2023 Y6 H2 Chemistry Preliminary Examinations Paper 2 Suggested Solutions

1 **(a)** The volatilities of the halogens decrease from chlorine to iodine.

From Cl_2 to I_2, the electron clouds of the halogens become larger and more polarisable. Hence, more energy is required to overcome the increasing strength of the instantaneous dipole–induced dipole interactions between the halogen molecules down the group, leading to decreasing volatility.

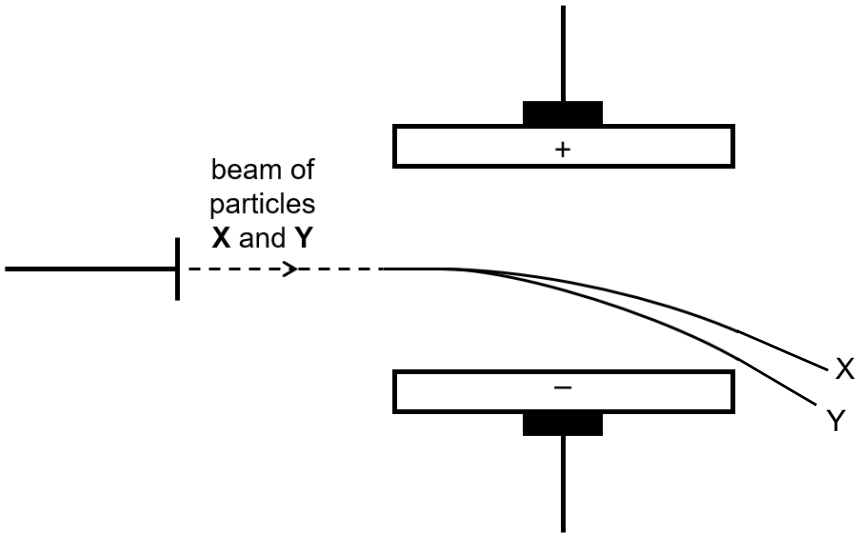
Examiner Comments
- Volatility is the tendency of a substance to evaporate and is related to the intermolecular forces of attraction.
- There were a number of candidates who did not realise that volatility involves intermolecular forces of attraction and **not** covalent bond strength (volatility does not involve separating the molecule into its atoms).
- Terms used should be spelt out in full i.e., "instantaneous dipole–induced dipole interactions", not "id-id".
- Some students talked about the trend in boiling point, which was irrelevant in this question.

(b) **(i)**

	X	**Y**	**Z**
nucleon number	140	<u>103</u>	37
charge	+1	+1	<u>0</u>

Examiner Comments
- Very well done, with a small number of candidates making mistakes most likely due to not reading the question carefully enough.

(ii)



Examiner Comments
- A number of candidates drew the path for Z instead. Do read the question carefully.
- The paths drawn should end outside of the "+" and "–" plates. Please also note that within the electric field, the paths for X and Y are curved, as shown in the above diagram.

- It should be very clear to the examiner that Y deflects to a **larger** extent than X.
- A number of candidates drew a longer horizontal line for X before deviation, with a deflection angle similar to that of Y. Please note that the deviation should start at the same spot.

(iii) nucleon number = 103 = 31 + 35 + 37
There is 1 ^{35}Cl atom in Y.

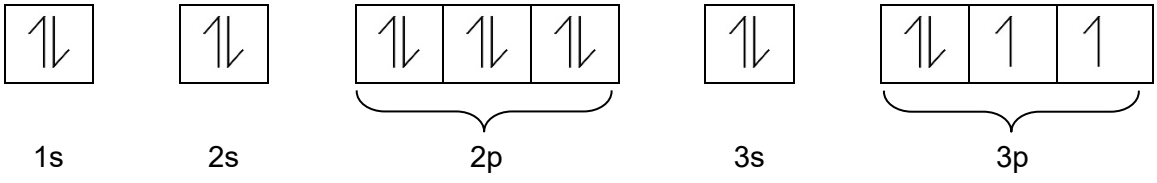
Y is PCl_2^+.
Its shape is bent.

Examiner Comments
- Note that there is one lone pair on the central atom P.

(c) **(i)** $P(g) + e^- \longrightarrow P^-(g)$

Examiner Comments
- Very well done, except some missed out giving state symbols. Note that state symbols should be shown **without** being asked whenever an equation is used to reflect the terms in Energetics e.g., ionisation energy, enthalpy change of combustion, enthalpy change of atomisation, etc

(ii)



Examiner Comments
- Very well done, except some candidates gave the arrangement for the P atom instead of the P^- ion.

(iii) ① Nuclear charge increases from A*l* to C*l* but shielding effect remains effectively constant. Effective nuclear charge increases. Electrostatic attraction between the nucleus and the incoming electron increases, resulting in an increase in the energy released.

Examiner Comments
- Be precise in your answer – "approximately constant" is not the same as "constant".
- The attraction is between the nucleus (not atom) and an **incoming** electron here, *not* with a "valence" electron. Note: P atom has 5 valence electrons, and the incoming electron enters the valence shell.

② The attraction between the nucleus and incoming electron is weakened due to inter-electronic repulsion between this electron and the one already present in the 3p orbital. Hence, less energy is released as the first electron affinity.

Examiner Comments
- Be very clear with the terms used and do not use them loosely or interchangeably.
- A number of candidates were confused and used incorrect terminology: a 3p **orbital** is not the same as a 3p **subshell**.
- Note: "electrons" cannot be *filled up*, "orbitals" cannot be *paired*.
- A "partially filled 3p subshell" does not mean it contains one electron in each of the 3p orbitals – such a phrase just means it can contain between 1 to 5 electrons in total.
- Some phrases implied that inter-electronic repulsion only exists between the incoming electron and the electron in the 3p orbital – note that repulsion exists between inner electrons, as well as between the single electrons in each of the half-filled 3p orbitals.

