Section A

1(a)(i) Both diamond and silicon have giant covalent structures. During melting, strong Si–Si and C–C covalent bonds between atoms are broken in silicon and diamond respectively.

Si–Si covalent bonds are weaker than C–C as the valence orbitals of Si are more diffuse than that of C, thus overlapping of the orbitals of Si is less effective than that of C. Hence less energy is required to break the weaker Si–Si bonds during melting compared to C–C bonds in diamond.

Examiner's Comment

- This question was not well answered. Many students misread the question and tried to compare SiO_2 instead of Si with diamond.
- Note that when melting a giant covalent structure, the covalent bonds between Si **atoms** are broken in silicon, and between C atoms in diamond. To compare the strengths of covalent bonds between atoms, we need to compare the effectiveness of overlap between Si orbitals, with overlap between C orbitals.
- It is not acceptable to use bond energy values to compare covalent bond strengths, without further explanation.
- Some students were unsure of the structure of Si, mistaking it for being simple covalent, or similar to that of graphite.
- Please be clear and specific with terms used e.g. the orbital overlap is between the atoms, **not** molecules.

1(a)(ii) Al_2O_3 is amphoteric/reacts with both acids and bases, while SiO_2 is acidic/reacts with bases only.

$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$
$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq)$
$SiO_2(s) + 2OH^-(conc) \rightarrow SiO_3^{2-}(aq) + H_2O(l)$

or

$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$
$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na^+[Al(OH)_4]^-(aq)$
$SiO_2(s) + 2NaOH(conc) \rightarrow Na_2SiO_3(aq) + H_2O(l)$

Examiner's Comment

- Students generally recognised that Al_2O_3 is amphoteric and SiO_2 is acidic, but had difficulty balancing the equations for their reactions.

1(b)(i) For reaction 2, $\Delta H^{\ominus} = 2(-110.5) - (-910.9) = +689.9$ kJ mol^{-1}

Assuming that $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are independent of temperature,
$\Delta G^{\ominus}_{2500K} = +689.9 - (2500)(+361 \times 10^{-3}) = -213$ kJ mol^{-1} (3s.f.)

Reaction 2 has negative $\Delta G^{\ominus}_{2500K}$ and is spontaneous, whereas reaction 1 has positive $\Delta G^{\ominus}_{2500K}$ and is non–spontaneous. Hence reaction 2 is the preferred method for the extraction of Si from SiO_2.

Examiner's Comment

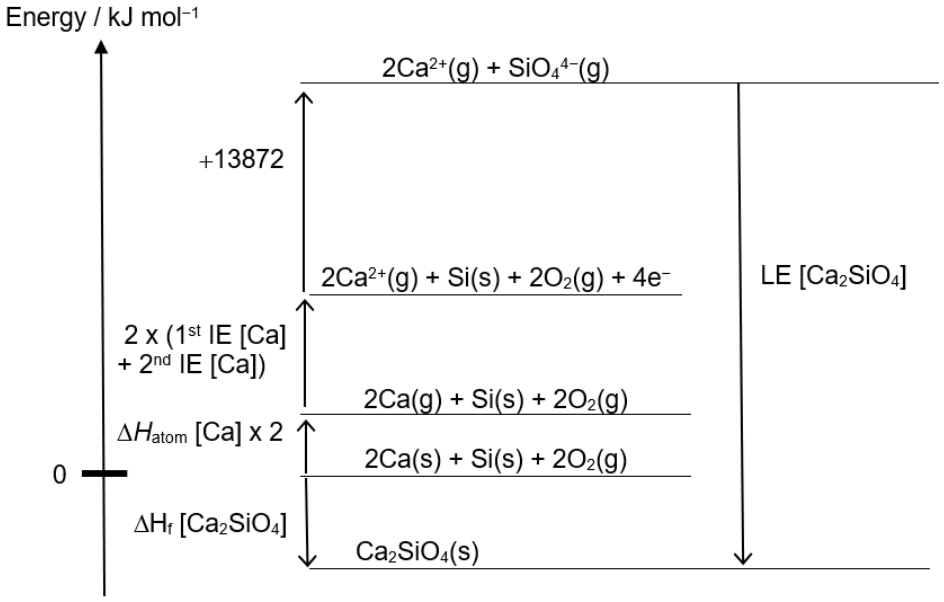
- To calculate $\Delta G^{\ominus}$ for reaction 2 at 2500 K, $\Delta H^{\ominus}$ for reaction 2 needs to be calculated first, using $\Delta H_r^{\ominus} = \Sigma n \Delta H_f^{\ominus}$ (products) $-$ $\Sigma m \Delta H_f^{\ominus}$ (reactants). Many students also calculated $\Delta H^{\ominus}$ correctly by using an energy cycle.
- Students are reminded to present their final calculated answers for each part of a question to 3 significant figures, and to include the correct units in their answers.
- A number of students used "−110" instead of "−110.5" as given in the question in their calculations. Please always use exactly what is given in a question (or in the Data Booklet).

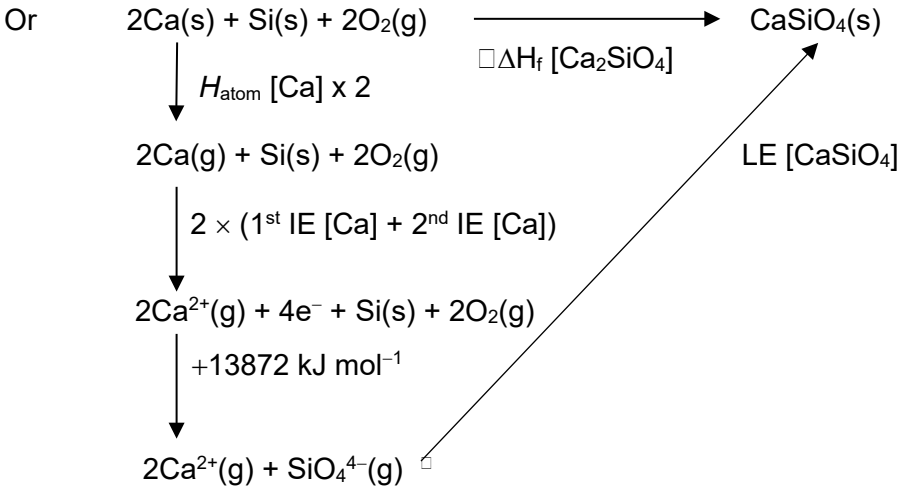
1(b)(ii) $\Delta S^{\ominus}$ is positive as there is an increase in the number/moles/amount of gaseous particles (from 0 to 2) in the equation.

Examiner's Comment

- This question was generally well answered. Note that it is important to mention "gaseous" particles in the answer.
- A number of candidates reported the increase incorrectly e.g. forming **1** mol of gas when the equation clearly shows 2 moles of CO molecules formed. Some students also cited gaseous ions / atoms, which were incorrect here.

1(c)





Using Hess' Law,
$-2306 = 2(+121) + 2(+590 + 1150) + 13872 + \text{LE } [Ca_2SiO_4]$
LE $[Ca_2SiO_4]$ = $\underline{-19900 \text{ kJ mol}^{-1}}$ (3s.f.)

