2021 H2 Chemistry Prelim Paper 2 – Suggested Solutions

General comments

- There is a common theme in the examiner comments it is apparent that many students do not read the question carefully to answer the question. Many students do not give the necessary details <u>dictated by</u> <u>the question</u>. Please read carefully!
- The handwriting of some scripts left much to be desired. No marks are awarded for answers which cannot be read. Please write clearly for your own sake.
- Please space out the answers. Do not squeeze the drawing of structures into the space of one line. Structures which cannot be clearly seen were not awarded marks. There is sufficient space given for each part.
- In the drawing of mechanisms, please show the lone pair of electrons clearly make them bigger and darker.
- Please use ink throughout. Do not use pencil as pencil markings are often unclear and may be deemed as rough work.
- **1(a)(i)** Heat gained by water = 4.18 x 10.0 x 300 = 12540 J Heat gained by copper can = 0.384 x 10 x 250 = 960 J Total heat gained = 12540 + 960 = 13500 J = 13.5 kJ

Examiner Comments

- This was generally well done.
- Some students forgot to account for the heat gained by copper can even though the question clearly stated that consideration.
- **1(a)(ii)** Amt of ester = 0.980 / 74.0 = 0.0132 mol Theoretical heat energy released = 0.0132 x 1592 = 21.1 kJ

Examiner Comments

- This was generally well done.
- Note that there is no need for put negative sign here as the heat energy calculated is for the heat *released*.
- A sign would be necessary for heat *change* as it could be a positive or negative change.
- **1(a)(iii)** <u>Method 1 Find % heat loss to surroundings</u> 13.5 kJ (expt) / 21.1 kJ (theoretical) = 64% of heat energy transmitted (36% heat loss) Amt of ethyl ethanoate = 0.948 / 88.0 = 0.010773 mol Heat transferred = $4.18 \times 11.5 \times 300 + 0.384 \times 11.5 \times 250 = 15525$ J = 15.5 kJ Theoretical heat released = 15525 / 0.64 = 24257 J = 24.3 kJ $\Delta H = -24.3$ kJ / 0.01077 = -2252 = -2250 kJ mol⁻¹

 $\begin{array}{l} \underline{\text{Method 2 - Find thermal capacity of apparatus OR by proportion}} \\ \hline \text{Thermal capacity = theoretical energy released / observed temperature change} \\ \hline \text{Thermal capacity = 21.1 kJ / 10 K = 2.11 kJ K^{-1}} \\ \hline \text{Theoretical heat produced from combustion = 2.11 kJ K^{-1} x 11.5 K = 24.3 kJ} \\ \hline \text{Amt of ethyl ethanoate = 0.948 / 88.0 = 0.010773 mol} \\ \Delta H = -24.3 \text{ kJ / 0.01077 = -2252 = } \underline{-2250 \text{ kJ mol}^{-1}} \\ \hline \end{array}$

- Similar to part (i), students must account for the heat transfer to both water and the copper can.
- It is stated clearly in the question that the *percentage* heat loss (not absolute heat loss) is the same across both experiments. A number of students failed to consider this important information resulting in loss of marks.
- Many students struggled with the calculation of percentage heat loss to determine the theoretical heat transferred during reaction. Firstly, students need to realize that the heat that

was *transmitted* (100% – *heat loss%*) is that which made it to the calorimeter and observed to raise the temperature. So the calculated q (from mc Δ T) represents 64% of the total heat given out by the reaction. Secondly, to scale any quantity from x% to 100%, we need to divide by x to get 1% and then x 100 for 100%, OR to use simple ratios and take q_{total}/q_{transmitted} = 100/64, and therefore q_{total} = q_{transmitted} x100/64). Students need to master these basic mathematical manipulation.

- As there is no such thing as %loss or %transmission of ΔH, it is not acceptable to calculate those terms. The question specifically hinted at the use of % loss of heat, which is not the same as ΔH.
- Quite a few students also made careless mistakes in calculations or did not read the question and make use of the Mr data that has been given .









1(b)(ii) pK_a for **P** will be smaller.

The conjugate base for \mathbf{P} CH₃CH(OH)COO⁻ is more stable than CH₃CH₂COO⁻. The –OH group is electron-withdrawing and disperses the negative charge on O of –COO⁻ to a large extent. Hence, \mathbf{P} is a stronger acid than propanoic acid.