2 **(a)** Au has a <u>smaller atomic size</u> and thus have more atoms per unit volume. It also has a <u>larger atomic mass</u> than Ba. Hence it has a greater mass per unit volume (i.e. higher density) as compared to Ba.

Examiner Comments
- This question, covering a fundamental concept, was not well done. Many students incorrectly thought that the *atomic radius* of Au and Ba are similar or did not mention about Au having a larger *atomic mass*.
- It is insufficient to just state that "Au has a larger mass per unit volume" without comparing the atomic size and atomic mass of the two metals as the question already mentioned that Au has a higher density than Ba. That answer simply paraphrased the question.
- Many incorrect and lengthy answers went on to talk about shielding effect, effective nuclear charge, charge density etc, all of which are all unrelated to explaining density, a macro physical property which is defined as mass/volume.

(b) max % of Au in amalgam = 100% − 40% = 60%
max mass of Au in 250 g of amalgam = 0.6×250
= 150 g

Examiner Comments
- This question was well done.

(c) conc of Hg vapour
= 1 g of Hg / 1 m^3 of air
= 1 g of Hg / 1.19 kg of air
= 1 g of Hg / 1190 g of air
= $(\frac{1}{1190})$ g of Hg / 1 g of air
= $(\frac{1}{1190} \times 10^6)$ g of Hg / 10^6 g of air
= 840.3 g of Hg / 10^6 g of air
≈ 840 ppm

Examiner Comments
- This question was quite well done.

(d) **(i)** Water prevents / reduces the vaporisation / evaporation of the collected mercury.

Examiner Comments
- This question was well done.
- A handful of students incorrectly thought that mercury dissolves in water or react with water. Such answers received no credit.

(ii) When heated, the mercury in the amalgam vaporises and then condenses on the cooler inner surface of the glass bowl. Then it slides back down to accumulate on the sand to be collected and recovered.

Examiner Comments
- This question was well done with most students recognising that the mercury first vaporises upon heating and then condenses.

(iii) advantage
- low cost/convenient to set up because of the use of simple household items or no need special equipment (e.g. metal apparatus)
- no mercury-contaminated wastewater produced

disadvantage
- the mercury collected will mix with the sand and hence be harder to recover
- the setup is not as airtight as Method I, i.e. mercury vapour has higher chance to escape back into the atmosphere
- when the bowl is removed, mercury can vaporise again whilst collecting the mercury from the sand
- mercury poisoning from re-use of cooking pot used in the extraction for cooking purposes

Examiner Comments
- For full credit, students should substantiate their answers appropriately.
- Most students correctly recognised that method II would be cheaper or only required household items/less specialised equipment which are an advantage for the miners who are often from poverty-stricken communities (this info was given in the question).
- Discussion on scale or efficiency of process were not given credit as the diagrams were labelled to be not drawn to scale and hence insufficient info to draw conclusion on scale or efficiency.

(e) **(i)** $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Examiner Comments
- Most students were able to obtain the correct half-equation from the *Data Booklet*. The clue in the question was in the presence of *oxygen*, in an *aqueous* solution, to give *hydroxide ions*.
- As the question already mentioned O_2 is reduced, students should use the *irreversible arrow* instead of the reversible arrow to illustrate reduction reaction.

(ii) mol ratio $4Au : 1O_2 : 4e^-$
Each Au atom loses 1 e^- to form Au^+.

The oxidation state of Au is +1.

Examiner Comments
- This question was quite well done.
- A handful of students gave the formula Au^+ instead of the oxidation state.

(iii) CN^- is the ligand in D.
The complex anion which is linear would be formed as such: $^-NC\rightarrow Au^+ \leftarrow CN^-$.

D is $[Au(CN)_2]^-$.

Examiner Comments
- Students should realise the ligands are $:CN^-$. Given that it is linear about Au, there are two ligands.
- A handful of students mistakenly wrote Ag (silver) instead of Au (gold).

(f) **(i)** Metallic bond is the electrostatic attraction between a lattice of positive ions and delocalised electrons.

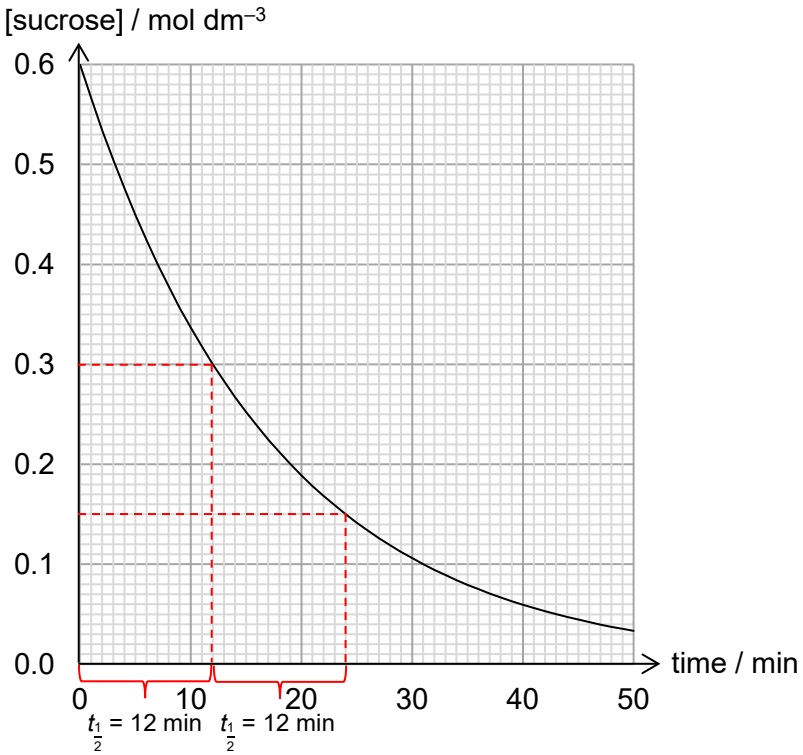
Examiner Comments
- This question interestingly revealed some misconceptions regarding metallic bonding. Some students thought metallic bond is between *one cation* and the sea of delocalised electrons, which is erroneous and showed lack of appreciation that the metallic bonding extends throughout the entire metallic lattice.
- Students need to mention *electrostatic attraction* (not just bond) in their answer and state clearly that this electrostatic attraction is between positive metal ions (not a singular cation) and the sea of delocalised electrons.

