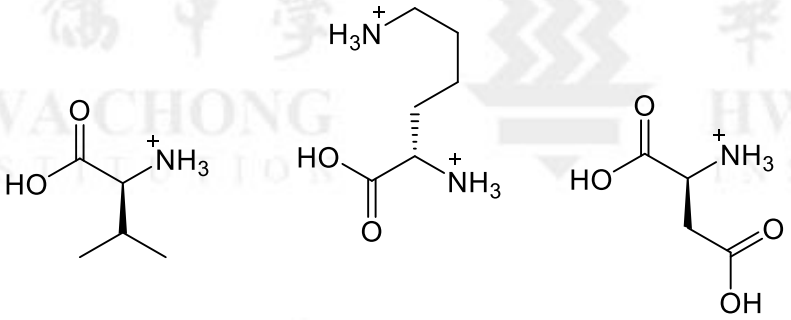
Paper 3

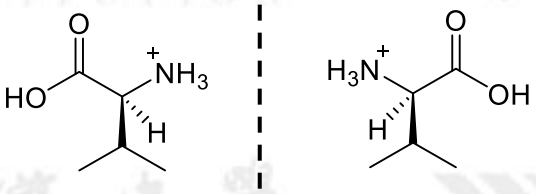
1 (a) (i)



[1] each x 3

1 (a) (ii) [1] Pick one of the products from (a)(i) and draw mirror images using stereochemical formula with appropriate dash/wedge, showing the tetrahedral shape about the chiral carbon, and dotted line to show the mirror plane.

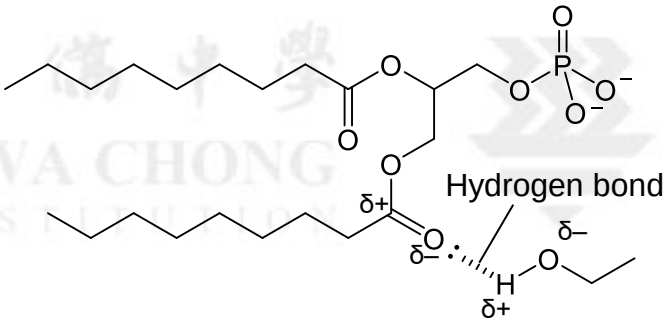
e.g.



The product has two isomers that are [1] <u>non-superimposable mirror images</u>, hence they are enantiomers.

1 (a) (iii) [1] The host cell recognises a specific conformation/chirality of the spike protein. If the amino acid in the protein is swapped with its enantiomer, it changes the conformation/3-dimensional arrangement of the protein, and the host cell no longer recognises it and the virus cannot enter

1 (b) (i)



[2] Draw one ethanol molecule and indicate correct hydrogen bond with appropriate illustrations. Students may choose any part of the phospholipid that can form hydrogen bond with the ethanol.

1 (b) (ii) [1] Dispersion forces of attraction forms between the hydrocarbon chains of the soap and phospholipid ions

[0.5] Water forms hydrogen bonding with the carboxylate group on the soap.

[0.5] The above, together with the mechanical action of water forces the phospholipid particles to be pulled apart/ separated from each other/ washed away, hence breaking up the membrane.

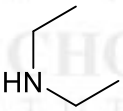
1 (b) (iii) [1] Surface charge of the fiber polarises/distorts the electron cloud of the non-polar dust molecules

[1] Forms ion – induced dipole attraction, OR electrostatic force of attraction between the charge on the fiber and the induced dipole on the dust molecule

1 (c) Copper metal is made up of a [1]giant metallic lattice held together by the [1]electrostatic forces of attraction between the Cu^{2+} metal ions and the sea of delocalised electrons

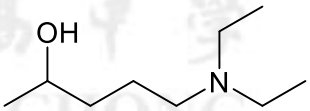
1 (d) (i)

[1] P:

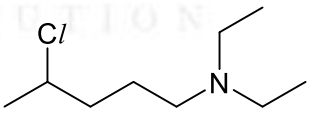


1 (d) (ii) [1] Step 2: $LiAlH_4$/ dry ether OR $NaBH_4$ OR H_2/ Ni/ high pressure
[1] Step 3: PCl_3 OR PCl_5 OR $SOCl_2$/ warm OR concentrated HCl/ $ZnCl_2$/ heat
[1] Step 4: ethanolic concentrated ammonia, heat in sealed tube

[1] R:



[1] S:



1 (d) (iii) [1/2] Lone pair of electrons on N_a is delocalised into the aromatic ring(s), making the lone pair [1/2] less available for donation/ accept a proton.

