

2011 A LEVEL PRELIM P1 SOLUTIONS

1	A	11	D	21	B	31	D
2	D	12	A	22	C	32	B
3	B	13	C	23	C	33	B
4	C	14	C	24	C	34	A
5	D	15	C	25	D	35	A
6	B	16	C	26	D	36	B
7	A	17	A	27	A	37	D
8	C	18	C	28	C	38	A
9	A	19	B	29	C	39	B
10	C	20	D	30	B	40	C

2011 Prelims (P2): Suggested Answer

- 1 (a) No of moles of $\text{H}_2\text{SO}_4 = 10/1000 \times 1 = 0.01 \text{ mol}$
 No of moles of $\text{NaOH} = 40/1000 \times 1.50 = 0.06 \text{ mol (excess)}$
 No of moles of H_2O formed = 0.02 mol
 Amount of heat produced = $0.02 \times 57\,400 = 1148 \text{ J}$
 Temperature rise = $1148/(50 \times 4.18) = 5.5 \text{ }^\circ\text{C}$

(b)

Volume of FA 1 / cm^3	10	20	30	40
Volume of FA 2 / cm^3	40	30	20	10
Temperature rise, ΔT / $^\circ\text{C}$	5.5	11.0	8.2 / 8.3	4.1 / 4.2

(c)

- Measure 10.0 cm^3 of **FA 1** using a 20 cm^3 measuring cylinder.
- Pour the **FA 1** into a styrofoam cup.
- Measure the temperature of **FA 1** in the cup using a thermometer.
- Measure 40.0 cm^3 of **FA 2** using another 50 cm^3 measuring cylinder. Measure the temperature of **FA2**.
- Take the average of the temperatures of **FA1** and **FA2** as the initial temperature.
- Pour the **FA 2** into the Styrofoam cup containing **FA 1** and stir using the thermometer.
- Record the maximum temperature of the mixture.
- Repeat the experiment using the various volumes of **FA 1** and **FA 2** shown in the table in (b).

OR

- Measure 10.0 cm^3 of **FA 1** using a 20 cm^3 measuring cylinder.
- Pour the **FA 1** into a styrofoam cup.
- Measure 40.0 cm^3 of **FA 2** using another 50 cm^3 measuring cylinder.
- Pour the **FA 2** into the Styrofoam cup containing **FA 1**.
- Stir the mixture gently and record the initial temperature of the mixture using a

thermometer.

6. Record the maximum temperature of the mixture.
7. Repeat the experiment using the various volumes of **FA 1** and **FA 2** shown in the table in (b).

(d) **Source of error and suggestion to minimise error**

Heat absorbed by the calorimeter	Calibration of calorimeter to account for heat absorbed (see calibration of calorimeter)
Heat loss to surrounding	Provide lagging on the body of the calorimeter OR Use a lid to cover the calorimeter OR Consider cooling correction (see next section)
Measuring cylinders not precise in measuring volumes of FA 1 and FA 2 .	Use a burette to measure accurately the volumes of FA 1 and FA 2 .

- (e) From the graph, find the point of **intersection of the two lines** to obtain the vol of **FA 2** with maximum temperature rise.

Assume vol of H_2SO_4 in **FA 1** is $V_1 \text{ cm}^3$ at point of intersection

$$V_1/1000 \times [\text{H}_2\text{SO}_4] = (50 - V_1) / 1000 \times 1.5/2$$

$$[\text{H}_2\text{SO}_4] = \frac{(50 - V_1) \times 1.5}{2 V_1}$$

- 2 (a) (i) Powdered iodine has **larger surface area** for effective collision.
Thus the **rate of reaction will increase.**
- (ii) The reaction is exothermic and has to be kept in control OR iodine may **oxidise** ethanol.
- (iii) To ensure the reaction is complete.
- (b) (i) $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{I} \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{HI}$
Iodoethane undergoes nucleophilic substitution with ethanol acting as the nucleophile.
- (ii) $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^- \quad E^\theta = +0.54$
 $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \quad E^\theta = +1.23$
 Overall: $4\text{I}^- + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{I}_2 + 2\text{H}_2\text{O}$
 $E^\theta_{\text{overall}} = +1.23 - +0.54 = +0.69 \text{ V}$
- (c) (i) To remove / react **H_3PO_3** .
- (ii) To remove **water soluble** impurities / ethanol / ether / last traces of sodium carbonate.
- (iii) K_2CO_3 / CuSO_4 / CoCl_2 / MgSO_4 / Na_2SO_4 / CaSO_4
- (iv) The boiling temperature of fixed at 71°C to ensure that the distillate is **pure**.

(d) (i) Cl is more electronegative than I will pull bond pairs of electrons towards itself. Hence, there is lesser repulsion between the bond pairs and the bond angle of PCl_3 is smaller.



(iii) **White fumes** were seen for the reaction of PCl_3 and water due to the **formation of HCl gas**. The HI formed for the reaction of PI_3 and water undergoes thermal decomposition **to form purple I_2 fumes**.

The **size of I is bigger than Cl**. Thus the atomic overlap between H and I atoms is less effective. The **bond strength of H-I is weaker**, hence it is more easily broken to form I_2 .

