Question 1

(a) Finely powdered Ca metal has a large surface area which increases its rate of reaction with water vapour in the air to produce hydrogen gas.

$$Ca + H_2O \rightarrow CaO + H_2$$

The heat produced causes hydrogen gas to combust spontaneously with oxygen gas in the air, causing explosions.

$$2H_2 + O_2 \rightarrow 2H_2O$$

This generates more water which spark off further explosive reactions with finely powdered Ca metal.

(b)(i) $Q = I \times t = n_e \times F$

$n_e = \frac{1\times10^5\times3\times60\times60}{96500} = 1.12\times10^4 \text{mol}$

$Ca^{2+}(l) + 2e^- \rightarrow Ca(s)$

Mass of Ca formed = $\frac{1.12\times10^4}{2}\times 40.1 = 2.24\times10^5 g = 0.224 \text{ tonnes}$

(b)(ii) From Data Booklet,

$2H_2O + 2e^- \rightarrow 2H_2 + 2OH^-$ $E^\ominus = -0.83V$

$Ca^{2+} + 2e^- \rightarrow Ca$ $E^\ominus = -2.87 V$

Since $E^\ominus(H_2O/H_2)$ is less negative than $E^\ominus(Ca^{2+}/Ca)$, H_2O will be preferentially reduced at the cathode instead of Ca^{2+}. No Ca metal will be obtained.

(c)(i) $Ca(CH_3CO_2)_2 \rightarrow \underset{\text{solid } \mathbf{M}}{CaCO_3} + CH_3COCH_3$

(c)(ii) White residue contains $CaCO_3$ and CaO.

Method 1

Amount of $CaCO_3$ formed at 450 °C = Amount of $Ca(CH_3CO_2)_2 = \frac{2.0}{158.1} = 0.01265$ mol

Let the amount of CO_2 evolved = y mol.

Amount/mol	$CaCO_3$	$\longrightarrow$	CaO	+	CO_2
Initial	0.01265		-		-
Change	-y		+y		+y
Final	0.01265 - y		y		y

Mass of $CaCO_3$ in the residue = (0.01265 – y)(100.1) = (1.266 – 100.1y) g

Mass of CaO in the residue = 56.1y g

$$\frac{\text{mass of } CaCO_3 \text{ in the residue}}{\text{mass of CaO in the residue}} = \frac{70}{30}$$

$$\Rightarrow \quad \frac{1.266 - 100.1y}{56.1\,y} = \frac{7}{3}$$

$$1.266 - 100.1y = 130.9y$$

$$y = 0.005483$$

Amount of CO_2 evolved = 0.005483 mol

Mass of CO_2 evolved = (0.005483)(44.0) = **0.241 g**

Method 2

Mass of $CaCO_3$ formed at 450°C = 2 /158.1 x 100.1 = 1.266 g

	$CaCO_3$	$\longrightarrow$	CaO	+	CO_2
mass after partial decomp / g	1.266 – x – y		x		y

Since mass of white residue = (1.266 – y) g and %(CaO in white residue) = 30%

$$\Rightarrow \frac{x}{1.266 - y} = 0.3$$

Since amt of CaO formed = amt of CO_2 formed,

$$\Rightarrow \frac{x}{56.1} = \frac{y}{44}$$

Solving simultaneous equations, y = mass of CO_2 lost = 0.241 g

Method 3

Let mass of white residue be x g and mass of CO_2 evolved by y g.

Mass of CaO = (0.3x) g

Since $CaCO_3 \rightarrow CaO + CO_2$,

amt of CaO = amt of CO_2

$$\frac{0.3x}{56.1} = \frac{y}{44}$$

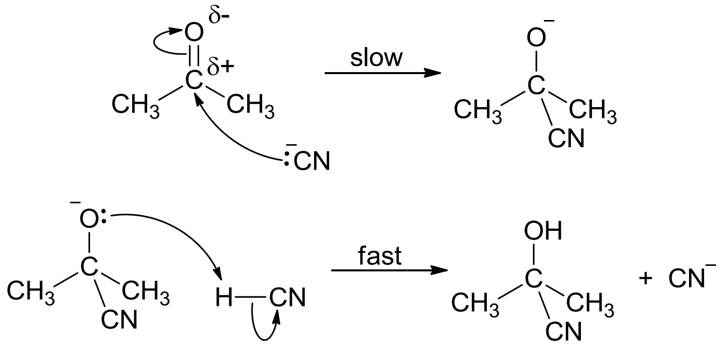
By conservation of mass, x + y = 1.266 g

Solving simultaneous equations, y = 0.241 g.)