[1/2] N_b has 3 electron donating alkyl groups attached to it, making its [1/2] lone pair of electrons more available for donation/ accept a proton.

[1] N_b more basic than N_a.
Awarded only if there is some attempt at explaining the difference.

1 (d) (iv) [1] Reagent/Test
[1/2] Positive observation
[1/2] Negative observation

$K_2Cr_2O_7(aq)$/ $H_2SO_4(aq)$/ heat. Orange $K_2Cr_2O_7$ turns green for hydroxychloroquine but remains orange for chloroquine
or
$KMnO_4(aq)$/ $H_2SO_4(aq)$/ heat. Purple $KMnO_4$ decolourises for hydroxychloroquine but remains purple for chloroquine
or
PCl_5. Or $SOCl_2$/ warm. White fumes of HCl for hydroxychloroquine but no white fumes for chloroquine
or
Na(s). Effervescence of (colourless odourless) H_2 gas that gives pop sound with burning splint for hydroxychloroquine but no effervescence for chloroquine

2 (a) (i) Off-white precipitate **[1/2]** turns brown **[1/2]** upon reacting with dissolved oxygen.

Reject: white ppt for $Mn(OH)_2$, brown ppt of MnO_2 (wrong species)

2 (a) (ii) No. of moles of iodine formed = ½ x (12.60/1000 x 0.01) = 6.30×10^{-5} mol

No. of moles of Mn^{3+} that reacted = $2(6.30 \times 10^{-5}) = 1.26 \times 10^{-4}$ mol

No. of moles of dissolved oxygen = $1.26 \times 10^{-4} / 4 = 3.15 \times 10^{-5}$ mol **[1]**

[dissolved oxygen] = $3.15 \times 10^{-5} / 500 \times 1000 = 6.30 \times 10^{-5}$ mol dm^{-3} **[1]**
= 0.002016 g dm^{-3}
= 2.02 mg dm^{-3} + conclusion **[1]**

Fish will not be able to survive in this sample as the dissolved oxygen is lower than what is needed.

Ecf is allowed if no. of moles of oxygen is calculated wrongly as long as student draws the correct conclusion based on the calculated concentration.

2 (b) (i) $K_{sp} = [Cu^{2+}][OH^-]^2$ **[1]**
$K_{sp} = (3 \times 10^{-6})(2 \times 3 \times 10^{-6})^2 = 1.08 \times 10^{-16}$ **[1]**
units = $mol^3\ dm^{-9}$ **[1]**

2 (b) (ii) $[OH^-] = 10^{-(14-8.73)} = 5.3703 \times 10^{-6}$ **[1]**

$K_{sp} = [Cu^{2+}][OH^-]^2$
$[Cu^{2+}] = Ksp \div [OH^-]^2 = 3.7448 \times 10^{-6}$ mol dm^{-3}
= 0.238 mg dm^{-3} + conclusion **[1]**

Conclusion: $[Cu^{2+}]$ lower than MCLG hence water is possible for consumption.

Ecf is allowed based on wrong Ksp from (b)(i).

2 (c) (i) Electrode with ethanol: negative
Electrode with oxygen/air: positive **[1] both correct polarities**

Electron flow from the electrode with ethanol towards electrode with oxygen (to be drawn in the external circuit) **[1]**

Reject: Arrow that is drawn on the electrolyte.