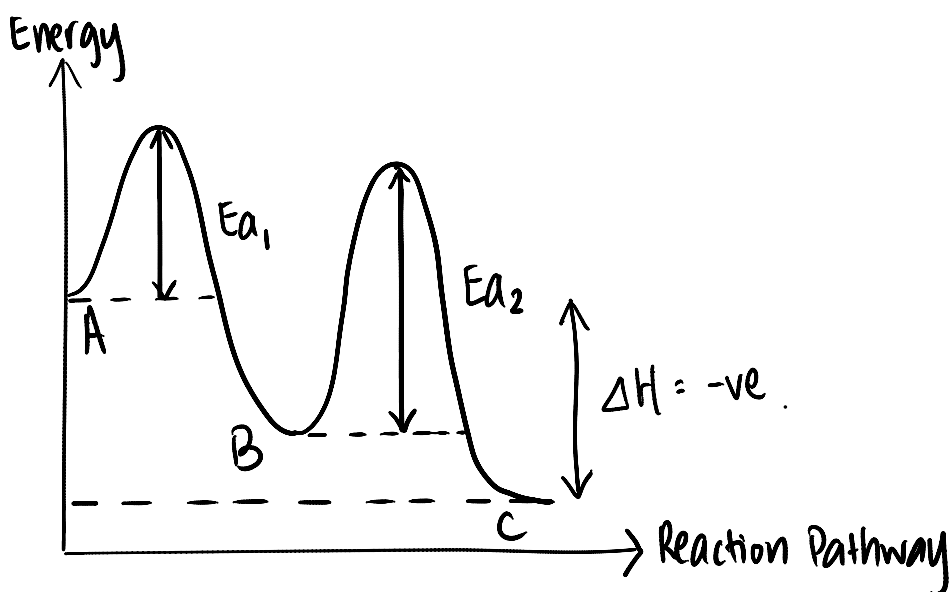
3 (a) (i) The formation of B is faster than C OR Step 1 is faster than Step 2 as it has a steeper gradient OR the maximum concentration is attained faster in the formation of B than C.

(ii) Step 2

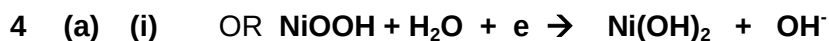
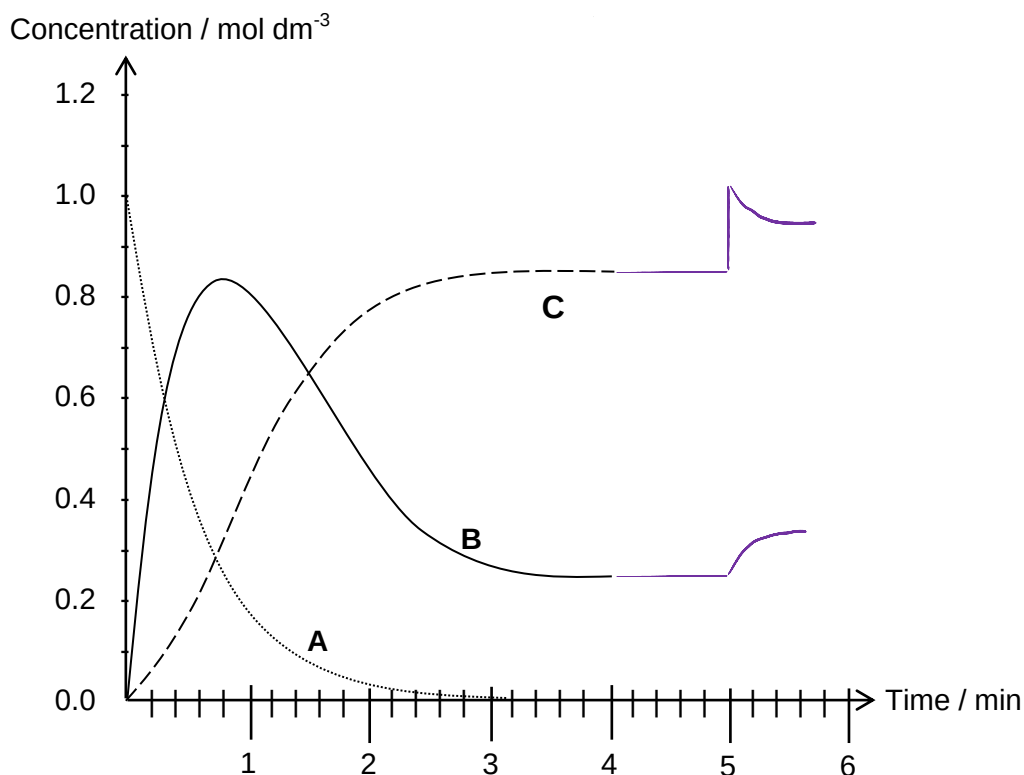
(iii) $t_{1/2} = 0.40 \text{ min}$

2 half-lives constant

(iv)



(b)

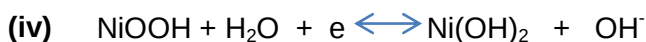


(ii) Iron to Nickel oxide-hydroxide

(iii) $1.2 = E^\circ_{\text{cell}} (\text{NiOOH}) - (+0.55)$

Thus,

$E^\circ_{\text{cell}} (\text{NiOOH}) = +1.75\text{V}$

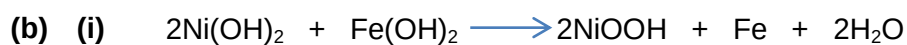


When the acid is added, it removes the OH^- ions and hence reduces its concentration leading to the **equilibrium above to shift to the right** to replenish the OH^- ions removed.

