1(a)(i) $B^{3+}(g) \longrightarrow B^{4+}(g) + e^-$

Comments:
- State symbols are essential for this equation to avoid ambiguity as the definition of fourth ionisation energy requires the ions to be in gaseous state. Any differences in state will cause the enthalpy change of the reaction to be different.
- Some students are unfamiliar with the element boron and wrote Be^{3+} or Br^{3+} instead.

1(a)(ii) B^{3+}: $1s^2$ C^{3+}: $1s^2\ 2s^1$

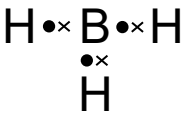
C^{3+} has one more electron shell than B^{3+}; the 2s electron in C^{3+} is further away from the nucleus than the 1s electron in B^{3+}. Shielding experienced by the 2s electron in C^{3+} is greater than the 1s electron in B^{3+}.

Despite the greater nuclear charge in C^{3+}, electrostatic attraction between the nucleus and the 2s electron in C^{3+} is weaker than the 1s electron in B^{3+}. Less energy is required to remove the 2s electron in C^{3+} compared to the 1s electron in B^{3+}.

Thus, B has a higher fourth ionisation energy than C.

Comments:
- Answers for this question were poorly phrased and lacking in key points. Many students focused only on the difference in electron shell from which the electrons are removed and did not discuss shielding effect and nuclear charge in their answer.
- Students are reminded to phrase their answers in terms of B^{3+} and C^{3+} instead of ambiguous terms like "boron/B" and "carbon/C" as it is open to interpretation whether the answer is referring to the atom or the ion. For example, "C has one more electron shell than B" would be incorrect for the case of C and B atoms.
- Common poor phrasing include:
  - "$1s^2$ electron", it should be "1s electron"
  - "1s shell", 1s is not an electron shell, it is an orbital/subshell depending on the context used
  - "inner 1s subshell", the comparison should be in terms of electron shell and not subshell
- Students are reminded that in both cases, the electrons to be removed are from the valence electron shell of B^{3+} and C^{3+}.

1(b)(i)



Comments:
- Generally well done.
- A number of students erroneously included a lone pair of electrons for B.

1(b)(ii) shape: <u>trigonal planar</u>
bond angle: <u>120°</u>

Comments:
- Generally well done.
- Students are reminded that the command verb for the question is "state", thus no explanations are required.

1(b)(iii) ΔH_r = energy required to break bonds – energy released from bonds formed

$= 3BE(B–H) + \frac{3}{2} BE(O=O) – BE(B=O) – BE(B–O) – 3BE(O–H)$

$= 3(330) + \frac{3}{2} (496) – 837 – 536 – 3(460)$

$= –1019 \text{ kJ mol}^{–1}$

$= \underline{–1020 \text{ kJ mol}^{–1}}$ (3 s.f.)

Comments:
- Generally well done.
- Common mistakes include not considering:
  - The coefficient of ½ in the equation for B_2O_3
  - The two O−H bonds in H_2O

1(b)(iv) The standard enthalpy change of combustion of borane is more exothermic than ΔH_r as <u>energy is released to condense steam to water</u> and to <u>convert B_2O_3 from gaseous to solid state</u>.

Comments:
- Students generally found this question challenging as they did not realise that $\Delta H_c^{\ominus}$ referred to B_2O_3 in its standard state (as a solid given in the question) while the calculated $\Delta H_r^{\ominus}$ involves B_2O_3 in its gaseous state.

1(c)(i) Aluminium in $AlCl_3$ has a vacant, low-lying orbital to accept a lone pair of electrons from the chlorine atom of another $AlCl_3$ molecule.

Comments:
- Generally well done.
- Students should consider that Al in $AlCl_3$ is sp^2 hybridised and hence has an empty unhybridised p orbital which is energetically accessible (low-lying) to accept a lone pair of electrons from Cl. Some students indicated that 3d orbitals were involved, which is incorrect in this context as Al does not have an expanded octet in Al_2Cl_6.
- A small number of students wrongly considered $AlCl_3$ as an ionic compound and provided explanations in terms of charge density and polarising power.

1(c)(ii) sp^2 to sp^3

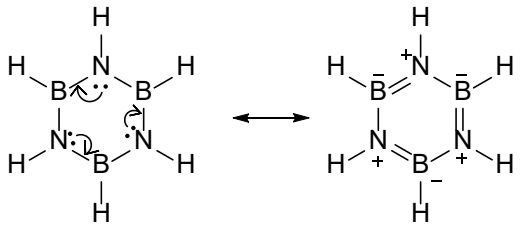
Comments:
- Generally well done.

1(c)(iii) There is less electron density in each B–H_b bond / fewer shared bonding electrons, hence resulting in weaker attraction to the nuclei.

Comments:

- Students generally found this question challenging as they were unable to account for the factor that leads to a weaker B−H_b bond than B−H_a and hence resulting in different bond lengths.
- Some students attempted to explain in terms of hybridisation / s−character. However, B is sp^3 hybridised in both B−H_a and B−H_b and H does not have a p orbital in the first principal quantum shell for hybridisation. Hence, it is not possible to compare and explain the phenomenon in terms of hybridisation / s−character.

1(d)(i)



X **Y**

Comments:

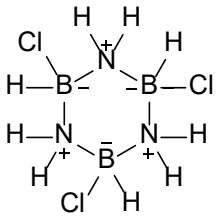
- A significant number of students appeared to have overlooked this question and did not attempt it. Students are reminded to take note of the question part labels "(i)", number of marks for each question "[1]" and to read the question carefully "complete Fig 1.2".