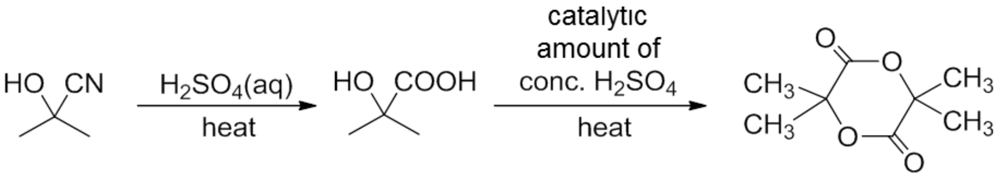
(c)(iii) $Ba(CH_3CO_2)_2$ will decompose at a higher temperature. Ba^{2+} ion has a larger ionic radius as compared to Ca^{2+} ion resulting in a lower charge density. Ba^{2+} ion therefore has weaker polarizing power, hence weakening the covalent bonds within $CH_3CO_2^-$ ions to a smaller extent as compared to Ca^{2+} ion, resulting in higher thermal decomposition temperature.

(d)(i) Nucleophilic addition

$$KCN \longrightarrow K^+ + CN^-$$



(d)(ii)



(e)(i) Compare experiments 1 and 2.

When [**Q**] is increased 1.25 times, rate is increased 1.25 times.

$\Rightarrow$ rate $\propto$ [**Q**]

$\Rightarrow$ Order of reaction with respect to **Q** = 1

Compare experiments 1 and 3.

When [propanone] is doubled, rate is doubled.

$\Rightarrow$ rate $\propto$ [propanone]

$\Rightarrow$ Order of reaction with respect to propanone = 1

Comparing experiments 2 and 4:

$$\frac{(0.200)(0.100)^n}{(0.100)(0.150)^n} = \frac{5.28\times10^{-5}}{3.96\times10^{-5}} \Rightarrow 2\times(\frac{2}{3})^n = \frac{4}{3}$$

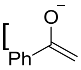
Hence, n = 1

$\Rightarrow$ Order of reaction with respect to OH^- = 1

The rate equation is:

rate = k [**Q**] [propanone] $[OH^-]$

(e)(ii) Step **B** is the slow step i.e. the rate-determining step.

From the slow step: rate = k' [] $[H_2O]$ [propanone]

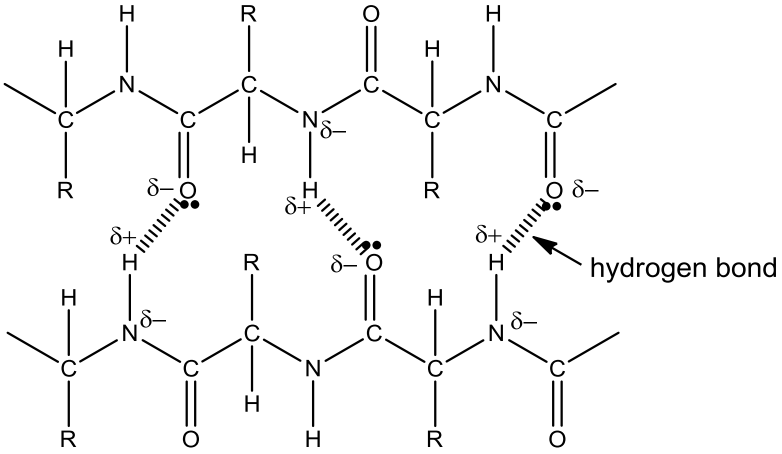
= k [Q] $[OH^-]$ [propanone]

The rate equation obtained agrees with that in **(e)(i)**.

