HWA CHONG INSTITUTION
2022 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS (PAPER 3)

---

1 (a) (i) **[½]** working
[½] answer to nearest integer (*n* must be 65)

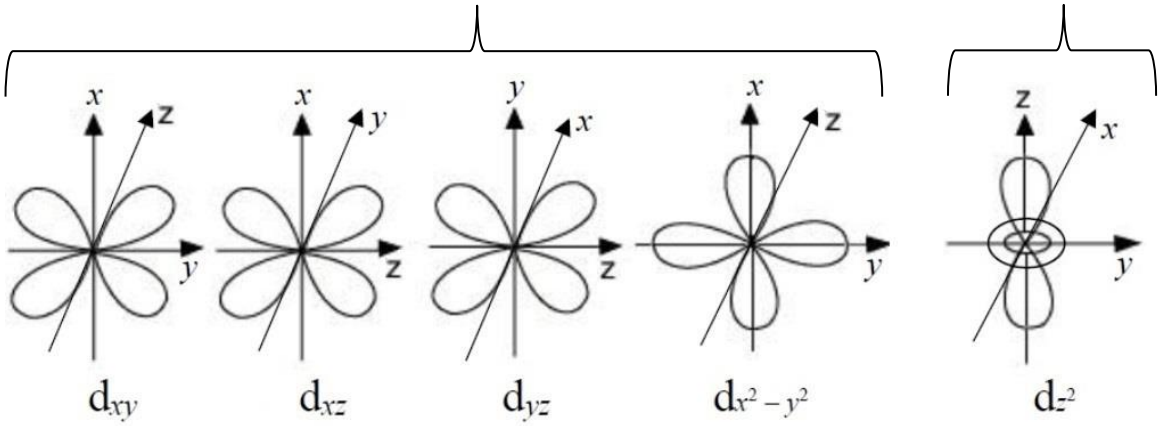
$$63 \times \frac{74.1}{100} + n \times \frac{25.9}{100} = 63.5$$

$$25.9n = 6350 - 4668.3$$

$$\therefore n = \frac{1681.7}{25.9} = 65$$

1 (a) (ii) **[1]** nucleon number is the <u>total number of protons and neutrons</u> in the nucleus of an atom

1 (a) (iii) **[1]** draw any one of these **[1]** draw this



For each 1m: ½m for drawing the shape
½m for labelling x y z axes AND 'naming' that orbital
(students who drew, say, the d_{z^2} orbital but named it as $d_{x^2-y^2}$ are penalised)

1 (b) (i) **[½]** Zn oxidised to Zn^{2+}
AND justify in terms of $E^{\ominus}(Zn^{2+}/Zn)$ vs. $E^{\ominus}(Cu^{2+}/Cu)$ and $E^{\ominus}(Au^{3+}/Au)$

[½] Explain why Zn^{2+} is not reduced at the cathode
in terms of $E^{\ominus}(Zn^{2+}/Zn)$ vs. $E^{\ominus}(Cu^{2+}/Cu)$

[½] Au is collected as anode sludge / Au falls off the anode
(Reject 'Au remains on the anode' / 'remains as anode' / 'remains on the Shakudo')

[½] Explain why Au is not oxidised in terms of $E^{\ominus}(Au^{3+}/Au)$ vs. $E^{\ominus}(Cu^{2+}/Cu)$

<u>Sample write-up:</u>

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^{\ominus} = -0.76$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^{\ominus} = +0.34$ V
$Au^{3+} + 3e^- \rightleftharpoons Au$ $E^{\ominus} = +1.52$ V

At the anode,
$E^{\ominus}(Zn^{2+}/Zn)$ is the least positive (or most negative), so Zn oxidises to Zn^{2+} (which enters the solution).
$E^{\ominus}(Au^{3+}/Au)$ is more positive than $E^{\ominus}(Cu^{2+}/Cu)$, therefore Au is not oxidised, Au sinks to the bottom of the container as anode sludge.

