B1(a) $K_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^{+}]}$

B1(b)(i) Assume the concentration of Ag^+ = concentration of SCN^- = 0.045 mol dm^{-3}, or
Assume 25.00 cm^3 SCN^-(aq) was required for titration,
(Assume a titre volume between 20.00 cm^3 – 25.00 cm^3)

Amount of Ag^+ = $\frac{25}{1000}$ x 0.045 = 0.001125 mol
Amount of SCN^- in 25.00 cm^3 = 0.001125 mol
Amount of SCN^- in 250 cm^3 = 0.001125 x 10
= 0.01125 mol
Mass of KSCN(s) = 0.01125 x (39.1 + 32.1 + 12.0 + 14.0)
= 1.0935
= 1.09 g

Examiner's Comments

- Many students did not explicitly state the key assumption required to *calculate* the suitable mass of KSCN to be used.
- After calculating the amount of SCN^- in the titre volume assumed, many students did not scale up to find the amount of SCN^- in 250 cm^3 of solution in the volumetric flask. This is stated as a requirement in the question – "You are to prepare a suitable concentration of KSCN solution *in a 250cm³ volumetric flask* that is…" Please learn to read the question properly and answer the question!
- Note that the amount of Fe^{3+} at equilibrium is irrelevant in this calculation. SCN^- reacts with all the Ag^+ present. Once all the Ag^+ is consumed, the excess drop of SCN^- added with reacts with Fe^{3+}, changing the colour of the solution, indicating the end point.
- Also, since the solution in the conical flask being titrated does not contain any Ag solid, there is no shifting of the position of equilibrium when the titration is carried out.

B1(b)(ii)

1. Using an electronic mass balance, weigh accurately about 1.09 g of KSCN(s) in a dry and clean weighing bottle.
2. Quantitatively transfer KSCN(s) from the weighing bottle to a 100 cm^3 beaker. Rinse the weighing bottle a few times with small volumes of deionised water and transfer all washings into the beaker.
3. Dissolve the KSCN(s) in the 100 cm^3 beaker.
4. Transfer the solution from the beaker quantitatively into a 250 cm^3 volumetric flask with the aid of a funnel and glass rod.
5. Make up to the 250 cm^3 mark using more deionised water, use a dropper when nearing the mark.
6. Stopper the volumetric flask and shake the volumetric flask well to ensure a homogeneous solution is obtained.

Examiner's Comments

- You are advised to write your procedure in clearly numbered steps.
- Quantitative transfer

- It is the important that quantitiative transfer of KSCN(s) occurs from the weighing bottle to the beaker and from beaker to volumetric flask. This ensures that the entire mass of KSCN is dissolved in the volumetric flask.
- A handful of students described the quantitative transfer process poorly. The ideas of "transferring" and "rinsing" should be clearly described.

- Students are reminded to consider carefully their choice of words. For example, "fill up the volumetric flask with deionised water ***to the 250cm^3 mark***" does not mean the same meaning as "fill up the volumetric flask with deionised water". Please revise and be familiar with common terms used to describe these processes.
- Some common mistakes made are highlighted in the following table and explanations of why these should not be done are included. Please take note of these and do not repeat these mistakes.

Common mistake	Why this should not be done	What should be done
Many students take a shortcut by directly transfer the solid from weighing bottle to volumetric flask.	1. The mouth of the volumetric flask is very narrow. It is very likely that the student will spill the solid during transfer. 2. It is very difficult to agitate the mixture sufficiently to dissolve a solid in the volumetric flask. This is why only solutions, not solids, are added to the volumetric flask.	After weighing the solid in the weighing bottle, dissolve the solid in a beaker before transferring the solution into the volumetric flask.
Many students tried to dissolve the solid in the weighing bottle.	The weighing bottle is very small with very little space to stir with a glass rod to dissolve the solid. Very often, some of the solution is spilt, leading to loss of the chemical.	Transfer the solid from the weighing bottle to a beaker before trying to dissolve it.
Some students used the method of difference to weigh the solid i.e. 1. Measure mass of empty weighing bottle with solid 2. Measure mass of emptied weighing bottle. 3. Take the difference of the two values to obtain the actual mass of solid used. This method is problematic when students rinse the emptied weighing bottle with water before measuring the mass of the emptied weighing bottle.	Rinsing the emptied weighing bottle effectively transfers all the solid into the beaker, making the use of the reweighing method unnecessary. More importantly, if the emptied weighing bottle is rinsed before its mass is measured, the mass would include water left over from the rinsing, making the mass calculated extremely unreliable.	If you wish to use the method of difference, you should not rinse the weighing bottle with water. In this experiment, it is easier to use the tare method.

B1(c) 1. During titration, as SCN^- is added, Ag^+ is removed. The position of equilibrium may shift left so as to counteract the change. Ag reacts with Fe^{3+}, producing more Ag^+. This would lead to inaccurate titration results.

2. The actual volume of solution pipetted would be less than 25.0 cm^3 since the Ag(s) occupies some of the volume. This would lead to inaccurate titration results.