(e)(iii) The hydroxide ion acts as a base. OR The hydroxide ion acts as a catalyst.

Question 2

(a)(i)



- All peptide linkages are involved in intra-chain hydrogen bonding.
- It is stabilized by hydrogen bonds between the C=O group of a peptide in one strand and the N-H group of another peptide in the adjacent strand
- R groups (side chains) project above and below the sheet and are 90° to the plane of the pleated sheet.

(a)(ii) Methionine and tyrosine exists as zwitterions and they can form ion-dipole interactions with water , making them highly soluble in aqueous state.

(a)(iii) $-NO_2$ group is electron withdrawing which disperses the negative charge on the O atom of the phenoxide ion , stabilizing the phenoxide ion, making nitro-tyrosine a stronger acid.

(a)(iv) At physiological pH of 7.34-7.45, the phenol group on nitrotyrosines is deprotonated and forms phenoxide ion. With the increase in negatively charged phenoxide ions, it will be bonded to positively charged R groups like ($-NH_3^+$) via ionic bonding in the tertiary structures, promoting fibril formation. (or disrupts existing hydrogen-bonding)

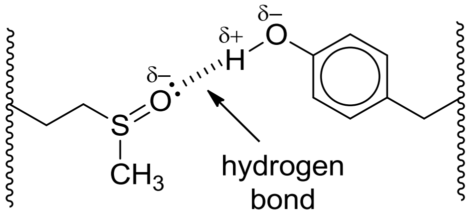
OR

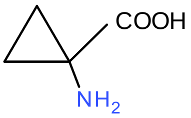
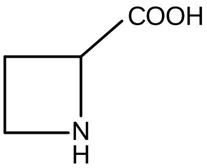
At physiological pH of 7.34-7.45, the phenol group on nitrotyrosines is deprotonated which allows it to form ionic interactions with positively charged R-groups and disrupts the original hydrogen-bonding between the R-groups , causing a conformation change in the tertiary structure.

OR

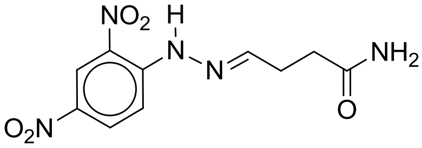
The intramolecular hydrogen-bond between the –OH and $–NO_2$ of the nitrotyrosine R-group reduces the formation of hydrogen-bonds with R-groups of other amino acid residues. This causes a conformation change in the tertiary structure.

(a)(v) Hydrogen bonding



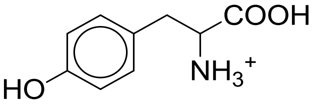
(b)(i) X: 	**(b)(ii)** Nucleophilic Substitution **Y** 

(b)(iii) Orange ppt formed

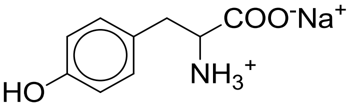


(c)(i) The second and third K_a of protonated tyrosines are too close as they are only about 1 unit apart (i.e. 9.1 vs 10.1). Hence, the titration curve cannot show a distinct sharp rise for the second and third equivalence points.

(c)(ii)



and



(c)(iii) $H_2T^- \rightleftharpoons H^+ + HT^{2-}$ or $H_2T^- + H_2O \rightleftharpoons H_3O^+ + HT^{2-}$

pH = 5.7 ⇒ $[H^+] = 10^{-5.7} = 2.00 \times 10^{-6}$ mol dm^{-3}

(c)(iv)

$$K_{a2} = \frac{[H^+][HT^{2-}]}{[H_2T^-]} = 10^{-9.1}$$

$$K_{a2} = \frac{[10^{-5.7}]^2}{[H_2T^-]} = 10^{-9.1}$$

$$[H_2T^-] = 5.01 \times 10^{-3}$$

$[H_3T] = 2 \times [H_2T^-] = 2 \times 5.01 \times 10^{-3} = 0.0100$ mol dm^{-3}

Question 3

(a)(i) Due to the presence of partially filled d-subshells in transition metals, reactant molecules can form weak interactions with the surface of the catalyst.

