

2016 H2 Chemistry Preliminary Examination Paper 3 – Suggested Answers

- 1 (a) (i) The two bond energies of bonds between C and O in the *Data Booklet* are $E(\text{C}=\text{O})$: $+740 \text{ kJ mol}^{-1}$ and $E(\text{C}-\text{O})$: $+360 \text{ kJ mol}^{-1}$, which are double and single bonds respectively. The bond between C and O in carbon monoxide is however a triple bond which is stronger than both the double and single carbon-oxygen bonds. [1m]

(ii) Energy due to bond formation
 $= -E(\text{C}=\text{O}) - 3E(\text{H}-\text{H}) = -1046 - 3(436) = -2354 \text{ kJ mol}^{-1}$
 Energy due to bond breaking
 $= 4E(\text{C}-\text{H}) + 2E(\text{O}-\text{H}) = 4(410) + 2(460) = +2560 \text{ kJ mol}^{-1}$
 Enthalpy change of reaction
 $= +\Sigma \text{BE}(\text{bonds broken}) - \text{BE}(\text{bonds formed})$
 $= -2354 + 2560$ [1m]
 $= +206 \text{ kJ mol}^{-1}$ [1m]

- (b) (i) $\Delta G = \Delta H - T\Delta S$; Since $\Delta H = +206 \text{ kJ mol}^{-1}$, and $\Delta G = +142 \text{ kJ mol}^{-1}$.
 Hence at 298K, $+142 = +206 - (298)\Delta S$ [1m]
 $\Delta S = +0.215 \text{ kJ mol}^{-1} \text{ K}^{-1}$ [1m]

- (ii) When the reaction just becomes feasible, $\Delta G = 0$.
 Assuming ΔH and ΔS do not change over a large temperature change,
 $\Delta H = T\Delta S$, hence $T = \underline{958 \text{ K}}$ [1m] for correct ans + 3sf + units

- (c) (i)
- | | | | | | | | |
|-------------------------|---------------------------------|---|---------------------------------|---|-----------------------|---|-------------------------|
| | $\text{CH}_4(\text{g})$ | + | $\text{H}_2\text{O}(\text{g})$ | = | $\text{CO}(\text{g})$ | + | $3\text{H}_2(\text{g})$ |
| Initial pressure/ atm | 10/3 | | 5/3 | | 0 | | 0 |
| Change in pressure/ atm | $-1.8/3 = -0.6$ | | $-1.8/3 = -0.6$ | | $+1.8/3 = 0.6$ | | +1.8 |
| Eqm pressure/ atm | $3.33 - 0.6 = \underline{2.73}$ | | $1.67 - 0.6 = \underline{1.07}$ | | <u>0.6</u> | | +1.8 |
- [1m]

(ii)

$$\underline{K_p} = \frac{P_{\text{CO}} \cdot (P_{\text{H}_2})^3}{P_{\text{CH}_4} \cdot P_{\text{H}_2\text{O}}} \text{ [1m]}$$

$$K_p = [0.6 \times (1.8)^3] / [2.73 \times (1.07)]$$

$$= \underline{1.20 \text{ atm}^2} \text{ [1m]}$$

1 (c) (iii) Percentage yield of $H_2 = (1.8/5) \times 100 = \underline{36\%}$ [1m]

(iv) The yield will be higher at a higher temperature. (✓)

This is because higher temperature favours the endothermic reaction as the reaction that absorbs heat is favoured at higher temperature and position of equilibrium shifts right. [1m]

The yield will be increased at a lower pressure. (✓)

This is because since the forward reaction produces more gaseous molecules than the backward reaction, a lower pressure favours the forward reaction that produces more gaseous molecules to counteract the decrease in pressure so that position of equilibrium shifts right, thus increasing the yield. [1m]

2(✓): [1m]

(d) (i) When an alkaline electrolyte (e.g. warm KOH) is used, the reactions are as follows:

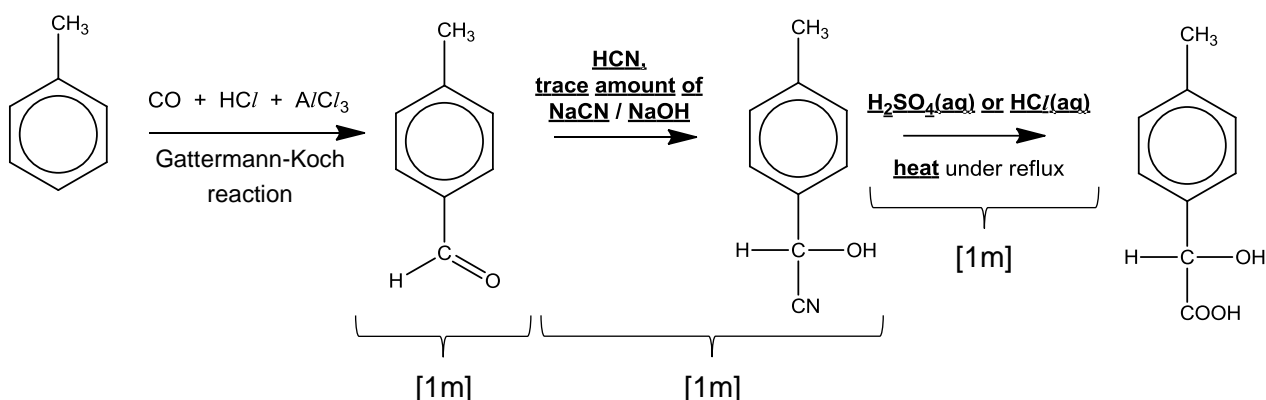
At the anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$ [1m] ss not req'd

At the cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ [1m] ss not req'd

(ii) $E_{cell} = (+0.40) - (-0.83) = + \underline{1.23V}$ [1m]

(iii) Eradicate/Prevent/Avoid/Remove the possibility of alkali leakage from the fuel cell. [1m]

(e)

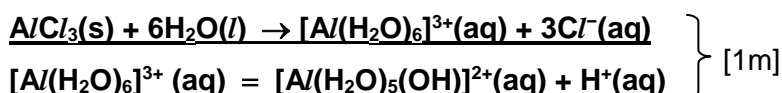


2 (a) (i) Pale greenish-yellow colour of Cl_2 gas fades
OR

Aluminium glows / burns. [1m]

(ii) $AlCl_3$ dissolves in water to give $[Al(H_2O)_6]^{3+}$, which hydrolyses (to a large extent) in water to give H^+ ions / to give a weakly acidic solution. [1m]

Hence, the **solution** turns red / pinkish-red. [1m]



- 2 (a) (iii) On addition of a small quantity of NaOH(aq), $[Al(H_2O)_6]^{3+}$ / $Al^{3+}(aq)$ **forms** the white **$Al(OH)_3$ precipitate**.

On addition of **excess NaOH(aq)**, **$Al(OH)_3$ / white precipitate forms a soluble**, colourless **complex** $Al(OH)_4^-$.

OR

As **$Al(OH)_3$ is an amphoteric hydroxide**, so it can further react with NaOH(aq).

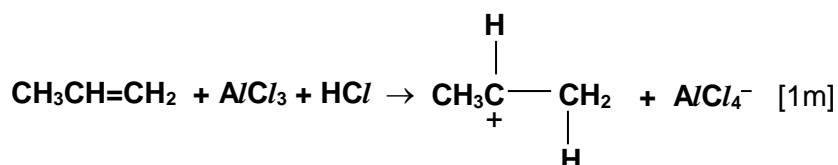
[1m]



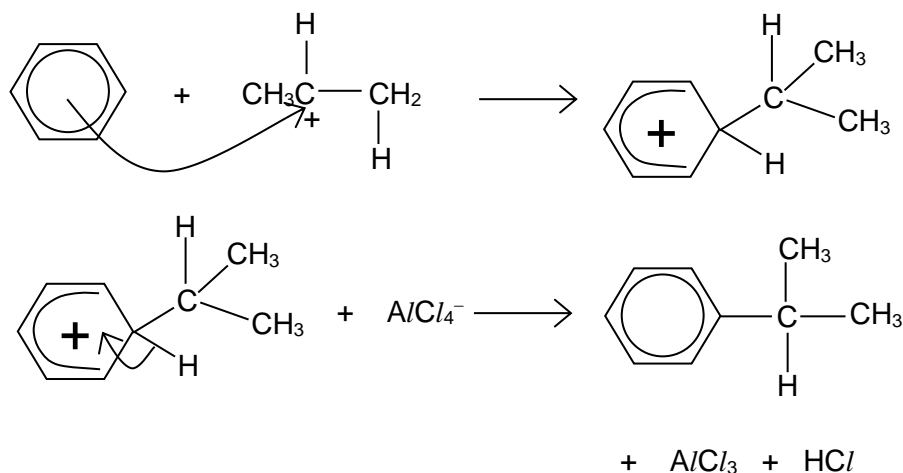
[Note: Accept $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$]