Examiner Comments

- This question allowed incorrect understanding of the effect of –OH group to be surfaced.
- A good number of students incorrectly thought that –OH is electron-donating, resulting in the wrong conclusion drawn on relative acidicity. Note the –OH is only "electron-donating" when it is attached to a benzene ring.
- -OH in phenol contributes to resonance (which outweighs inductive effect) because the lone pair of electrons on O can be delocalised into the pi electron cloud of benzene ring, resulting in increased electron density of the ring. This is only possible because, there is π overlap between the orbital containing the lone pair electrons of O, and the p-orbital of the neighbouring C of the benzene ring. No such thing happens in **P**.
- Students should note that resonance effect is possible only if resonance structures are allowed, which usually require some sort of π overlap. Students should not overgeneralize –OH groups as "electron donating". In fact, –OH groups are electron withdrawing by default (due to electronegative O). Sharing of lone-pair electron density by resonance is a separate phenomenon that is expected only in structures that allow resonance.
- Any answer that implies resonance is present in P is not accepted (such as "electrons are spread over 3 electronegative O atoms in P")
- Students should also avoid wasting time on irrelevant points, such as similarities between P and propanoic acid. Both compounds have the COOH group, and gives the -COO⁻ in their conjugate bases which is resonance stabilized. There is thus no need to write about -COO⁻ resonance stabilization at all.

1(b)(iii) $[H^+] = 10^{-2.43} = 3.72 \text{ x } 10^{-3} \text{ mol } dm^{-3}$

 $K_a = (3.72 \times 10^{-3})^2 / (0.10 - 3.72 \times 10^{-3}) = 1.43 \times 10^{-4} \text{ mol dm}^{-3}$ $pK_a = -\log 1.43 \times 10^{-4} = 3.84$

Since [H⁺] is known, there is no need to make assumption here. With assumption made, K_a is 1.38 x 10^{-4} mol dm⁻³ and p K_a is 3.86. This answer was also accepted.

Examiner Comments

• This calculation was straightforward and well done.

1(c)(i)



Examiner Comments

- The first reaction involving hot KOH(aq) is a hydrolysis reaction, and the ester is hydrolysed to an alcohol (linalool) and a carboxylic acid. However, due to the alkaline conditions, the carboxylic acid reacts with KOH to form the carboxylate salt.
- Students should remember to include the correct counter ion (K⁺) in **C**, since the identity of the reagent (which provided the counter ion) was known.
- When skeletal structures are drawn, the usual practice is to leave out the H atoms, but in the case of compound **C**, including the H adds clarity to the structure. A small number of students drew a bond without H, which implies ethanoate instead of methanoate.
- On the other hand, if non-skeletal structures are drawn (e.g. labelling the central C atom in **C**), you must show the H atom.
- Compound D was correctly identified by most students. However, some students did not position the ester group correctly in D, or incorrectly deprotonated the alcohol groups in D. Students should remember that alcohol groups do not react with OH⁻.



12

Examiner Comments Most students were able to identify compound **E** correctly, as well as two of the three alkenes. Most students did not identify the structure shown in H, possibly because they did not notice • that one of the expected alkenes (G in this case) exhibits cis-trans isomerism. Among the answers, a common incorrect alternative structure was suggested: [°]C [™]CH₂ Please note that such structures with two consecutive C=C bonds, known as allenes, exhibit different chemical properties and should not be considered unless all other structures, which can be explained using H2 Chemistry content, have been exhausted. Many students drew skeletal formulae of compounds with poor distribution of bond lines. For is more accurately represented as ~ . The substructure example. was particularly ambiguous as the groups on the right side of the trisubstituted alkene deviated greatly from the correct geometry, and it was unclear whether the student meant to show a structure containing or

1(c)(iii) Both nucleophile and base have a pair of electrons available for donation.

A nucleophile attacks an electrophile (or an electron-deficient species) to form a bond, as shown in reaction 1.

A base accepts a H^+ (proton) as shown in reaction 2.

Examiner Comments

- This question was poorly attempted because answers tended to include definitions of *nucleophile* and *Bronsted base* without clearly identifying a similarity and a difference between them.
- One common example was the statement "nucleophiles are electron pair donors, while Bronsted bases accept a H⁺ ion". While the conjunction 'while' can indicate a contrast between two things, it is a weak argument here because Bronsted bases <u>also</u> donate an electron pair in the process of accepting a H⁺ ion. A good answer would therefore contrast the identity of the electron pair acceptor as the main difference.
- A common misconception is that a <u>lone pair</u> must be donated by a nucleophile, and might be due to familiarity with only nucleophiles which donate *lone pairs* e.g. OH⁻, NH₃, etc. Recall in electrophilic substitution of benzene, the benzene nucleophile donates π electrons to the electrophile present. Thus, it is more correct to refer to the donation of an <u>electron pair</u> by nucleophiles.
- Other poor choice of terms include, "give / lose electrons" (this means oxidation), "attracted to..." (ambiguous as this could simply lead to formation of intermolecular forces among other interactions), "nucleophiles are electron-rich" (this is merely a property of nucleophiles and does not imply the nucleophile is about to participate in a reaction).

1(c)(iv) reaction 1: <u>aqueous</u> KOH, <u>heat</u>

reaction 2: KOH in ethanol, heat

Examiner Comments

 This question was not well answered. Incorrect answers did not specify the need for heating, or did not distinguish between the different solvents required to favour substitution over elimination, or vice versa.