(ii) In mercury, poor shielding results in the outermost electrons being held so tightly by the nucleus that it is very difficult (or requires a lot of energy) for the outermost electrons to be delocalised.

Hence, only weak metallic bonds are formed, resulting in mercury being a liquid and not a solid at room temperature.

Examiner Comments
- Most students recognised that the metallic bonds in mercury are weaker due to mercury being a liquid at r.t. and having a lower melting point than other metals.
- Students need to state clearly that it is the *valence or outermost* electrons that are delocalised.
- Wrong concepts include confusing the attraction between the positive nucleus and the valence electrons as metallic bond!
- Some students incorrectly thought that no electrons are delocalised and thus mercury has a simple covalent structure.

3 (a) (i)

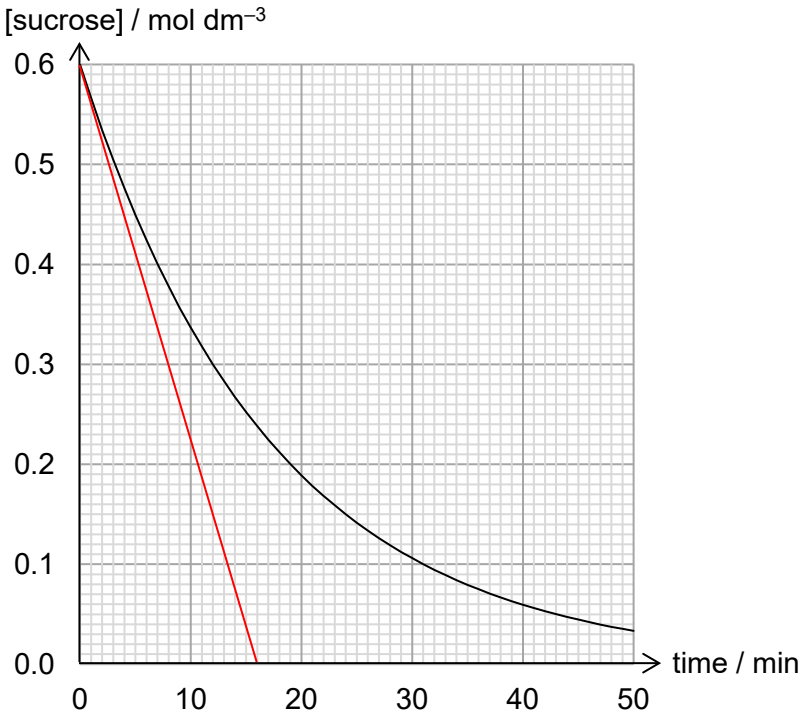


Since half-life is <u>constant</u> at 12 min, order of reaction with respect to sucrose = 1, hence $x = 1$.

Examiner Comments

- Generally well done.
- It is necessary to explicitly state the value of half-life for full credit to be awarded.

(ii)



initial rate of reaction

$= \left|\frac{0.60 - 0.00}{16 - 0}\right| = 0.0375$ mol dm^{-3} min $^{-1}$

Examiner Comments

- A handful of students drew poor tangents. Please consult your tutor if you are uncertain on the drawing of tangents.
- Candidates are reminded to take coordinates that are at least 3 big squares apart to obtain a more accurate reading. You can review your practical notes for this.

(iii) Ratio of the rate of reaction of experiment **1** and **2**
= (0.0375 / 0.0125)
= 3

Comparing expt **2** to **1**, when $[H^+]$ x 3, initial rate x 3 $\Rightarrow$ rate $\propto [H^+]$, hence order of reaction with respect to $H^+ = 1$, $y = 1$.

Examiner Comments

- Generally well done.
- However, candidates are reminded to use present their answers with appropriate statements to explain their working, rather than just a series of mathematical equations. Please avoid the expectation of having the marker interpret your working. The command word in question is “deduce”, requiring some working that exemplified understanding to be shown.

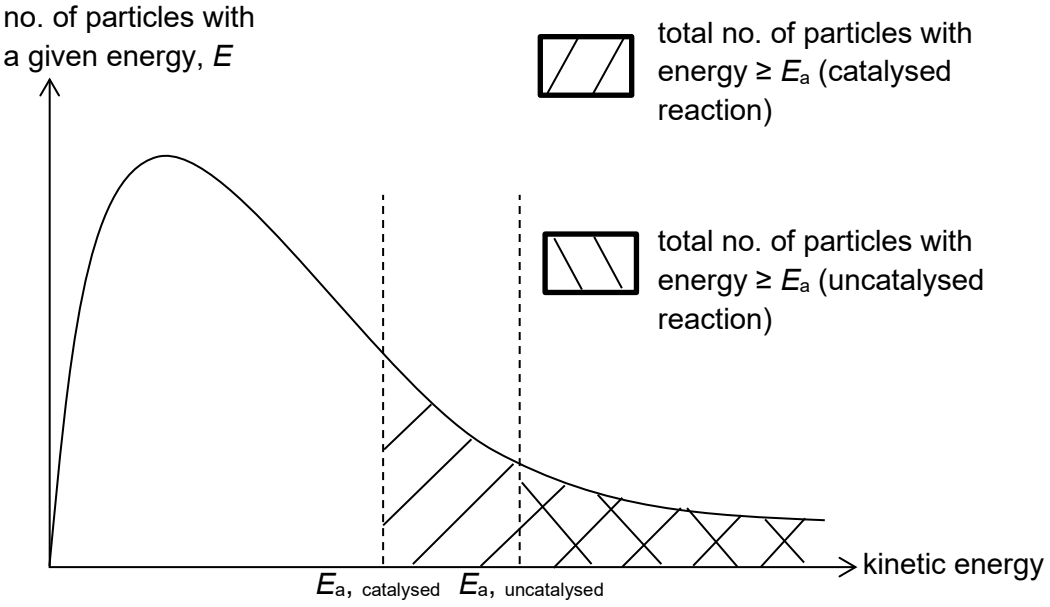
(iv) from **(a)(i)** and **(a)(iii)**; rate = k[sucrose][H^+]
from **(a)(iii)**; initial rate = 0.0125 mol dm^{-3} min^{-1}