Hence the E°_{cell} at the cathode becomes greater than +1.75V, resulting in the **e.m.f becomes greater than +1.2V**

(v) When the volume of the hydroxide increase, there is **no change in concentration of the OH^-** hence no shift in equilibrium

Hence, there is **no change in e.m.f**



(ii) Mass of Fe required = $3 \times 0.95 = 2.85\text{g}$

No. of moles of Fe = $2.85/55.8 = 0.05107$

No of moles of electrons required = $0.05107 \times 2 = 0.1022$

Thus,

Total amount of electricity required = $0.1022 \times 96500 = 9857.5\text{C}$

Thus minimum current = $9857.5 / (2 \times 60 \times 60) = \underline{1.37\text{A}}$

(iii) Total amount of electricity = $1.37 \times (2 \times 60 \times 60) = 9864\text{C}$

Total number of electrons = **total number of nickel oxide-hydroxide**

= $9864 / 96500 = 0.102$ [1]

Total mass of nickel oxide-hydroxide = $0.102 \times (58.7 + 32 + 1) = 9.35\text{g}$

Actual mass of nickel oxide-hydroxide = $9.35/0.95 = \underline{9.85\text{g}}$

(iv) $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-$ $E^\circ_{\text{red}} = +0.40\text{V}$

Having a **more negative than +1.75V** (E°_{red} of the reaction at the nickel (III) oxide-hydroxide), the hydroxide ions are also discharged to produce oxygen gas.

5 (a) (i) $\text{Fe(s)} + 3/2 \text{Cl}_2(\text{g}) \longrightarrow \text{FeCl}_3(\text{s})$

(ii) $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^5$

(iii) $\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \longrightarrow [\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+} + \text{H}_3\text{O}^+$
 $2\text{H}^+ + \text{CO}_3^{2-} \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$

(iv) **A:** $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} \cdot 3\text{Cl}^-$ OR $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$ OR $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

B: $\text{Fe}(\text{OH})_3 (\text{s})$

C: $\text{Fe}(\text{OH})_2 (\text{s})$

D: neutral $\text{FeCl}_3(\text{aq})$

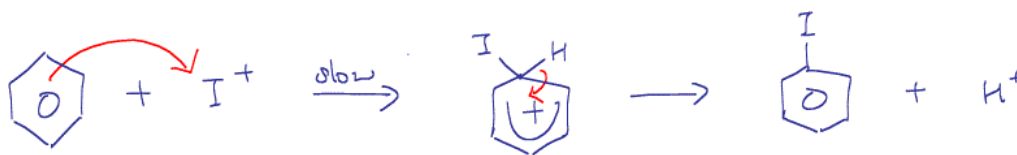
(v) Ligand exchange

$[\text{Fe}(\text{EDTA})]^-$

(b) (i) $\text{I}_2 + 2\text{Cu}^{2+} \longrightarrow 2\text{I}^+ + 2\text{Cu}^+$

Redox

(ii) Electrophilic substitution



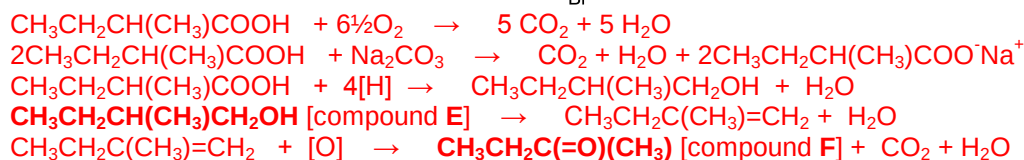
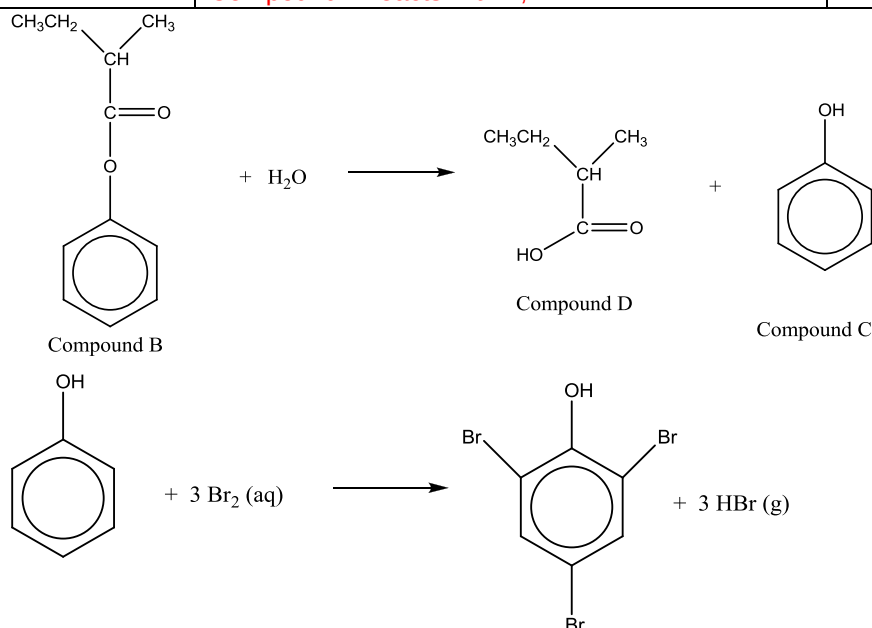
Suggested Solution P3 2011 Prelim H2 Chemistry