Examiner's Comment
- Some students did not show a good understanding of the definitions of enthalpy changes, or were careless in writing equations. Many students neglected to multiply ΔH_{atom} or IE by 2 times.
- Note that the lattice energy of an ionic compound is the energy **released** when 1 mole of the solid ionic compound is formed from its constituent gaseous ions under standard conditions, hence it is an exothermic reaction. Some students wrote the equation for LE as the breaking of the ionic lattice instead and obtained a positive answer for LE.
- Students are reminded to read the question carefully and to make use of the equation given for the formation of SiO_4^{4-}. Since electrons are required for this reaction, Ca should be ionised $\underline{\text{first}}$ to obtain 4 electrons.
- Equations were often not balanced in terms of charges due to missing/additional electrons.
- Where energy level diagranms are drawn as the answer, the vertical axis should be drawn and labelled with "Energy/kJ mol^{-1}".

1(d)(i) The standard electrode potential, $E^{\ominus}$, of a half–cell is the $\underline{\text{electromotive force / potential difference, measured at 298 K, between the half–cell and the standard hydrogen electrode}}$, in which the concentration of any reacting species in solution is $\underline{1 \text{ mol dm}^{-3}}$ and any gaseous species is at a pressure of $\underline{1 \text{ bar}}$.

Examiner's Comment
- This question was poorly answered. Students are reminded to learn their definitions well.
- The standard conditions need to be specified clearly.

1(d)(ii) Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (x2)

Overall: $O_2 + 2H_2O + 2Fe \rightarrow 4OH^- + 2Fe^{2+}$

$E^{\ominus}_{cell} = +0.40 - (-0.44) = +0.84$ V

Examiner's Comment
- This question was generally well-answered, although some students calculated $E^{\ominus}_{cell}$ wrongly.
- An irreversible arrow should be used for the overall equation.

1(d)(iii) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell} = -4(96500)(+0.84) = -324240 \text{ J mol}^{-1} = \underline{-324 \text{ kJ mol}^{-1}}$

Examiner's Comment
- This question was generally well-answered, although some students missed out the negative sign for the formula for $\Delta G^{\ominus}$.
- Note that the units for $\Delta G^{\ominus}$ using this formula is J mol^{-1}.

1(d)(iv) (I) Oiling the bicycle chain <u>minimises contact between H_2O / O_2 and Fe</u>, thus rusting stops/slows down.

(II) $Zn^{2+} + 2e^- \rightleftharpoons Zn$ $\quad E^\ominus = -0.76$ V

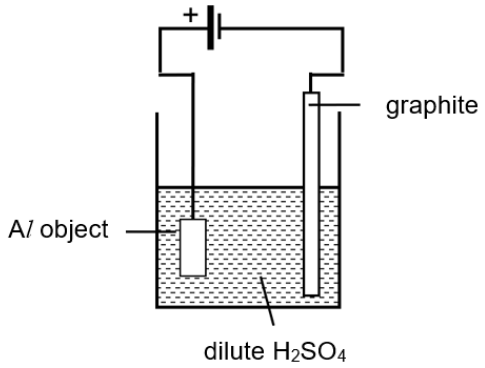
$Fe^{2+} + 2e^- \rightleftharpoons Fe$ $\quad E^\ominus = -0.44$ V

Zn is more easily oxidised than Fe, since <u>$E^\ominus(Zn^{2+}/Zn)$ is more negative than $E^\ominus(Fe^{2+}/Fe)$</u>. Hence <u>Zn rusts in place of Fe</u>.

Examiner's Comment

- This question was generally well-answered.
- Students are reminded that standard electrode potentials, $E^\ominus$, represent <u>reduction</u> processes. Hence if $E^\ominus(Zn^{2+}/Zn)$ is more negative than $E^\ominus(Fe^{2+}/Fe)$, it means that the reduction of Zn^{2+} to Zn is less spontaneous than that of Fe^{2+} to Fe, so the oxidation of Zn is more spontaneous than that of Fe.
- Students also need to compare the standard electrode potentials of $E^\ominus(Zn^{2+}/Zn)$ and $E^\ominus(Fe^{2+}/Fe)$, rather than just quoting the values.

1(e)



Examiner's Comment

- This question was not well attempted. Students are reminded that the industrial process of anodising of aluminium is part of the learning outcomes of the chapter on electrolysis.
- Many students incorrectly drew electrochemical cells or setups with a salt bridge, when an electrolysis cell was required.
- Many students omitted labelling the electrolyte or labelled it wrongly as containing Al^{3+}. Note that the Al object is coated with Al_2O_3 and not Al.
- At the anode (attached to the positive terminal of the battery), water is discharged forming O_2, hence the Al object to be anodised should be placed at the anode, so that O_2 evolved at the anode reacts with the Al forming a layer of Al_2O_3.
- The cathode should be an inert electrode like graphite.

2(a)(i) High temperature and low pressure.

Examiner's Comment

- Generally well done.
- Some students confused conditions with assumptions.

2(a)(ii) $V = (5.2)(8.31)(15+273)/101300 = 0.123\ m^3 = \underline{123\ dm^3}$

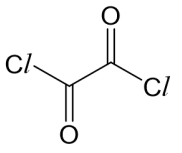
Examiner's Comment

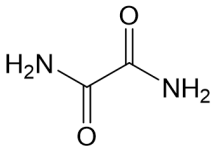
- Generally well done, though some students had trouble converting the units from m^3 to dm^3. ($1\ m^3 = 1000\ dm^3$)

2(a)(iii) Hydrogen bonding in ammonia caused the molecules to be closer to one another, thus the gas occupies a volume smaller than expected.

Examiner's Comment
- This was poorly done.
- It was surprising that many students were unable to state that the intermolecular forces between ammonia molecules is hydrogen bonding.
- In addition, it is insufficient to merely state the intermolecular forces. Students are required to justify further that the presence of hydrogen bonds held the molecules closer together (compared to the negligible intermolecular forces in an ideal gas), resulting is a lower measured volume.

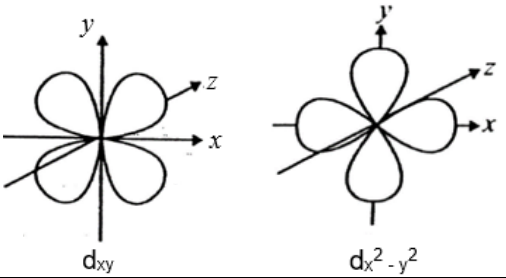
2(b) Step 2: NH_3
Step 3: LiA*l*H_4, dry ether

A is 

B is 

Examiner's Comment
- Generally well done.
- Students should note that ammonia gas is the reactant in step 2. Aqueous ammonia or ammonia dissolved in ethanol are not suitable as water and ethanol will react with the acyl chloride functional groups, forming side-products. Also, the reaction of NH_3 and acyl halide to form amide can take place without heating.
- Students should also note that other reducing agents like H_2, Ni or $NaBH_4$ are not suitable for reduction of amides to amines.