Examiner's Comments

- Very few candidates scored both marks in this part due to various misconceptions. The most prevalent misconception involves understanding how a solid affects (or does not affect) the position of a system in equilibrium. Students should consult their tutors clarify this concept if they are unsure.
- Other common problems / misconceptions are described below.
  - Many students failed to understand that with or without the Ag(s) accidentally pipetted, the mixture being pipetted is already at equilibrium and its concentrations are the equilibrium concentrations.
  - The Ag(s) is present as part of the original equilibrium mixture. Even if some of it is pipetted, the mixture is <u>still</u> at equilibrium. Many students incorrectly thought that the additional Ag(s) disturbed the system at equilibrium and went on to describe how the position of equilibrium shifted in response.
- Students have to show understanding that the equilibrium is disrupted as the titration takes place as *the Ag+ is being removed by reaction with SCN^-*, so the backwards reaction can take place, now that Ag(s) is present in the sample that was pipetted, producing more Ag^+.
- A handful of students suggested that Ag(s) may interfere with the end point colour change observation. The solution before end point is originally cloudy (due to the solid AgSCN produced), so that small amount of Ag(s) accidentally transferred is unlikely to cause any significant colour differences.
- Students are advised to communicate their ideas clearly. A reduction in the volume of solution pipetted does not change the concentration of the ions present in the solution. However it does mean that fewer moles of Ag^+ are being pipetted and titrated. So it leads to a lower ***calculated [Ag^+]*** based on the titration data instead.

B1(d) Yellow-green → Orange (yellow + red) or Blood red

Examiner's Comments

- When asked for the colour <u>change</u> at end point, students are expected to state the colour just before end point and the colour at end point.
- Students should consider the colour of the species present in the mixture before end point and at end point, then consider the overall colour.

Species present just before end point	**Species present at end point**
Fe^{2+} (pale-green), Fe^{3+} (yellow), Ag^+ (colourless), AgSCN (white solid)	Fe^{2+} (pale-green), Fe^{3+} (yellow), AgSCN (white solid), $FeSCN^+$ (blood red)

B1(e)

	$Fe^{2+}(aq)$	+	$Ag^+(aq)$	⇌	$Fe^{3+}(aq)$	+	Ag(s)
Initial conc / mol dm^{-3}	$\frac{0.1}{2}$		$\frac{0.1}{2}$		0		
Change in conc / mol dm^{-3}	–x		–x		+x		

Equilibrium conc / mol dm^{-3}	0.045	0.045	x

x = 0.05 – 0.045 = 0.005 mol dm^{-3}

$K_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^{+}]} = \frac{0.005}{(0.045)^2}$ = 2.47 mol^{-1} dm^3

Examiner's Comments

- "25.0 cm^3 of 0.100 mol dm^{-3} Fe^{2+} solution is mixed with 25.0 cm^3 of 0.100 mol dm^{-3} Ag^+ solution in a volumetric flask."
  Many students did not consider how mixing (doubling of the volume) results in dilution. The initial $[Fe^{2+}]$ and $[Ag^+] = \frac{0.1}{2}$ mol dm^{-3} and not 0.1 mol dm^{-3}.
- Note that it is stated in the question that "The concentration of Ag^+ in the equilibrium mixture was verified to be 0.045 mol dm^{-3}." i.e. equilibrium $[Ag^+]$ = 0.045 mol dm^{-3}. With the initial concentrations known, the change in concentrations and hence equilibrium $[Fe^{2+}]$ and $[Fe^{3+}]$ can be determined.
- It is conceptually wrong to think that equilibrium $[Ag^+] = [Fe^{2+}] = [Fe^{3+}]$ simply because they are in a 1:1:1 ratio in the chemical equation. Rather, it is the change in concentration of $[Ag^+] : [Fe^{2+}] : [Fe^{3+}]$ = 1:1:1.

B1(f) According to Le Chatelier's Principle, at higher temperature, the position of equilibrium shifts left to favour the backward endothermic reaction that absorbs heat. Hence, the concentration of Ag^+ in the equilibrium mixture will increase.

Examiner's Comments

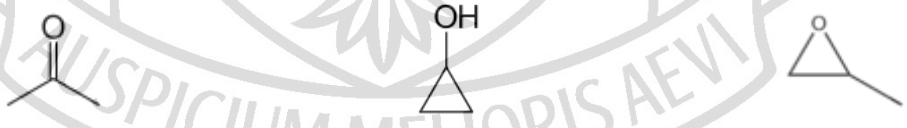
- Generally well done.
- Some students were confused with the symbolic representations, e.g. $\Delta H < 0$, interpreting this as an endothermic reaction rather than an exothermic reaction.

B2(a) Constitutional isomers have the same molecular formula but different structural formula i.e. different arrangement of atoms.

Examiner's Comments

- Generally well-done. Students who wrote 'same chemical formula' instead of 'same molecular formula' were not given credit. This is because for organic compounds, chemical formula includes empirical formula. Students who wrote 'same structure' instead of 'same structural formula' were not given credit. An example is that the cis and trans isomers have the same structural formula but different structures.

B2(b)



P **Q** **R**

Examiner's Comments

- Some students misread the question and did not show skeletal formula but condensed structural formula.
- In the drawing of skeletal formula, the H atoms attached to C should not be drawn, but the H atom attached to O atom must be shown in **Q.** Similarly, in **R,** the $-CH_3$ group should not be drawn.
- Some students gave the same structures for both **Q** and **R**.
- Quite a number of candidates gave the structure of **P** as 

. Such a structure is inaccurate. Students should draw **P** as shown i.e. in a trigonal planar manner.
- For **Q**, some students drew the bond to be situated in the middle of O and H, hence not correctly indicating that it is a C–O bond.

B2(c)(i) 4 electron pairs

Examiner's Comments

- Please read the question carefully. The question did not ask for the number of lone pairs on O atom but the number of *electron* pairs which includes both bond pairs and lone pairs.

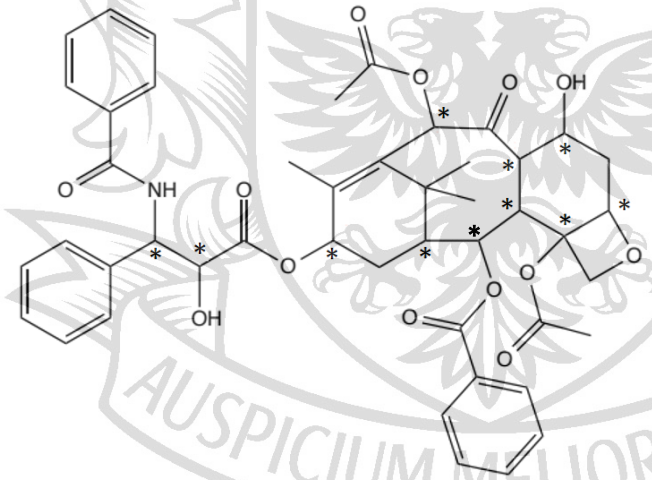
B2(c)(ii) 90°

The ring structure causes the bond angle to be smaller than the expected 105° (2 lone pairs and 2 bond pairs) and nearer to that of an angle in a square.

Examiner's Comments

- Most students were not able to deduce from the given structure of oxetane, a four-membered ring / cyclic compound, that the C–O–C bond angle would deviate greatly from the ideal case of 105° and approach that of the angle in a square. (However, do note that oxetane is not a planar molecule as all the atoms in the ring is sp^3 hybridised.)

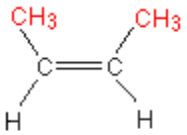
B2(c)(iii) 11



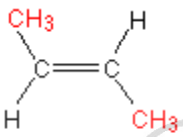
Examiner's Comments

- There was a variety of answers to this but a large majority were able to identify the correct number of chiral carbons.

B2(d)



cis-but-2-ene



trans-but-2-ene

There is <u>restricted rotation</u> at the C=C bond and <u>each C</u> of the C=C bond is <u>bonded to two different groups</u>. Hence these are two different compounds.

Examiner's Comments

- The cis and trans isomers were well drawn. Please clearly show that the C atoms of the C=C bond are trigonal planar for cis-trans isomers. Vertical (or right-angled) bonds were not accepted.
- The explanation lacked clarity for most students. Students often forgot that there are two criteria to be satisfied for cis-trans isomerism and often just quoted one of them. The answers were often poorly phrased; phrases like 'restricted movement', '2 different groups attached to the C=C bond' were incorrect.
- No credit is given to any structure that only has "C" drawn in i.e. missing out the attached "H".

B3(a)

$$pV = nRT \quad \Rightarrow \quad pV = \frac{m}{M}RT \quad \Rightarrow \quad pM = \left(\frac{m}{V}\right)RT \quad \Rightarrow \quad pM = \rho RT$$

$101325 \times 44.0 = \rho \times 8.31 \times 293$

$\rho = 1831.05 \text{ g m}^{-3} = 0.00183 \text{ g cm}^{-3}$

Examiner's Comments

- Most candidates were able to obtain the correct numerical answer. Common errors were incorrect values of temperature/ pressure/ M_r substituted into the equation, and/or incorrect conversion of the units of volume.
- Some were still unclear of the conditions at room temperature and pressure – 20 °C (293K) and 1 atm (101325 Pa), which can be easily obtained from the *Data Booklet*.

B3(b)

At constant T and P, $V \alpha n$

Molar heat capacity of air
= [20.79 x 0.96 + 29.12 x 78.1 + 29.38 x 20.9 + 36.94 x 0.04] / 100
= 29.1 J mol^{-1} K^{-1} (3 s.f.)

Examiner's Comments

- A good majority of the candidates answered this question correctly. Candidates are reminded to leave their calculated answers in 3 s.f. unless otherwise stated.

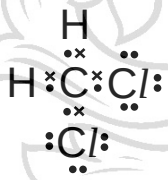
B3(c) No, moist air is <u>less dense</u> than dry air.

Moist air contains <u>water vapour which has lower M_r than N_2 and O_2 (accept any gas except noble gases) / moist air has lower average M_r</u>**.** When the amount of water vapour increases, the amount of O_2 and N_2 decrease per unit volume and thus density decreases because mass is decreasing.

Examiner's Comments

- A significant number of candidates misinterpreted the question as water vapour being *added* to dry air, instead of water vapour *replacing* the major constituents of dry air, despite the question stating that the volume of air considered is fixed.
- Some candidates were also unable to appreciate the data fully and thus, did not make good use of the % composition by volume information in their explanation. Candidates should note that N_2 and O_2 are major components of air.

B3(d)(i)



Examiner's Comments

- A good majority of the candidates answered this question correctly. All candidates are reminded to present all answers in ink, except for graphical work.

B3(d)(ii) C*l*–C–C*l* bond angle > H–C–H
C*l* atoms are bigger and experience greater repulsion in their electron clouds.

OR

C*l*–C–C*l* bond angle < H–C–H (actual data)
C*l* is more electronegative than H. C*l* draws the C–C*l* bond pair closer to itself. The C–C*l* bond pair of electrons are thus further away from nucleus of C and exert less repulsion than those in the C–H bond.