1. a) i.	Unique sequence of amino acids held by peptide bonds. Any permutation of Ala, Gln and Lys. To take note of Isoelectric point with respect to pH = 7.3. Diagram involving 3 amino acids. Either diagram below is accepted. E.g Ala - Gln - Lys $ \begin{array}{c} \text{O} & \text{H} & \text{H} & \text{O} & \text{H} & \text{H} & \text{O} & \text{H} \\ & & & & & & & \\ -\text{O}-\text{C}-\text{C}-\text{N}- & -\text{C}-\text{C}-\text{N}- & -\text{C}-\text{C}-\text{N}- & \text{H}_3^+ \\ & & & \\ \text{CH}_3 & (\text{CH}_2)_2 & (\text{CH}_2)_4 & \\ & & & \\ & \text{CONH}_2 & \text{NH}_3^+ & \end{array} $ $ \begin{array}{c} \text{O} & \text{H} & \text{H} & \text{O} & \text{H} & \text{H} & \text{O} & \text{H} \\ & & & & & & & \\ -\text{C}-\text{C}-\text{N}- & -\text{C}-\text{C}-\text{N}- & -\text{C}-\text{C}-\text{N}- & \\ & & & \\ \text{CH}_3 & (\text{CH}_2)_2 & (\text{CH}_2)_4 & \\ & & & \\ & \text{CONH}_2 & \text{NH}_3^+ & \end{array} $ Note At pH = 7.3 Ala: $-\text{O}-\text{C}(=\text{O})-\text{CH}(\text{CH}_3)-\text{NH}_2$ Gln: $\text{H}_2\text{N}-\text{CH}(\text{CH}_2)_2-\text{C}(=\text{O})-\text{NH}_2$ Lys: $\text{HO}-\text{C}(=\text{O})-\text{CH}(\text{CH}_2)_4-\text{NH}_3^+$
1. a) ii.	disrupting the tertiary (<u>R-groups of glutamine would form hydrogen bond OR lysine will form ion-dipole interactions with the -OH functional group in ethanol</u>) disrupting the secondary structure (<u>peptide linkages would now form hydrogen bonds with ethanol instead of other peptide linkages</u>) Diagrams drawn are as represented below to illustrate the same points above: (GLN) OR (LYS) Diagram 1 (GLN): $ \begin{array}{c} \text{O}=\text{C} \\ \\ \text{H}-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{N}-\text{H} \\ \quad \quad \quad \delta^- \\ \text{H}-\text{N} \quad \quad \quad \text{H}-\text{O}-\text{CH}_2-\text{CH}_3 \quad \delta^+ \end{array} $ H-bond Diagram 2 (LYS): $ \begin{array}{c} \text{O}=\text{C} \\ \\ \text{H}-\text{C}-(\text{CH}_2)_4-\text{N}^+-\text{H} \\ \quad \quad \quad \delta^- \\ \text{H}-\text{N} \quad \quad \quad \text{H}-\text{O}^-\text{CH}_2\text{CH}_3 \end{array} $ ion dipole Diagram 3 (Secondary structure): $ \begin{array}{c} \text{O}=\text{C} \\ \\ \text{N}-\text{H} \quad \delta^+ \quad \quad \text{H}-\text{O} \quad \delta^- \\ \quad \quad \quad \text{H-bond} \quad \quad \quad \text{H}-\text{CH}_2\text{CH}_3 \end{array} $
	causing <u>the tertiary and secondary structures to unwind and become a random coil thus denaturing / loses the unique 3D conformation of</u> the protein.
1. b) i.	1. acidified potassium dichromate, heat and distill 2. HCN, trace amounts of NaOH (aq), @ 10 – 20 °C 3. H₂SO₄(aq), heat
	ii. 1. alkaline iodine solution, heat 2. acidify with mineral acid / H⁺ (aq)
1. c) i.	$\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 4\text{H}^+ + 4\text{e}^-$ $3\text{CH}_3\text{CH}_2\text{OH} + 2\text{Cr}_2\text{O}_7^{2-} + 16\text{H}^+ \rightarrow 3\text{CH}_3\text{COOH} + 4\text{Cr}^{3+} + 11\text{H}_2\text{O}$
	ii. CrO_4^{2-} / chromate (VI) ions / Na₂CrO₄
	iii. In the isolated gas phase, d orbitals are degenerate. In the presence of ligands, d orbitals split with a <u>small energy gap</u> between them. An electron will undergo d-d transition (where <u>a d electron jumps from a lower energy to the higher energy</u>) and absorbs from the <u>visible light</u> of the electromagnetic spectrum. The colour of the compound seen is the light that is <u>complementary of the visible light absorbed</u>.