1(d)(ii) N is more electronegative than B, and this reduces the extent of electron delocalisation (partially delocalised) compared to benzene.

Comments:

- Students generally found this question challenging due to a lack of understanding of the structure of borazine. The question indicated that "Borazine is similar in structure to benzene" and that its structure "can be represented by two different resonance structures". Some students contradicted these statements by suggesting that "delocalisation of electrons in borazine does not occur throughout the ring" or there is "no continuous side-on overlap of orbitals" in borazine.
- Another common error suggests that there are less number of delocalised electrons in borazine than benzene. This is incorrect as both borazine and benzene have 6 delocalised electrons. For benzene, each carbon atom contributes only 1 electron for delocalisation. For borazine, each nitrogen atom contributes 2 electrons for delocalisation and each boron atom does not contribute any electrons for delocalisation as its p orbital is empty.

1(d)(iii)



Comments:

- Students generally found this question challenging as they did not consider the structure of the product formed using the resonance structure **X** and did not ensure that the atoms are conserved in an addition reaction.
- In resonance structure **X**, the N atom has a lone pair of electrons for coordination with H in HC*l*. At the same time, the B atom has an empty p orbital to accept electrons from C*l* in HC*l*.
- In addition reactions, the total number of atoms must be conserved before and after the reaction. Hence, when "1 mole of X reacts completely with 3 moles of HC*l*", the equation should be $B_3N_3H_6 + 3HCl \longrightarrow B_3N_3H_7Cl_3$ where the product should have 3 additional H and C*l* respectively.
- Several reasonable structures of **Z** were accepted.

2(a)(i)

$NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O \quad E^\ominus = +0.87\ V$

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \quad E^\ominus = +1.23\ V$

$E^\ominus_{cell} = +1.23 - (+0.87) = +\underline{0.36\ V} > 0$ (reaction is spontaneous)

Comments:

- Generally well done.
- A small number of students made the mistake of multiplying +1.23 with a coefficient of 2 when calculating $E^\ominus_{cell}$ and/or using −0.87. Students are reminded that $E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$ without any coefficients (even if the half-reaction is multiplied by a coefficient) and both $E^\ominus_{cathode}$ and $E^\ominus_{anode}$ are standard reduction potentials from the *Data Booklet* without changing the sign.
- A positive $E^\ominus_{cell}$ value is sufficient to show that the reaction is spontaneous without having to calculate $\Delta G^\ominus$. If $\Delta G^\ominus$ is calculated, the correct number of moles of electrons transferred (8 mol in this case) should be used.

2(a)(ii) The beneficial bacteria provide <u>enzymes</u> which act as biological catalysts to speed up the nitrification process.

Comments:

- Generally well done.
- The beneficial bacteria is not the actual catalyst for the reaction as it is not consumed and regenerated in the reaction.

2(b)(i) Day 9 or 10

Comments:
- Generally well done.
- Beneficial bacterial **A** produces NO_2^- during the first part of nitrification and hence the presence of NO_2^- between day 9 and 10 first indicates that beneficial bacterial **A** has been established.

2(b)(ii) Day 29

Comments:
- Generally well done.

2(b)(iii) $[NO_3^-]$ before water change = 35 ppm

$[NO_3^-]$ after water change = $\frac{100-25}{100} \times 35 = \underline{26.3 \text{ ppm}}$

Comments:
- Generally well done.
- A small number of students wrongly considered the original concentration of 35 ppm as 125% instead of 100%.

2(b)(iv) Using Henderson-Hasselbalch equation, $pH = pK_a + lg(\frac{[NH_3]}{[NH_4^+]})$,

$7.4 = 9.25 + lg(\frac{[NH_3]}{[NH_4^+]})$

$\frac{[NH_3]}{[NH_4^+]} = 10^{7.4-9.25} = 0.014125$

$[NH_3] = 0.014125[NH_4^+]$

$z = \frac{[NH_3]}{TAN} = \frac{[NH_3]}{[NH_3] + [NH_4^+]} = \frac{0.014125[NH_4^+]}{0.014125[NH_4^+] + [NH_4^+]} = \frac{0.014125}{0.014125 + 1} = \underline{0.0139}$

OR

Let mole fraction of NH_3 be z, hence mole fraction of $NH_4^+ = 1 - z$

$\frac{z}{1-z} = 0.014125$

$z = \frac{0.014125}{1 + 0.014125} = \underline{0.0139}$

Comments:
- Students need to be familiar with the Henderson-Hasselbalch equation, $pH = pK_a + lg(\frac{[NH_3]}{[NH_4^+]})$. If calculating pH, the acid should be in the denominator. If calculating pOH, the base should be in the denominator.
- Common mistakes for this equation include:
  - $pH = pK_a + lg(\frac{[NH_4^+]}{[NH_3]})$, $pH = pK_a - lg(\frac{[NH_3]}{[NH_4^+]})$, $pH = pK_a + lg(\frac{[NH_3]}{TAN})$

  Similar mistakes were noted when students used the basic form of the Henderson-Hasselbalch equation.
- Some students made the mistake of applying a negative sign to the exponential while solving $lg(\frac{[NH_3]}{[NH_4^+]}) = -1.85$ while some students made mistakes when substituting $[NH_3] = 0.014125[NH_4^+]$ into the equation for z.