(0.0125) = k(0.6)(2.0)

k = <u>1.04 × 10^{-2}</u> mol^{-1} dm^3 min^{-1}

Examiner Comments
- This question was generally well done.
- A small group of students used the $t_{\frac{1}{2}} = \frac{\ln 2}{k}$ equation and the $t_{\frac{1}{2}}$ found from **(a)(i)** to find the value of k. This method is wrong because this is a pseudo first order reaction, hence this equation and the $t_{\frac{1}{2}}$ used are invalid.
- A number of students also failed to use the data from experiment 2, which are the [HCl] and initial rate, as stated in the question.

(b)



A catalyst provides an <u>alternative pathway of lower activation energy</u> ($E_{a,\ catalysed}$) than the uncatalysed reaction. <u>More</u> molecules possess <u>energy greater than or equal to $E_{a,\ catalysed}$</u>, hence <u>the frequency of effective collision increases</u>, and the <u>rate of reaction increases</u>.

A lower $E_{a,\ catalysed}$ also results in a larger rate constant.

Examiner Comments
- A significant proportion of candidates incorrectly stated that catalysts lower the activation energy without the mention of an alternative pathway.
- Candidates who did not have a legend should make reference to the different shaded areas in their explanation. This would allow the increase in number of particles with energy ≥ E_a to be illustrated in the written answer.

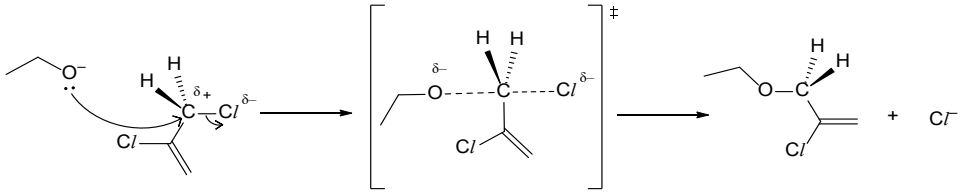
- The legend should describe two kinds of shading – 1 for E_a(catalysed)  and 1 for E_a(uncatalysed)  . It is incorrect to label  for E_a(uncatalysed), as this implies that E_a(catalysed) does not extend to the right side of the graph – this makes no sense at all. Please refer to the notes to revise the shading for Boltzmann distribution.
- Students should use 'higher frequency of effective collisions' instead of merely 'more effective collisions' as 'frequency' has the units of time in it, which is absent in 'more'.

(c) **(i)** *a*: –1, *b*: 3

Examiner Comments

- The question stated that it is a reaction that proceeds via a S_N2 mechanism, which is bimolecular. Students were supposed to deduce the units of the rate constant of the rate equation, rate = k[R–C*l*][$CH_3CH_2O^-$].

(ii)



Examiner Comments

- Students are required to show understanding that the S_N2 mechanism involves a backside attack through the arrows drawn. Essentially, the leaving group and the nucleophile should be at opposite sides of the molecule. Student who failed to draw the arrow (denoting the attack of the nucleophile) towards the <u>opposite</u> side of the C*l* atom were penalised.
- A handful of students are unaware that it is necessary to draw the pentavalent transition state, and with the correct features. Common mistakes include the lack of dipole charges on O and C*l*, positive dipole on central C or O, and lack of transition state sign.
- Some students did not balance the equation with Cl^- as a side product.
- "Slow" and "fast" steps were also commonly seen in the mechanism. Please be reminded that S_N2 mechanism is a <u>one</u> step mechanism.

(iii) The <u>p-orbital of C*l*</u> in **C** <u>overlaps</u> with the <u>π-electron cloud of the C=C</u> bond, causing the <u>lone pair of electrons on C*l*</u> atom to <u>delocalise</u> into the C=C bond. This causes the <u>C–C*l* bond</u> in C to have a partial double bond character and is <u>strengthened</u>. Hence, more energy is required to break this bond. This results in a higher activation energy for the reaction and therefore a smaller value of the rate constant, *k*.

Examiner Comments

- Many students did not provide the complete explanation. Some students stated the delocalisation of electrons without mentioning the overlapping of the p-orbitals with the π-electron cloud, and vice

versa. A handful also used the phrase "resonance-stabilised" to sum up the entire explanation, which is insufficient.

- A common error made by candidates was the incorrect direction of delocalisation where many stated that the "π-electrons in C=C delocalise into the p-orbital of C*l*".
- Some students attributed the stronger C–C*l* bond in compound **C** to the higher s-character of the C–C*l* bond in **C**.

  compound **C** : C_{sp2}–C*l*

  compound **A** : C_{sp3}–C*l*

  This concept is correct, but it is not the biggest contributing factor.
- Some students mentioned that the electron deficient C atom in compound **C** has a lower partial positive charge compared to that in **A** due to the delocalisation of the lone pair of electrons of C*l* into the π-electron cloud of C=C. Again, this is not the main factor attributing to the small rate constant.
- Some students incorrectly claimed that there is delocalisation of electrons in the 2 carbons of C=C bond. Delocalisation is only possible when >2 p-orbitals overlap side-on. Overlapping of 2 p-orbitals is simply the formation of a π-bond.
- Students are reminded to use proper terminology. Orbitals overlap with other orbitals or electron clouds, **not** with (double) bonds nor electrons. Charges can be dispersed or intensified, not stabilised or destabilised.