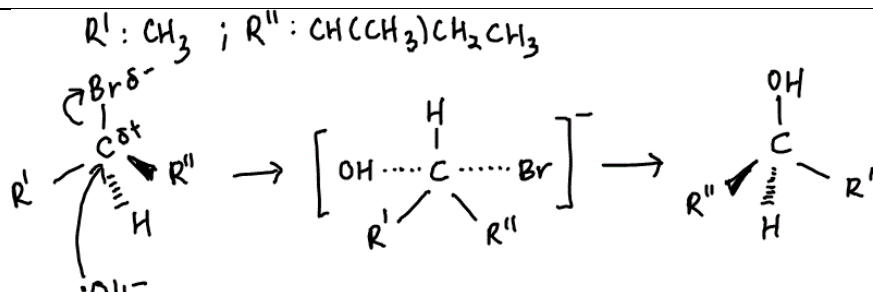
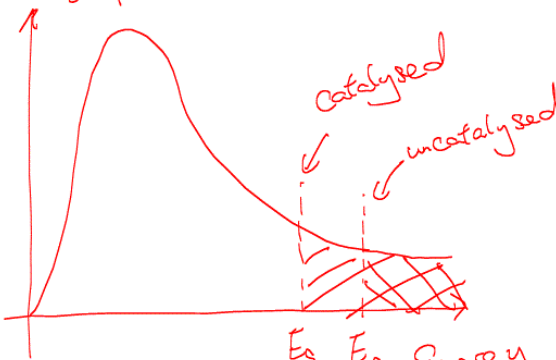
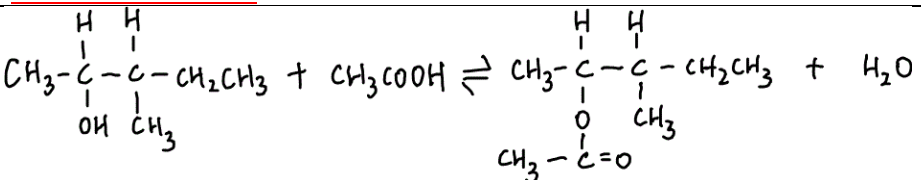
		iv.	amount of potassium dichromate = $0.015 \times 0.017 = 2.55 \times 10^{-4}$ mol amount of ethanol needed = $2.55 \times 10^{-4} \times 3/2 = 3.825 \times 10^{-4}$ mol (ecf) min. Vol of ethanol = $(3.825 \times 10^{-4}) \times 8.31 \times (273 + 36.9) / 101325 = 9.72 \text{ cm}^3$	
1.	d)	i.	$\text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O} + 2\text{O}_2$ $\swarrow -1371$ $\swarrow -876$ $2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$ $\Delta H^\circ_{\text{oxidation}} = +(-1371) - (-876) = -495 \text{ kJ mol}^{-1}$	
2.	a)	i.	$\text{Cl}^{4+}: [\text{Ne}]3s^23p^1$ $\text{S}^{4+}: [\text{Ne}]3s^2$ OR The 5 th electron is removed from the 3p subshell for chlorine and 3s subshell for sulfur. <u>3p subshell is further from the nucleus as compared to the 3s subshell and experiences a larger screening effect due to the filled 3s subshell.</u> These factors <u>outweigh the increase in nuclear charge</u> , resulting in a lower effective nuclear charge. <u>Less energy is required</u> to remove the 5 th electron from chlorine as compared to sulfur.	
		ii.	Hydrogen fluoride and hydrogen chloride are both simple covalent molecules. <u>HCl exhibits induced dipole-induced dipole and permanent dipole-permanent dipole interactions OR VDW.</u> For hydrogen fluoride, it also exhibits hydrogen bonding. Due to the additional hydrogen bonding interaction, hydrogen fluoride molecules exhibit stronger intermolecular forces of attraction as compared to hydrogen chloride molecules.	
		iii.	<u>Bond strength of C-Cl is stronger</u> as compared to bond strength of C-Br. AgCl ppt is formed at a slower rate than AgBr.	
2.	b)		$\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}_2 + \text{I}-\text{Cl} \xrightarrow{\text{slow}} \text{CH}_3-\text{C}(\text{CH}_3)(\text{I})-\text{CH}_2\text{I} + \text{Cl}^-$ $\downarrow \text{fast}$ $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{CH}_2\text{I}$ Arrows / polarity on ICl : Intermediate / Final product:	
2.	c)	i.	$\text{H}-\text{C}(\text{H})-\text{C}(\text{H})-\text{C}(=\text{O})-\text{OH}$ H H H $\text{H}-\text{C}-\text{C}-\text{C}=\text{O}$ H Cl $\text{O}-\text{H}$	
		ii.	Concentration of HA after dissociation = $10^{-3} - 14.1 / 100 \times 1 \times 10^{-3} = 8.59 \times 10^{-4}$ Concentration of $[\text{H}^+] = 14.1 / 1000 \times 10^{-3} = 1.41 \times 10^{-4}$ $K_a = \frac{([\text{H}^+])^2}{[\text{HA}]_{\text{after dissociation}}}$ $= \frac{(1.41 \times 10^{-4})^2}{8.59 \times 10^{-4}}$ $= 2.31 \times 10^{-5} \text{ mol dm}^{-3}$	
		iii.	Amount of NaOH added : $0.01 \times 5 \times 10^{-4} = 5 \times 10^{-6} \text{ mol}$ Amount of $\text{A}^- = 5 \times 10^{-6} \text{ mol}$ Amount of HA initially : $0.01 \times 1 \times 10^{-3} = 1 \times 10^{-5} \text{ mol}$ Amount of HA finally : $1 \times 10^{-5} - 5 \times 10^{-6} = 5 \times 10^{-6} \text{ mol}$ $\text{pH} = \text{p}K_a + \lg([\text{A}^-] / [\text{HA}])$ $[\text{A}^-] = [\text{HA}]$ OR maximum buffer capacity. $= -\lg(2.31 \times 10^{-5}) + \lg(5 \times 10^{-6} / 0.02) / (5 \times 10^{-6} / 0.02)$ $= 4.64$ (ecf based on the K_a calculated in (ii))	