The H_2 and O_2 molecules adsorb onto the surface of the Pt catalyst. The adsorption increases the surface concentration of H_2 and O_2 on the Pt surface and weakens the covalent bonds in H_2 and O_2 for reaction. After reaction, the product (H_2O) desorbs from the surface, allowing more reactants to adsorb.

(a)(ii) An acid-metal reaction between Zn and H_2SO_4 produces H_2 gas:

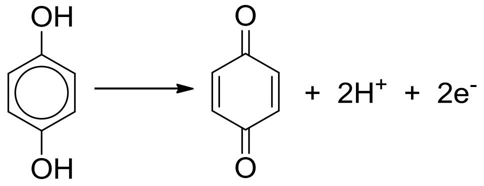
$$Zn(s) + H_2SO_4(g) \longrightarrow ZnSO_4(aq) + H_2(g)$$

The H_2 gas evolved travels out of the outlet and mixes with O_2 from the air on the surface of the Pt catalyst , undergoing an exothermic reaction which ignites the remaining H_2 gas exiting the outlet.

(b)(i) Oxidation state of C in C=O in quinone = +2
Oxidation state of C in C–O in hydroquinone = +1

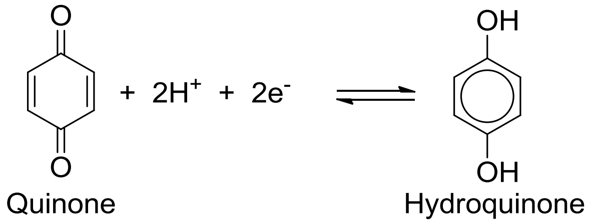
Since there is a decrease in oxidation state from quinone to hydroquinone, reduction has occurred.

(b)(ii) Cathode: $Ag^+(aq) + e^- \longrightarrow Ag(s)$
Anode:



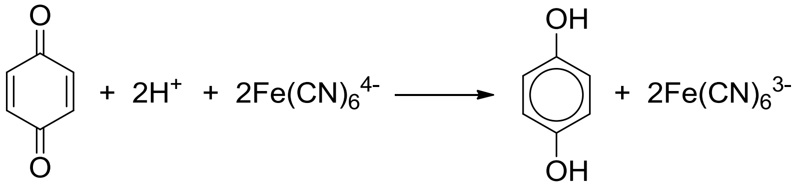
(b)(iii) Reading on voltmeter = $E^\ominus_{cell} = 0.80 - (+0.70) = +0.10$ V

(b)(iv)



+0.70 V

$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ +0.36 V



Since E_{cell} = +0.70 –(+0.36) = **+0.34 V** >0, the above reaction occurs. This causes the

- [**hydroquinone] to increase and [quinone] to decrease**.

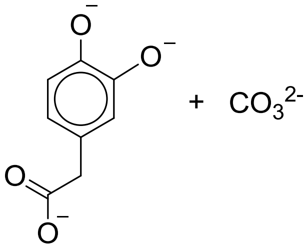
- **$E_{(quinone/hydroquinone)}$ to become less positive** (become smaller than +0.70V)
- Reading on voltmeter to become **more positive**.

(c)(i) **i.** I_2, NaOH, warm
ii. HC*l*(aq)

(c)(ii) $COCl_2$

(c)(iii) Test: To separate samples of the compounds, add neutral $FeCl_3$ (aq)
Observation: Violet colouration observed in **Y**. No violet colouration observed in **Z.**

(c)(iv) Products:



Question 4

(a)(i) Al: [Ne] $3s^2 3p^1$
Mg:[Ne] $3s^2$

The 3p electron to be removed from Al is at a higher energy level than the 3s electron to be removed from Mg. Hence less energy is required to remove the 3p electron in Al than the 3s electron in Mg and so the first ionisation energy of Al is lower than that of Mg.