- (b) (i)



- (ii)

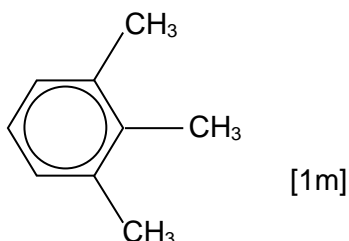


[2m]

- (iii) **$CH_3CH_2\overset{+}{C}H_2$** carbocation is **less stable** than **$CH_3\overset{+}{C}HCH_3$** as **it has one less electron-donating alkyl group**. [1m]

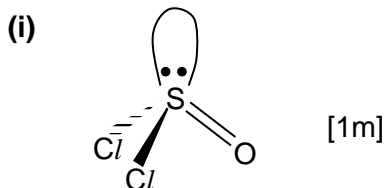
Hence, the positive charge on $CH_3CH_2\overset{+}{C}H_2$ is less dispersed and this carbocation is formed in a smaller quantity.

- (iv)



- 5 (c) (v) Test: Add **acidified KMnO_4** to each compound separately and heat. **Pass** any **gas evolved through limewater**. [1m]

Observations: Both cumene and the isomer in (iv) will decolourise purple KMnO_4 but **only** the **cumene** will **give** CO_2 **gas which gives a white ppt with limewater**. [1m]



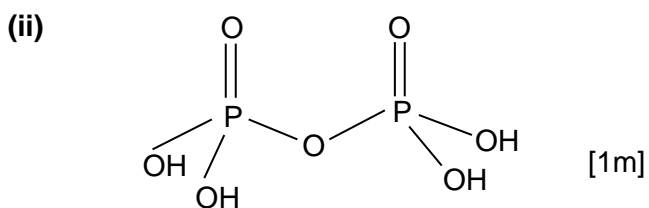
- (ii) **POCl_3 has more electrons per molecule** than SOCl_2 . [1m]

As a result, more energy is required to overcome the **stronger van der Waals' forces / induced dipole-induced dipole attractions between POCl_3 molecules** than the **weaker van der Waals' forces / induced dipole-induced dipole attractions** (and permanent dipole-permanent dipole attractions) **between SOCl_2 molecules**. [1m]

- (d) (i)

	P	O	H
% by mass	34.8	62.9	2.3
Amount/mol	1.12	3.93	2.3
Ratio	1	3.5	2
	2	7	4

The empirical formula of **W** is **$\text{P}_2\text{O}_7\text{H}_4$** . [1m]



- (iii) **$5\text{H}_3\text{PO}_4 + \text{POCl}_3 \rightarrow 3\text{P}_2\text{O}_7\text{H}_4 + 3\text{HCl}$** [1m]

3 (a) (i) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ [1m]

(ii) At 500 °C, the solids present are MgO and CaCO_3 .

At 900 °C, the solids present are MgO and CaO.

So, mass of $\text{CO}_2 = 3.06 - 2.03 = 1.03 \text{ g}$

Since $\text{CaC}_2\text{O}_4 \equiv \text{CaCO}_3 \equiv \text{CO}_2$,

Amount of $\text{CaC}_2\text{O}_4 = \frac{1.03}{44.0} = 0.0234 \text{ mol}$ [1m]

Mass of MgO = $3.06 - \text{mass of CaCO}_3$
 $= \underline{3.06 - (0.0234 \times 100.1)}$
 $= 0.718 \text{ g (or 0.717)}$ } [1m]

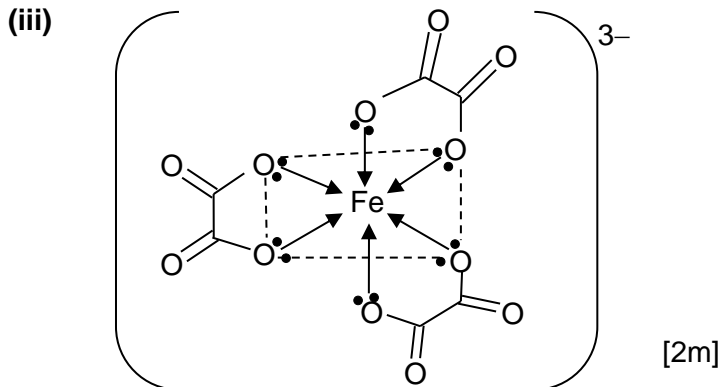
OR Mass of MgO = $\underline{2.03 - (0.0234 \times 56.1)} = 0.717 \text{ g}$