		iv.	(1) Calculation of concentration of the salt formed. Amount of $\text{Ca}(\text{OH})_2$ added : $0.01 \times 2.5 \times 10^{-4} = 2.5 \times 10^{-6} \text{ mol}$ Amount of OH^- added : $5.0 \times 10^{-6} \text{ mol}$ <table border="1"><tr><td>(mol)</td><td>OH^-</td><td>HA</td><td>H_2O</td><td>A^-</td></tr><tr><td>Initial</td><td>5.0×10^{-6}</td><td>5.0×10^{-6} (iii)</td><td>0</td><td>5.0×10^{-6} (iii) ecf</td></tr><tr><td>Change</td><td>-5.0×10^{-6}</td><td>-5.0×10^{-6}</td><td>$+5.0 \times 10^{-6}$</td><td>$+5.0 \times 10^{-6}$</td></tr><tr><td>Final</td><td>0</td><td>0</td><td>5.0×10^{-6}</td><td><u>1×10^{-5}</u></td></tr></table> $[\text{A}^-] = 1 \times 10^{-5} / 0.03 = \underline{3.33 \times 10^{-4}} \text{ mol dm}^{-3}$ (2) Balanced equation. $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$ (3) pH of salt formed. $K_b = K_w / K_a = 1.264 \times 10^{-9} \text{ mol dm}^{-3}$ $[\text{OH}^-]_{\text{contribution by hydrolysis}} = (K_b \times [\text{A}^-])^{1/2} = (1.264 \times 10^{-9} \times (1 \times 10^{-5} / 0.03))^{1/2}$ $= \underline{6.49 \times 10^{-7} \text{ mol dm}^{-3}}$ $[\text{OH}^-] = 6.49 \times 10^{-7} + (2.92 \times 10^{-14})^{1/2} = 8.20 \times 10^{-7} \text{ mol dm}^{-3}$ $\text{pOH} = -\lg(8.20 \times 10^{-7}) = 6.09$ $\text{pH} = \text{p}K_w - \text{pOH} = -\lg(2.92 \times 10^{-14}) - 6.09 = \underline{7.44} \text{ (3 s.f.)}$	(mol)	OH^-	HA	H_2O	A^-	Initial	5.0×10^{-6}	5.0×10^{-6} (iii)	0	5.0×10^{-6} (iii) ecf	Change	-5.0×10^{-6}	-5.0×10^{-6}	$+5.0 \times 10^{-6}$	$+5.0 \times 10^{-6}$	Final	0	0	5.0×10^{-6}	<u>1×10^{-5}</u>	
(mol)	OH^-	HA	H_2O	A^-																				
Initial	5.0×10^{-6}	5.0×10^{-6} (iii)	0	5.0×10^{-6} (iii) ecf																				
Change	-5.0×10^{-6}	-5.0×10^{-6}	$+5.0 \times 10^{-6}$	$+5.0 \times 10^{-6}$																				
Final	0	0	5.0×10^{-6}	<u>1×10^{-5}</u>																				
Q3 (a)			Information	Deduction																				
B	the molecular formula $\text{C}_{11}\text{H}_{14}\text{O}_2$			C:H ratio close to 1:1 possesses a benzene function group																				
	sparingly soluble in water			large molecule possesses functional groups (-OH, -COO-) which can form hydrogen bonding with water.																				
	does not decolourise aqueous bromine			absence of alkene and phenol functional group																				
	Upon heating with acidified potassium manganate(VII) solution, it does not decolourise the purple solution, but forms 2 organic products, compounds C and D.			- does not undergo oxidation - acidic hydrolysis occurred																				
C	forms a violet colouration when neutral iron(III) chloride solution is added.			presence of phenol functional group																				
	Upon reaction with aqueous bromine (in a stoichiometric ratio of 1:3), it forms a white precipitate and copious white fumes which turns blue litmus paper red.			- electrophilic substitution occurred - positions 2, 4 and 6 wrt phenol are hydrogen - white precipitate is 2,4,6-tribromophenol																				
D	able to rotate plane-polarised light			possesses a chiral carbon																				
	Upon combustion with excess oxygen, 0.1 mol of compound D produces 34.7 dm^3 of gas under 150°C and 101325 Pa . The volume is halved when the gaseous products was passed through anhydrous calcium chloride.			34.7 dm^3 of gas = 1 mol of gas (inclusive of water vapour) 0.1 mol of D undergoes complete combustion to form 0.5 mol of CO_2 and 0.5 mol of H_2O - D has 5 carbon atoms and 10 hydrogen atoms [Note: anhydrous calcium chloride is a drying agent which removes water vapour]																				
	reacts with sodium carbonate powder, in a ratio of 2:1, to give effervescence			possesses 1 carboxylic acid functional group																				
	reacted with lithium aluminium hydride in dry ether to form compound E.			undergoes reduction																				
E	Compound E is then reacted with excess concentrated sulfuric acid.			undergoes elimination of water to form an alkene																				

	Product of elimination is oxidised by KMnO_4 (aq)	Terminal $\text{C}=\text{C}$
F	Compound F reacts with 2,4 DNPH	Ketone