- As the same base is involved in both substitution and elimination, students have to recognise that elimination would be more favoured in an alcoholic medium as it makes the hydroxide ion a stronger base. Thus, "aqueous ethanol" is not as good an answer as the presence of water dilutes the enhancement of basicity brought about by an alcoholic medium.
- As with other "reagents and conditions" type of questions, it is important to specify a particular reagent to use; i.e. "ethanol" instead of "alcohol".



Examiner Comments

- Many students did not obtain full credit because the requirement to show the stereochemistry (in this case, the 3D structure around the chiral centre) of the reactant and products was not fulfilled. Since the reactant possesses a chiral centre, a proper 3D tetrahedral structure should be shown at the chiral centre. Because the S_N1 reaction would lead to the formation of a racemic mixture if the products are chiral, both enantiomers of the product need to be clearly shown.
- In addition, there were a significant number of drawings which could be improved on. Some examples include:
 - Rv is not planar but is. The former seems to suggest that the three groups attached to the positively charged carbon did not redistribute into a planar arrangement after the loss of the chloride leaving group.
 - is an incorrect representation of a tetrahedral geometry.
 - Students are also reminded to name the mechanism clearly $(S_N 1)$ as part of the answer, and not scribbled in the margin somewhere. If written in full, the correct name is unimolecular nucleophilic substitution. Please also note the correct notation for $S_N 1$, not SN_1 or $_{SN} 1$.

2(a)(i)

Examiner Comments

111.

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sp²

- This question was surprisingly not as well done. A significant number of students wrote "sp³" even though boron has only 3 regions of electron density around it.
- Students should note that the number "2" should be written as a superscript and not a subscript.

2(a)(ii) Since the boron atom is sp² hybridised and it only has 6 valence electrons around boron, there is an empty unhybridised p orbital which can accept a pair of electrons and thus, is an electrophile.

Examiner Comments

- This question was poorly answered.
- Many students did not include the accepting of a pair of electrons in their explanation. This is necessary as electrophiles are defined as such. "Accept electrons" is not accepted as this can refer to 3 or 5 electrons while "accept electron" refers to only 1 electron which is incorrect. An electrophile need not accept a lone pair of electrons as the electron pair can come from a bond pair like in the following mechanism.
- Students should note that an unhybridized orbital need not be empty, it can contain electrons like in the case of the unhybridized p orbitals in alkenes. Some students conveniently wrote "boron has empty orbitals" when boron only has 1 empty p orbital which is available to accept an electron pair.
- Some students wrongly identified boron as having 5 valence electrons even it is from Group 13. Other students ignored the context of the question and indicated that boron (as an element) has 3 valence electrons and did not indicate how many valence electrons the boron in BH₃ has. A small number of students wrongly stated that boron has no valence electrons as they are all used in bonding. This is incorrect as electrons do not disappear when they participate in bonding.
- Students should avoid explanations such as "boron does not have an octet configuration" or "boron needs 2 more electrons" as these do not clearly indicate that boron can accept a pair of electrons.
- **2(b)(i)** Since B is less electronegative than H, B would develop δ^+ while H would be δ^- .



- Generally well answered.
- Common mistakes made by students include absence of charges, absence of H⁻ as a product of step 1 and absence of lone pair of electrons on the H⁻ nucleophile in step 2.
- A small number of students did not realise that H should have the partial negative charge as indicated by the electronegativity table and did not adhere to the requirement to form a carbocation and hydride ion after the first step. Wrong mechanisms would involve the formation of BH₂⁺ and H⁻ from BH₃ as the first step.
- Students are reminded to show the slow and fast steps for relevant mechanisms which they have learnt in the H2 syllabus and clearly show curly arrows pointing at relevant atoms and not charges.

2(b)(ii) The more stable tertiary carbocation is formed if the electron deficient B atom forms a bond with the doubly bonded carbon with more hydrogen atoms.

The H atom of BH₃ is therefore bonded to the doubly bonded carbon with fewer hydrogens, forming a product which does not follow Markovnikov's rule.

Examiner Comments

- This question was not well answered.
- Many students lack clarity in their answers, such as not being specific about which intermediate carbocation they are referring to and which carbon atom are they referring to.
- Many students did not make reference to the intermediate formed in their mechanism in (b)(i) as required by the question and merely stated difference in positions of the substituents.
- Some students indicated that the more stable carbocation had 2 electron-donating alkyl groups when there were 3. Similarly, there should be 2 instead of only 1 electron-donating alkyl group for the less stable carbocation.
- A small number of students described the electrophile as BH₂⁺ when this species is not formed in the mechanism.