2 (c) (ii) $CH_3CH_2OH + H_2O \rightarrow CH_3CO_2H + 4H^+ + 4e^-$ **[1]**

2 (c) (iii) $CH_3CH_2OH + O_2 \rightarrow CH_3CO_2H + H_2O$ **[1]**

Ecf accepted only if they've combined the eqn in **(c)(ii)** with $O_2 + 4H^+ + 4e \rightarrow 2H_2O$

2 (c) (iv) $\Delta G^\ominus_r = -(-174) + (-389) + (-237) = -452$ kJ mol^{-1} **[1]**

$\Delta G^\ominus_r = -nFE^\ominus_{cell}$
$-452000 = -4(96500)\ E^\ominus_{cell}$
$E^\ominus_{cell} = +1.17$ V **[1]**

Ecf accepted if $E^\ominus_{cell}$ is calculated from wrong $\Delta G^\ominus_r$

2 (c) (v) Cigarette smoke contains volatile compounds (e.g aldehydes or other alcohols) that may be oxidised in the cell. **[1]**

3 (a) (i) The standard enthalpy change of combustion is the heat evolved when **one mole** of the substance is completely burnt in oxygen / burnt in excess oxygen at 298 K and 1 bar. **[1]**

3 (a) (ii) Heat absorbed by water, $q = mc\Delta T = 200 \times 4.18 \times (67.0 - 20.0)$
$= 39292$ J or 39.292 kJ **[1]**

Amount of cyclobutane used $= \dfrac{1.00}{12.0 \times 4 + 1.0 \times 8} = 0.01786$ mol

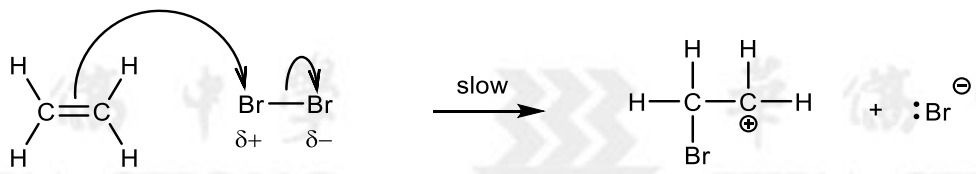
ΔH_c(cyclobutane) $= -39.292 / (0.01786 \times 0.8) = -2.75 \times 10^3$ kJ mol^{-1} **[1]**

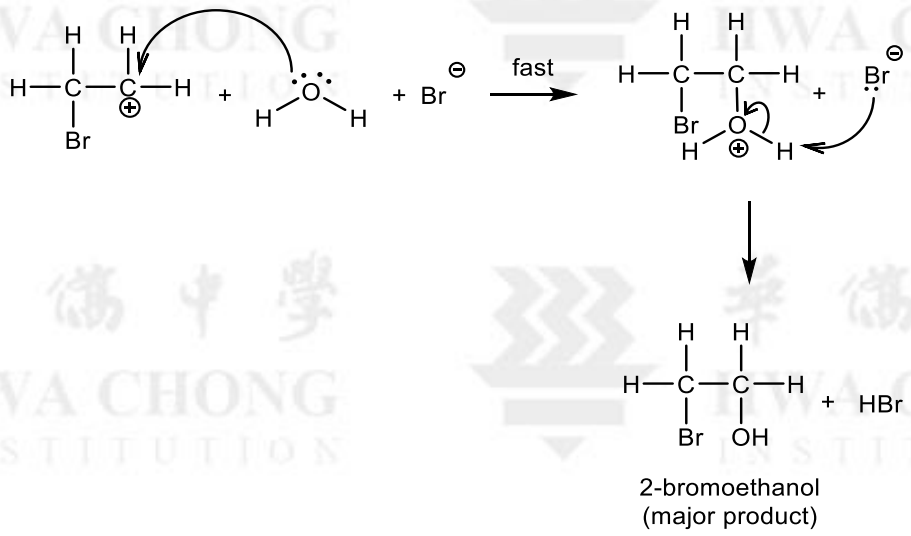
Ecf 2nd mark if student divided by correct moles and factored in 0.8