At the cathode,
$E^{\ominus}(Zn^{2+}/Zn)$ is less positive (or more negative) than $E^{\ominus}(Cu^{2+}/Cu)$, therefore Zn^{2+} is not reduced (but remains as Zn^{2+} in the solution).

1 (b) (ii) $Q = n(\text{electrons}) \times F = n(\text{electrons}) \times L \times e = It$

$$\frac{0.26}{63.5} \times 2 \times L \times 1.60 \times 10^{-19} = 1.10 \times 12 \times 60$$

$$L = 6.04 \times 10^{23}$$

[2]
Any mistake loses 1m
No ½m for this part

1 (c) (i) **[1]** no electron-rich centres / no region of high electron density / no $\delta+$ carbon / non-polar C–C and C–H bonds

1 (c) (ii) **[½]** *difference in reaction condition*: Benzene needs conc. H_2SO_4 as catalyst while propoxybenzene doesn't. (Reject discussion of temperature ∵ for benzene, even at higher temperature (55 °C), the reaction still doesn't work if conc. H_2SO_4 catalyst isn't added. The question also never label the temperature for propoxybenzene's nitration, so students shouldn't be looking at temperature.)

[½] *difference in organic products*: Benzene only mono-nitration / mono-substitution or draw out the nitrobenzene, while propoxybenzene is tri-substituted.

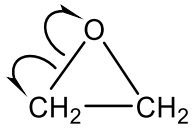
[½] *regarding the lone pair on O*: Oxygen's lone pair delocalises over the benzene ring. (Reject: 'O is electron donating' / '$OCH_2CH_2CH_3$ is electron donating' ∵ that could refer to an inductive effect.) (Reject: 'alkyl group electron donating' – must discuss about the lone pair on O)

[½] *so what if that lone pair delocalises*: This increases electron density in the benzene ring, making it more reactive towards electrophile / more susceptible towards electrophilic substitution.

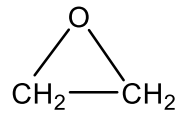
1 (d) **[1] P**: $HOCH_2CH_2CHO$ **[1] R**: $HOCH_2CH_2CH_2OH$
(allow ecf from P only if student's P can be reduced to student's R using the H_2/Pt)

[1] Q: $HOCH_2CO_2H$
(all three structures must fit their given molecular formula)

1 (e)

initiation:  $\rightarrow$ $^{\bullet}CH_2CH_2O^{\bullet}$

[½] two curly half-arrows 'fly out' from <u>one</u> C–O bond, 'fly to' the correct atoms
[½] correct product radical, • at correct atoms

propagation: $^{\bullet}CH_2CH_2O^{\bullet}$ +  $\rightarrow$ $^{\bullet}CH_2CH_2O–CH_2CH_2O^{\bullet}$

[½] correct radical reacts with epoxyethane
[½] correct product radical, • at correct atoms

2 (a) (i) No. of moles of thiosulfate needed to react with 25 cm^3 of solution = 12.0/1000 x 0.50 = 0.006

No. of moles of I_2 in 25 cm^3 of solution = 0.006/2 = 0.003 mol [1]

No. of moles of I_2 formed from solid NaI = 0.003 x (100/25) = 0.012 mol

$2I^- + 2e \rightarrow I_2$

No. of moles of electrons lost by iodide on reacting with conc H_2SO_4 = 0.012 x 2 = 0.024 mol

No. of moles of electrons gained per mole of sulfuric acid = 0.024 / 0.003 = 8 [1]

Oxidation state of sulfur product = +6 – 8 = **–2** [1]

2 (a) (ii) $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^{\ominus}$ = +1.36 V or $E^{\ominus}$ (Cl_2/Cl^-)= +1.36 V
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^{\ominus}$ = +0.54 V or $E^{\ominus}$ (I_2/I^-)= +0.54 V
[1] for quote $E^{\ominus}$ and comment on more/less positive $E^{\ominus}$