2(c)(i) When small amount of $OH^-(aq)$ is added,
$HCO_3^-(aq) + OH^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l)$

When small amount of $H_3O^+(aq)$ is added,
$CO_3^{2-}(aq) + H_3O^+(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$

Comments:
- Students must use the irreversible arrow $\longrightarrow$ for equations showing the action of a buffer. This is so that the equations show the net change after the shift in position of equilibrium.
- This is in contrast to explaining buffer action using Le Chatelier's principle where the reversible arrow $\rightleftharpoons$ should be used to show the shift in position of equilibrium of a particular equilibrium reaction.
- This is analogous to the use of the irreversible arrow $\longrightarrow$ when writing equations for reactions at the cathode and anode in electrochemistry even though the species are in equilibrium.

2(c)(ii) Tank water with a higher carbonate hardness has a higher buffer capacity to partially offset increase in $[H^+]$ due to the nitrification process.

Comments:
- Generally well done.
- Buffer capacity is affected by the number of moles of CO_3^{2-} and HCO_3^{2-} present. A greater amount (and hence concentration due to same total volume) of CO_3^{2-} and HCO_3^{2-} can react with a greater amount of H^+ and OH^- respectively.

2(d)(i) $n(S_2O_3^{2-}) = 13.40 / 1000 \times 0.0100$
$= 0.000134$ mol
mole ratio of $O_2 : I_2 : S_2O_3^{2-}$
$= 0.5 : 1 : 2$
$= 1 : 2 : 4$
$n(O_2) = 0.000134 / 4 = 0.0000335$ mol
$[O_2] = 0.0000335 / 100 \times 1000$
$= 3.35 \times 10^{-4}$ mol dm^{-3} (within recommended range)

Comments:
- Generally well done.
- A few students made mistakes when considering the mole ratios of the various substances or did not conclude if the concentration falls within the recommended range.
- Students are reminded that the thiosulfate ion has the formula $S_2O_3^{2-}$ instead of $S_4O_6^{2-}$.

2(d)(ii) Oxidation: $N_3^-(aq) \longrightarrow \frac{3}{2} N_2(g) + e^-$

Reduction: $8H^+(aq) + 2NO_2^-(aq) + 6e^- \longrightarrow N_2(g) + 4H_2O(l)$

Overall: $4H^+(aq) + 3N_3^-(aq) + NO_2^-(aq) \longrightarrow 5N_2(g) + 2H_2O(l)$

Comments:

- Students must always check that all half-equations and overall equations are mass and charge balanced. Any equation that is not mass or charge balanced will definitely be wrong.
- Some students are still making the mistake of trying to write overall redox equations directly without first writing out the individual half-equations. This often results in an overall equation that is mass balanced but not charge balanced.
- Other mistakes include overlooking that N_2 is the only nitrogen-containing product and/or using O_2 instead of H_2O to balance O while constructing half-equations.
- A handful of students mistook N_3^- as N^{3-}.
- Students are reminded to label their equations so that it is clear which equation is the overall equation. Also, the half-equations should be written on the answer lines since they are required by the question.

2(e) Decreasing basicity: N(1) > N(2) > N(3)

N(1) is a primary amine. The electron-donating $-CH_2-$ group increases the electron density on N(1), making the lone pair of electrons on N more readily available to form a dative covalent bond with a proton.

N(2) is an aromatic amine. The orbital containing the lone pair of electrons on the nitrogen atom overlaps with the π electron cloud of the benzene ring and the lone pair of electrons is delocalised and is less available to form a dative covalent bond with a proton.

N(3) is a sulfonamide which has similar basicity as amides. It has the lowest basicity among the three nitrogen-containing groups because the orbital containing the lone pair of electrons on the N atom overlaps with the π electron cloud of the adjacent S=O group and the lone pair of electrons is delocalised to a greater extent, and hence least/not available to form a dative covalent bond with a proton.

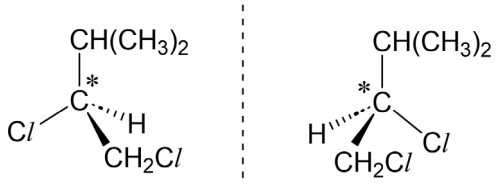
Comments:

- Students who gave clear and thorough explanations were able to get full credit for this question.
- Students are advised to rank N1, N2 and N3 explicitly.
- Students should recognise the parallels between the sulfonamide group and the amide group. Just like in an amide, where the lone pair of electrons on N can delocalise into the pi electron cloud of C=O, the lone pair of electrons on N can also delocalise into the pi electron cloud of S=O in the sulfonamide.
- Common mistakes include:
  - Not specifying coordination/donation to a proton/H^+

- Not describing the overlap of orbitals that lead to the delocalisation of electrons. The orbitals have to first overlap to allow for the delocalisation of electrons.
- "empty" orbital containing lone pair of electrons on N (contradictory as the orbital containing lone pair of electrons on N is not empty)
- Overlaps with the π electron cloud of the adjacent "C=O" group (there is no C=O group in compound **P**)
- Dispersing the "negative charge" on N (unlike the case of $-COO^-$, there is only a partial negative charge on NH_2).
- "Lone pair of electrons on N overlaps" with the pi electron cloud of the benzene ring. (It is not the electrons that overlap with the pi electron cloud, but the orbitals containing the lone pair of electrons that do.)
- N2 is bonded to the "benzylic" carbon (benzylic carbon refers to the carbon directly bonded to the benzene ring and not the carbon in the benzene ring)
- N1 is bonded to an electron-donating "methyl" group (a methyl group is $-CH_3$ which is not what N1 is bonded to)
- Lone pair of electrons on N1 is "delocalised" into the benzene ring (the lone pair of electron on N1 is unable to delocalise into the benzene ring due to the absence of continuous side-on overlap of orbitals since N1 is bonded to a sp^3 carbon)
- N1 is more basic than N2 as it is "further away" from the electron-withdrawing sulfonamide group (the sulfonamide groups is equal number of carbons away from both N1 and N2)