Examiner's Comments

- A significant number of candidates answered this question without justifying their choice of how the C*l*–C–C*l* bond angle is when compared to the H–C–H bond angle.
- Some candidates also showed misconceptions in their answers e.g. stated that the C*l*–C–C*l* bond angle is larger due to the higher electronegativity of C*l*, which is a contradiction.

B3(d)(iii) Both caffeine and CH_2Cl_2 are polar molecules while CO_2 is non-polar.

Since the permanent dipole-permanent dipole interactions and instantaneous dipole-induced dipole (id-id) interactions between caffeine and CH_2Cl_2 is stronger than the id-id interactions between CO_2 and caffeine, caffeine dissolves better in CH_2Cl_2, making CH_2Cl_2 a better solvent.

Examiner's Comments

- This question was poorly-answered. A significant number of candidates were unable to answer the question fully and presented poor concepts in Chemical Bonding. Since the question requires the use of intermolecular forces to explain the solubility of caffeine in two different solvents, the comparison must be clearly and explicitly shown, with the respective solute-solvent interactions stated and *why* CH_2Cl_2 is the better solvent.

B3(d)(iv) Possible answers include:

- Supercritical CO_2 is easily removed from the system after extraction of caffeine by allowing it to evaporate.
- CO_2 is non-toxic, non-flammable, renewable.
- High pressure used, rate of extraction is increased.

Examiner's Comments

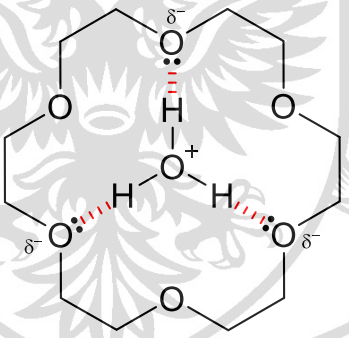
- Many candidates were unable to give reasonable answers for this question. Vague answers were not accepted.

B3(e)(i) Trigonal pyramidal
3 bond pairs and 1 lone pair

Examiner's Comments

- A significant number of candidates were able to answer this question correctly.
- All candidates are to note that a good and complete answer should include consideration of *both* bond pairs and lone pairs present in the molecule.

B3(e)(ii)



The interactions shown are hydrogen bonds.

Examiner's Comments

- A significant number of candidates gave incomplete answers which did not show all the hydrogen bonds which can be formed.

- Candidates are strongly encouraged to label the interactions presented for greater clarity of their answers.
- Candidates are also reminded to present all answers in ink, except for graphical work.

C1(a) $CH_3CH_2CH_2CH_3$ molecules form <u>weaker instantaneous dipole-induced dipole interaction</u> with one another while $CH_3CH_2CH_2CH_2C\mathit{l}$ molecules form <u>stronger permanent dipole-permanent dipole interaction</u>.

<u>Less energy is needed to overcome the weaker id-id interaction than that needed to overcome the stronger pd-pd interaction</u>. Hence, $CH_3CH_2CH_2CH_3$ has a lower boiling point than $CH_3CH_2CH_2CH_2C\mathit{l}$.

Examiner's Comments

- Students must understand that boiling is a process that involves a change from the liquid state to the gaseous state. Hence, molecules in the liquid state need to overcome the intermolecular forces of attraction in order to escape into the gaseous state. Thus, this is an assessment on the ability to identify the types and respective strengths of the intermolecular forces of attraction. It is therefore wrong to compare energies needed to break the covalent bonds in discussing differences in boiling points. Some even claimed that C-C*l* bond is stronger than C-H bonds without realising that the bond energy data in the Data Booklet states otherwise.
- Some students only compared the difference in the strength of id-id interaction, attributing it to a difference in the size of electron cloud without recognising that 1-chlorobutane is polar and forms pd-pd interactions as well.
- Students must always remember not to assume that their assessors understand their own acronyms. Merely writing "id-id and pd-pd interactions" without first introducing the terms in full would not have warranted any credit.
- It is an important exam skill to be able to craft succinct answers that answer the question according to the marks allocated for the section. Students who provided detailed answers to explain why 1-chlorobutane is polar and hence forms pd-pd interactions would have spent unnecessary time on this section.

C1(b) $\Delta H = (410 + 244) - (340 + 431) = -117 \text{ kJ mol}^{-1} < 0$

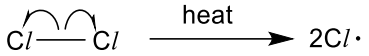
Since there is no change in the number of gaseous particles, <u>$\Delta S \approx 0$</u>.
Since $\Delta G = \Delta H - T\Delta S$, ΔG is always negative (or < 0).
The reaction is always exergonic. The reaction is spontaneous.

Examiner's Comments

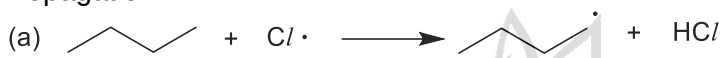
- Many students are able to determine the value for ΔH correctly.
- When asked to explain if a reaction is *spontaneous*, students must immediately understand that they need to discuss it in terms of ΔG. It is wrong to assume that all exothermic reactions are spontaneous because spontaneity is indicated by ΔG and is affected by both ΔH and ΔS.
- In so doing, students must recognise that $\Delta S \approx 0$. Simply stating that ΔS is very small is not precise enough because a sufficiently high T will make the $-T\Delta S$ significant in the ΔG equation. The idea that the magnitude of ΔS is negligible must be communicated.