2(c)(i)



Examiner's Comment
- Generally well done.
- Students are encouraged to draw the relevant two axes (depending on which orbital) as horizontal and vertical, instead of diagonal.

Students must label the diagrams drawn with the orbital type.

2(c)(ii) In an octahedral environment, lone pairs on the ligands approach the central metal ion along the x, y and z axes.

$3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals have their greatest electron density along the co-ordinate axes on which the ligands are situated. Hence electrons in these orbitals are pointing towards the lone pairs of ligands and will be repelled by them.

$3d_{xy}$, $3d_{yz}$, $3d_{xz}$ orbitals have their greatest electron density in between the co-ordinate axes. Hence the repulsion between electrons in these orbitals and those of the approaching ligands will be less compared to electrons in $3d_{x^2-y^2}$ or $3d_{z^2}$ orbitals.

Hence, $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are at a higher energy level and $3d_{xy}$, $3d_{yz}$, $3d_{xz}$ orbitals are at a lower energy level.

Examiner's Comment

- Some students did not read the question carefully to account for all 5 3d orbitals. Students should justify both the extents of repulsion i.e. stronger or weaker repulsion by stating if the greatest electron density is along or between the axes.
- Students should note that the ligands approach along the x, y and z axes in an octahedral complex (not in between the axes).

2(d)(i) $Cr(OH)_3$

Examiner's Comment

- A sizeable number of students stated that the ppt is $Cr_2(CO_3)_3$, which does not exist. Students should recall from QA that Cr^{3+} is acidic hence will react with CO_3^{2-} to give CO_2 and $Cr(OH)_3$ ppt.

2(d)(ii) Oxidation

Examiner's Comment

- Generally well done.
- It is not ligand exchange reaction as there are no ligands in CrO_4^{2-}.
- Since this is a 'state' question, justification for the reaction type is not required.

2(d)(iii) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

This reaction involves the combination of two ions with the elimination of a small molecule, H_2O.

Examiner's Comment

- Poorly done.
- Students are required to apply knowledge from organic condensation reactions like the esterification or reaction of carbonyls with 2,4-DNPH, where 2 molecules/ions are added together with the elimination of a small molecule.
- Students should note that the 2 molecules/ions added together is 2 CrO_4^{2-} ions, not $CrO_4^{2-} + H^+$ ions.
- Condensation involves the release of a small molecule, not necessarily H_2O molecules. H_2O is an example of such a small molecule.
- The reaction is not a redox reaction as both CrO_4^{2-} and $Cr_2O_7^{2-}$ ions contains chromium in the +6 oxidation state. Hence, e^- should not appear in the equation.

2(d)(iv) OH^- and H_2O are different ligands of different strength. The d orbitals of Cr^{3+} are hence split into two sets of slightly different energy levels to different extents, creating different energy gaps for different complexes, which in turn absorb energies of different wavelengths from the visible light spectrum for d-d transitions, thus displaying different colours.

Examiner's Comment

- Students should specify that the d orbitals are being split.
- Students need to mention that different wavelengths are absorbed, instead of merely stating that the energy gaps correspond to different wavelengths.
- Do note that OH^- is the ligand in $[Cr(OH)_6]^{3-}$, not OH.

2(d)(v) The ability to display variable oxidation states in their compounds.

This is due to the close similarity in energy of the 3d and 4s electrons, which thus allows for different number of these electrons to participate in chemical bonding.

Examiner's Comment

- Generally well done.
- Students should note that having partially filled 3d subshell is not the primary reason why transition elements are able to exhibit variable oxidation states.

2(e)(i) $AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+Cl^-(aq)$

Examiner's Comment

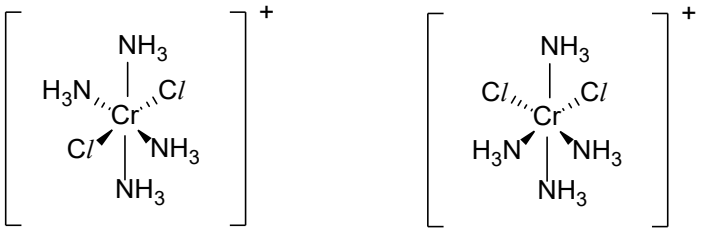
- This was poorly done.
- A sizeable number of students cannot recall the soluble complex cation, $[Ag(NH_3)_2]^+$ from QA. Examples of wrong complexes are $[Ag(NH_3)_4]^+$ or $[Ag(NH_3)_6]^+$.
- Given that the question stated that a white ppt was observed when $AgNO_3$ was added, students should indicate that X in AgX is actually Cl.

2(e)(ii) Cation: $[Cr(NH_3)_4Cl_2]^+$ Anion: Cl^-

Examiner's Comment

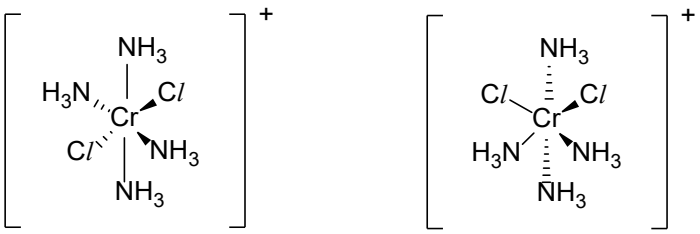
- Poorly done.
- Many students do not understand that Cl^- can exist either as a ligand or counter anion. Students who concluded that $[Cr(NH_3)_4]^{3+}$ is the cation failed to understand that 1 mol (not 3 mol) of AgCl is formed from 1 mol of $Cr(NH_3)_4Cl_3$. This means that 1 Cl^- ion exists as the counter anion and the other 2 Cl^- ions are bonded to the chromium centre as ligands. Since Cl^- is the counter anion, then the cation has to be a singly positively charged cation comprising of Cr^{3+} as the central ion with 2 Cl^- and 4 NH_3 ligands.
- Students should give the formula of the cation and anion with the known identity of X.

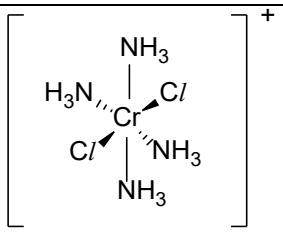
2(e)(iii)



Examiner's Comment

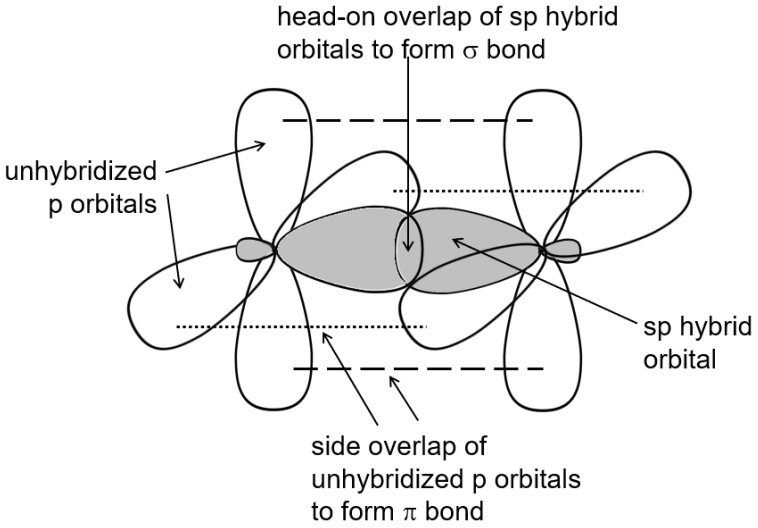
- This was poorly done.
- Students should note that 3D structures are perspective drawings and should be drawn with a chosen point-of-view. The following are **incorrect** 3-D representations (where the first two suggests hexagonal planar):