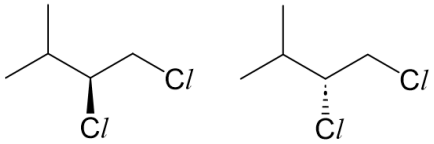
- A few students included the concept of "partial double bond" which is irrelevant in this context as the C−N and S−N bonds are not broken during protonation.

3(a)(i)



Comments:

- Many students did not indicate the presence of the mirror plane. A good complete answer should include the mirror plane.
- A good answer should also show the correct representation of the tetrahedral geometry around the chiral carbon atom.
- Many students were not sure how to draw enantiomers using skeletal formula, especially when it involves the use of wedged and dashed bonds. So, they chose to use a combination of skeletal and condensed formulae. Please avoid doing this. Choose to use either condensed formula as shown in the answer above or skeletal formula as shown below.

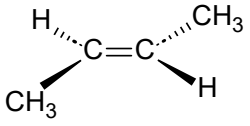


- Many students made mistakes when drawing the $–CH(CH_3)_2$ group attached to the chiral carbon, either giving an incorrect number of hydrogen atoms or incorrect structure. Note that representing the group as $–CHCH_3CH_3$ is not accurate, as the first CH_3 group is a branch on the first carbon. Please represent it as $–CH(CH_3)_2$ instead.

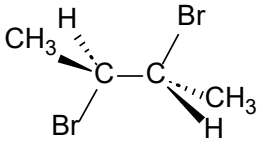
3(a)(ii) The carbocation that is produced in the reaction is trigonal planar with respect to the positively charged carbon. Cl^- can attack the positively charged carbon from either side of the trigonal plane with equal likelihood. This results in the formation of a racemic mixture. The optical activity of each enantiomer cancels out each other. The product mixture is unable to rotate plane-polarised light.

Comments:
- A number of students did not state the shape of the intermediate, as required by the question.
- Students who have learnt the electrophilic addition mechanism well would have known that the positively charged carbon of the carbocation is attacked by the nucleophile Cl^-, and not electrophile Cl^+.

3(a)(iii)

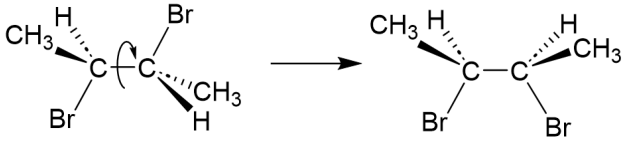


alkene **E**



product

For visualization,



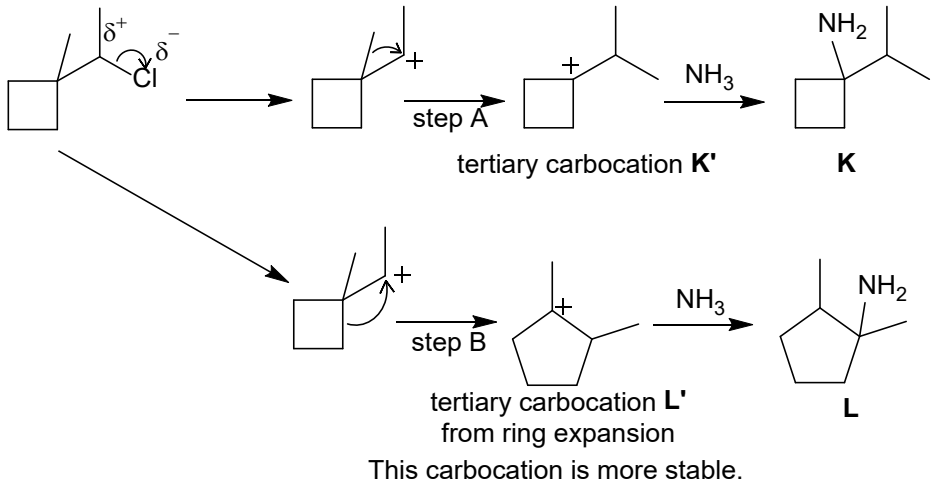
Comments:
- Students who were able to visualise three-dimensional structures and rotation about carbon–carbon single bond did well. Those who understood the definition of a meso compound as given in the question and drew the product with an internal plane of symmetry were also given the credit.

3(b)(i) In this reaction, a secondary carbocation, **F'**, rearranges to form a tertiary carbocation, **G'** which is more stable because it has more electron donating alkyl groups bonded to the positively charged carbon. This helps to disperse the positive charge. **G** will be formed in a larger proportion.

Comments:
- Some students merely stated the fact that G' is a tertiary carbocation while F' is a secondary carbocation without explaining the phenomenon in terms of electron donating effect of the alkyl group. This approach is inadequate as the question requires students to use the concept of electronic effect for their explanation.