Iodide is a <u>stronger reducing agent</u> than chloride due to <u>less positive</u> $E^{\ominus}(I_2/I^-)$. Iodide is more easily oxidised to iodine and is able to <u>reduce sulfur atom from +6 to a product with a lower oxidation state</u> or <u>chloride is unable to reduce H_2SO_4.</u> [1]

2 (b) (i) <u>Strong ionic bonds</u> in **P** require <u>large amounts of energy</u> to overcome, hence **P** has high melting point and exists as a solid. [1]

<u>Weak dispersion forces</u> between molecules of **Q** require <u>lesser energy</u> to overcome, hence **Q** has low melting point and exists as a liquid. [1]

2 (b) (ii) **P**: $MgCl_2$ [1]

Q: $SiCl_4$ [1]

2 (b) (iii) **P** undergoes <u>slight/partial hydrolysis</u> in water [½]

$Mg(H_2O)_6^{2+} + H_2O \rightleftharpoons Mg(H_2O)_5(OH)^+ + H_3O^+$ [1]

Q undergoes <u>complete hydrolysis</u> in water [½]

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ [1]

2 (c) (i) $K_p = P_{Cl2}\ P_{PCl3} / P_{PCl5}$ [1]

2 (c) (ii)

	$PCl_5(g)$	⇌	$PCl_3(g)$	+	$Cl_2(g)$
Initial pressure/kPa	84 + x		0		0
Change in pressure/kPa	–x		+x		+x
Eqm pressure/kPa	84		x		x

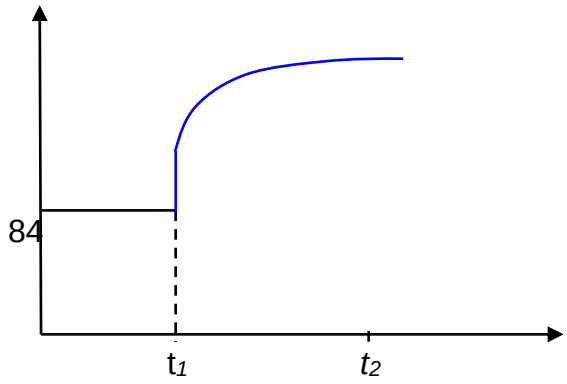
Total equilibrium pressure = (84 + 2x) kPa

(84 + x) / (84 + 2x) = 0.70 [1] correctly set up initial P/total eqm P = 0.7

84 + x = 58.8 + 1.4x → x = 63 [1] find partial pressure of PCl_3 or Cl_2

$K_p = 63^2 / 84 = 47.3$ kPa or 47300 Pa [1]
*must use 84 as equilibrium pressure of PCl_5 is given in question.

2 (c) (iii) partial pressure of PCl_5 / kPa



[1] correct sketch at t_1 (sharp increase) + explain: volume reduced hence pressure increased

[1] correct sketch between t_1 and t_2 (increase at decreasing rate) + explain: POE shifts <u>left</u> to lower total pressure by forming <u>fewer gaseous molecules</u>

2 (d) **X** undergoes **<u>oxidation /</u> iodoform** reaction with warm alkaline aqueous iodine I_3 → **X** contains **<u>$CH_3CH(OH)$–</u>** (structure must be drawn out, there is no name for this structure)

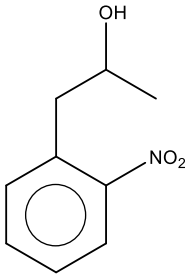
X undergoes (nucleophilic) **<u>substitution</u>** reaction with PCl_5 → **X** contains an <u>alcohol</u> group

Y is **<u>reduced</u>** by tin, conc HC*l* → **Y** contains **<u>nitrobenzene</u>** or **Z** contains **<u>phenylamine</u>**.

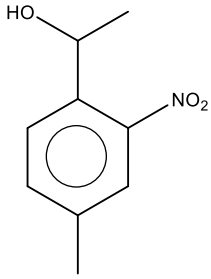
This is followed by an intramolecular **<u>nucleophilic substitution</u>** reaction between **<u>chloroalkane and phenylamine</u>** to form **Z**.