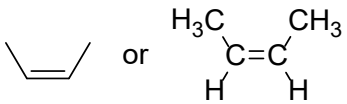


- Cis-trans isomerism can exist in complexes with octahedral geometry. In the cis-isomer, the pair of identical ligands occupies positions adjacent to each other (i.e. 90° apart). In the trans-isomer, the pair of identical ligands occupies positions diagonally opposite each other (i.e. 180° apart).
- Students are reminded that overall charge of the complex ion should be indicated using [ ]^{charge}.
- Some students incorrectly drew mirror images without realising they were identical compounds and thus not enantiomers.

3(a)(i) The carbon atoms in C≡C are <u>sp</u> hybridised.
The <u>σ bond</u> is formed from <u>head-on overlap</u> of <u>sp hybrid orbitals</u> of each atom.
<u>2 π bonds</u> are formed. Each π bond is formed from the <u>side-on overlap</u> of one unhybridised <u>p-orbital</u> from each atom.



Examiner's Comment
- Generally well done.
- Students should label their diagrams clearly.
- Many student omitted the type of overlap which occurred to give rise to each type of bond e.g. <u>head-on overlap</u> to form σ bond. It is important to include such details.
- If students drew a diagram, the type of overlap could be inferred from the diagram. However, for questions which did not require a diagram, students need to be accurate and detailed in their description.

3(a)(ii)  or

Examiner's Comment

- Generally well done. The trigonal planar shape about each doubly bonded C must be clearly shown for the isomerism to be clearly illustrated.

3(a)(iii) But-2-yne and hydrogen <u>adsorb</u> onto the surface of the Lindlar's catalyst through the formation of weak bonds / interactions with the surface of the catalyst.

This <u>increases the surface concentration</u> of the reactants and brings the reactants in <u>closer proximity</u> and proper orientation for reaction to take place. This also <u>weakens</u> the covalent <u>bonds</u> <u>within</u> reactant <u>molecules</u>, <u>lowering the activation energy</u> for reaction.

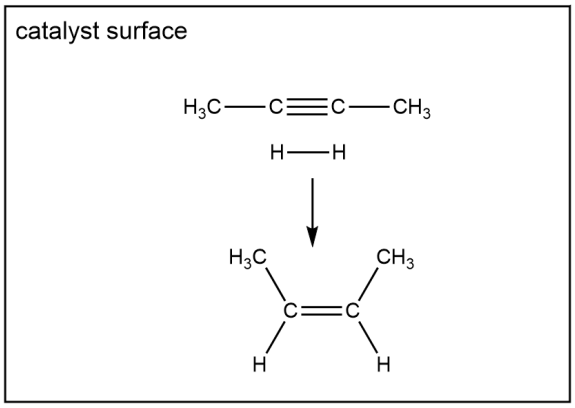
Once formed, the product molecules can easily <u>desorb</u> from the surface of the catalyst.

Examiner's Comment

- Students who recognised this part as requiring students to describe heterogeneous catalysis generally did well. Some students merely describe general catalysis which was insufficient for the question.

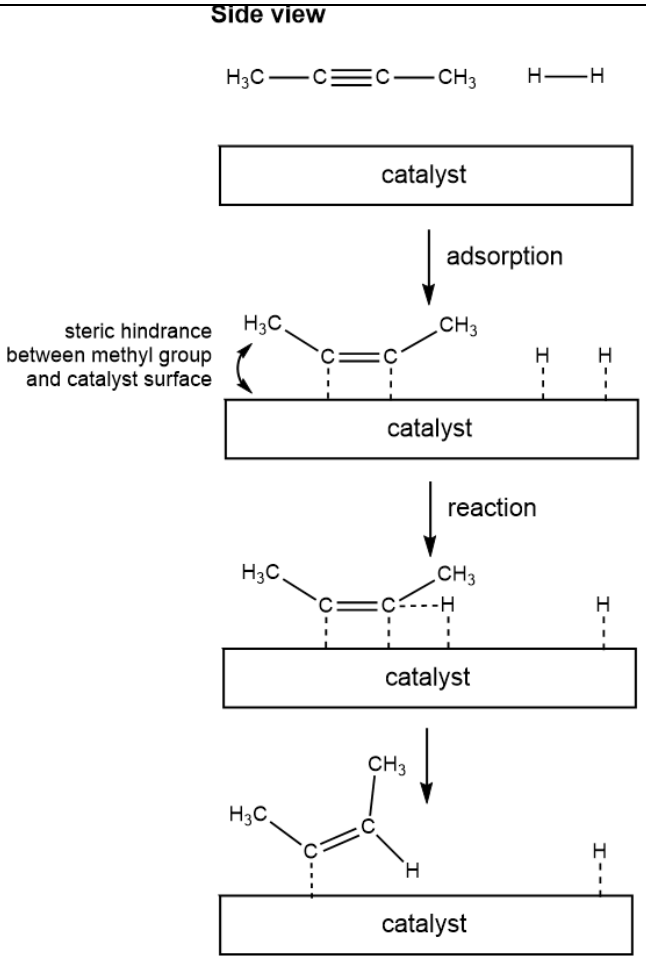
3(a)(iv) Upon adsorption of but-2-yne and H_2 on the catalyst surface, <u>H_2 collides and forms bonds with one side of the alkyne molecule</u> at the same time, adding two H atoms to the same side.

Top view



OR

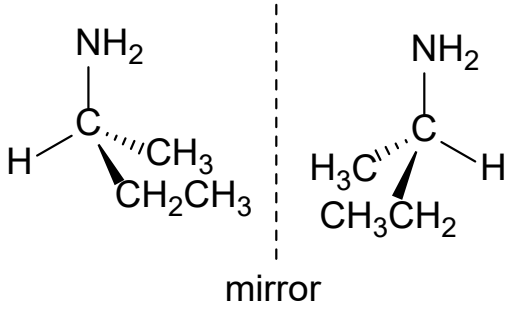
Upon adsorption of but-2-yne and H_2 on the catalyst surface, the bulky methyl groups on but-2-yne experience electronic repulsion from the catalyst surface and point away from the catalyst surface. The H atoms then add to the side of the alkyne that was previously temporily bonded to the catalyst surface.