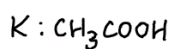
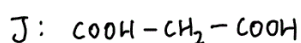
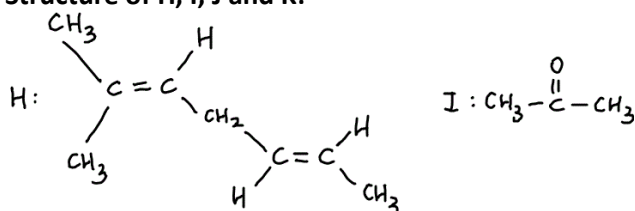
3	(b)	(i)	Temperature = 298 K $[\text{I}^-] = [\text{I}_2] = 1 \text{ mol dm}^{-3}$ $[\text{MnO}_4^-] = [\text{Mn}^{2+}] = [\text{H}^+] = 1 \text{ mol/dm}^3$ Half cell at anode, Half cell at cathode including concentration and temperature, salt bridge, voltmeter. $E_{\text{cell}} = 1.52 - 0.54 = +0.98 \text{ V}$	
3.	b)	ii.	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad +1.52\text{V}$ $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+} \quad +0.77\text{V}$ $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^- \quad +0.54\text{V}$ $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$ $E^\ominus_{\text{cell}} = +0.75\text{V}$ $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{Fe}^{2+}$ $E^\ominus_{\text{cell}} = +0.23\text{V}$ <u>MnO_4^- and I^- repel one another</u> hence rate of reaction is very slow. OR Fe^{2+} acts as a catalyst that will <u>increase the rate of reaction due to attraction between oppositely charged ions.</u>	
4.	a)	i.	Using experiments 1 and 2, as the overall volume is the same, concentration is directly proportional to the volume used, [FA3] is constant, [FA4] increases by 1.2069 times, rate increases by 1.2069 time.	

			Since the increase is between [FA4] and rate are approximately the same, the <u>order of reaction with respect to [FA4] is 1.</u> Using experiments 1 and 3, [FA3] increases by 7.5 times, [FA4] decreases by 11.6 times, rate decreases by 1.55 (original rate $\times 7.5 / 11.6$) times. Hence the <u>order of reaction with respect to [FA3] is 1.</u>																					
4	a	ii.	$r = k[2\text{-bromo-3-methylpentane}][\text{sodium hydroxide}]$ ecf on (i)																					
		iii.	$R^I: \text{CH}_3$; $R^{II}: \text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$  • reflection of reactant and product i.e. inversion • Arrows / lone pair / polarity.																					
		iv.	Using data from experiment 1, ecf based on rate equation in (ii). $8.17 \times 10^{-7} = k(0.001 \times 0.01 / 0.05)(0.029 \times 0.01 / 0.05)$ $k = 0.704$ Units: $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$																					
		v.	Proportion of particles  Catalyst would <u>lower the activation energy with alternative pathway</u> needed for the reaction to take place, resulting in an <u>increase in the proportion of molecules with energy greater than or equal to the activation energy (OR with legend in the diagram)</u> This results in <u>an increase in frequency of effective collisions</u> and hence the <u>rate of reaction increases.</u>																					
4.	b.	i.																						
4	b	ii.	amount of KOH used = $0.0248 \times 0.08 = 1.984 \times 10^{-3} \text{ mol}$ amount of ethanoic acid in 10 cm^3 of ether = $1.984 \times 10^{-3} \text{ mol}$ amount of ethanoic acid in 100 cm^3 of ether = $1.984 \times 10^{-2} \text{ mol}$																					
			<table border="1"> <thead> <tr> <th></th><th>Compound G</th><th>Ethanoic acid</th><th>Ester</th><th>Water</th></tr> </thead> <tbody> <tr> <td>Initial / mol dm^{-3}</td><td>0.400</td><td>0.200</td><td>-</td><td>-</td></tr> <tr> <td>Change / mol dm^{-3}</td><td>-0.0016</td><td>-0.0016</td><td>+0.0016</td><td>+0.0016</td></tr> <tr> <td>Equilibrium / mol dm^{-3}</td><td>0.3984</td><td>0.1984</td><td>0.0016</td><td>0.0016</td></tr> </tbody> </table>		Compound G	Ethanoic acid	Ester	Water	Initial / mol dm^{-3}	0.400	0.200	-	-	Change / mol dm^{-3}	-0.0016	-0.0016	+0.0016	+0.0016	Equilibrium / mol dm^{-3}	0.3984	0.1984	0.0016	0.0016	
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			$K_c = 3.24 \times 10^{-5}$																					