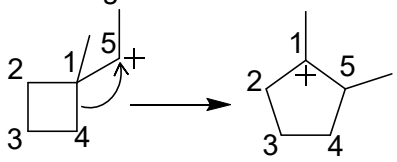
- A significant number of students used symbols such as e^- to represent the word 'electron' without explaining it to the marker. Students are strongly encouraged to spell out the word once before using the symbols. For example, write it as "electron (e^-) donating" instead of "e^- donating".

3(b)(ii)



Comments:

- Students who find it difficult to visualise ring expansion are encouraged to associate each carbon in the ring with a number.



- Labelling each carbon in the ring helps in visualising ring expansion.

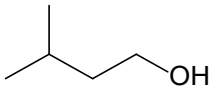
3(b)(iii) Although both carbocations are tertiary carbocations, **L'** is more stable as there is less repulsion between bond pairs of electrons in the cyclopentane ring, compared to **K'**. **L'** is formed faster and hence, **L** is the major product.

Comments:

- A number of students recognised the greater ring strain in K' than that in L' but did not mention the effect this has on the relative stability of the carbocations.
- Students who answered **(b)(iii)** using the difference in stability of a secondary and a tertiary carbocation did not notice that both **K'** and **L'** are tertiary carbocations. Hence, the difference in the yield of **K** and **L** cannot be attributed to the number of alkyl groups bonded to the positively charged carbon atom.

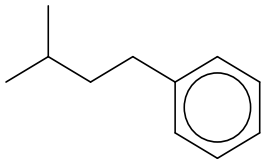
3(c)(i)

M:



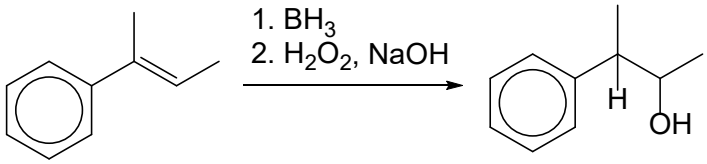
Step 2: PCl_5 / PCl_3 / $SOCl_2$, or dry HCl, $ZnCl_2$, heat

P:

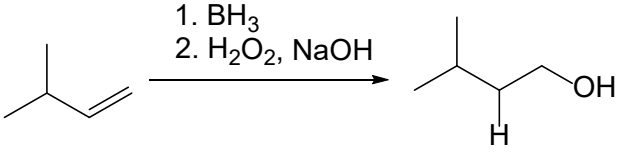


Comments:

- Generally well done. For the structure of **M**, students will need to follow the pattern given in Fig. 3.6 to realise this reaction does not follow Markonikov's rule.
- Refer to Fig. 3.6,



Therefore,



3(c)(ii) 1-chloro-3-methylbutane

Comments:

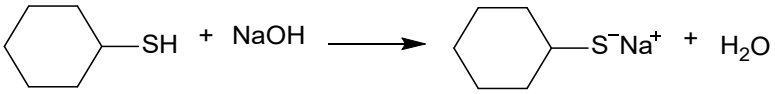
- Students are expected to follow all the rules for writing the systematic names of organic compounds. In this case, the chloro group must be written before methyl as the substituents are written in alphabetical order. Also, remember to include the numbers for the substituents.

3(c)(iii) Electrophilic substitution

Comments:

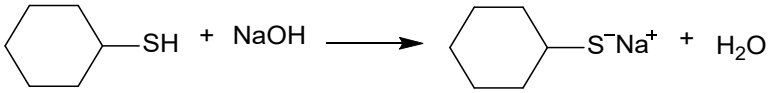
- Step 4 involves the reaction of benzene and a Lewis Acid $AlCl_3$. Hence, it is electrophilic substitution.

3(c)(iv)



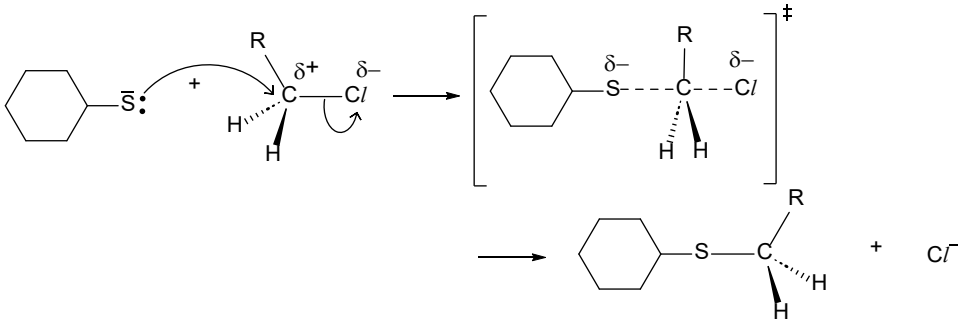
Comments:

- Since the question states that this is an acid-base reaction, then the equation must be:



proton donor (acid) proton acceptor (base)

3(c)(v) S_N2



Comments:

- Compound **N** is a primary halogenoalkane. It reacts via an S_N2 mechanism.
- Students are reminded to learn how to draw the structure of the transition state accurately. They should indicate the distribution of δ– charges correctly.
- Students are reminded to start drawing the curly arrow from the lone pair of electrons on sulfur, and not to forget to break the C−C*l* bond.
- A number of students forgot to include the Cl^- by-product.
- This is a single step reaction mechanism, hence there is no slow or fast step.

3(c)(vi) To 1 cm^3 of each compound, add 1 cm^3 NaOH(aq), followed by 2 to 3 drops of $KMnO_4$. Heat the solution.