(iv) The carbocation from the S_N1 reaction of compound **B** is stabilised as the empty p-orbital of the positively charged carbon overlaps with the π-electron cloud of the C=C bond. The π electrons delocalises into the empty p-orbital dispersing the positive charge on the carbocation, hence stabilising it.

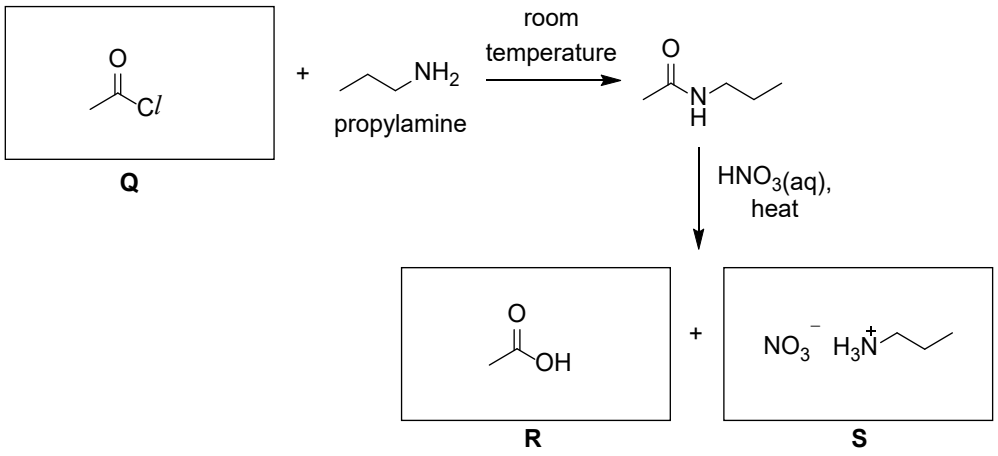
For S_N2, the presence of bulky C*l* atoms bonded to the electron deficient carbon causes the approach of the nucleophile to be sterically hindered.

Examiner Comments

- It is insufficient to merely state that there is steric hindrance as the question already indicated that there is a steric effect. Students need to specify which bulky groups are sterically hindering the attack of the nucleophile.
- Some students incorrectly stated that electronegative C*l* atom disperses the positive charge on the C^+. An ***electron-withdrawing*** C*l* would *intensify* the positive charge instead of *dispersing* it.
- Similar to **(c)(iii)**, incomplete explanation for overlapping of orbitals and delocalisation of electrons were provided.
- Some students also incorrectly indicated that electrons were delocalising from the p-orbital of the carbon with positive charge to the π-electron cloud of C=C bond. However, there is no electron in the empty p-orbital of C^+.
- Students should only claim that the $–CH=CH_2$ group is electron donating (to the C with the partial positive charge) if they justify that this is possible due to p-orbital of the positively charged carbon overlapping with the π-electron cloud of the C=C bond, hence allowing the π electrons to delocalise into the empty p-orbital.
- Students should not suggest that C*l* atom is "electron-donating"

since C*l* is electronegative (compared to C). Instead, students should explain that due to overlap between the empty p-orbital of the positively charged carbon with the p-orbital of the C*l* atom, the lone pair of electrons on C*l* delocalises into the empty p-orbital.

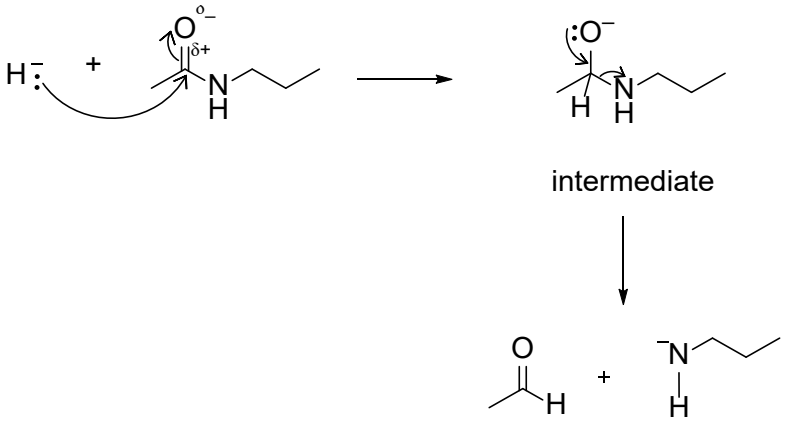
4 **(a)**



Examiner Comments

- Many students were able to identify **Q** as ethanoyl chloride, and that **R** and **S** are the products of amide hydrolysis.
- However, since HNO_3 was used for amide hydrolysis, the products would be formed in an acidic medium. Hence, the amine product will be protonated and with NO_3^- as the counteranion. The most common mistake was omitting the NO_3^- anion. Some students were also careless in the number of H atoms on the protonated amine.
- Another common mistake was identifying ethanoic acid as **Q**. Note that when a carboxylic acid reacts with an amine, a salt and water is formed, i.e., this is a neutralisation reaction. This condensation reaction occurred without acid catalysis and requires an acyl chloride.

(b)



Examiner Comments

- Many students showed an understanding of the mechanism being described, but were careless in drawing the arrows, lone pairs or partial charges.
- Note that arrows must start from (lone pair or bond) and point to (atom or

bond) the correct positions.