(a)(ii) **E**: SiO_2 **F**: P_4O_6 **G**: Al_2O_3

(a)(iii) **E** (SiO_2) has a giant covalent structure with strong covalent bonds between its atoms, resulting in its high melting point. It conducts electricity poorly as there are no charged particles in the molten state.

F (P_4O_6) is a simple covalent molecule with weak van der Waals interactions resulting in its low melting point. It does not conduct electricity as there are no charged particles in the molten state.

G (Al_2O_3) has giant ionic lattice structure with strong electrostatic forces of attraction between its cations and anions resulting in its high melting point. It conducts electricity in the molten state as its ions become mobile.

(a)(iv) The pH values for E, F and G are 7, 2 and 7 respectively.
$P_4O_6(s) + 6H_2O(l) \longrightarrow 4H_3PO_3(aq)$

(a)(v) Heat a mixture of S_8 and Cl_2 above 115°C .
The product can be purified by simple distillation, collecting it at 137°C.

(b)(i) $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$
$K_{sp} = [Fe^{2+}(aq)][OH^-(aq)]^2 \quad mol^3\ dm^{-9}$

(b)(ii) mass concentration of Fe^{2+} not yet precipitated $= 0.05 \times (256.8 \times 10^{-3})$
$= 0.01284\ g\ dm^{-3}$

$[Fe^{2+}(aq)] = 0.01284 \div 55.8$
$= 2.30 \times 10^{-4}\ mol\ dm^{-3}$

$K_{sp} = [Fe^{2+}(aq)][OH^-(aq)]^2$
$8.0 \times 10^{-16} = (2.30 \times 10^{-4})[OH^-(aq)]^2$
$[OH^-(aq)] = 1.865 \times 10^{-6}\ mol\ dm^{-3}$

pH = 14 – pOH
= 14 – 5.73
= 8.27

(b)(iii) 6.4

(b)(iv) X is $\mathbf{Fe^{3+}}$.

(b)(v) Upon exposure to air, Fe^{2+} was oxidised to Fe^{3+}.

$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$

The Fe^{3+} ion underwent hydrolysis in aqueous solution, producing H_3O^+ ions which caused the pH of the solution to decrease.

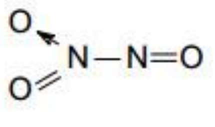
(c)(i) Assume 100 g of P.

	H	As	O
mass / g	2.1	52.8	45.1
M_r	1.0	74.9	16.0
amt / mol	2.1	0.704	2.81
simplest ratio	3:	1:	4

From the balanced equation, it can be seen that the empirical formula is the same as the molecular formula
i.e. P is H_3AsO_4.

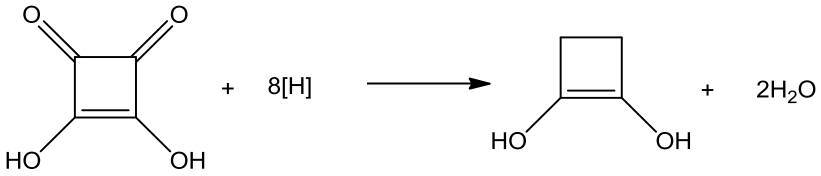
(c)(ii) **Q** is N_2O_3.

(c)(iii)



Question 5

(a)(i)



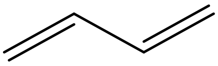
(a)(ii) Compound **A** is more acidic than **C**.

While both conjugate bases of **A** and **C** are resonance stabilized, the negative charge in **A** is **delocalized/dispersed over more atoms** as compared to **C**.