Examiner's Comment

- This question required students to propose a reasonable hypothesis for the situation. Sensible answers which involved sound chemical concepts were given credit. Two possible answers are shown above.
- There were many good attempts to answer this question.
- Some students had the incorrect idea that H_2 attacks but-2-yne from the top, i.e. the opposite side of the catalyst where but-2-yne is adsorbed. Please be reminded that for heterogeneous catalysis, both but-2-yne and hydrogen are adsorbed and thus, an attack from the top by H_2 is impossible to happen.
- Some answers focused on the catalyst's active sites putting the reactants in a specific orientation that only allows the cis-isomer to be formed. This is vague as there was no further elaboration of how this orientation led to the cis configuration.

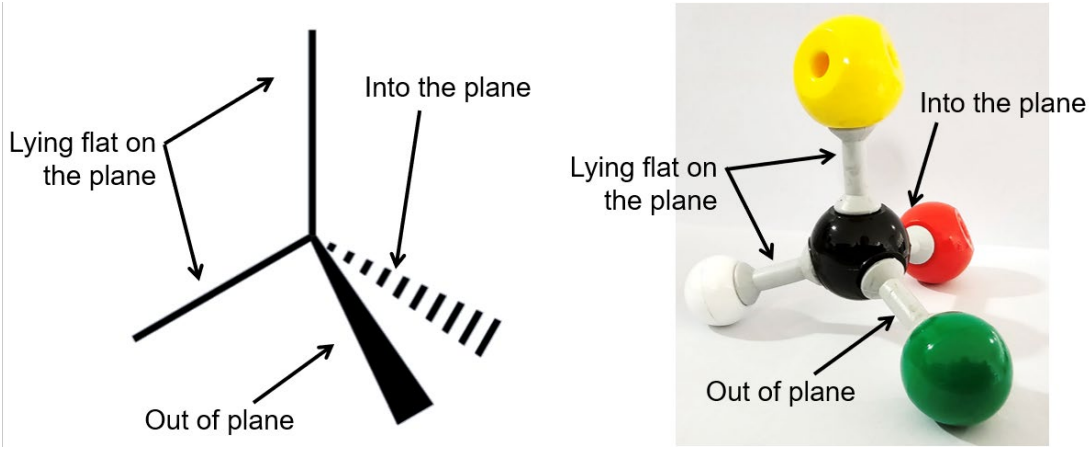
3(b)(i)



Examiner's Comment

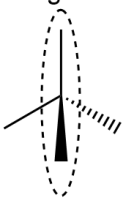
This question required students to make use of 3D representation to show the structures of the two enantiomers, which differed in their orientation in 3D space. While almost all students attempted to draw a tetrahedral structure, many drew the tetrahdedral structure incorrectly.

The tetrahedral structure is drawn as such to emulate what is seen in the molecular model. Take note of the following when comparing the drawing to the molecular model.



1. There are two bonds that are lying on a plane – 1 bond pointing up, the other bond pointing to the left. The bond angle here should be near 109°.
2. The other two bonds are generally pointing to the right – 1 pointing out of plane, the other pointing into the plane. But both are pointing in the same general direction (to the right).

Common mistakes made by students are shown below.

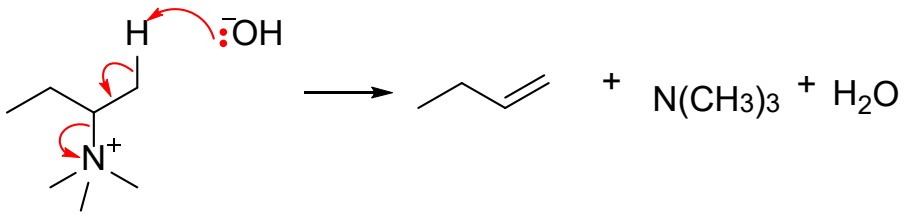
Mistake	Examples of mistake
Bond angles of 90° or 180°. The bond angle in tetrahedral shape is 109.5° and thus, in the diagram there should not be any bond angles of 90° or 180°.	incorrect 90 deg bond angle  incorrect 180 deg bond angle 
Wedge and dash bonds not pointing to the same side.	Incorrect 
Pointing the bond to the incorrect atom e.g. H instead of C.	Incorrect : NH_2– Correct : –NH_2.
–CH_3CH_2 instead of –CH_2CH_3 OR –NH_3 instead of –NH_2.	--

$H_3CH_2C–$ instead of $–CH_2CH_3$. Students are reminded that for any side chains of ≥ 2C, they should not be writing it backwards. In addition, if there are ≥ 3C, branching is possible and students should write out the structural formula to show the bonding.	--

3(b)(ii) excess CH_3I in ethanol, heat in a sealed tube

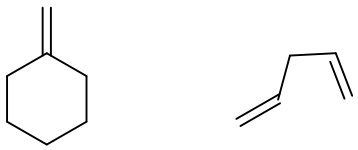
Examiner's Comment:
Common mistakes include:
- Using the wrong halogen. The counter anion in the question is I^-, so CH_3I has to be used.
- No mention of 'excess'. Since multiple nucleophilic substitutions occured, there must be excess of CH_3I used.
- CH_2I instead of CH_3I

3(b)(iii)



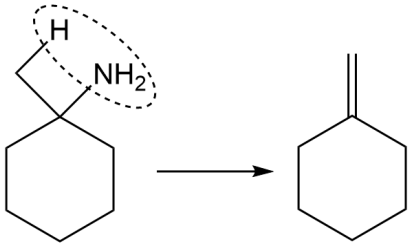
Examiner's Comment
- Generally well done. Clues can be obtained by looking at the species in the products.
  - H_2O hints that the OH^- needs to form a bond with H^+
  - $N(CH_3)_3$ hints that the C–N bond needs to break
  - The new π bond implies that the electrons from the broken C–H must be transferred to form the π bond.
- Observing, interpreting and understanding the above would facilitate the drawing of curly arrows.

3(b)(iv)

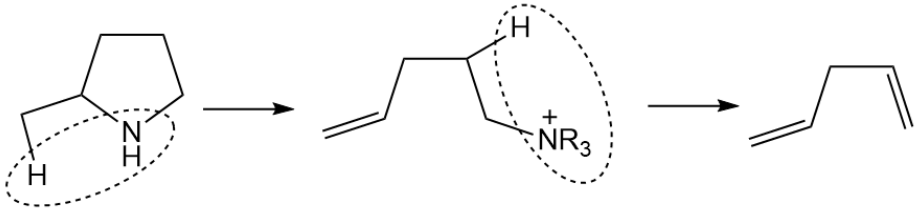


compound **D** compound **E**

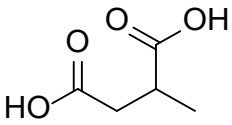
Examiner's Comment
- Compound **D** was generally well done. From the information provided, the Hoffman elimination gives the less substituted alkene as the major product – a contrast to Saytseff's rule. The elimination can be visualised as follows.