- In the first step, an arrow points from the lone pair on H^- to the $\delta+$ C atom on the amide, hence forming a C–H bond in the intermediate. In the second step, an arrow points from the lone pair on O^- to the C–O bond, reforming the C=O bond. A second arrow points from the C–N bond to the N atom, thus the C–N bond breaks.

(c) **(i)** $CH_3CH_2CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2CH_2NH_3^+ + OH^-$

Examiner Comments

- This question was generally well attempted, although some students used → instead of ⇌. Note that since propylamine is a **weak** base, it ionises only partially in water, hence ⇌ should be used.

(ii) $pOH = -\lg\sqrt{4.7\times10^{-4}\times1.3}$

$= 1.606$

$pH = 14 - 1.606$

$= 12.4$

Examiner Comments

- This question was generally well attempted.

(iii) $n_{HCl} = 0.025 \times 1.3 \times ½ = 0.01625$ mol

$V_{HCl} = 0.01625 / 0.80 = 0.02031\ dm^3 = 20.3\ cm^3$

$pH = -\lg\frac{10^{-14}}{4.7\times10^{-4}} = 10.67 = 10.7$

Examiner Comments

- Many students recognised correctly that a buffer with maximum buffering capacity is obtained at the half equivalence point of this titration. From the Henderson- Hasselbalch equation, $pOH = pK_b$ since $[CH_3CH_2CH_2NH_3^+] = [CH_3CH_2CH_2NH_3]$.
- A number of students incorrectly answered that V was the equivalence point volume, instead of half of the equivalence point volume.

(iv) When H^+ is gradually added to the buffer solution, it reacts with $CH_3CH_2CH_2NH_2$. Therefore, $[CH_3CH_2CH_2NH_2]$ decreases, concentration of $CH_3CH_2CH_2NH_3^+$, increases and the position of equilibrium shifts slightly towards the left. Since the ratio of the amine to its conjugate acid remains relatively constant, pH remains unchanged.

Examiner Comments

- This question was poorly attempted. Students are reminded to read the question carefully and use their answer in **(c)(i)**, i.e. $CH_3CH_2CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2CH_2NH_3^+ + OH^-$.
- In this buffer solution, there is a large reservoir of the unreacted amine, $CH_3CH_2CH_2NH_2$ (B) and its conjugate acid, $CH_3CH_2CH_2NH_3^+$ (BH^+). On addition of a small amount of acid, the amine present should react with the added acid:

$$CH_3CH_2CH_2NH_2 + H^+ \rightarrow CH_3CH_2CH_2NH_3^+$$

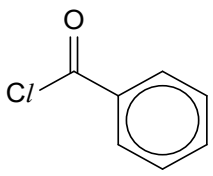
decreasing [B] and increasing $[BH^+]$. Hence the position of

equilibrium of the equation in **(c)(i)** will shift to the left (not right).
- Incomplete answers did not account for the very slight shift in the position of equilibrium, and thus the relatively constant pH.
- Many incorrect answers stated that the H^+ from HC*l* would react with OH^- from the hydrolysis of the amine. This is incorrect. The acid reacts with the large reservoir of the amine as OH^- is present only in very low concentrations.
- Other incorrect answers include simply defining a buffer, or restating the question.

5 **(a)** Oxybenzone absorbs radiation over a larger range of wavelengths because the π electrons in oxybenzone are delocalised over a larger number of atoms resulting in greater extent of delocalisation. Hence oxybenzone is a better choice for sunscreen because it absorbs both UVA and UVB radiation whereas compound **U** absorbs only UVB radiation.

Examiner Comments
- It was necessary for students to **compare** the structures of oxybenzone and compound **U** to account for the greater extent of delocalisation of π electrons in oxybenzone. Many students only referred to the structure of oxybenzone.
- Due to continuous side-on overlap of p orbitals in oxybenzone, the π electrons are able to delocalise over the C atoms in the benzene rings and C=O group, O and N atoms while in compound **U**, π electrons are only able to delocalise over the C atoms in the C=C and C=O groups, O and N atoms. Hence, the π electrons in oxybenzone are delocalised over a larger number of atoms.
- While majority of students were able to identify oxybenzone as the better sunscreen, many explained it as a result of the wide range of wavelengths, without addressing whether the range of wavelengths is suitable i.e. whether it protects against UVA and UVB. It is important to make use of contextual information on the wavelengths of UVA and UVB radiation to suggest why oxybenzone is better. Students are reminded to consider contextual information given and apply them in their answers where relevant, especially for data-response questions.
- A handful of students stated that 'oxybenzone had 2 benzene rings, whereas **U** had none' as their reason for different extents of delocalisation. However, having benzene rings is not the criteria for delocalisation. Delocalisation can still happen across C=C and C=O double bonds, as well as the O and N atoms involved.
- This is a two-part question. A handful of students only answered the first but not the second part of the question, failing to identify which sunscreen was better.

(b) **(i)**



Examiner Comments
- Generally well done.
- Students are reminded that electrophilic substitution (Friedel-Crafts acylation) of an arene occurs with an acyl halide, not with a carboxylic acid.

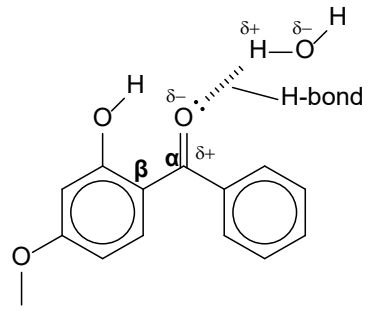
(ii) Test: Add 2,4-DNPH to each sample placed in separate test tubes.

Observation:
For 3-methoxyphenol, no orange ppt formed.
For oxybenzone, orange ppt formed.