C1(c) Free radical substitution

Initiation

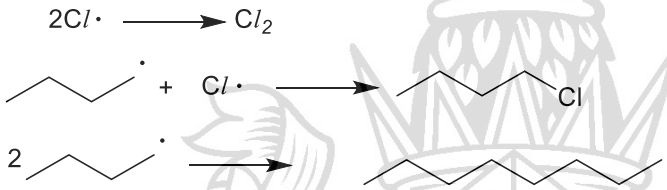


Propagation



Then (a), (b), (a), (b)…

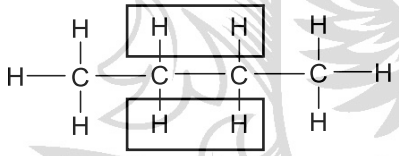
Termination



Examiner's Comments

- Many students who have revised the free radical substitution mechanism gained full credit for this section.
- Students must be aware that arrows need not be shown in the propagation and termination steps unless otherwise instructed. Students who chose to show the arrows in the propagation and termination steps must ensure that they are shown correctly.
- Students are strongly encouraged to use chemical equations to describe mechanisms as opposed to writing word statements.

C1(d)(i)

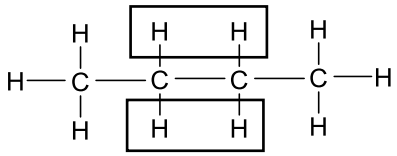


There are 6 primary hydrogen atoms and 4 secondary hydrogen atoms. Therefore, the ratio of the products formed is 6:4, which is 3:2

Examiner's Comments

- Part (d) presents students the room for presenting their answers creatively yet unambiguously. The assessors saw a variety of presentation, ranging from diagrams to labelling.
- Part (d)(i) was quite well done. Students who simplified their ratio of 6:4 directly to 3:2 to account for the presence of 6 primary hydrogen atoms and 4 secondary hydrogen atoms were penalised.

C1(d)(ii)



If all hydrogen atoms were equally reactive, 1-chlorobutane should constitute 60% of the chlorobutanes formed. But experimentally, 1-chlorobutane was found to constitute only 30% of the chlorobutanes formed. Hence, the secondary hydrogen atoms (hydrogen atoms in the box) are more reactive.

Alternative answer:

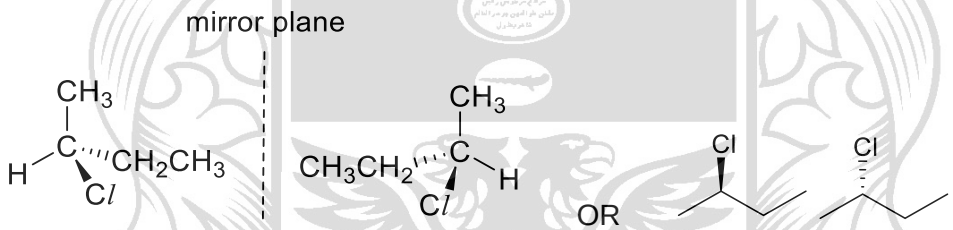
	Secondary H	Primary H
Relative ratio of H atoms	2	3
Experimental ratio of products	7	3
Relative reactivity	3.5	1

Secondary H atoms are 3.5 times more reactive.

Examiner's Comments

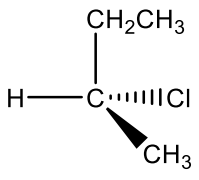
- Students often did not make it clear that they were comparing the relative stabilities of the primary and secondary radicals. A number of students erroneously compared the relative stabilities of primary and secondary carbocations or that of 1-chlorobutane and 2-chlorobutane.
- A number of students concluded that "secondary hydrogen atoms are more reactive and hence stable" without even realising that the statement is contradictory.
- Students who chose to work out the numerical ratio of the relative reactivities have to ensure that they gave the correct the numerical answer. Otherwise, a clearly worded comparison suffices for this section.

C1(e)(i)

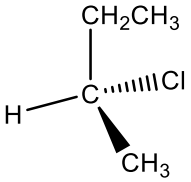


Examiner's Comments

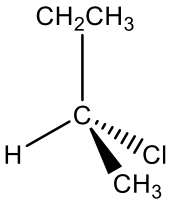
- Students MUST learn that it is critical to show the stereochemical representations clearly. The following are just some examples of incorrect representations.



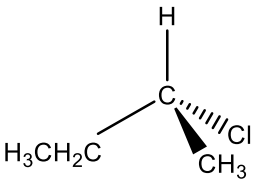
wrong shape



wrong shape



must show C-C bond to ethyl group



flipping ethyl group brings ambiguity

- Students must label the mirror plane correctly. There are too many scripts without labelling the mirror plane while many others label it as a "mirror"!
- Due care must be given to draw stereochemical formulae accurately.
- Many students misread the question and drew the stereochemical representation of the free radical instead.

C1(e)(ii) There is equal chance for the Cl• / Cl_2 to attack the free radical from both sides of the plane, forming equal proportion of the two enantiomers (or a racemic mixture).

Examiner's Comments

- Many students merely stated that the mixture exists as a racemic mixture without explaining how the racemic mixture arises.
- Many students misread the question and defined racemic mixture instead.
- Some students merely stated that there is equal probability of finding lone electron on the p orbital of the radical as shown in the diagram without explaining that the racemic mixture arises due to the eventual bond formation.
- Once again, students seem fond of the word "carbocation" when in fact, the diagram in the question clearly shows a free radical.