2(c)(i)

or any correct conformations of this stereochemistry.

compound V Examiner Comments

- Students who answered this question incorrectly either did not consider the approach of BH₃ from the top side of the plane or switched the orientation of the given BH₃ molecule and ended up with the Markovnikov's product. Students should note that the choice of where to place the substituents in the product is not arbitrary as you are not drawing both enantiomers in a racemic mixture.
- You can make use of the following augmented reality (AR) tool to help you visualize the process.
 - Scan the QR code below with your phone camera and point it at the Hiro Marker below.
 - Compare the structure of the loaded model with the diagram in your question paper.
 - Touch the screen with 3 fingers to animate the reaction.
 - Once the reaction is complete, press the button at the bottom of the screen to change the orientation of the paper plane and compare it with the diagram in the answer above.





Examiner Comments

- Generally well answered.
- Some students did not realise that **V** and **W** are no longer alkenes and there is no restricted rotation for cis-trans isomerism to occur.
- Some students were not specific, indicating "stereoisomerism" as their answer, which is not accepted as it could refer to either enantiomerism or cis-trans isomerism.

2(d)(i)

OH

Examiner Comments

- Generally well answered.
- Some students did not recognise the hydroboration-oxidation pattern from (a) and gave a structure with a –BH₂ substituent when the use of 'H₂O₂, NaOH' would have converted (stage 2) the –BH₂ to –OH.
 - A small number of students gave a tertiary alcohol as their answer which is not formed as the H atom is not added to the doubly bonded carbon with more hydrogen atoms, according to **b(ii)**.

2(d)(ii)



Examiner Comments

- Common mistakes for organic product of X include missing/extra carbon along the chain or methyl groups, and giving an aldehyde instead of carboxylic functional group. Students are reminded to count all carbons carefully and under strong oxidation conditions, all aldehydes will be oxidised to carboxylic acids.
- Common mistake for organic product of **Y** include missing methyl groups and oxidation of methyl groups to carboxylic acids. Students should note that oxidation of methyl group is only possible under strong oxidation conditions if the methyl group is bonded to a benzene ring.
- **3(a)** Both VSO₄ and $V_2(SO_4)_3$ have giant ionic lattice structure with strong ionic bonds.

The ionic bond strength is dependent on lattice energy (LE)

lattice energy
$$\left| \propto \; \left| \frac{q_+ \, \times \, q_-}{r_+ \, + \, r_-} \; \right. \right|$$

Since V³⁺ has a higher charge and smaller cationic radius than V²⁺ and they have the same anion, the lattice energy of V₂(SO₄)₃ is more exothermic / magnitude of lattice energy of V₂(SO₄)₃ is larger than that of VSO₄. More energy is required to overcome the stronger ionic bonds in V₂(SO₄)₃ and thus it has a higher melting point.

- Students need to be rigorous in learning how to describe the structure and bonding of compounds and how to explain the properties observed. It is insufficient to simply state that "VSO₄ and V₂(SO₄)₃ are ionic compounds". This statement does not clearly illustrate the nature of the "giant ionic lattice".
- Students should use lattice energy to explain ionic bond strength. Students are also reminded to spell "lattice energy" and not merely use abbreviation such as "LE".

- It is also not enough to only highlight the difference in charge of the ions, ignoring the fact that V³⁺ has a smaller ionic radius than V²⁺. Elaborating the effect of ionic charges and radii on lattice energy will make the discussion on lattice energy much clearer.
- It is also important to be clear that lattice energy is an exothermic term. Hence, merely stating that "lattice energy is larger" is ambiguous. It is much clearer to state that "the *magnitude* of lattice energy is larger".
- Many student erroneously quoted charge density in the explanation of ionic bond strength. Do note that there is no charge density term in the lattice energy expression.
- Some students went on to explain the existence of covalent character in ionic compound. Students should note that there is no direct correlation between covalent character in an ionic compound to its melting point.

3(b)(i)
$$VO_2^+ + 2H^+ + e \Rightarrow VO^{2+} + H_2O$$
 $E^{\ominus} = +1.00 V$
 $V^{3+} + e \Rightarrow V^{2+}$ $E^{\ominus} = -0.26 V$

 $E_{cell}^{\ominus} = 1.00 - (-0.26) = +1.26 \text{ V}$ Examiner Comments • This is generally well done.

3(b)(ii)
$$VO_2^+ + 2H^+ + e \Rightarrow VO^{2+} + H_2O$$
 $E^{\ominus} = +1.00 V$

If the battery is allowed to run at higher pH, [H⁺] would decrease and position of equilibrium for the above equilibrium would shift to the left.

 $E(VO_2^+/VO^{2+})$ would become less positive, causing E_{cell} to become less positive.

Examiner Comments

- Surprisingly, quite a lot of students mistakenly related a higher pH to a higher [H⁺]. This shows the need to be clear-minded before making an incorrect judgement that will result in a wrong conclusion.
- Some students made no attempt to be clear in writing which electrode potential they are referring to. A good habit is to write it in the form E^o(VO₂⁺/ VO²⁺).
- There is a need to differentiate between E_{cell} and E°_{cell} . Remember that when the electrochemical cell is no longer at standard conditions, it is more correct to express the cell potential as E_{cell} and not E°_{cell} .

3(b)(iii) Tank **A**: the solution turns from grey (violet-green) to green. Tank **B**: the solution turns from green to blue.

- Many students forgot to consider the species present in the tanks initially which resulted in the mixing of colours. For example, an equal concentration of VO²⁺ and VO₂⁺ in tank B would result in an initial green solution.
- Again, the expressing your ideas clearly is important. Some students chose to indicate the tanks as "cathode" and "anode" instead of "tank A" or "tank B" and left it to the markers to decide. Marks are not awarded for such answer.
- Students are also reminded to always indicate colour *change* from the *initial* colour to the *final* colour. It is insufficient to only give the final colour in each tank.

3(b)(iv) H⁺ ions flow from Tank **A** towards Tank **B**.

To maintain electrical neutrality. As the reaction proceeds, the electrolyte in Tank **A** becomes increasingly positive (due to a more highly positively charged ion being formed) while the electrolyte in Tank **B** becomes decreasingly positive (due to consumption of H^+).

OR To maintain/replenish [H⁺] as it is being used up in Tank B.

Examiner Comments

- It is important to be clear when explaining why H⁺ ions flow from tank A towards tank B. It is not enough to simply state that H⁺ is being used up in tank B without elaborating on the effect of consumption of H⁺ on an imbalance of electrical charges in the solution or on the need to maintain or replenish [H⁺].
- It is also not sufficient to state the need to maintain electrical neutrality without further elaboration on how the charge imbalance were formed in the first place.
- An alternative perspective is to recognise that H⁺ ions are used up in tank B and this causes a concentration gradient of H⁺ ions between tanks A and B. Thus, H⁺ ions diffuse from a region of high H⁺ concentration to a region of low H⁺ concentration.
- Some students associated the built up of negative charge in tank B to the flow of electrons into the electrolyte. Students must note that electrons cannot flow into the electrolyte.
- As oxidation occurred in Tank A, electrons were released into the wire which will then move from tank A to tank B. The species in Tank A, which lose electrons due to oxidation, will become positive, causing Tank A to be increasingly positive. The species in Tank B will undergo reduction by receiving electrons from the electrode in Tank B and Tank B becomes decreasingly positive.

3(b)(v) The porous electrodes would allow liquid to pass through, thus <u>increasing the surface area</u> for contact, allowing the exchange of electrons to occur faster.

Examiner CommentsThis is generally well done.

3(c)(i) $V^{3+} + VO^{2+} + H_2O \rightarrow VO_2^+ + V^{2+} + 2H^+$

Examiner Comments

- This is generally well done. Only a handful of students failed to read the carefully and made the careless mistake of writing the overall equation for the discharging process.
- **3(c)(ii)** $\Delta G^{\ominus} = -nFE^{\ominus}$
 - = (1)(96500)(-1.26)= +1.22 x 10⁵ J mol⁻¹

Examiner Comments

- Surprisingly quite a number of students forgot the relationship $\Delta G^{\theta} = -nFE^{\Theta}$ despite having encountered it many times.
- Since this is a charging process, students are reminded to use the correct E^{\ominus} value.
- There are also students who forgot that the units of ΔG° is J mol⁻¹ or kJ mol⁻¹.
- Additionally, it is important to display the sign for ΔG° .

4(a)(i) The concentration of dissolved NaCl increases linearly as the time of electrolysis increases. *Examiner Comments* Generally well done.

 4(a)(ii) The reactions at the cathode and anode remove water. With less water in the mixture, the concentration of dissolved NaCl increases.
Examiner Comments
Most students noticed from the equations of the reactions at the anode and cathor

Most students noticed from the equations of the reactions at the anode and cathode that water was removed during electrolysis.

- Some went to great lengths to prove that the given reactions will indeed happen. There is no need to do so the questions already told you that those reactions take place.
- Many students incorrectly talked about how "electrolysis of NaCl(aq) causes Cl⁻ to be oxidised to Cl₂, therefore more NaCl(s) will dissolve to increase the concentration of Cl⁻". There is no undissolved NaCl(s) in seawater, what was described above cannot possibly happen.

4(a)(iii) A white solid of NaC*l* will be observed at the bottom of the setup.

Examiner Comments

- A good number of students got this correct.
- From (a)(ii), there is less water in the electrolytic tank and the [NaCl] would increase, as seen from 0 to 90 h. From 90 to 120 h, water is still being lost as electrolysis carries on. By 90 h, so much water has lost that there is insufficient water to completely dissolve the NaCl. At this point, the maximum amount of NaCl remains dissolved, the NaCl that cannot dissolve would precipitate out.
- Common mistakes
 - The question started with "<u>apart from</u> the evolution of gases...". Students should look for observations that are not related to the evolution of gases. A common incorrect answer here would be that the solution turned yellowish-green due to the production of chlorine gas".
 - The question required students to state observations i.e. what is seen. Observations such as pH changes cannot be seen, these have to be tested.
 - Some students gave the observation that the liquid level in the tank would decrease. Take note that generally, we do not comment on the liquid levels as an important observation when there are more important observations. For example, in QA, we do not talk about the level of solution rising when NaOH is added to FA 1 as an observation. Only use that as the observation if you are certain that is the only important observation.

4(a)(iv) A greater proportion of chlorine gas will be produced.

Examiner Comments

- From (a)(ii), due to the loss of water during electrolysis, the concentration of Cl⁻ increases. In your study of electrolysis, you would have learnt that when [Cl⁻] is higher (e.g. in brine), Cl⁻ is oxidised to Cl₂. In this setup, as electrolysis occurs, more water is loss, [Cl⁻] increases, more Cl⁻ will be oxidised to Cl₂ gas.
- Incorrect answers can usually be attributed to students not seeing / understanding the words "composition", "products" and "anode" in the question.
 - Composition would refer to the proportion of various products. Many students simply talked about forming more products *in total* over time, which is the nature of many reactions. We want to know how the proportion of various products change.
 - Some students commented on the quantity of Cl^- ions, but Cl^- ions are not products.
 - Some students talked about products at the *cathode* instead.
- **4(a)(v)** Increasing the concentration of NaOH increases the concentration of the common ion, Na⁺. This causes the position of equilibrium of NaC*l*(s) \Rightarrow Na⁺(aq) + C*l*⁻(aq) to shift to the left, precipitating NaC*l*(s), reducing the concentration of dissolved NaC*l*.

- There were good answers seen.
- Most students get the idea of what is happening, but do not explain their answers sufficiently.
- It is insufficient to talk about "Na⁺ being a common ion" or "Na⁺ exerts a common ion effect". Students need to explain the effect of the common ion on the position of equilibrium.
- Students need to show clearly what equilibrium they are referring to when they say "position of equilibrium shifted left". The clearest way to show this is to write the chemical equation for the equilibrium you are referring to.

- Credit was also awarded for students who gave clear explanations using ionic product and K_{sp}. Though, many who tried to use this approach did not understand the concept well enough to use it properly.
- **4(a)(vi)** 1. The oxidation of OH^- is favoured over the oxidation of Cl^- at the anode since $E^{\ominus}(O_2/OH^-)$ is less positive than $E^{\ominus}(Cl_2/Cl^-)$.

 $Cl_2 + 2e^- \rightleftharpoons 2Cl^- \qquad E^{\ominus} = +1.36 \text{ V}$ $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad E^{\ominus} = +0.40 \text{ V}$

2. The concentration of chloride in solution is significantly decreased, causing $E(Cl_2/Cl^-)$ to become much more positive, preventing Cl^- from being oxidised.

Examiner Comments

- Many students did not realise that part (v) and (vi) involve a new setup where NaOH is added to "the sample of seawater prior to electrolysis". This is not a continuation of the previous electrolysis.
- Given that this solution to be electrolysed is an alkaline solution of NaOH, OH⁻ is the species that is oxidised at the anode, not water. Many students incorrectly discussed the reaction as anode in terms of O₂ + 4H⁺ + 4e⁻ ⇒ 2H₂O E[⊕] = +1.23 V and went on to elaborate on how OH⁻ reacts with H⁺ and cause the position of equilibrium to shift left and E to become less positive.
- The second reason was correctly explained by students who made use of observation 1, which mentioned that [Cl⁻] was very low. Due to the very low [Cl⁻], Cl⁻ will not be oxidised an idea in electrolysis that you should be familiar with.
- Some students talked about Cl₂ reacting with the OH⁻. However, Cl₂ was not formed in the first place!
- **4(b)(i)** Amount of Fe = 0.04(15000)/55.8 = 10.75 mol Amount of O₂ consumed by Fe = 0.75(10.75) = 8.06 mol

Amount of $NaClO_3 = 0.88(15000)/(106.5) = 123.9 \text{ mol}$ Amount of O_2 produced from $NaClO_3 = 1.5(123.9) = 185.9 \text{ mol}$

Overall amount of O_2 produced = 185.9 - 8.06 = 177.8 mol Volume of O_2 produced = 177.8 (24.0) = 4267 dm³ = 4270 dm³ (to 3 sf)

- This question was well answered by many students. They recognised that the net volume of oxygen released is affected by Fe, which consumes oxygen, and NaClO₃, which gives out oxygen.
- Common mistakes would include the following.
 - The contents of the candle weigh 15.0 *kilograms*. Students need to convert it to 15000 g before calculating the number of moles of Fe or NaC/O₃.
 - When calculating the number of moles of O₂ from Fe, many students forgot to multiply the amount of Fe by ³/₄.
 - The question instructed students to ignore the contribution from phosphorus.
 - $\circ\,$ Some students summed up the volumes of O_2 from the equations involving Fe and NaClO_3 instead of subtracting.
 - Some students chose to use pV = nRT to derive the volume at r.t.p., even though they could have used 24 dm³ mol⁻¹. Common mistakes using the ideal gas equation are shown below.
 - Room temperature is 20 °C (293 K), not any other temperature.
 - If p is in Pa, n is in mol, R is 8.31, and T is in K, then the units of V will be m³, not dm³.

4(b)(ii) With 3 bond pairs and 1 lone pair around each P atom, the bond angle should be 107°. The bond angle in P₄ is 60°, leading to increased bond pair-bond pair repulsion, which makes the molecule less stable and more reactive.

Examiner Comments

- This question was not well-attempted because many students did not understand the requirements of the question.
- Many students saw "VSEPR" and went on a long exposition about why the bond angle around a central atom with 3 bond pairs and 1 lone pair should be 107°. The question requires you to recognise the situation presented to you i.e. P₄. Each face of the tetrahedron is an equilateral triangle and the bond angle is 60°. The "VSEPR" is to guide students to discuss the reactivity in terms of concept of electron-pair repulsions, *specifically*, increased bond pair-bond pair repulsions due to the smaller than expected bond angle.





3bp + 1lp bond angle of 107^o is the outcome of the lp-bp and bp-bp repulsions

bond angle in the P_4 structure is forced to be 60° , the bp's are closer than a typical situation with 3 bp and 1 lp. - increased bp-bp repulsion

- It is important to recognise and explain the situation required by the question. Many students tend to see only some words (e.g. VSEPR) and tried to explain something that the question did not ask for.
- Some students recognised that with 3bp and 1lp, the lone pair-bond pair repulsion is stronger than the bond pair-bond pair repulsion leading to the bond angle of 107°, which is smaller than 109.5°. However, they went on to talk about how this makes the molecule unstable. This is not true – many stable molecules with 3bp and 1lp exist. NH₃ is the most common example of this.
- Many students noticed that the P–P–P bond angle is 60° and explained the reactivity in terms of ring strain, angle strain, bond strain. These answers were not accepted because the requirement of the question was to discuss in terms of VSEPR i.e. focus on the repulsion between bond pairs in this case.
- Some phenomenon have multiple perspectives to explain. Some questions are more open in their design and intend to allow a variety of perspectives; others are more specific, testing students whether they are adept at explaining in terms of particular concepts. This question belong to the latter category.
- **4(b)(iii)** P₄, S₈ and Cl₂ are <u>simple covalent molecules</u> with <u>instantaneous dipole-induced dipole (id-id)</u> interactions between their molecules.

The <u>electron clouds of P_4 and S_8 are larger and more polarisable</u> than that of Cl_2 . More energy is required to overcome the <u>stronger id-id interactions in P_4 and S_8 compared to Cl_2 .</u>

- This question was generally well done. Explanations linking the size of electrons cloud of P₄, S₈ and Cl₂ to the strengths of their id-id interactions were clear.
- Many students were excessively long-winded in their answers. Please learn to organise your answers well so that you do not spend a disproportionate amount of time on simple questions like this.
- Some students did not remember that P_4 and S_8 are simple covalent molecules and incorrectly thought them to be giant covalent. You should refer to your Periodic Table 1 lecture notes to understand why.
- The question asked students to use "structure and bonding" the simple covalent structure of the three should be clearly described in your answer

4(b)(iv) 1st ionisation energy of P > 1st ionisation energy of S. The valence electron to be removed from S is a paired 3p electron which experiences additional inter-electronic repulsion, requiring less energy for removal.

 1^{st} ionisation energy of S < 1^{st} ionisation energy of C*l*. More energy is required to remove the valence electron of chlorine which experiences a higher nuclear charge but approximately constant shielding compared to sulfur.

Examiner Comments

- Many candidates did not clearly state that the electron to be removed is the *valence* electron, or indicate exactly which electron is being removed i.e. 3p.
- Note that repulsion exists even between the unpaired 3p electrons in S or Cl. It is because the 4th electron is paired with another electron within the same 3p orbital for S that there is additional repulsion present, thus requiring less energy for ionisation.
- Please note that the first IE trend across a Period needs to be explained in terms of shielding and nuclear charge, as required by the syllabus (stating only effective nuclear charge is not sufficient).
- From the general equation of the first IE, X(g) → X⁺(g) + e⁻, it can be seen that the process involves ionisation of gaseous atoms, X(g). Some candidates gave their answers incorrectly in terms of P₄, S₈, or Cl₂ losing the first valence electron.
- Note that the shielding effect is NOT negligible, it is the <u>increase</u> in shielding effect from S to CI that is negligible (or minimal).
- There are paired and unpaired electrons, but there's no such thing as an unpaired or paired *subshell*. Please use the terms correctly.
- Please use the proper conventions; it is unknown what is being referred to as a "3p³ electron" or "3p⁴ electron". Do not confuse an electronic configuration presentation when you wish to refer to a specific electron in a particular subshell.

4(c)(i)

HO

Examiner Comments

• Mostly well-attempted.

4(c)(ii) Step 1: Br₂(aq)

Step 2: Na(s)

Examiner Comments

- Common errors include Br₂(CCl₄) and NaOH(aq).
- Note that the use of $Br_2(CCl_4)$ will result in a dibrominated product (CH₂BrCH₂Br) and alcohol does not react with NaOH(aq)

4(c)(iii)



- Mostly well-attempted. Common mistakes include missing, or incorrect placement of, lone pair, δ + and/or δ -.
- A two-step (S_N1) mechanism whereby C–Br bond is first broken to generate a carbocation, which is then attacked by the lone pair on the negatively charged O is not accepted, as the primary carbocation formed is unstable. Candidates should propose a one-step (S_N2) mechanism.
- Candidates should read carefully as the instructions were to complete this part on the printed figure.

4(c)(iv) Use an excess of NH₃.

Using an excess of NH_3 increases the probability of ethylene oxide colliding with NH_3 instead of ethanolamine or diethanolamine to form the polysubstituted products.

Examiner Comments

- In their phrasing, some candidates did not clearly show that they understood that the increase in amount of NH₃ used is to favour the reaction with ethylene oxide, so that ethylene oxide has lower chances of colliding with ethanolamine etc. for further substitution.
- Some candidates elaborated on how poly-substitution takes place without addressing how the use of excess NH₃ or limited amount of epoxide reduces the yield of the mono-substituted product (ethanolamine).

4(c)(v) Methanal

Examiner Comments

- Many candidates were unable to give the correct IUPAC name of this aldehyde.
- The reagents and condition used suggest that a carbonyl compound, specifically methanal, undergoes nucleophilic addition in step 1 to yield the cyanohydrin.

4(c)(vi) H₂, Ni, heat OR LiA/H₄ in dry ether *Examiner Comments* Mostly well-attempted.

4(c)(vii) Temperature in chamber **A**: 40 °C Temperature in chamber **B**: 80 °C (**A** cooler than **B**, temperature difference of at least 40 °C)

At a cooler temperature in chamber **A**, larger K_c , the position of equilibrium lies to the right, encouraging ethanolamine to bond with CO_2 to remove CO_2 from the air in the submarine.

At a higher temperature in chamber **B**, smaller K_c , the position of equilibrium lies to the left, liberating CO₂ to be released.

- Some candidates forgot to give the units for the temperatures.
- This part should be answered in context i.e., how the selected temperatures will respectively aid the removal of CO₂ from the air from submarine in chamber A, and aid the expelling of CO₂ from the aqueous ethanolamine solution in chamber B. Just comparing the magnitudes of the K_c without clear reference to the entire CO₂ transfer process or the position of equilibrium is insufficient.
- Do note that both the forward reaction and backward reactions of Fig 4.4 are still taking place within *each* chamber some candidates phrased it as if only the forward reaction is occurring in chamber **A**, and only the backward reaction is occurring in chamber **B**.
- <u>Practical considerations</u>: while the answers for the temperatures were accepted based on the data given in Fig 4.5, some candidates were able to realise that it would be more reasonable to have the chamber temperatures to be below 100 °C (i.e., boiling point of water) so that the aqueous system does not turn gaseous. Furthermore, the lower temperature should not too low, so that the reaction rates (both forward and backward rates in chamber A) would not be too low.
- As data does not exist (or not given) below 20 °C or above 130 °C, candidates should not give values *outside* of the available data set. This is not a question where an extrapolation (of any trend) is needed or applicable.

4(d) Ba²⁺ has a larger ionic radius than Ca²⁺, resulting in Ba²⁺ having a lower charge density and polarising power than Ca²⁺.

 Ba^{2+} distorts the electron cloud of CO_3^{2-} to a lesser extent than Ca^{2+} , leading to less weakening of the covalent bonds within CO_3^{2-} .

More heat energy is required to break the covalent bonds within CO_3^{2-} in BaCO₃, leading to a higher temperature for thermal decomposition.

- An atom / element is not described to have a charge density nor polarising power please refer these terms clearly to the ion Ba²⁺ or Ca²⁺.
- Please note the proper usage of the terms:
 - o distortion of electron cloud of the anion (not distortion of covalent bond), and
 - weakening of the covalent bonds within the anion (some candidates used polarisation of the covalent bond, which leads to the formation of a dipole moment for a particular covalent bond due to the difference in electronegativities of the two atoms making up that bond, and is irrelevant to the phenomenon being described in this context).