3 (a) (iii) $\Delta H_1 = \Delta H_c(\text{cyclobutane}) - 2\Delta H_c(CH_2{=}CH_2)$
$= -2750 - 2(-1422)$
$= +94.0$ kJ mol^{-1} **[1]**

Ecf from a(ii)

3 (b) (i) Electrophilic addition **[1]**



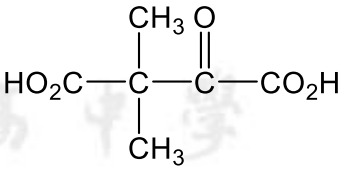


1m for slow step and 1m for the rest of the mechanism

3 (b) (ii) The electrons delocalise from the C=C to the C=O group, making the carbonyl carbon less electron deficient and hence less susceptible to attack by nucleophiles. This also reduces the electron density on the terminal carbon on the alkene / causes the terminal carbon on the alkene to be electron deficient and enable it to be attacked by CN^- nucleophile.

0.5m for each underlined point

3 (c) (i)



T: **[1]**

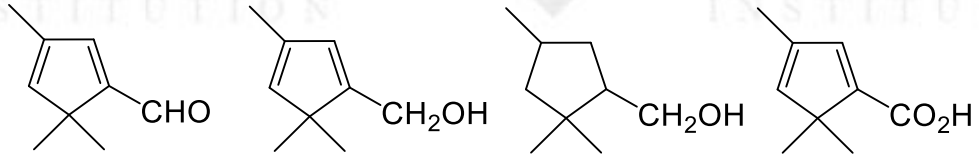
3 (c) (ii) **P** undergoes reduction with $NaBH_4$ to give **Q**
⇒ **P** contains an aldehyde

P undergoes reduction / catalytic hydrogenation to form **R**
⇒ **P** has C=C
⇒ Since **P** gains 6H atoms upon reduction (2H to reduce the carbonyl group), P has two C=C
⇒ **R** contains 1 alcohol group (give the mark if alcohol in **Q** mentioned instead for reduction of **P** with $NaBH_4$)

P undergoes oxidation with Tollen's reagent, followed by acidification to give **S**
⇒ **P** is an aldehyde
⇒ **S** contains a carboxylic acid

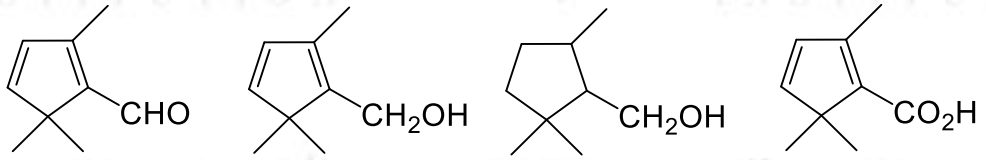
S undergoes oxidative cleavage to form **T** and **U**.

P: **Q:** **R:** **S:**



Alternative answer:

P: **Q:** **R:** **S:**



1m each structure, 0.5m each underlined point, total: 9m

4 (a) (i) Na^+ has <u>low charge density</u> [•] and hence <u>does not undergo hydrolysis</u>. [•]

Since <u>Al^{3+} has higher charge density</u> than Na^+ [•], it can undergo <u>partial hydrolysis</u> in aq solution, resulting in pH < 7**.** [•]

$[Al(H_2O)_6]^{3+}$ (aq) + $H_2O(l)$ ≪ $[Al(H_2O)_5OH]^{2+}$ (aq) + H_3O^+(l) **[1]**

$SiCl_4$ undergoes <u>complete hydrolysis</u> [•]

$SiCl_{4(l)} + 4\ H_2O_{(l)} \rightarrow SiO_2.2H_2O_{(s)} + 4\ HCl_{(aq)}$ (accept $Si(OH)_4$ as product) **[1]**

2 marks for all 5 [•]; 1 mark for 3 or 4 [•]

4 (a) (ii) Correct pH value suggestion: 3.1 – 5.0 **[1/2]**

From the Data Booklet, the ionic radius of the relevant ions can be obtained: Na^+ - 0.095 nm; Al^{3+} - 0.050 nm; Fe^{3+} nm – 0.055 nm **[1/2]**