C2(a) $C_8H_7N_3O_2 + 6OH^- \rightarrow C_8H_5NO_4^{2-} + N_2 + 4H_2O + 4e^-$

Examiner's Comments

- This question was poorly attempted. Common mistakes included: balancing equation in acidic medium, not balancing H correctly, using O_2 or H_2 to balance O and H, not balancing charge correctly.

C2(b)(i) % uncertainty = $\left(\pm\frac{0.20+0.20}{2.5+2.0}\times 100\right)$ = ± 8.89 %

Examiner's Comments

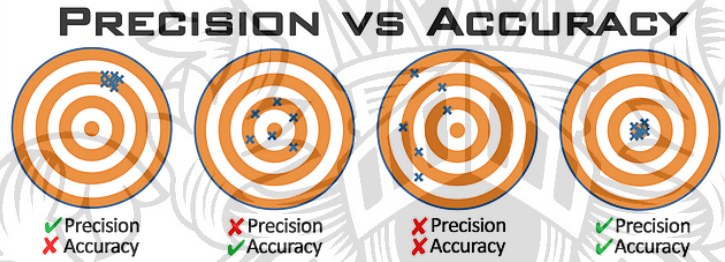
- Many students used the sum of relative uncertainties (and obtained ±18%) as the answer. The sum of relative uncertainties should only be used to calculate maximum uncertainty during titration experiments.
- A number of students omitted the ± sign in their answers.

C2(b)(ii) Any one of the below

- A <u>more precise apparatus</u>, such as a burette, could be used to measure the volumes.
- <u>Increase volumes</u> of FA1 and FA2 measured.

Examiner's Comments

- Students should be aware of the difference between *precise* and *accurate*.
- Precision is related to the uncertainty in a measurement. A <u>more precise</u> apparatus is able to measure a quantity with a smaller degree of uncertainty. For example, a burette is more precise than a measuring cylinder. A measuring cylinder is more precise than a beaker.
- Accuracy is related to how close the measurement is to the true value. In contrast, a <u>more accurate</u> apparatus gives a measurement that is closer to the true value. For example, a measuring cylinder measures volume more accurately than a bucket.
- You may find this diagram useful in understanding precision and accuracy.



- Syringes or smaller/larger measuring cylinders were not acceptable answers unless explicitly stated as being more precise. A pipette was not accepted due to the small volumes used in this experiment.

C2(b)(iii) Any one of the below:

- Human reaction time in stopping the stopwatch when the flash of light was observed.
- Time lag between the mixing of FA1 and FA2 and starting the stopwatch due to human error.
- Uncertainty in measurement of time using the stopwatch.

Examiner's Comments

- Many students claimed "human error" as a source of error. Please elaborate on what the error is. Errors that may be avoided by competent use of lab equipment are not accepted, for example, using a stopwatch, recording of time, parallax error, rinsing of glassware, etc.

C2(c) This is so that the effect of changing the initial concentration of uric acid on the initial rate of the reaction can be studied and the order of reaction with respect to uric acid can be determined.

Examiner's Comments

- Students should avoid vague answers which do not show understanding of the question.

C2(d)(i) Calculate $\frac{[UA]}{T}$ for each experiment.

Experiment	$\frac{[UA]}{T}$ / mol dm^{-3} s^{-1}
1	$\frac{3.00 \times 10^{-5}}{450} = 6.67 \times 10^{-8}$
2	$\frac{3.00 \times 10^{-5}}{900} = 3.33 \times 10^{-8}$
3	$\frac{1.00 \times 10^{-5}}{300} = 3.33 \times 10^{-8}$
4	$\frac{0.50 \times 10^{-5}}{150} = 3.33 \times 10^{-8}$

Comparing experiments 1 and 2, when **[HRP] doubles, $\frac{[UA]}{T}$ doubles**. Therefore, [HRP] $\propto$ rate, and hence **order of reaction with respect to HRP is 1**.

Comparing experiments 2 and 3, when **[UA] triples, $\frac{[UA]}{T}$ remains constant. Order of reaction with respect to UA is 0.**

Comparing experiments 3 and 4, when **[H_2O_2] doubles** and [UA] doubles, $\frac{[UA]}{T}$ **remains constant**. **Order of reaction with respect to H_2O_2 is 0.** Note that the order of reaction with respect to UA has been found to be 0.

Examiner's Comments

- Despite being told to calculate initial rate using the relationship given, many students used Time or 1/T to compare rates of reaction, leading to incorrect rates and therefore, incorrect orders.
- Students should show appropriate working/reasoning and state clearly the order of reaction with respect to each reactant. Note that no credit is awarded if working/reasoning is incorrect/missing, even if the correct order was obtained.
- A number of students interpreted the relationship initial rate $\propto$ [UA]/T given to mean that the rate is directly proportional to [UA], hence the reaction is first order with respect to UA. This is not the case because [UA]/T is derived from the definition of rate as Δ[UA]/Δtime.
- When comparing Expt. 1 and 2, avoid using 'decrease' when 'increase' can be used because confusion may arise. Do **not** write in the following ways:
  - When [HRP] is decreased by 2 times, [UA]/T is decreased by 2 times.
  - When [HRP] is decreased 2 times, [UA]/T is decreased 2 times.
  - When [HRP] is decreased by ½, [UA]/T is decreased by ½.