2 marks for any 4 underlined points from above.
1 mark for 2-3 underlined points from above.

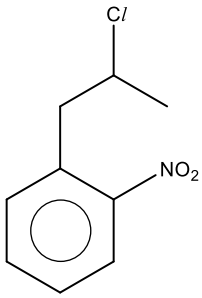
X:



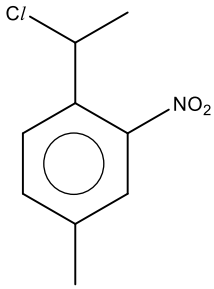
alternative structure:



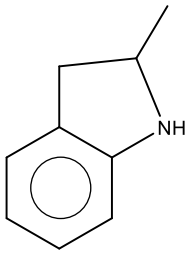
Y:



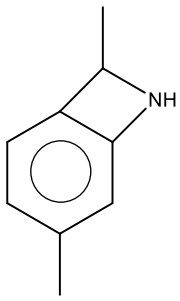
alternative structure:



Z:



alternative structure:



Z must be in 1,2 position otherwise no intramolecular reaction.

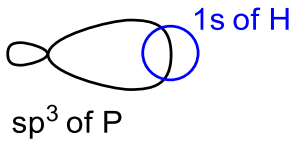
3 (a) (i) Nitrogen is in Period two of the Periodic Table whereas phosphorus is in Period three. Phosphorus has energetically accessible 3d subshells to accommodate beyond eight electrons in its valence shell. However, for nitrogen, the next available subshell beyond 2p is 3s, which is not energetically accessible. [1]

(credit is awarded for an idea of nitrogen being unable to “expand octet”.)

3 (a) (ii) σ: 6
π: 1

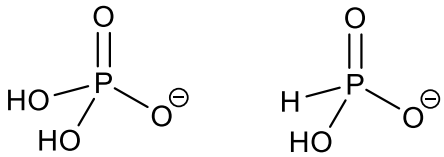
[1] for **both**

3 (a) (iii) For P–H: head-on overlap between the sp^3 orbital P and the 1s orbital of H to form an sp^3–1s σ bond. [1]



[1] correct labels are required to score this credit.

3 (a) (iv) The structures of the conjugate base of H_3PO_4 and H_3PO_3 are shown below.

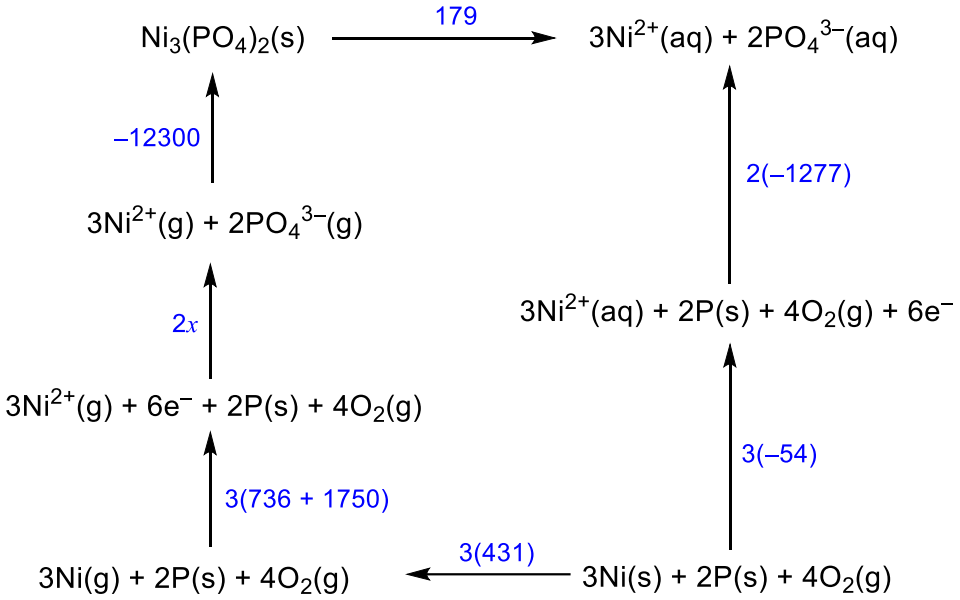


H_3PO_4 has a higher pK_a than H_3PO_3, implying that the latter has a large K_a and thus H_3PO_3 ionises to a greater extent than H_3PO_4. [0.5]