Charge density of Fe^{3+} is much higher than Na^+ but slightly lower than Al^{3+}; its degree of hydrolysis is slightly lower than Al^{3+}, hence, the pH of $FeCl_3$ is in between that of NaCl and $AlCl_3$ (but closer to $AlCl_3$) **[1]**

4 (b) (i) E^o (Fe^{2+}/Fe) = –0.44 V
E^o (O_2/OH^-) = +0.40 V
E^o_{cell} = +0.40 – (–0.44) = +0.84 V **[1]**

4 (b) (ii) When $Fe(OH)_2$ is formed, [Fe^{2+}] decreases. This causes the position of equilibrium (Fe^{2+} + 2e ≪ Fe) to shift to the left. **[1/2]** $E_{Fe2+/Fe}$ will then become more negative. **[1/2]**

In addition, $[OH^-]$ decreases, causing the position of equilibrium ($O_2 + 2H_2O + 4e \ll 4OH^-$) to shift to the right. **[1/2]** Thus $E_{O2/OH-}$ becomes more positive. **[1/2]**

Since $E_{cell} = E_{O2/OH-} - E_{Fe2+/Fe}$, E_{cell} will become more positive. **[1]**

4 (b) (iii) $E^o_{cell} = +0.40 - (-0.56) = +0.96\ V > 0$
Hence $Fe(OH)_2$ readily becomes further oxidised. **[1]**

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ **[1]**

4 (c) (i) Step 1: Water will cause $FeBr_3$ to no longer act as a Lewis acid catalyst as it will form ions in water. **[1]**

Step 2: $K_2Cr_2O_7$ is not strong enough to oxidise the alkyl side chain. **[1]**

Step 3: The lone pair of electrons on Br can delocalised into the benzene. This results in a partial double bond and thus the Br group cannot be easily substituted. **[1]**

Step 4: The $-CO_2H$ group is 3-directing while the –OH group is 2,4-directing. The product shown in the scheme will not be the major product. **[1]** (Accept multi-substitution)

4 (c) (ii) Sn, concentrated HC*l*, heat (followed by controlled addition of NaOH(aq))

4 (d) When H^+ is added to the blood, the following reaction occurs
$H^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq)$ **[1]**

When OH- is added, it is removed by the carbonic acid.
$H_2CO_3(aq) + OH^- \rightarrow HCO_3^-(aq) + H_2O(l)$ **[1]**

The amount of HCO_3^- (relative to the amount of CO_2) decreases; however, the amount of the change is tiny compared to the large amount of HCO_3^- present in the blood.
As the original amounts of H_2CO_3 and HCO_3^- are large compared to the amount of H^+ or OH^- ions added, the ratio $[HCO_3^-] / [H_2CO_3]$ remains almost constant.
Since $K_a = [H^+][HCO_3^-] / [H_2CO_3]$, and K_a is a constant, so $[H^+]$ and pH remains almost constant. **[1]**

5 (a) (i) MgO is a **<u>basic oxide</u>** and Al_2O_3 is an **<u>amphoteric oxide</u>**, hence, **<u>both reacts with acids.</u>** [0.5]

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O \quad [0.5]$$
$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \quad [0.5]$$

P_4O_{10} is an **<u>acidic oxide</u>** and Al_2O_3 is an **<u>amphoteric oxide</u>** (only need to see once), hence, **<u>both reacts with bases</u>**. [0.5]

$$P_4O_{10} + 12NaOH \rightarrow 4Na_3PO_4 + 6H_2O \quad [0.5]$$
$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4 \quad [0.5]$$

5 (a) (ii) No. of moles of kaolinite = 1.8 / 258 = 0.006977 mol
No. of moles of H_2O = 0.251 / 18.0 = **0.01394 mol**
z = 0.01394 / 0.006977 = **2** [1]