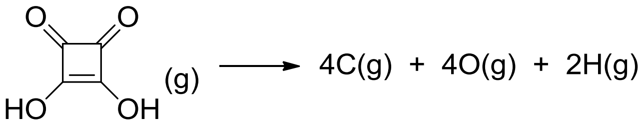
(a)(iii) Step III: $LiAlH_4$ in dry ether

Step IV: excess conc. H_2SO_4, 170°C

(a)(iv)



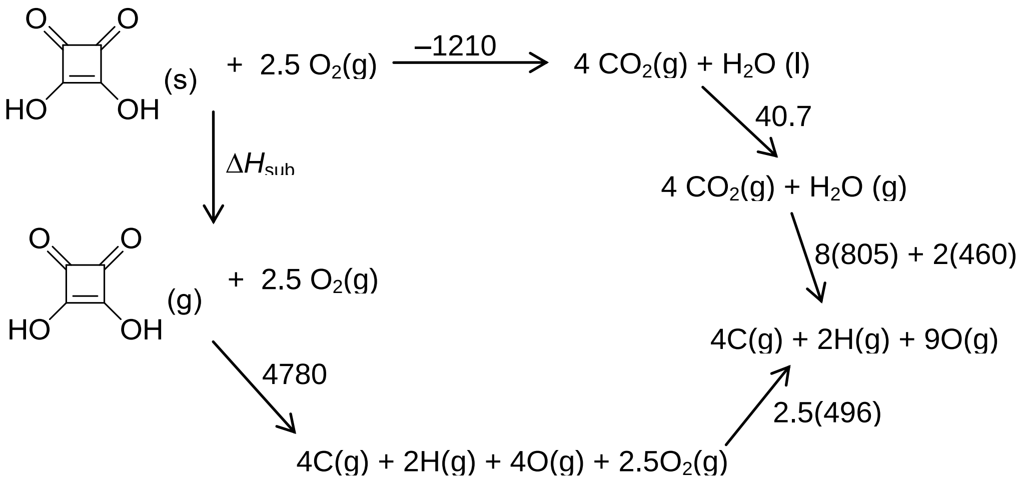
(b)(i)



(b)(ii) Using bond energy data from data booklet,

$$\Delta H_{atom}\,[\mathbf{A}(g)] = BE(C{=}C) + 3\,BE(C{-}C) + 2\,BE(C{=}O) + 2BE(C{-}O) + 2\,BE(O{-}H)$$
$$= 610 + (350x3) + (740x2) + (360x2) + (460x2)$$
$$= +4780 \text{ kJ mol}^{-1}$$

(b)(iii)

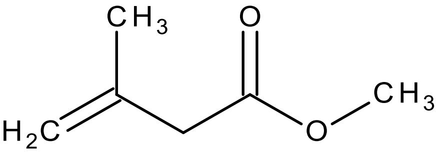
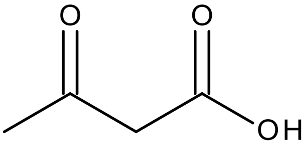


Applying Hess' Law,

$$\Delta H_{sub} = -1210 + (40.7) + 8(805) + 2(460) - 2.5(496) - 4780$$
$$= +170.7 \text{ kJ mol}^{-1}$$

(c)

J + $Br_2 \rightarrow C_6H_{10}Br_2O_2$	- Electrophilic addition occurred ⇒ 1 C=C (alkene) present
J $\xrightarrow[\text{prolonged heating}]{\text{excess } KMnO_4/H^+}$ **K**($C_4H_6O_3$) + 2 CO_2	- Oxidative cleavage / oxidation of C=C with CO_2 gas evolved ⇒ =CH_2 present - Possible acidic hydrolysis of ester to form an alcohol that could be oxidised to CO_2 (mark for either) ⇒ methanol
K ($C_4H_6O_3$) $\xrightarrow[\text{warm}]{I_2 / NaOH}$ yellow ppt	- oxidation reaction OR positive iodoform test ⇒ CH_3CO– group present
K ($C_4H_6O_3$) $\xrightarrow[\text{reaction}]{\text{Clemmensen}}$ **K** ($C_4H_8O_2$)	Reduction of carbonyl group ($RCOCH_3$) to alkane (RCH_2CH_3)
K / **L** $\xrightarrow{Na_2CO_3}$ effervescence of CO_2	- Acid-carbonate (or acid base) reaction ⇒ RCOOH present in **J** and **K**

J 	
K 	**L**