  Write your statement in one of the following ways:
  - When [HRP] is doubled, [UA]/T is doubled.
  - When [HRP] is increased 2 times, [UA]/T is increased 2 times.

- When [HRP] x 2, [UA]/T x 2.
- When [HRP] is halved, [UA]/T is halved.
- When [HRP] x ½, [UA]/T x ½.

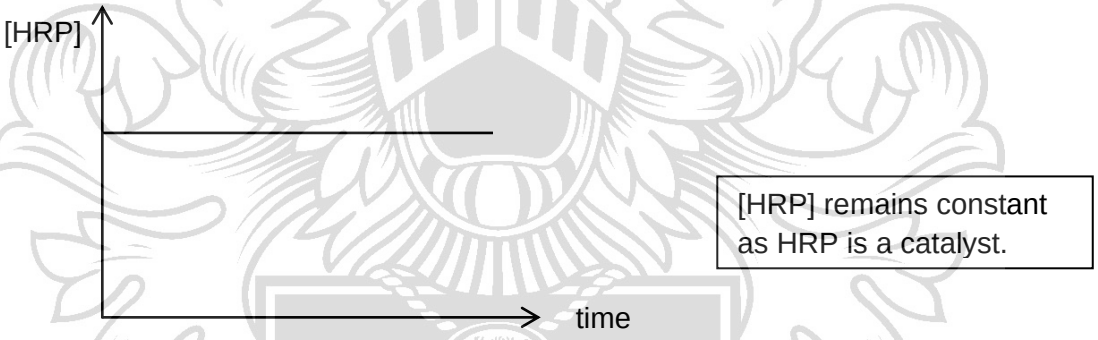
C2(d)(ii) Rate = k[HRP]

Units of k is s^{-1}

Examiner's Comments

- Many students wrote the units of *k* immediately after the rate equation, e.g. rate = k[HRP] s^{-1}. The units of *k* are not the units of rate.
- A number of students wrote the rate equation in the wrong form, e.g. "rate equation = k[HRP]" or "rate = [HRP]"

C2(d)(iii)



Examiner's Comments

- The question hinted at several different junctures that HRP is a catalyst.
- Since the reaction was first order with respect to HRP, many students drew a first order curve with a constant half-life. Partial credit was awarded.

C2(e) HRP is in the same phase/state as the other reagents. HRP takes part / used in the chemical reaction / reacted with H_2O_2 in Step 1 by being converted into intermediate X and subsequently regenerated in Step 3.

Examiner's Comments

- Students must explain that the catalyst is homogeneous as HRP is in the same aqueous state as H_2O_2.
- As stated in the question, answers must use evidence from the partial mechanism given. Therefore, refer to the reactants and intermediates given in the mechanism, or make reference to the two key steps.
- In general, students should check for 3 criteria to show that a chemical species is a *homogeneous* catalyst.
  1. The catalyst is in the same phase as the reactants.
  2. The catalyst is consumed in one step and regenerated in another.

3. The sum of the steps of the mechanism give the overall equation. (This is not applicable for this question because you were provided with only a *partial* mechanism)

C2(f) While keeping concentrations of all reagents in FA1 and FA2 constant, carry out the experiment at varying temperatures. Place FA1 and FA2 in a water bath of one temperature and mix the two solutions in the same water bath. Repeat this in a water bath of different temperatures.

Examiner's Comments

- There is no need to describe the procedure in detail as this question is only awarded 1 mark. However, answers need to clearly show that students recognise temperature as the *only independent variable* in the experiment.
- Many students simply stated "repeat the experiment" but which one? Repeating the entire experiment that is described in the question at a different temperature would have two independent variables – temperature and concentrations of the reactants.
- Note that the reagents need to be kept at the same temperature before mixing to ensure the entire reaction occurs at a fixed and controlled temperature.

C3(a) Hybridisation of N = sp^2 and hybridisation of C = sp^2
Since C has 3 regions of electron density, the hybridisation is sp^2.

Examiner's Comments

- The hybridisation of N is sp^2 as there are 3 regions of electron density, namely in the N=C bond, N-C bond, and the lone pair on N.
- The hybridisation for C can also be explained in terms of C having 3 sigma bonds and 1 pi bond, hence requiring 3 hybrid orbitals, i.e. sp^2 hybridisation.

C3(b)(i) The standard enthalpy change of hydration H^+ is exothermic because the process only involves the formation of ion-dipole interactions and the formation of such interactions is exothermic.

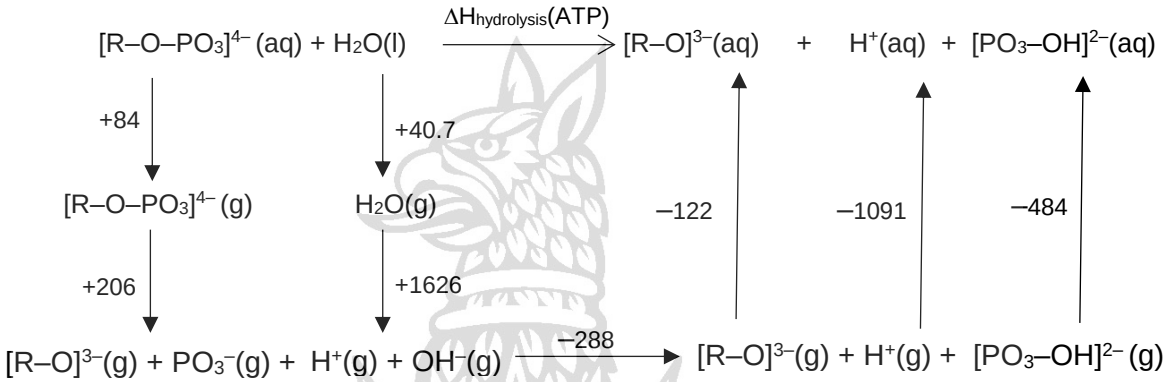
The vaporisation of H_2O requires energy to overcome the hydrogen bonds between the water molecules.