No. of moles of HCl = 1.20 x 35/1000 = 0.0420 mol

No. of moles of Al_2O_3 = 0.0420 **/ 6** = 0.00700 mol [1] ecf

x = 0.00700 / 0.006977 = **1** [1]

Mass of Al_2O_3 = 0.006942 x 102.2 = 0.709 g
Mass of SiO_2 = 1.8 – 0.709 – 0.251 = **0.840** g
No. of moles of SiO_2 = 0.840/60 = 0.0140 mol

y = 0.014 / 0.006977 = **2** [1]

5 (b) Al_2O_3 has a **<u>giant ionic lattice structure</u>** where Al^{3+} and O^{2-} are electrostatically attracted to one another through **<u>strong ionic bonding</u>**. A lot of energy is needed to overcome the strong ionic bonding, hence, a high melting point. [1]

SiO_2 has a **<u>giant molecular covalent structure</u>** where Si and O atoms are held together by strong covalent bonds. SiO_2 has a high m.p because a lot of energy is needed to overcome the **<u>extensive amount of strong covalent bonds</u>** in the giant molecular structure. [1]

[1] For the mention of the word **energy**

5 (c) (i) Cathode: $Al^{3+} + 3e^- \rightarrow Al$ [1]
Anode: $2O^{2-} \rightarrow O_2 + 4e^-$ [1]

5 (c) (ii) $Al^{3+} + 3e^- \rightleftharpoons Al$ -1.66V
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ -0.83V
citing the 2 correct half-eqns / citing the 2 correct $E^\ominus$ values in an unambiguous way e.g. $E^\ominus(Al^{3+}/Al)$ [1]

The reduction potential of water is **<u>less negative (or more positive)</u>** than Al^{3+}. Hence, water will be **<u>preferentially reduced</u>** at the cathode over Al^{3+}. [1]

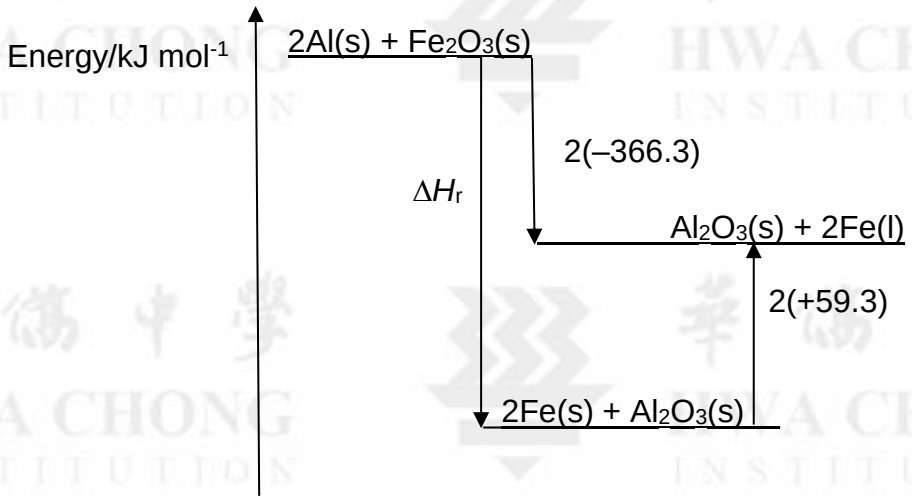
5 (c) (iii) Mass of Al_2O_3 in bauxite = **60/100** x 2.28 x 10^6 = 1.368 x 10^6 kg
No. of moles of aluminium = 1.368 x 10^9/102 **x 2** = 2.6824 x 10^7 mol [1]

No. of electrons required = 2.6824 x 10^7 **x 3** = 8.0471 x 10^7 mol **ecf mole ratio from half-eqn in (i)**

Q = nF = 8.03 x 10^7 x 96500 =**7.7654 x 10^{12} = 7.77 x 10^{12} C** [1]

Mass of aluminium = 2.6824 x 10^7 x 27.0 = **7.24 x 10^8 g** [1]

5 (d)



Hess' Law: ΔH_r = 2(–366.3) – 2(+59.3) = –851.2 kJmol^{-1}