$H_2PO_4^-$ is therefore less stable than that of $H_2PO_3^-$ and because the former has 2 -OH groups and the latter has 1 -OH group [0.5], it can be inferred that the negative charge on O^- in $H_3PO_4^-$ is likely to be intensified by the presence of the extra -OH via an electron-donating effect. [0.5]

The lone pair of electrons on O^- in $H_2PO_3^-$ delocalises over P=O to a greater extent than that in $H_2PO_4^-$ (due to the former having only 1 -OH group). [0.5]

3 (b) Let the standard enthalpy change of formation of $PO_4^{3-}(g)$ be x.



Credit is awarded based on the following correct enthalpic terms illustrated in the cycle (state symbols and molar ratios are included):

[1] ΔH_f for **both** $PO_4^{3-}(aq)$ and $Ni^{2+}(aq)$.
[1] First and second ionisation energies for Ni(g)
[1] The rest of the enthalpic terms, i.e. ΔH_{soln} $Ni_3(PO_4)_2(s)$, ΔH_{atm} Ni(s) and LE $Ni_3(PO_4)_2(s)$
[1] **Close cycle** drawn and correct application of Hess' law (ecf allowed)

Using Hess' Law,

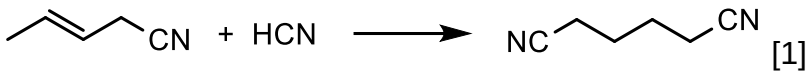
$2x = -3(736 + 1750) - 3(431) + 3(-54) + 2(-1277) - 179 + 12300 = +654$ kJ mol^{-1}
$x = +327$ kJ mol^{-1}

3 (c) (i) The melting point of Ni is higher compared to that of Ca. As compared to Ca, more energy is required to overcome the stronger metallic bonds between the Ni^{2+} ions and the sea of delocalised electrons, since both 3d and 4s electrons are involved in the metallic bonding. [1]

The density of Ni is higher compared to that of Ca, because Ni has a smaller atomic radius (or cationic radius) and a larger A_r than Ca. Since density is the mass per unit volume, assuming that the atoms are spherical in shape, Ni will have a higher density as compared to Ca. In addition, having a smaller atomic radius also means that its structure is more closely packed. [1]

3 (c) (ii) CO undergoes a ligand exchange reaction and displaces O_2 from oxyhaemoglobin. CO binds more strongly / irreversibly (or CO is a stronger ligand) [1] to haemoglobin than O_2 thus preventing oxygen transport (in the blood/tissues etc.) [1]

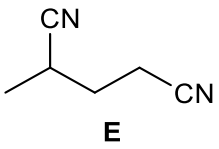
3 (d) (i)



[1]

3 (d) (ii) Ni is being <u>oxidised from 0 to +2</u> [1] and HCN is being added to NiL_3 as –H and –CN ligands. [1]

3 (d) (iii)



E [1]

3 (e) (i) HCN and alkene are in excess and <u>the change in their concentration during the reaction is negligible</u>/ <u>their concentration appears to be unchanged</u>. Hence both concentration terms can be subsumed into *k*'. [1]

3 (e) (ii) From the graph, $m = \dfrac{1.10 - (-0.55)}{-0.78 - 0.04} = -2.01$

Order of reaction with respect to L is –2. [1]

3 (e) (iii) When [L] doubles, rate will be reduced to a quarter of its original value. [1]
(allow ecf)

4 (a) Because its molecules are non-polar, they can form dispersion forces with the non-polar molecules in skin and be absorbed. [1]

It has a simple molecular structure with only weak dispersion forces between its non-polar molecules, therefore little energy is required to overcome these forces, causing it to be easily vapourised. [1]