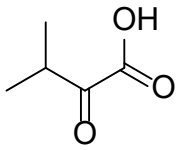


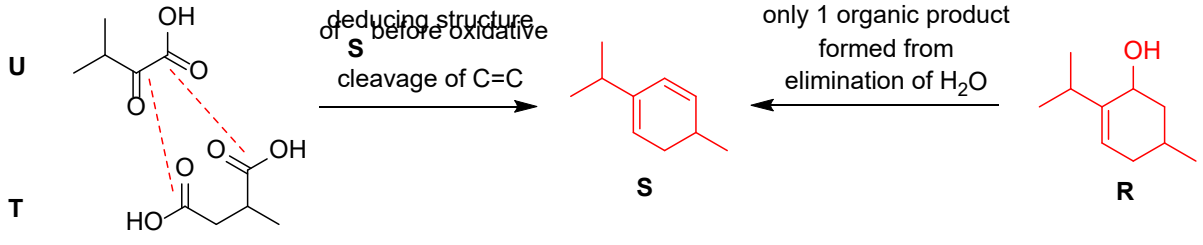
- Deducing the structure of compound **E** proved to be difficult. Two Hoffmann eliminations occurred one after another to obtain the correct product.

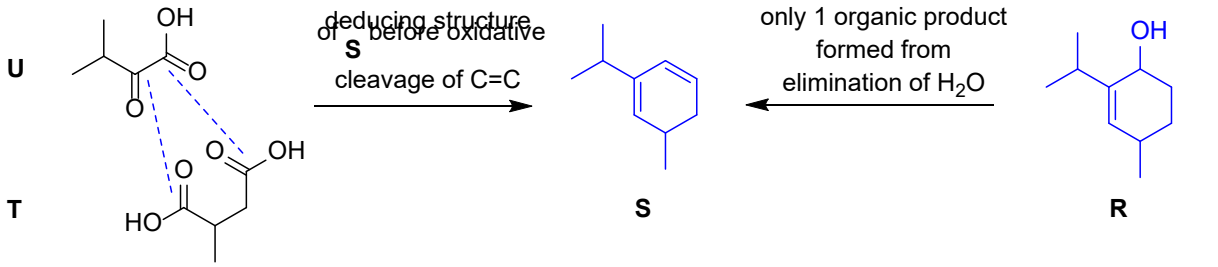


3(c)

Evidence	Deduction
R ($C_{10}H_{18}O$) $\xrightarrow{PCl_5}$ product	Nucleophilic substitution - **R** contains an alcohol.
1 **R** + 1 Br_2 ⟶ product	Electrophilic addition - **R** contains 1 C=C.
R ($C_{10}H_{18}O$) $\xrightarrow[\text{heat}]{\text{conc. } H_2SO_4}$ **S** ($C_{10}H_{16}$) only product	Elimination of 1 H_2O / dehydration - Formed a C=C in **S** or **R** contains an alcohol
S $\xrightarrow[\text{heat}]{\text{acidified } KMnO_4}$ **T** ($C_5H_8O_4$) + **U** ($C_5H_8O_3$).	Strong oxidation / oxidative cleavage - **S** contains C=C - **T** and **U** do not contain any primary/secondary alcohol or aldehydes
1 **T** + 2NaOH ⟶ product 1 **U** + 1NaOH ⟶ product	Acid-base reaction - **T** contains 2 –COOH groups - **U** contains 1 –COOH group - **T** has 5 carbons, 2 –COOH and 1 chiral centre. 
U $\xrightarrow{\text{2,4-DNPH}}$ orange ppt	Condensation reaction - **U** contains carbonyl / ketone group
U $\xrightarrow{\text{alkaline } I_2}$ no yellow ppt	No oxidation reaction - does not contain $COCH_3$

U $\xrightarrow[\text{uv}]{Cl_2}$ 2 products.	<u>Free radical substitution</u> - <u>**U** contains two types of hydrogen.</u>  **U**



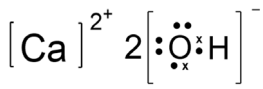


Examiner's Comment

- There is evidence of hard work and practice in students' work. The deductions were generally very well-written, and most students were able to obtain full credit for them. Not all who wrote good deductions went on to deduce the structures. Students need to continue to hone their elucidation and problem solving skills through more practice.
- In the nucleophilic substitution of **R** with PCl_5, students should specify that **R** contains an alcohol group as "−OH" may also refer to phenol. It is also incorrect to deduce that **R** may contain −COOH because **R** only contains 1 O atom.
- In the acid-base reaction of **T** ($C_5H_8O_4$) and **U** ($C_5H_8O_3$) with NaOH, it is incorrect to deduce that they may contain phenol functional group because their molecular formula shows that they only contain 5 C atoms.
- When there are two mono-chlorinated products formed from free radical substitution, the deduction should be 'the alkane contains two types of hydrogen' instead of that it contains an alkane.

Section B

4(a)



Examiner's Comment

- Some students used incorrect symbols like circles or triangles to represent the electron gained. This is a dot-and-cross diagram – students need to alternate the use of dots and crosses to indicate electrons of different origins.
- Some students incorrectly drew a covalent compound's dot-and-cross diagram for the ionic compound $Ca(OH)_2$.
- When drawing dot-and-cross diagrams for cations, students should not draw electrons about Ca^{2+} as only electrons in the valence shell electrons need to be drawn.

4(b) Mass of hydroxyapatite lost = $0.75 \times 2.5 = 1.875$ g
Amount of hydroxyapatite lost = $1.875 / 502.5 = \underline{3.731 \times 10^{-3} \text{ mol}}$

Amount of $Ca(OH)_2$ required = $5 \times 3.731 \times 10^{-3} = 0.01866$ mol
Mass of $Ca(OH)_2$ required = $0.01866 \times 74.1 = \underline{1.38 \text{ g}}$

Examiner's Comment

- This question is generally well done.

4(c)(i) $K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-]$

Examiner's Comment

- This question is generally well done.

4(c)(ii) Let the solubility be y mol dm^{-3}.

$(5y)^5(3y)^3(y) = 6.80 \times 10^{-37}$
$84375\ y^9 = 6.80 \times 10^{-37}$
$y = 2.717 \times 10^{-3} = \underline{2.72 \times 10^{-5}}$

Solubility of hydroxyapatite = 2.72×10^{-5} mol dm^{-3}

Examiner's Comment

- This question is generally well done.

4(c)(iii) Solubility of hydroxyapatite <u>increases</u> in an acidic environment.
<u>$[OH^-]$ is low / H^+ reacts with OH^-</u> and PO_4^{3-} anions shifting position of equilibrium to the <u>right</u>.

Examiner's Comment

- A handful of students were unclear about the cause-effect relationship in the shifting of position of equilibrium. Common wrong answers stated that "POE shifts right to produce more OH^- to react with H^+". Students should understand that POE shifted because OH^- was consumed, and the system is responding but favouring the forward reaction to produce more OH^-. OH^- was **<u>not</u>** produced to react with H^+. Cause: $[OH^-]$ reduced, effect: POE shifts right.

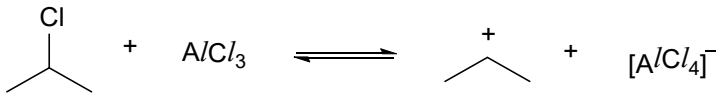
4(c)(iv) In fluoride-treated water, hydroxyapatite is converted to the <u>less soluble</u> fluorapatite with a <u>lower K_{sp}</u> value, making teeth less susceptible to tooth decay.

Examiner's Comment

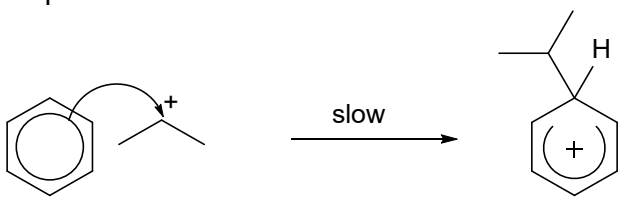
- Question indicated to use the data provided in the table, however, many students still did not use K_{sp} to explain. Students should understand that when both salts have the same number of ions per unit formula of compound, K_{sp} can be used to compare solubility.
- Some students stated that there is a "decrease in K_{sp} as F^- replaces OH^-". This is a false statement as 2 salts of different formula have different K_{sp}. The K_{sp} of each salt did not change. K_{sp} will only increase or decrease in the event of a change in temperature.
- While some students mentioned that "since K_{sp} of fluorapatite is low, it will dissolve first in place of hydroxyapatite". This is contradictory as a lower K_{sp} will indicate a lower solubility in this context.
- Many students mentioned that "K_{sp} of fluorapatite is low, hence will precipitate out first". This is not a situation of selective precipitation. With lower K_{sp}, fluorapatite will form readily in the case that hydroxyapatite dissolves, hence preserving the teeth. It further reduces decay because it is less soluble than hydroxyapatite.

4(d)(i) **Electrophilic Substitution**

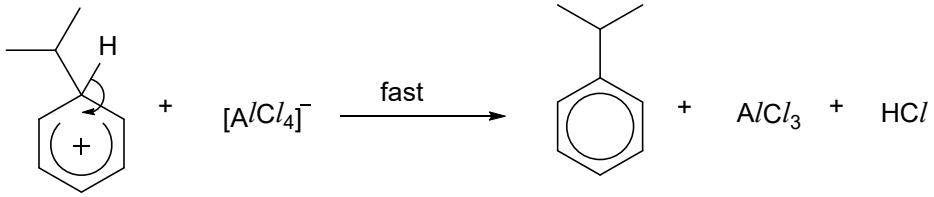
Generation of electrophile:



Step 1:

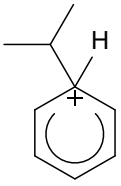


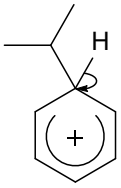
Step 2:



Examiner's Comment

- This question is generally well done.
- Some students included elaborate mechanism for the generation of electrophile and step 2. This was unnecessary.
- Some students wrongly generated a 4-carbon electrophile,  .

- Some students wrongly drew the carbocation as 

, where the positive charge is localised on the substituted carbon. This is a misconception as the carbon that is substituted has 4 bonds and is not electron deficient. The positive charge should be delocalised among the remaining 5 carbons. Hence, the positive charge is drawn in the middle of the "◡".
- Another misconception is that the bond-pair of electrons in the C–H bond was given to the substituted carbon (

). This shows that student did not understand that the bond-pair of electrons is returned to the benzene ring to restore the resonance stabilisation.
- Many students incorrectly omitted the regeneration of A*l*C*l*$_3$ catalyst, and generation of HC*l* in step 2 of the mechanism.

4(d)(ii) Lewis acid is an <u>electron pair acceptor</u>.

Examiner's Comment

- A few students stated that Lewis acids are "molecules that accept electron pairs" or "cations that accept electron pairs". This is not accurate as Lewis acids can be a molecule or cation, and not necessarily either only.
- Many students stated that Lewis acids accept lone-pair of electrons, which is wrong. For instance, in the electrophilic substitution mechanism drawn, benzene ring is not a lone-pair donor. The electron pair came from the π-electron cloud.

4(d)(iii)

- <u>Alkyl</u> groups are <u>activating / electron donating</u> so the <u>electron density in benzene ring increases / benzene ring becomes more electron rich / more susceptible to electrophilic attack</u>.

- The alkyl group in cumene is <u>2,4-directing</u>, hence the 1,3-disubstituted product is not favoured / benzene ring is further substituted at the 2,4-positions.

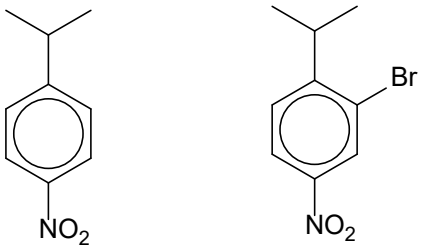
- The bulky –CH(CH_3)$_2$ <u>sterically hinders</u> the electrophilic <u>attack</u> at the 2-position; thus the 4-position product is favoured. / <u>Steric hindrance</u> between two bulky –CH(CH_3)$_2$ groups causes the 1,2-disubstituted product to be <u>unstable</u>, hence produced in less amounts.

Examiner's Comment

- Some students mentioned the high electron density of benzene due to its π-electron cloud, allowing it to undergo di-substitution. This is incorrect as a nitrobenzene will not undergo di-substitution readily, despite having the π-electron cloud. This is due to the deactivating nature of the nitro group which makes the benzene ring in nitrobenzene less susceptible to electrophilic substitution. Students should realise that the first alkyl group substituted affects the second substitution.

- Some students wrongly suggested that the alkyl group is electron donating through resonance effect. The carbon bonded to the benzene ring is an sp^3 hybridised carbon, there is no p-orbital available to overlap with the π-electron cloud of benzene.
- Many students attributed the lack of 1,2-disubstituted product to steric hindrance, without further explanation of the cause of the hindrance. No credit was awarded for such cases.

4(e)(i)(ii)



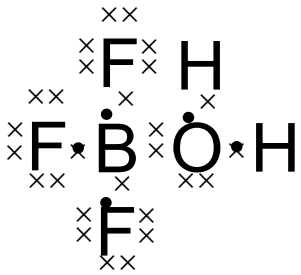
F **G**

Step 1: conc. HNO_3, conc. H_2SO_4, 30°C
Step 2: Br_2, $FeBr_3$
Step 3: Sn, conc. HC*l*, heat under reflux, followed by NaOH(aq)

Examiner's Comment
- This question is generally well done.
- Common errors include the substitution of Br using Br_2 in CC*l*$_4$, use of Br_2(aq) with anhydrous $FeBr_3$, reduction of the nitro group using LiA*l*H_4 in dry ether, and the lack of stepwise neutralisation of $–NH_3^+$.

5(a)(i) Lewis acid is an <u>electron pair acceptor</u>.

5(a)(ii)



5(a)(iii) Tetrahedral, 109°

Examiner's Comment
- These three parts were generally well done. Students are reminded to use only dots and crosses to indicate electrons of different atoms. The lone pairs of F must also be included.
- Hence, using the diagram above as an example, it must be clear that boron has 3 valence electrons (3 dots around B) and oxygen has 6 valence electrons (6 crosses around O).

5(b)(i) $K_{sp} = [Co^{2+}][C_2O_4^{2-}]$ units: $mol^2\ dm^{-6}$

Examiner's Comment
- This part was generally well done though some students left out the units or made careless mistakes when deriving the units.