Hence, amount of $\text{MgC}_2\text{O}_4 = \text{amount of MgO} = \frac{0.718}{40.3} = 0.0178 \text{ mol}$

So, the ratio is $\frac{0.0178}{0.0234} = \underline{0.761}$ (or 0.760) [1m]

(b) (i) A ligand is an anion or molecule which has at least one lone pair of electrons to form dative / co-ordinate bonds with metal ion or atom. [1m]

(ii) +3 [1m]



(iv) The colour of the complex arises due to electron transition between the d orbitals. The presence of ligands causes the 3 d orbitals in Fe^{3+} to split into two different energy levels with relatively small energy difference.

Radiation from the visible light region of the electromagnetic spectrum is absorbed when an electron transits from a d-orbital of lower energy to an unfilled / partially-filled d-orbital of higher energy.

The colour seen is the complement of the colour absorbed. [3m]

(v) Fe has energetically accessible vacant orbitals that can accept lone pair of electrons from ligands to form dative covalent bonds / coordinate bonds, unlike calcium. [1m]

- 3 (c) **K** undergoes alkaline hydrolysis with NaOH(aq) on warming to give anion of **L** and NH₃ gas.

K is a primary amide.

L is carboxylic acid.

L undergoes condensation reaction with 2,4-DNPH to give positive test.

L is a carbonyl compound / is either a ketone or an aldehyde

L has no reaction with Fehling's solution

L is not an aldehyde / **L** is a ketone

L undergoes acid-hydrogencarbonate reaction with NaHCO₃(aq)

L is carboxylic acid.

L undergoes reduction reaction with LiAlH₄.

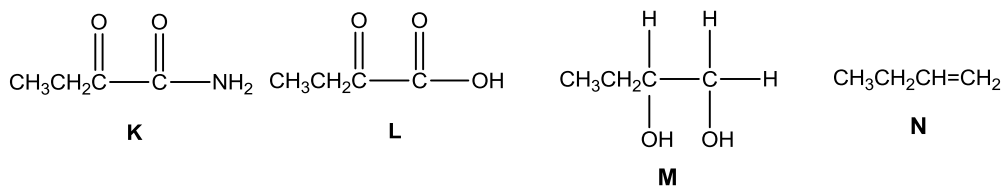
M is a primary alcohol and secondary alcohol.

N undergoes mild oxidation to give **M**.

M is a diol.

N is an alkene.

Explanation: [4m]



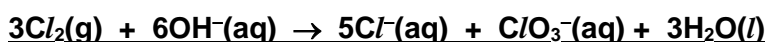
[1m] each

- 4 (a) Type of reaction: Disproportionation

[1m]

Products formed: Cl⁻(aq), ClO⁻(aq) [or NaCl(aq), NaClO(aq)]

[1m]



[1m]

[OR $3\text{Cl}_2(\text{g}) + 6\text{NaOH}(\text{aq}) \rightarrow 5\text{NaCl}(\text{aq}) + \text{NaClO}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$]

(ss not reqd)

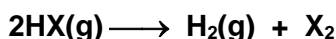
- (b) Bond energy and bond strength of H-X decreases down the Group.

} [1m]

Hence, down the Group, HX becomes less thermally stable.

Thermal decomposition of HX involves the reaction (for X = I and Br)

} [1m]



With HI, copious violet fumes of I₂ are seen.

With HBr, some red-brown / orange fumes of Br₂ are seen.

With HCl, no fumes observed (or no observation).

} [1m]

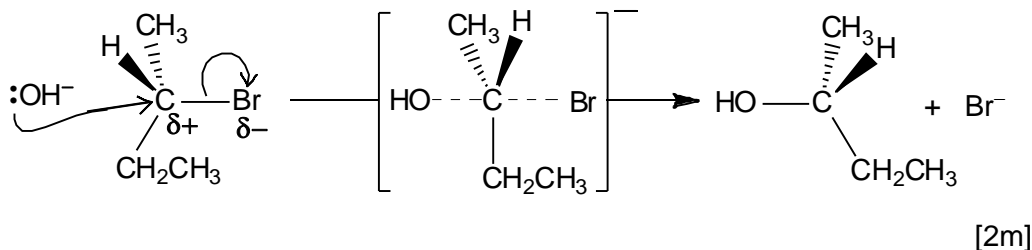
- 4 (c) (i) Energy must be supplied to break the covalent bond between C & Br, hence reaction I has high E_a [1m] and must be heated.