4 (b) (i) 2-chloro-6-methylheptane [1]

4 (b) (ii) The central A*l* atom in these molecules are only surrounded by six valence electrons, therefore it is electron-deficient / contains a vacant low-lying orbital that can accept an electron pair. [1]

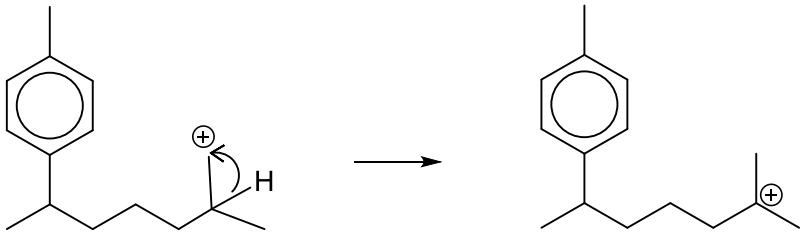
4 (b) (iii) constitutional / structural / positional isomers [1]

The $–CH_3$ group of methylbenzene is 2,4–directing and hence directs the electrophile to preferentially substitute on C2 or C4 instead of C3. [1]

4 (b) (iv) (limiting) Br_2, uv light [1]

4 (b) (v) There are <u>six equivalent H atoms</u> on the terminal $–CH_3$ groups that can be substituted to produce R, therefore there is a <u>high chance that the bromine radical will abstract one of those H atoms</u> to produce the corresponding alkyl radical. [1]

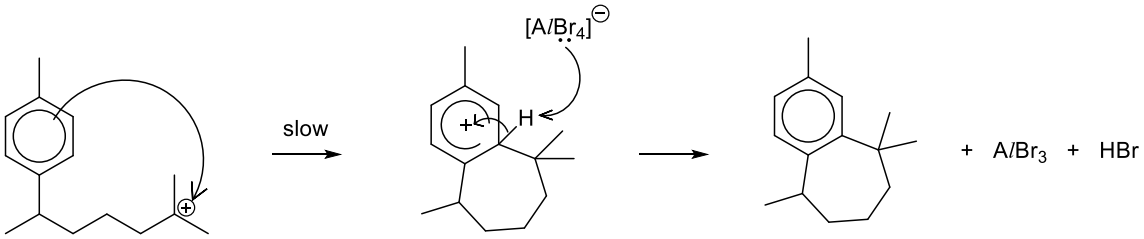
4 (c) (i)



[1]

4 (c) (ii) The carbocation II has three electron-donating alkyl groups bonded to the positively charged carbon while carbocation I only has one. [1] Therefore, the positively charge in carbocation II is more dispersed, resulting in carbocation II being more stable. [1]

4 (c) (iii) electrophilic substitution [1]



4 (d) (i) hydrolysis [1]

$ROCONHR' + H^+ + H_2O \rightarrow ROH + R'NH_3^+ + CO_2$ [1]

OR

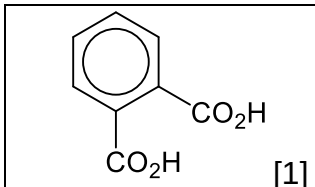
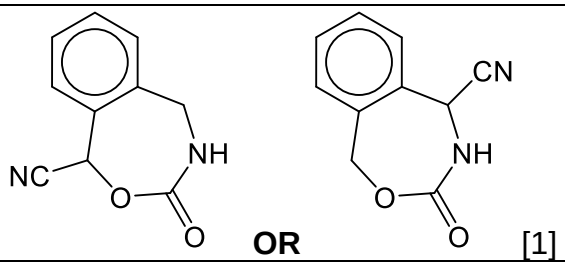
$ROCONHR' + H_3O^+ \rightarrow ROH + R'NH_3^+ + CO_2$

4 (d) (ii) The carbamate group contains as amide as well as an ester functional group, both of which are able to undergo hydrolysis. [1]