S: Purple $KMnO_4$ is decolourised. Black solid MnO_2 is formed.
T: Purple $KMnO_4$ remains.

Comments:

- When **S** and **T** are hydrolysed by NaOH, they produce 2-methylbutan-1-ol, a primary alcohol, and 2-methylbutan-2-ol, a tertiary alcohol, respectively. 2-methylbutan-1-ol is oxidised by $KMnO_4$, causing purple $KMnO_4$ to be decolourised. Black MnO_2 is formed as well. 2-methylbutan-2-ol, a tertiary alcohol, is resistant to oxidation. Hence, purple $KMnO_4$ remains.
- Many students chose to use ethanolic KOH to eliminate HC*l* from S and T to form alkenes. Subsequently, any use of $KMnO_4$ to distinguish both alkenes will

not be meaningful as both alkenes will be oxidised and $KMnO_4$ will also oxidise the ethanol from the previous reaction.
- Many students also chose to use ethanolic $AgNO_3$ to differentiate between S and T. However, Ag*Cl* will be precipitated for both reactions. There will also be no appreciable difference in the rate of formation of Ag*Cl* as both compounds are chloroalkanes.

3(d)(i) CFCs contain C–C*l* bonds which undergo homolytic fission in the presence of UV light to form chlorine radicals which catalyse the decomposition of ozone.

Comments:
- Refer to Halogen Derivatives lectures LO(g) and (h).
- While students are not expected to know the mechanistic details of how CFCs deplete the ozone layer, they are expected to know and understand the chemical inertness of fluoroalkanes and fluorohalogenoalkanes due to the strong C−F bond.

3(d)(ii) HFCs have higher GWP than CFCs. Hence, HFCs trap more heat and cause global warming to a larger extent than CFCs.

Comments:
- Generally well done.
- A small number of students simply indicate 'causes climate change' as their answer. Answers have to be specific to earn the credit.

4(a)(i) The order of reaction with respect to a particular reactant is the power to which the concentration of that reactant is raised in the rate equation.

The rate constant, *k*, is a constant of proportionality in the rate equation. It is constant for a particular reaction at a given temperature.

Comments:
- Students need to be familiar with all the definitions covered in the syllabus. Avoid rephrasing the definitions in your own words.
- Some students erroneously defined overall order of a reaction instead of order of reaction with respect to a reactant.
- Note that reactants appearing in the rate equation of the overall reaction need not necessarily be involved in the rate-determining step. In the example below, Cl_2 is not involved in the rate-determining step but appears in the rate equation of the overall reaction.

Reaction	$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$
Reaction mechanism	Step 1: $NO + Cl_2 \rightleftharpoons NOCl_2$ fast Step 2: $NO + NOCl_2 \longrightarrow 2NOCl$ slow
Rate equation	rate = $k [NO]^2 [Cl_2]$

4(a)(ii) From Fig. 3.1, first $t_{1/2}$ = 2nd $t_{1/2}$ = $\underline{2.3 \times 10^{-4}\ s}$
∴reaction is $\underline{\text{first order with respect to •OH}}$.

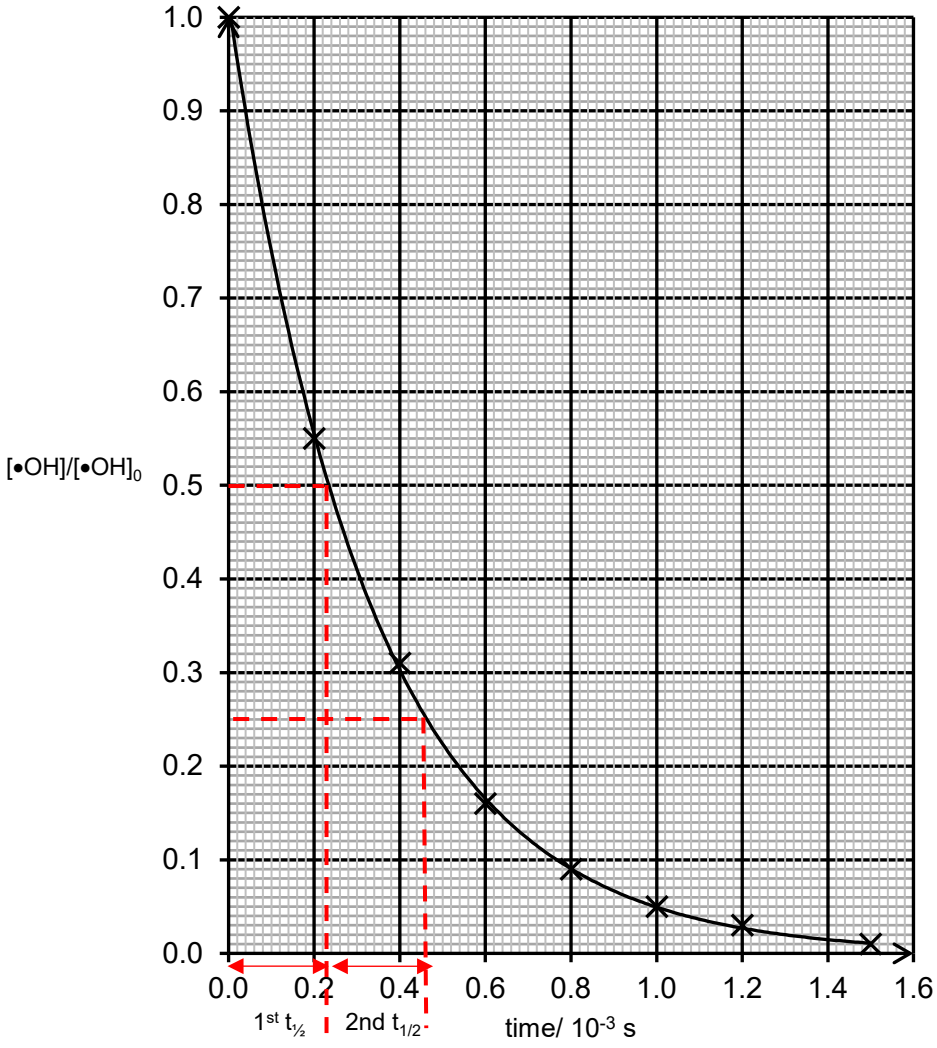


Fig. 3.1

Comments:

- Since the graph of $\frac{[\bullet OH]}{[\bullet OH]_0}$ against time is a downward sloping curve, we can conclude that the reaction is not zero order with respect to •OH. Hence, students should check if $t_{½}$ is constant to determine if the reaction is first order with respect to •OH. (Note: $t_{½}$ should be (approximately) constant. Otherwise, we cannot conclude that the reaction is second order with respect to •OH. To conclude that the reaction is second order with respect to •OH, we need a graph of rate against $(\frac{[\bullet OH]}{[\bullet OH]_0})^2$ to be a straight line with positive gradient passing through the origin.)
- As use of Fig. 4.1 is required in this question, students should show clearly the construction lines and demarcate clearly two $t_{½}$ on the graph (as shown in the

answer above). Students should also indicate the value of each $t_{½}$ on the graph and/or working. For the above graph, it is incorrect to write 2nd $t_{½} = 0.46 \times 10^{-3}$ s.

- Some students missed reading or appeared unsure of how to read the x-axis label 'time / 10^{-3} s'. For example, when $\frac{[\bullet OH]}{[\bullet OH]_0} = 0.5$,

$$\text{time} / 10^{-3}\ \text{s} = 0.23$$
$$\text{time} = 0.23 \times 10^{-3}\ \text{s}$$

- For the x-axis scale, one small square is 0.02×10^{-3} s. Several students misread the x-axis scale and incorrectly determined the value of $t_{½}$.

4(a)(iii) $k' = k[CH_3CHO]^n$

A straight line graph with positive gradient passing through the origin is obtained for the graph of k' vs $[CH_3CHO]$, OR $k' \propto [CH_3CHO]$, OR k' is directly proportional to $[CH_3CHO]$.

The reaction is first order with respect to CH_3CHO.

$$k = \text{gradient} = \frac{(4.0-0.0) \times 10^3}{(4.5-0.0) \times 10^{-7}} = 8.89 \times 10^9$$

Comments:

- As the use of Fig. 4.2 is required in this question, students should state clearly the overall shape of the graph, instead of reading off selected points on the graph to compare the relationship between k' and CH_3CHO.
- While most students recognised that k = gradient of graph, several students missed reading or appeared unsure of how to read the x- and y-axis labels, 'k' / 10^3 and '$[CH_3CHO]$ / 10^{-7} mol dm^{-3}' respectively *(refer to comments for **(a)(ii)**)*.

4(a)(iv) $\text{rate} = k[\bullet OH]\,[CH_3CHO]$

Comments:

- Generally well done. Some students erroneously gave 'rate = $k'[\bullet OH]$' without stating what k' refers to.
- Other common mistakes include:
  - rate equation = $k[\bullet OH]\,[CH_3CHO]$
  - $k = [\bullet OH]\,[CH_3CHO]$

4(a)(v) Yes I agree, since equation 1 shows a bimolecular reaction involving 1 •OH reacting with 1 ethanal which agrees with the rate equation in **(a)(iv)** showing that the reaction is first order with respect to both •OH and CH_3CHO.

Comments:

- While most students correctly agreed with the proposal that the reaction takes place in a single elementary step, few students were able to explain their responses well. It is important to explain that the molecularity of equation 1, i.e. bimolecular reaction involving one •OH and one CH_3CHO, agrees with the rate

equation in **(a)(iv)** which shows that the reaction is first order with respect to both •OH and CH_3CHO.

- Some students compared the order of reaction with respect to •OH and CH_3CHO to their stoichiometric ratio in equation 1, which is ambiguous as a stoichiometric ratio of 1:1 does not necessarily mean one •OH reacting with one CH_3CHO. Instead, it would have been clearer to refer to the stoichiometric coefficients of •OH and CH_3CHO in equation 1.

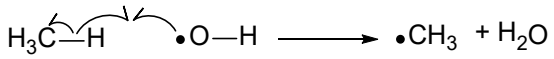
4(a)(vi) A catalyst will <u>increase</u> the magnitude of the <u>rate constant, *k*</u>, and <u>decrease the</u> magnitude of the <u>activation energy, E_a</u>.

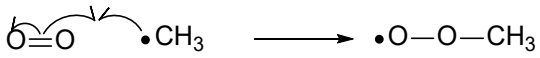
Comments:

- In the context of this question, students are required to compare the *k* and E_a of the catalysed reaction as compared to that of the uncatalysed reaction.
- While most students recognised that E_a decreases in the presence of a catalyst, some erroneously thought that *k* remains unchanged as temperature is constant. From the Arrhenius equation, when temperature increases and/or E_a decreases, *k* increases.