Examiner Comments

- A popular incorrect test was to use Tollens' reagent. Note that Tollens' reagent is used to identify aldehydes. The ketone group present in oxybenzone does not react with Tollens' reagent.
- A small handful of students were unfamiliar with what 2,4-DNPH represents, 2,4-**d**i**n**itro**p**henyl**h**ydazine.
- Students are reminded to present the negative observation clearly, i.e. "No orange ppt formed". Answers like "No reaction", "no observation" or "no change" were not accepted.
- No credit was given for writing "orange solution" or "orange compound", as these do not describe the observation that a ppt was formed.

(c) **(i)**



Key drawing points

- dipoles on O and H atom of water, and O/ H on oxybenzone
- lone pair involved in hydrogen bond
- label "hydrogen-bond"

Examiner Comments

- While most students knew the correct interaction formed between oxybenzone and water, many did not include the essential stated in the "key drawing points". This is a standard requirement for drawing hydrogen bonds, students need to learn it well.
- A small handful of students labelled the bond as an ion-dipole interaction. Students are reminded that ion-dipole interactions should involve at least one ion (with full positive or negative charge).

(ii) At high temperatures, the intramolecular H-bonds in oxybenzone can be overcome. Hence oxybenzone would be able to form more extensive H-bonds with H_2O, increasing its solubility in water.

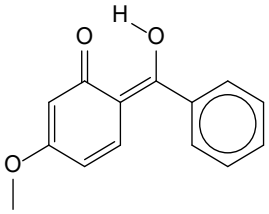
Examiner Comments

- Many students did not make use of the information given about the ease of rotation about the **α**−carbon and **β**−carbon bond to provide an explanation for the increased solubility.
- The restricted rotation about the α−C and β−C bond promotes the intramolecular H-bond between the –OH and C=O groups to form. At high temperatures, there is greater kinetic energy, allowing the intramolecular H-bonding to be overcome. The free rotation about the bond then moves the two groups further apart.
- From **(c)(i)**, Oxybenzone is able to form H-bonds with water even at low temperatures. It is important to recognise that at high

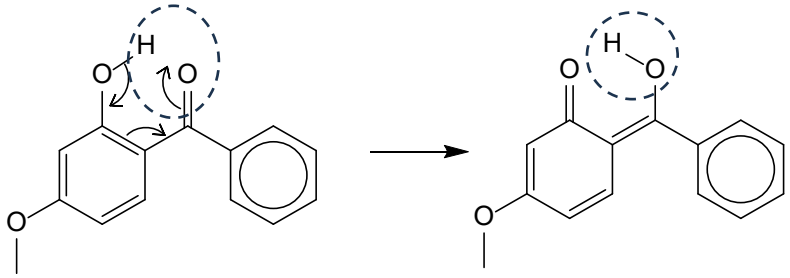
temperatures, oxybenzone can form <u>H-bonds (more extensive H-bonding)</u> with more water molecules, causing its increased solubility.

- A handful of students wrongly described oxybenzone forming 'stronger H-bonds with water'. It is the number of H-bonds with water that increase (more extensive), not the strength of the H-bonds.
- Steric factor is of low significance in this context as the groups involved in H-bonding are at the terminal ends of the molecule and are highly exposed.

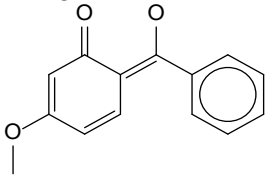
(d)



Examiner Comments

- 

There were a handful of students who interpreted incorrectly interpreted the arrow pushing in the circled region. The arrow is drawn from the C=O bond to the space between O and H atoms, this meant that the π electrons in the C=O moved to form a single bond with H as seen in the product. Students who thought that the π electrons moved to the O atom and drew



were not given credit as they did not account for the H atom.

(e) **(i)**

$$Zn(s) + H_2O(g) \rightleftharpoons ZnO(s) + H_2(g)$$

initial amount / mol	2.60	2.60	0	0
change in amount / mol	−2.58	−2.58	+2.58	+2.58
equilibrium amount / mol	0.02	0.02	2.58	2.58

partial pressure of H_2 at equilibrium = $\left(\frac{2.58}{0.02 + 2.58}\right)$ x 10

= <u>9.92 atm</u>

Examiner Comments

- The determination of equilibrium amounts was well done.
- Partial pressure of gas X = $\left(\frac{\text{amount of gas X}}{\text{total amount of } \textbf{gases} \text{ in mixture}}\right) \times P_{total}$

  There was a surprisingly large number of students who mistakenly included the amount of solid species, Zn and ZnO in the calculation of partial pressure.

(e) **(ii)** $K_p = \frac{p_{H_2}}{p_{H_2O}}$

$= \frac{\left(\frac{2.58}{2.60}\right) \times 10}{\left(\frac{0.02}{2.60}\right) \times 10} = 129$

Examiner Comments

- Students are reminded that solid species should not be included in the K_p expression and that K_p is expressed in terms of partial pressures instead of concentrations.
- Students are reminded to avoid writing p[H_2] or [p H_2] as square brackets are used to refer to molar concentration in Chemistry.

(iii) At lower temperatures, <u>position of equilibrium shifts right</u> to <u>favour</u> the forward <u>exothermic</u> reaction that releases heat, <u>increasing the yield</u> of zinc oxide.

Examiner Comments

- A handful of students did not recognise that $\Delta H < 0$ meant an exothermic forward reaction.
- Some students suggested that rate will decrease because of the decrease in temperature. While this is true, it will not lead to a lower yield of ZnO. It will only take a longer time to achieve a higher yield of ZnO.

6 **(a)** number of π electrons in styrene: 8

number of π electrons in acrylonitrile: 6

Examiner Comments

- Most students were able to recognise that styrene contained 8 π electrons; 6 π electrons from the benzene ring and 2 π electrons from the C=C bond.
- Few students were able to correctly deduce the number of π electrons in acrylonitrile. In acrylonitrile, the C=C bond contains 2 π electrons and the C≡N contains 4 π electrons, giving a total of 6 π electrons.