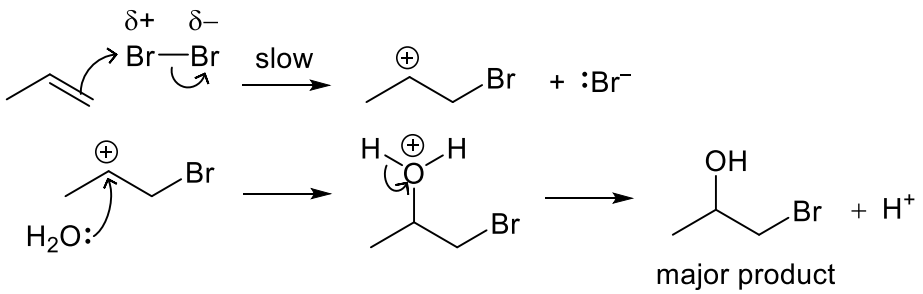
OR The carbamate C is very electron deficient and is able to attract the H_2O nucleophile.

4 (e) (i) nitrile [1]

4 (e) (ii)

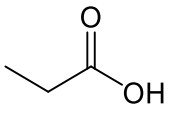
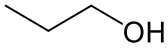
T	S
 [1]	 **OR** [1]

5 (a) (i)



[1] correct secondary carbocation and major product
[1] correct mechanism drawn

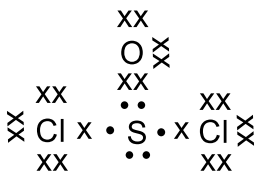
5 (a) (ii)

D:  **E**: 

Step 1: aqueous I_2 in NaOH warm, followed by dilute H_2SO_4
Step 2: LiA*l*H_4 in dry ether
Step 3: excess concentrated H_2SO_4, heat

[3] for correct structures of **D** and **E** and reagents and conditions in each step.

5 (b) (i)



[1]

Shape: trigonal pyramidal, bond angle: 107° [1] for both correct

5 (b) (ii) pH of **J** is 0.5, **H** is 2.5 and **G** is 3.0. [1]

J undergoes hydrolysis in water to produce HC*l*, which is a strong acid. Therefore, it has the lowest pH. [1]

G and **H** are carboxylic acids, which are weak acids. The conjugate base of **H** is more stable than **G** due to presence of electronegative C*l* atom, which withdraws electron density from the carboxylate ion, dispersing the negative charge, making **H** more acidic than **G**. [1]

J hydrolyses in water to produce Cl^- ion, forming AgCl white ppt. [1]

J undergoes hydrolysis more readily than **H** as the C-Cl carbon in **J** is much more electron deficient, having bonded to 2 highly electronegative atoms O and Cl, making it more susceptible to nucleophilic attack, than the C-Cl carbon in alkyl chloride **H**. [1]

5 (c) (i) [Cl^-] in water sample = $0.0500 \times 21.60 / 25.0 = 0.0432$ mol dm^{-3} [1]

5 (c) (ii) IP = $(0.1 \times 0.05 / 25.1) (25 \times 0.0432/25.1) = 8.57 \times 10^{-6}$. [1]
Since IP > K_{sp}, precipitate will be formed. [1]

5 (c) (iii) [Ag^+] = $10^{-4.87} = 1.349 \times 10^{-5}$ mol dm^{-3}
[Cl^-] = $1.80 \times 10^{-10} \div (1.349 \times 10^{-5}) = 1.33 \times 10^{-5}$ mol dm^{-3} [1]

5 (c) (iv) Before point **E**, the Ag^+ added is used to precipitate AgCl continuously, hence the [Ag^+] remains relatively the same, so pAg value decreases steadily. [1]

As it passes through point **E**, all AgCl ppt has been formed. Ag^+ added is not used to precipitate AgCl. [Ag^+] increases quickly, causing pAg to decreases sharply. [1]

5 (c) (v) NH_3(aq) will form $[Ag(NH_3)_2]^+$ complex [1], consuming more Ag^+, causing titre value to be larger, and hence larger calculated [Cl^-]. [1]