Arrhenius equation: $k = A\, e^{-\frac{E_a}{RT}}$

4(b)(i)

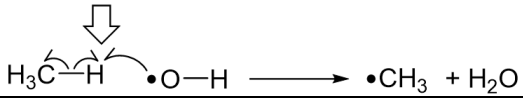
Step 1: 

Step 2: 

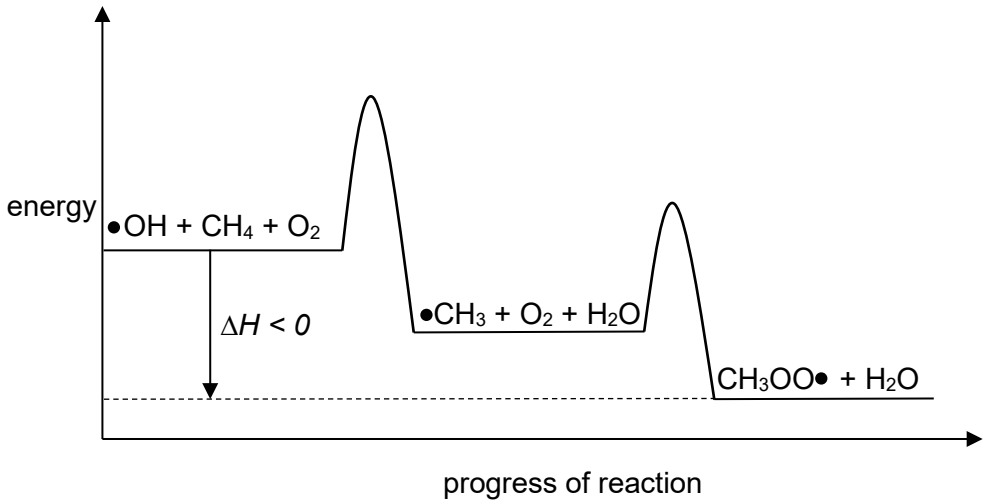
Comments:

- In general, most students referred to the information given and correctly gave the two steps of the reaction mechanism. However, only a handful were able to draw the curly arrows correctly.
- As the two steps involved formation/reaction of radicals, homolytic bond cleavage and formation must have occurred. Hence, use of the half curly arrows is required.
- When drawing reaction mechanisms, students need to show clearly where the curly arrows start and end. For example, in the formation of the O-H bond in step 1, students should show clearly the two half curly arrows ending in between the H and O atoms (i.e. where the O-H bond is forming) instead of ending the two half curly arrows on the H atom.

incorrect



4(b)(ii)



Comments:

- Some students showed confusion between energy profile diagram and energy level diagram.
- As the energy profile diagram is for the first two steps of the reaction, there should be two transition states in the diagram. Note that transition states should be higher in energy level than both the reactants and products of the corresponding step.
- As the question required a labelled energy profile diagram, students need to label clearly:
  - axis labels
  - ΔH for the overall enthalpy change with correct direction of arrow (pointing downwards since the overall enthalpy change of the first and second steps is exothermic)
  - all reactants, intermediates and products.
- Note that for the labelling of the reactants, intermediate and products, each step must be both mass and charge balanced.
- Some common mistakes for the axis labels include:
  - 'ΔH' or 'enthalpy change' for y-axis
  - 'time' or 'reaction' for x-axis

4(c)(i) $2H_2O_2 \longrightarrow \bullet OH + HOO\bullet + H_2O$

Comments:

- Generally well done. Note that all chemical equations should be both mass and charge balanced. Equations should also be simplified, e.g. any common species on both sides of the equation should be removed.

4(c)(ii) Fe^{2+} is a homogeneous catalyst as it is in the same phase as H_2O_2.
It is used in equation 2 and regenerated in equation 3.

Comments:

- Most students correctly identified Fe^{2+} as the catalyst for the reaction. As use of equations 2 and 3 are required, it is insufficient to simply state that Fe^{2+} is regenerated at the end of the reaction. Students need to also state the consumption/involvement of Fe^{2+} in equation 2 to form the intermediates.

4(c)(iii) Add aq, NaOH/aq. Na_2CO_3 to precipitate out $Fe(OH)_2$ / $Fe(OH)_3$.
OR
Add aq. NaS_2O_3 (or other known reducing agent of H_2O_2) to react with H_2O_2.
OR
Add a large volume of water (dilution).

Comments:

- Students should specify the reagent used to quench the reaction, instead of giving general answers such as quenching reagent or oxidising/reducing agent.
- Several students incorrectly used a large volume of acid to react with OH^- or to dilute the reaction mixture. Note that OH^- is a product in the generation of •OH by Fenton's reagent and removal of OH^- will not stop/slow down the formation of •OH. Also, to dilute the reaction mixture, a large volume of water should be used instead of acid.
- To quench the reaction, the reagent used should stop/slow down the reaction quickly. Although MnO_2 catalyses the decomposition of H_2O_2, the decomposition of H_2O_2 will still take time and hence MnO_2 will not be a suitable/efficient quenching agent.
- From equations 2 and 3, students should recognise that either Fe^{2+} or Fe^{3+} can catalyse the generation of •OH from H_2O_2 (i.e. either equations 2 or 3 can take place first). Hence, any reagent that converts $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$ and vice versa, will not be able to stop/slow down the formation of •OH.