In aqueous state, HBr and NaOH are dissociated into ions OR exist as ions as they are strong acid and strong base. Net reaction is the formation of bonds between H^+ and OH^- ions to give water. Since neutralisation involves attraction of oppositely charged ions H^+ and OH^- which requires low E_a , rate of reaction II is faster. [1m]

- (ii) Rate of reaction will be slower [1m].

The carbon-halogen bond is broken in the rate-determining step and since C-Cl bond (340 kJ mol^{-1}) is stronger than C-Br bond (280 kJ mol^{-1}), more energy will be required to break the C-Cl bond and hence the rate will be slower [1m].

- (iii) Since the stereochemical configuration of the product is reversed, the reaction follows the S_N2 mechanism.



- (iv) Rate = $k[\text{CH}_3\text{CHBrCH}_2\text{CH}_3][\text{NaOH}]$ [1m]

Rate of reaction decreases by 4 times [1m] as concentration of each reactant is halved [1m].

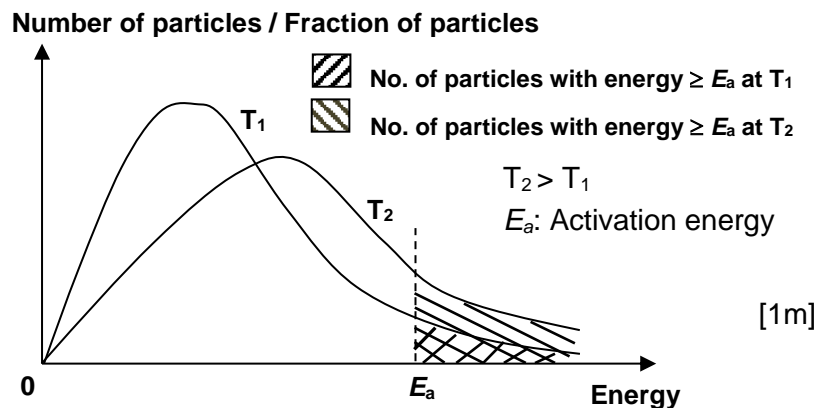
OR

Diluting the solution with equal volume of solvent will lower the concentrations of both reagents by half [1m] and hence, the rate will be decreased by four times [1m].

- 4 (c) (v) As the temperature is increased, more reactant particles / molecules have (kinetic) energies greater than or equal to the activation energy [1m]

Hence the frequency of effective collision between reactant particles/ molecules increases and reaction rate increases. [1m]

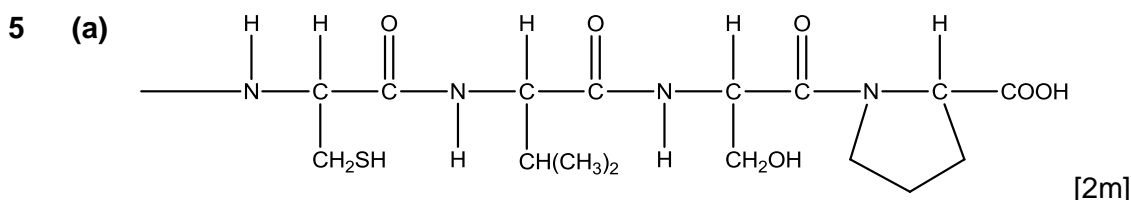
This is evident from the Boltzmann distribution curve of kinetic energies as shown below:



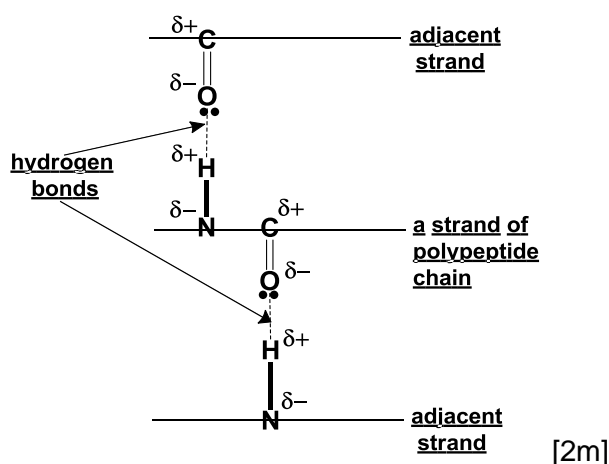
Effect of temperature on Boltzmann distribution of molecular energies

- (d) Add NaOH(aq) (or alkaline), I₂(aq), then heat.