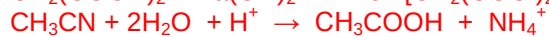
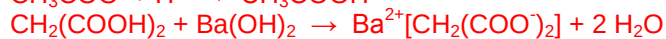
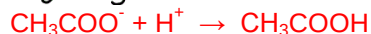
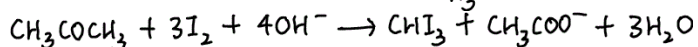
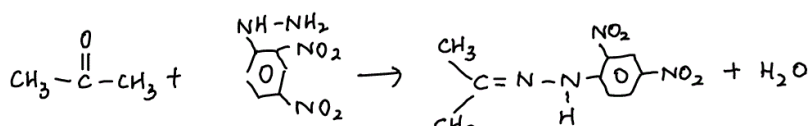
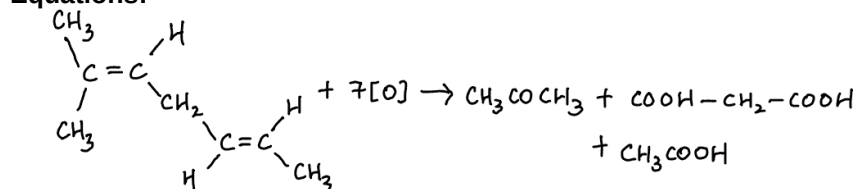
		iii.	The esterification process is endothermic . With increase in temperature, the equilibrium favours reactions which absorb heat (favouring endothermic process) . Hence the equilibrium would shift towards the right (favouring the formation of the ester) so as to remove the excess heat applied to the system.	
4.	c)	i.	Method 1: Reagents : 1. NaOH(aq) and heat 2. alkaline iodine solution and heat OR NaOH (aq), I ₂ (aq), heat. Observations: 2-bromo-3-methylpentane will form yellow CHI ₃ precipitate and 3-bromo-2-methylpentane will not form yellow CHI ₃ precipitate Method 2: Reagents : 1. Hot ethanolic NaOH 2. hot acidified KMnO ₄ Observations: 2-bromo-3-methylpentane will decolourise purple KMnO ₄ and form effervescence of CO ₂ , which will form white precipitate with calcium hydroxide. 3-bromo-2-methylpentane will decolourise and not form effervescence	
		ii.	acidified potassium manganate(VII) and heat (N-ethyl)methanamide will decolourise purple KMnO ₄ and form effervescence of CO ₂ , which will form white precipitate with calcium hydroxide (N-methyl)ethanamide will decolourise purple KMnO ₄ but not form effervescence	
5.	a)		As the Group II <u>metal ion increases in size</u> , the charge density and hence, the polarising power of the ions decreases down the group. Thus, Mg ²⁺ being the smallest cation, <u>has the greatest charge density</u> <u>Mg²⁺ has the best ability to polarise/distort the large electron cloud of the carbonate ion compared to other ions of lower charge density.</u> <u>Ease of decomposition of group II carbonates decreases down the group.</u> $\text{XCO}_3 \rightarrow \text{XO} + \text{CO}_2 \text{ (where X = Group II metal)}$	
5.	b)	i.	$K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$	
		ii.	Let the solubility of Ba(OH) ₂ be x mol dm ⁻³ $K_{sp} = [\text{Ba}^{2+}][\text{OH}^-]^2$ $2.55 \times 10^{-4} = (x)(2x)^2$ $x = 0.039948$ $[\text{OH}^-] = 2 \times 0.039948 \text{ mol dm}^{-3}$ $\text{pH} = 14 - \text{pOH} = 12.9$	
		iii.		
			Initial / mol dm ⁻³	Ba ²⁺ 0.0005
			Change / mol dm ⁻³	- x
			Equilibrium / mol dm ⁻³	0.0005 - x
				SO ₄ ²⁻ 0.0005
				- x
				0.0005 - x
			$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$ $1.08 \times 10^{-10} = (0.0005 - x)^2$ $x = 4.8961 \times 10^{-4} \text{ mol dm}^{-3}$ mass of BaSO ₄ formed = $0.2 \times 4.8961 \times 10^{-4} \times (137 + 32.1 + 16 \times 4)$ = 0.0228 g (3 s.f.)	
5.	c)	i.	Lattice energy is the energy released when 1 mol of ionic compound is formed from its gaseous ions.	
		ii.	$\text{Ba}^{2+}(\text{g}) + \text{O}^{2-}(\text{g}) \xrightarrow{\Delta H_{LE}} \text{BaO}(\text{s})$ $\begin{array}{c} \uparrow \Delta H_{f, \text{BaO}}(\text{g}) \\ \text{1st + 2nd} \\ = -140 + 798 \end{array}$ $\begin{array}{c} \uparrow \Delta H_f = -548 \\ \text{Ba}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \end{array}$ $\begin{array}{c} \uparrow \Delta H_{\text{atm Ba}} + \Delta H_{\text{atm } \frac{1}{2} \text{O}_2(\text{g})} \\ = 186 + \frac{1}{2}(496) \end{array}$ $\begin{array}{c} \uparrow \Delta H_{\text{I.E.}}(\text{Ba}) \\ \text{1st + 2nd} \\ = 502 + 966 \end{array}$ $\text{Ba}(\text{g}) + \text{O}(\text{g})$ $\text{L.E.} = -(-140 + 798) - (+502 + 966) - (+186 + 0.5 \times 496) + (-548)$ $= -3104 \text{ kJ mol}^{-1}$	

Compound	Information	Deduction
H	decolourises bromine solution in the dark.	- undergoes electrophilic addition reaction - presence of alkene
	reacts with hot acidified potassium manganate(VII) solution, it forms compounds I , J and K .	- undergoes oxidation reaction - presence of 2 C=C
I	forms an orange precipitate with 2,4-dinitrophenylhydrazine	- undergoes condensation reaction - presence carbonyl functional group
	After reacting with alkaline iodine solution and acidifying the resulting mixture, it forms a yellow precipitate and compound K .	- yellow precipitate is CHI₃ - presence of -COCH₃ group
J	0.104 g of compound J , a dicarboxylic acid, neutralises 25.0 cm ³ of FA5 .	- amount of Ba(OH)₂ used = 9.99 x 10⁻⁴ mol - M_r of J = 104.1
K	Compound K can be formed by boiling ethanenitrile with sulfuric acid.	undergoes acidic hydrolysis

Structure of H, I, J and K:



Equations:



-END-