5(b)(ii) $[Co^{2+}] = \frac{5.84}{58.9} = 0.0991$ mol dm^{-3}

When 94% of Co^{2+} has precipitated,
$[Co^{2+}]$ remaining $= \frac{6}{100} \times 0.0991 = 5.95 \times 10^{-3}$ mol dm^{-3}

Since the remaining leach solution is saturated,
$(5.95 \times 10^{-3})\ [C_2O_4^{2-}] = 2.7 \times 10^{-9}$

Therefore, $[C_2O_4^{2-}] = \frac{2.7 \times 10^{-9}}{5.95 \times 10^{-3}} = 4.54 \times 10^{-7}$ mol dm^{-3}

Examiner's Comment
- Many students used the concentration of Co^{2+} precipitated (i.e. 94% of the original concentration) to calculate $[C_2O_4^{2-}]$. The concentration of Co^{2+} ***left*** in solution is in equilibrium with the $C_2O_4^{2-}$ ions.

5(b)(iii) $[Ni^{2+}] = \frac{4.93}{58.7} = 0.0840$ mol dm^{-3}

When $[C_2O_4^{2-}] = 4.54 \times 10^{-7}$ mol dm^{-3},
$[Ni^{2+}][C_2O_4^{2-}] = (0.0840)(4.54 \times 10^{-7}) = 3.81 \times 10^{-8}$ mol^2 dm^{-6}

Since the ionic product $[Ni^{2+}][C_2O_4^{2-}]$ < K_{sp} of NiC_2O_4, the precipitate will not form.

Examiner's Comment
- Most students were able to solve this part by using $[C_2O_4^{2-}]$ from the previous part. Here, the remaining $C_2O_4^{2-}$ ions are present with the original concentration of Ni^{2+} ions. Hence, the ionic product of $[Ni^{2+}][C_2O_4^{2-}]$ will determine if the system is at equilibrium (IP = K_{sp}) or not at equilibrium (IP < K_{sp}).

5(b)(iv) As pH decreases, $[H^+]$ increases. The equilibrium positions of the acid dissociation reactions shift to the left, thus $[C_2O_4^{2-}]$ decreases.

$$CoC_2O_4(s) \rightleftharpoons Co^{2+}(aq) + C_2O_4^{2-}(aq)$$

This causes the equilibrium position of the dissolution of CoC_2O_4 to shift right, increasing the solubility of CoC_2O_4.

Examiner's Comment
- Many students incorrectly thought that decreasing pH meant decreasing $[H^+]$. Do be careful in reading the question.
- Students who identified that $[H^+]$ increased were able to explain the decrease in $[C_2O_4^{2-}]$ using the equations provided.
- However, answers which then concluded the solubility of CoC_2O_4 increased without an explanation were not awarded full credit.
- Students are reminded to explain Le Chatelier's Principle always in terms of *concentration* of the species, and not amount.

5(b)(v) A <u>complex ion / soluble complex was formed</u> between Co^{2+} and $C_2O_4^{2-}$.

The formation of the soluble complex <u>decreases</u> the uncomplexed <u>[Co^{2+}]</u> in the solution.

To counteract the decrease in [Co^{2+}], the equilibrium position of $CoC_2O_4(s) \rightleftharpoons Co^{2+}(aq) + C_2O_4^{2-}(aq)$ shifts to the <u>right</u>, resulting in more CoC_2O_4 dissolving and the solubility of CoC_2O_4 is increased.

Examiner's Comment

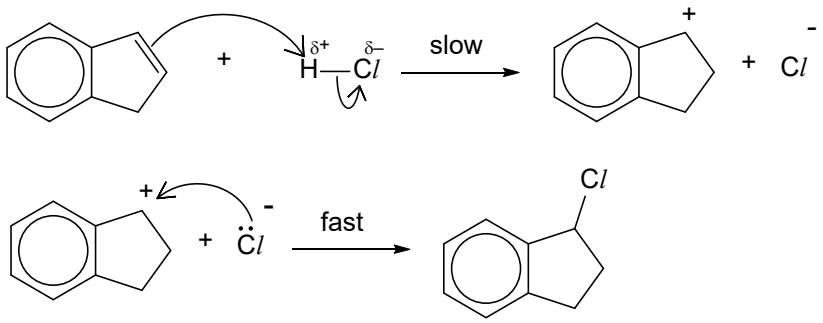
- This question was less well-attempted. Many students thought the same explanation applied here as from the previous part. It's important to recognise that when there is an increase in solubility due to an increase in concentration of one of the component ions, the only explanation is because of complex formation.

5(c) <u>Trans</u> isomer is not stable due to <u>angle/ring strain</u>.

Examiner's Comment

- Poor answers did not make mention specifically to the *trans* isomer, and claimed that both isomers were unstable. This is incorrect as the *cis* isomer was already shown in the structure of indene.

5(d)(i) Electrophilic addition

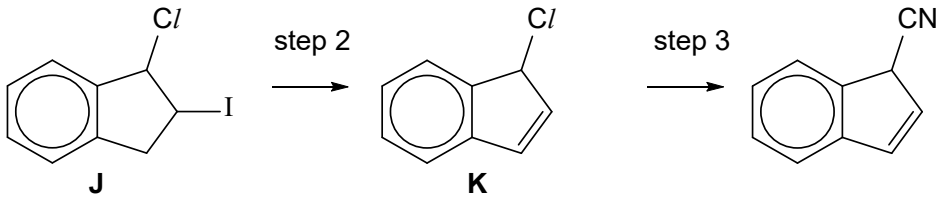


5(d)(ii) The major product is formed because the benzylic carbocation is resonance-stabilised. In this carbocation, the <u>empty p orbital of the positively charged carbon overlaps with the π electron cloud of the benzene ring</u>. The π electrons of the benzene ring <u>delocalise over the positively charged carbon</u> and disperse the positive charge.

Examiner's Comment

- Most students were able to draw the correct mechanism and identify the major product. However, some students were careless and forgot the Cl^- ion in the first step.
- The explanation for why the major product was formed was considerably poorer. Students should refer to the positively charged carbon atom clearly. Avoid ambiguous references such as:
  - the carbocation refers to the entire intermediate ion, not a single C atom;
  - the sp^2 carbon could be any of the C atoms on the benzene ring;
  - the benzylic carbon could be either of the C atoms bonded to the benzene ring.

5(e)(i)(ii)



J **K**

Step 2: ethanolic KOH, heat

Step 3: ethanolic KCN, heat

Examiner's Comment

- Students who were able to identify **J** correctly were able to complete the rest of the question well. **J** is formed via electrophilic addition, like the example you drew for HC*l* in part **(d)(i)**.
- In HC*l*, the bond is polar and H bears the $\delta+$ charge. In IC*l*, the bond is also polar. Since chlorine is more electronegative than iodine, iodine bears the $\delta+$ charge.
- As for the rest of the synthesis, the elimination step comes before the nucleophilic substitution step because the C-I bond is weaker than the C-C*l* bond.