(b) **(i)** $\Delta H = \sum$ BE of bonds broken in rxts – $\sum$ BE of bonds formed in pdts

= BE(C=C) – 2BE(C-C)

= 610 – 2(350)

= <u>–90.0 kJ mol^{-1}</u>

Examiner Comments

- This question was poorly done. Many students possibly interpreted the BE value of C=C from the *Data Booklet* incorrectly which resulted in calculating an incorrect answer of "+260 kJ mol^{-1}" obtained by the working of (610 – 350). Note that the BE(C=C) = +610 kJ mol^{-1} refers to the energy required to breaking of <u>both</u> the σ and π bond of the C=C bond.

(ii) Entropy is a <u>measure</u> of <u>disorderliness</u> of the system. The more disordered the system is, the larger its entropy.

Examiner Comments
- This question was well done.
- Note that entropy is <u>not</u> a quantity directly equal to the number of possible arrangements of particles / number of ways energy is distributed.

(iii) There is a decrease in entropy because there is a <u>decrease in number of particles</u>, and hence a decrease in number of ways to arrange the particles and their energies.

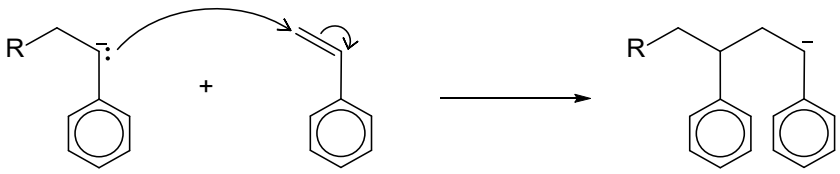
Examiner Comments
- This question was well done.
- Note that explanations involving breaking / formation of bonds do not quite pinpoint the key contributor of entropy change, in this case, the number of particles.

(b) **(iv)** $\Delta G = \Delta H - T\Delta S$

At high temperatures (i.e. $T > \frac{\Delta H}{\Delta S}$), <u>$\Delta G > 0$ because the positive $-T\Delta S$ outweighs the negative ΔH</u>.

Examiner Comments
- This question was well done.
- Students are reminded to use the modulus sign if they are trying to compare relative magnitudes. For example, a statement of "$-T\Delta S$ is more positive than ΔH" is not meaningful in this context, because the $-T\Delta S$ term is always positive and thus always more positive than the negative value of ΔH.
- Explanations regarding a shift in position of equilibrium were not valid as an equilibrium reaction is not being examined in this question.

(c) **(i)**



Examiner Comments

- This question was well done.

(c) (ii) The intermediate from styrene is stable, whereas the intermediate from acrylonitrile is unstable.

For the intermediate from styrene, the empty p orbital of the positively charged carbon overlaps with the π electron cloud of the benzene ring. π electrons from the benzene ring are able to delocalise into the empty p orbital, dispersing the positive charge, hence stabilising the intermediate.

For the intermediate from acrylonitrile, the −CN group is electron-withdrawing and therefore further intensifies the positive charge on the positively charged carbon, hence making the intermediate even less stable.

Examiner Comments

- Most students were able to correctly identify the relative stability of the intermediates.
- Many students gave incomplete answers in explaining the stability of the intermediate from styrene. Key terms involving the orbital overlap, delocalisation of π electrons and dispersal of charge must be clearly stated.
- Several misconceptions seen in the answers need to be corrected:
  - Many students referred to the positively charged carbon as the "carbocation", which is not accurate as the term "carbocation" refers to the entire species containing a positive charge on a carbon atom.
  - Delocalisation is actually possible in the intermediate of acrylonitrile as the empty p orbital of the positively charged carbon can overlap side-on with a C–N π bond, which allows π electron delocalisation. However, this is expected to be a small effect to be neglected due to the high electronegativity of nitrogen making this delocalisation less effective. This means that the electron-withdrawing inductive effect of the –CN group must be considered as the significant destabilising factor, which was absent in a number of answers.
  - Some answers said that "π electron delocalisation is more extensive in the intermediate of styrene as there are more (6) π electrons in benzene than in the intermediate of acrylonitrile (4)". Firstly, due to perpendicular arrangement of π bonds in the –CN group, only 2 π electrons can potentially participate in delocalisation. Secondly, this comparison is invalid here. The number of π electrons is a contributing factor only if there are no other differences in the two π systems compared, e.g. between CH_2=CH–CH_2^+ and CH_2=CH–CH=CH–CH_2^+ (the latter is more stable). If the length of the π system was always a significant factor, then the phenoxide ion would be deemed to be more

stable than the carboxylate ion (which is <u>not</u> true). From these examples, we can see how the presence of a highly electronegative atom can influence the stability of a π system. Therefore, one must consider carefully the differences in the π systems compared to determine the significant factors influencing their stability.

(d) <u>When two radicals of short chain lengths terminate</u>, they produce a short polymer chain. <u>When two radicals of long chain lengths terminate</u>, they produce a long polymer chain.

OR

The radical mechanism produces <u>radicals of different chain lengths</u> which <u>randomly combine/ terminate</u> to form polymers of different chain lengths.

Examiner Comments

- This question was fairly well attempted. To account for the wider distribution of polymer in chain lengths, students should suggest why polymers of both short chain length and long chain lengths are formed in the radical mechanism. Good answers clearly showed understanding that at an earlier stage of propagation, shorter chain radical intermediates can combine (i.e. terminate) randomly to form shorter polymer products, and radical intermediates can also continue to extend in length before combining with another radical to form longer polymer products.
- Explanations accounting for the narrower range of polymer size in the anionic mechanism were not always correct, but ignored as the anionic mechanism was not fully explained in the question. It would suffice to appreciate that the combination of two anionic growing chains is not possible due to repulsion beween anions.