Examiner's Comments

- Students are required to specify the *predominant* types of bonds formed during hydration of H^+, and broken during vaporisation.
- For the process involving enthalpy change of *hydration* of H^+, ion–dipole interactions are formed between H^+ and H_2O molecules.

- For the process involving enthalpy change of vaporisation of water, the predominant *intermolecular* forces overcome to convert H_2O from the liquid to the gaseous state is hydrogen bonds.

C3(b)(ii)



$\Delta H_{hydrolysis}(ATP) = 84 + 206 + 40.7 + 1626 - 288 - 122 - 1091 - 484 = -28.3$ kJ mol^{-1}

Examiner's Comments

- Students are reminded to draw an energy cycle with the enthalpy change value clearly labelled with every equation. Combining of enthalpy change values in a single step is not recommended.
- All equations must carry state symbols and the cycle should be closed.
- Some of the vaporisation and hydration steps were often missed out in students' answers, or the wrong sign for ΔH was used. Students are reminded to check the state symbols for reactants and products carefully.
- The working for the use of Hess' law to calculate $\Delta H^{\ominus}_{hydrolysis}$ should be shown clearly.

C3(c) The P–O bond in ATP is weakened as the pi or phosphate groups all carry negative charge. The –4 ion experiences a lot of internal repulsion between these negatively charged groups which repel each other, and weakens the bond.

OR

P is bonded to many electronegative oxygen atoms which withdraw electron density from P–O bond, weakening the bond.

Note: this is also why the P–O bond in ATP is a so called "high energy" bond. It is a weaker bond which breaks easily.

Examiner's Comments

- Students are reminded to read the given information in the question carefully. The *structure* of the given triphosphate group has to be referred to in the answer. Hence, it is not sufficient to explain the difference between $\Delta H_1^{\ominus}$ and BE(P–O) in terms of BE(P–O) being only the average value of bond dissociation energies of different P–O bonds.
- The P–O bond to be broken is *between* the phosphate groups. Hence, the repulsion between negatively charged phosphate groups weakens this P–O bond. It is irrelevant to say that the lone pairs on O atoms repel one another / repel electrons on P (P has

no lone pair in the phosphate group) as it does not affect the bond strength of this particular bond to be broken.

- It is incorrect to say that bond strain weakens the bond, as the O-P-O bond angle does not deviate from the VSEPR predicted angle for tetrahedral structure.
- Since $\Delta H_1^{\ominus}$ has smaller magnitude than BE(P–O), it is also irrelevant to explain in terms of delocalisation of electrons over the phosphate structure. The delocalisation of π electrons should cause the P–O bond to be *stronger*, not weaker.

C3(d)(i) There is an increase in number of aqueous particles (from 1 mol of aqueous reactant to 3 mol of aqueous product), resulting in an increase in disorder of the system.

OR

The disorder achieved in breaking up one ion ($[R–O–PO_3]^{4–}$) into three ions ($[R–O]^{3–}$, H^+, and $[PO_3–OH]^{2–}$) is greater than the ordering of water molecules around the ions.

Examiner's Comments

- The increase in *disorder* should be mentioned, together with the reason for the increase.

C3(d)(ii) maximum work done possible = $\Delta G^{\ominus} = \Delta H^{\ominus} – T\Delta S^{\ominus}$

$\Delta G^{o} = – 28.3 – 298(0.0077) = –30.6$ kJ mol$^{–1}$

Examiner's Comments

- Careless mistakes were common in students' answers, for example: not converting the units of $\Delta S^{\ominus}$ to kJ mol$^{–1}$, and using the wrong value of temperature for standard condition.

C3(d)(iii) The body temperature is higher than 298 K. $\Delta G^{\ominus}$ becomes more negative as $– T\Delta S^{o}$ is more negative.

Alternative answers in terms of any other deviation from non-standard conditions were acceptable.

1. Concentrations deviate from standard condition, because cells maintain high concentrations of ATP and low concentrations of ADP, which shift desired equilibrium position to favour hydrolysis and cause $\Delta G^{\ominus}$ to be more negative.
2. pH deviates from standard conditions, as physiological conditions, i.e. the body pH (near 7) is not standard.

Examiner's Comments

- In discussing the discrepancy between actual $\Delta G^{\ominus}$ values and calculated values, the deviation from standard conditions should be considered.
- Quite a number of students, especially those of biology background, gave answers that somehow imply that living things can accomplish more work done, without giving details as to how. Living things are not magically exempt from the laws of nature, and

accomplish the necessary outcomes by utilizing natural scientific principles, including Chemistry. These need to be given to answer the question.

- Quite a number of students use enzymes as a reason. Enzymes are catalysts; and while they are efficient and powerful, catalysts do not change ΔG or ΔH. They lower activation energy, which involves the transition state and not the products. Refer to your Kinetics lectures notes and reaction profile diagrams on catalysts.