Yellow precipitate formed for 2-bromopropane but no precipitate formed for 1-bromopropane. [1m]



- (b) (i) A β -pleated sheet consists of adjacent polypeptide strands stabilised by hydrogen bonds between the backbone C=O group of one strand and the backbone N-H group of the adjacent strand. [1m]

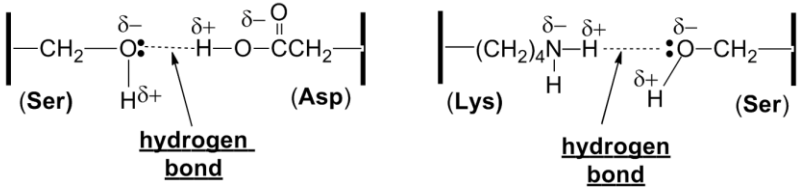
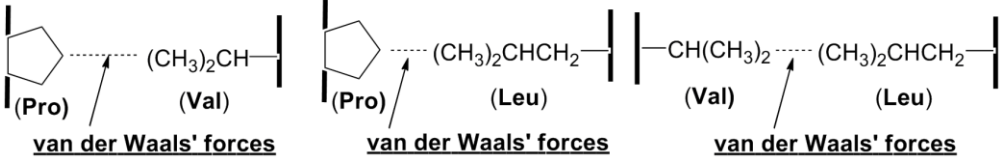


- 5 (b) (ii) Denaturation involves the disruption of R-group interactions / side-chain interactions of a protein, [1m]

leading to possible destruction of the secondary, tertiary and quaternary structures of the protein.

OR

which in turn alters the conformation/shape of the protein and causes the protein to lose its ability to perform its specific function. [1m]

Category	Diagram illustrating R group interaction (Any one of the suggested pairs)
hydrogen bond [1m]	<p>Suggested Pairs:</p>  <p>Asp - Lys pair: Rejected, as these two interact via ionic interactions</p>
van der Waals' forces [1m]	<p>Suggested Pairs:</p> 

- (b) (iii) Leucine, valine, proline, cysteine [1m]

(Any 3 of the 4 stated amino acid residues)

- 5 (c) Heavy metal ions have a high affinity for sulfur and will bind tightly (to -SH group / sulfur) group (of cysteine residue / in OVA). [1m]

Heavy metal ions form ionic interactions with -COO⁻. [1m]

These interactions between OVA and heavy metal ions may lead to precipitation and prevent the metal ions from being absorbed by the body.

- (d) The C₁-C₂ bond is a sp²-sp³ overlap, whereas the C₂-C₃ bond is a sp³-sp³ overlap.

OR

The C₁-C₂ bond is formed by the overlap of the sp² hybrid orbital of C₁ and the sp³ hybrid orbital of C₂. In contrast, the C₂-C₃ is formed by the overlap of the sp³ hybrid orbital of C₂ and the sp³ hybrid orbital of C₃.

The sp² orbital of C₁ contains greater s-character

where electrons can penetrate closer to the nucleus, the bonding electrons are more strongly attracted to the nucleus of the C₁ atom. Hence the bond formed by the sp²-sp³ overlap is shorter.

[1m]

- 5 (e) (i) The pK_a value of the α -COOH is lower, hence the α -COOH is a stronger acid than side-chain COOH [1m]

because the electron-withdrawing N / $-\text{NH}_2$ / $-\text{NH}_3^+$ is closer to the α -COOH group.

The negative charge of $\alpha\text{-COO}^-$ anion is more dispersed and the $\alpha\text{-COO}^-$ anion is more stable / stabilised to a larger extent. [1m]

(ii) $[\text{H}^+] = \sqrt{K_{a1} \times 0.050} = \sqrt{10^{-2.1} \times 0.050} = 0.0199 \text{ mol dm}^{-3}$

Hence, $\text{pH} = -\lg(0.0199) = \underline{1.70}$ [1m]

- (iii) The two species present in the buffer solution at pH 9.8:

