Section A

1 (a) (i)

Element	$E^{\ominus}$ / V
$\frac{1}{2}F_2 + e^- \rightleftharpoons F^-$	+2.87
$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$	+1.36
$\frac{1}{2}Br_2 + e^- \rightleftharpoons Br^-$	+1.07
$\frac{1}{2}I_2 + e^- \rightleftharpoons I^-$	+0.54

The order of oxidising strength of the halogens, as observed from the $E^{\ominus}$ values above, decreases down the Group.

Due to the strong oxidising power of F_2, the oxidation number of Phosphorus +5 in PF_5, +5 and +3 in PCl_5 and PCl_3, +3 in PBr_3 and PI_3 respectively. **[3]**

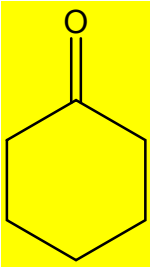
(ii)

The smaller the pK_a, the stronger the acid, indicating HI is the strongest acid, followed by HBr, HC*l* and HF. Down the group from F to C*l* to Br to I, atomic radius increases, effectiveness of orbital overlap between H and X decreases. The H–X bond becomes increasingly weaker, making it easier to lose the H^+. **[2]**

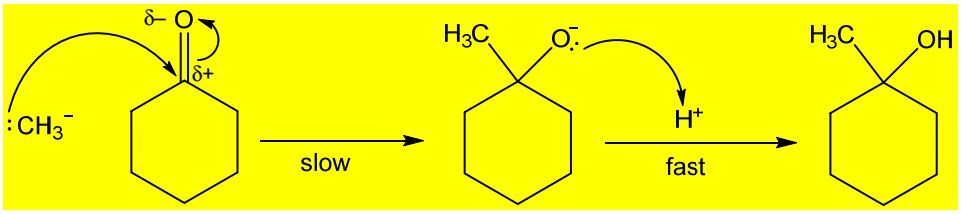
(b) (i)

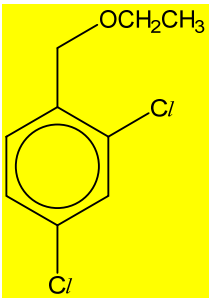
(Acidic) hydrolysis **[1]**

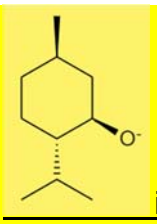
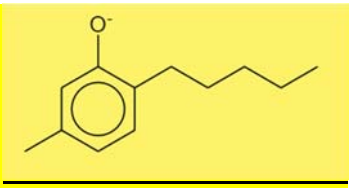
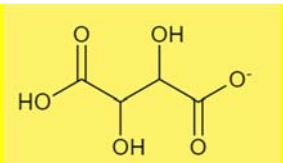
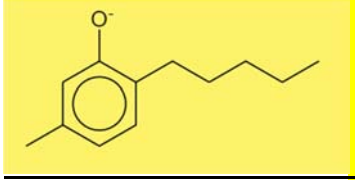
(ii)

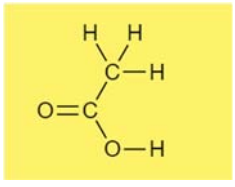


and CH_3MgBr **[2]**

		(iii)		**[3]**
	(c)	**(i)**	$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$	**[1]**
		(ii)	$[Ca^{2+}] = 1.14 \times 10^{-7} \times 3 = 3.42 \times 10^{-7}$ mol dm^{-3} $[PO_4^{3-}] = 1.14 \times 10^{-7} \times 2 = 2.28 \times 10^{-7}$ mol dm^{-3} $K_{sp} = (3.42 \times 10^{-7})^3(2.28 \times 10^{-7})^2 = \underline{2.08 \times 10^{-33} \text{ mol}^5 \text{ dm}^{-15}}$	**[2]**
		(iii)	Let the solubility of calcium phosphate in the presence of potassium phosphate be y. $2.08 \times 10^{-33} = (3y)^3(0.15 + y)^2$ Assume that y is small such that $0.15 + y \approx 0.15$ $2.08 \times 10^{-33} = (3y)^3(0.15)^2$ $y = \underline{1.51 \times 10^{-11} \text{ mol dm}^{-3}}$	**[2]**
		(iv)	An increase in $[SO_4^{2-}]$ causes the <u>equilibrium position of $CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$ to shift left</u>, <u>decreasing the solubility of $CaSO_4$</u>. Since the solubility of $CaSO_4$ is lowered, there will be <u>less Ca^{2+}</u> from dissolution of $CaSO_4$. <u>Equilibrium position of $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$ shifts right</u>, <u>increasing the solubility of $Ca_3(PO_4)_2$</u>.	**[2]**
				[Total: 18]

2	**(a)**	**(i)**	NaOH(aq), heat under reflux	**[1]**
		(ii)	The C–C*l* bond has a partial double bond character as the lone pair of electrons in the p orbital of the C*l* atom can delocalise into the π electron cloud of the benzene ring. This strengthens the C–C*l* bond, making it more difficult to break.	**[1]**
		(iii)		**[1]**
		(iv)	Add PC*l*$_5$ / SOC*l*$_2$ 2,4-dichlorobenzyl alcohol: white fumes (of HC*l*) observed amylmetacresol: no white fumes observed or Add Br$_2$(aq) 2,4-dichlorobenzyl alcohol: Br$_2$(aq) remains orange amylmetacresol: orange Br$_2$(aq) decolourises or Add neutral FeC*l*$_3$ 2,4-dichlorobenzyl alcohol: no violet complex formed amylmetacresol: violet complex formed	**[2]**

	(b)	Menthol < amylmetacresol < tartaric acid Menthol is the weakest acid.  is the least stable anion as the electron-donating alkyl group intensifies the negative charge on the oxygen atom in the anion.  Amylmetacresol is more acidic than menthol as the anion is more stable. The negative charge on the oxygen atom can be delocalised into the benzene ring.  Tartaric acid is the most acidic as the anion is the most stable. The negative charge on the oxygen atom is delocalised over the COO^- group, and the delocalisation is more effective than that in the  anion.	**[3]**
	(c)	**(i)**	Step 1: electrophilic substitution / electrophilic addition Step 2: reduction (Note: for step 1, the catalyst aids in the formation of $CH_3CHCH_3^+$ electrophile)	**[2]**
		(ii)	8 enantiomers Proportion = 0.125 / 12.5%/ 1/8	**[2]**

		(iii)	 (Accept: benzoate salt)	**[1]**
	(d)	**(i)**	When 0.00 cm^3 of NaOH is added, solution contains only tartaric acid. $[H^+] = \sqrt{(0.0100)(10^{-2.89})} = 3.59 \times 10^{-3}$ mol dm^{-3} pH = $-\lg(3.59 \times 10^{-3})$ = 2.45 When 12.50 cm^3 of NaOH is added, solution contains equal concentration of unreacted tartaric acid and tartrate mono-anion, giving rise to a buffer at its maximum buffering capacity. Hence, pH = pK_{a1} = 2.89. When 50.00 cm^3 of NaOH is added, solution only contains tartrate di-anion which undergoes hydrolysis to form OH^-. [Tartrate di-anion] = $(\frac{25.00}{1000} \times 0.0100) \div \frac{75.00}{1000}$ = 0.00333 mol dm^{-3} $[OH^-] = \sqrt{(0.00333)(\frac{1.00 \times 10^{-14}}{10^{-4.40}})} = 9.15 \times 10^{-7}$ mol dm^{-3} pOH = $-\lg(9.15 \times 10^{-7})$ = 6.04 pH = 14 – 6.04 = 7.96	**[4]**
		(ii)	The solid has a giant ionic lattice structure while tartaric acid has a simple covalent structure. More energy is needed to overcome the stronger electrostatic attraction between the cations and anions than the weak hydrogen bonds between tartaric acid molecules.	**[2]**
	(e)	**(i)**	Cold dilute acidified / alkaline $KMnO_4$(aq)	**[1]**
		(ii)		**[1]**

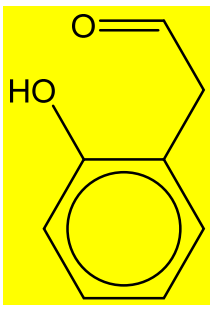
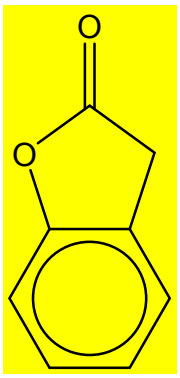
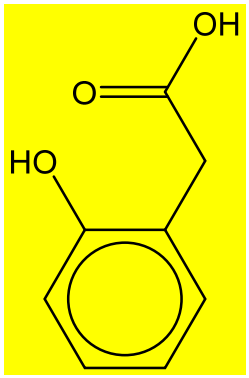
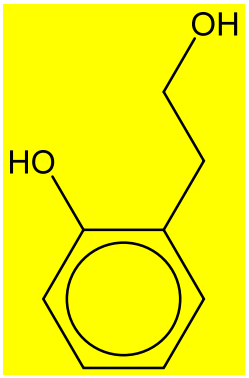
		(iii)	The gas is CO_2. $pV = nRT$ $p(500 \times 10^{-6}) = (\frac{0.36}{44.0})(8.31)(30 + 273)$ $p = \underline{4.12 \times 10^4 \text{ Pa}}$	**[2]**
				[Total: 23]

3	**(a)**	It is a substance that is at a different phase as the reactants, and it speeds up the rate of the reaction by providing an alternative reaction pathway with a lower activation energy.		**[2]**

	(b)	Zn/Zn^{2+} half-cell $E^{\ominus} = -0.76$ V
		VO_3^-/ VO^{2+} half-cell $E^{\ominus} = +1.00$ V
		VO^{2+}/ V^{3+} half-cell $E^{\ominus} = +0.34$ V
		V^{3+}/V^{2+} half-cell $E^{\ominus} = -0.26$
		$(VO_3^-/ VO^{2+}// Zn/Zn^{2+})$ $E^{\ominus}_{cell} = +1.76$ V
		Zn is able to reduce VO_3^- to VO^{2+}/ reduction of VO_3^- to $VO^{2+}$by Zn is spontaneous.
		$(VO^{2+}/ V^{3+}// Zn/Zn^{2+})$ $E^{\ominus}_{cell} = +1.10$ V
		Zn is able to reduce VO^{2+} to V^{3+}/ reduction of VO^{2+} to V^{3+} by Zn is spontaneous.
		$(V^{3+}/ V^{2+}// Zn/Zn^{2+})$ $E^{\ominus}_{cell} = +0.50$ V
		Zn is able to reduce V^{3+} to V^{2+}/ reduction of V^{3+} to V^{2+} by Zn is spontaneous.
		Hence, the solution changes from yellow to blue to green to violet.
				[3]

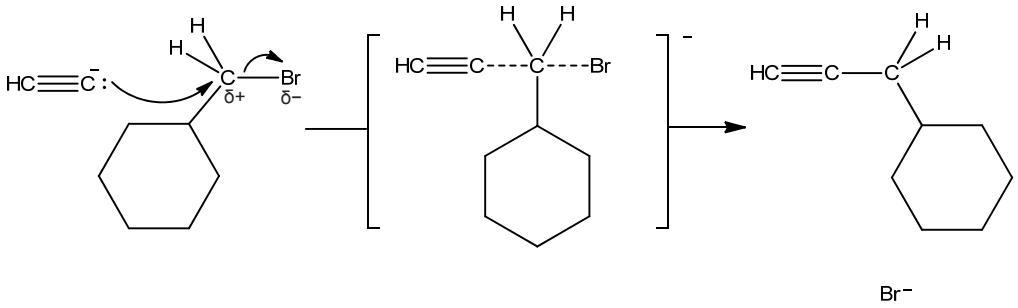
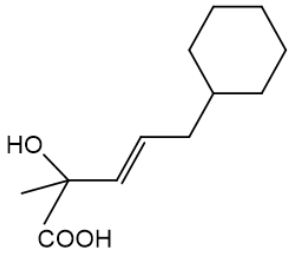
	(c)	**(i)**	$V^{3+}(aq)$	**[1]**
		(ii)	$5VO^{2+} + MnO_4^- + 6H_2O \rightarrow 5VO_3^- + Mn^{2+} + 12H^+$ **OR** $5VO^{2+} + MnO_4^- + H_2O \rightarrow 5VO_2^+ + Mn^{2+} + 2H^+$	**[1]**
		(iii)	$n_{KMnO_4} = \frac{20.63}{1000} \times 0.02 = 0.000413\ mol$	**[1]**

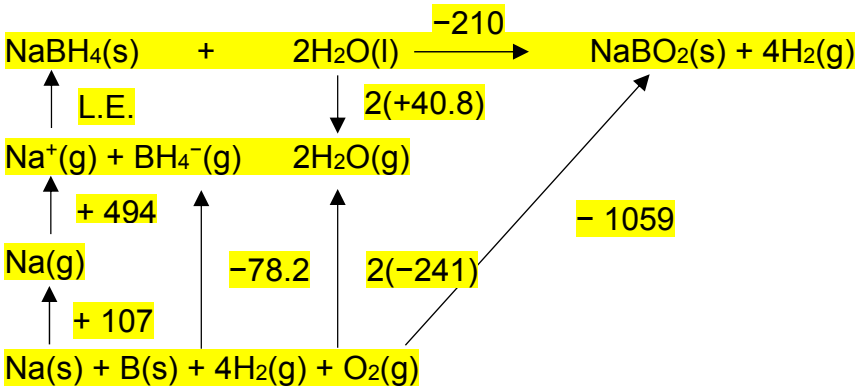
		(iv)	$n_{V^{3+}} + n_{VO^{2+}} = \frac{25}{1000} \times 0.05 = 0.00125$ mol $n_{V^{3+}} = 0.00125 - x$ n_{KMnO_4} reacted with $VO^{2+} = \frac{1}{5}x$ n_{KMnO_4} reacted with $V^{3+} = \frac{2}{5}(0.00125 - x)$ $\frac{2}{5}(0.00125 - x) + \frac{1}{5}x = 0.000413$ $0.0025 - 2x + x = 0.002063$ $x = 0.000437$ mol In 100 cm^3 of solution: $n_{V^{3+}} = 4(0.00125 - 0.000437) = 0.003252$ mol $n_{VO^{2+}} = 4x = 0.001748$ mol $m_{Zn} = 0.5[(65.4)(0.001748) + (65.4)(2)(0.003252)]$ $= 0.270$ g	**[4]**
	(d)	C:H ratio of **A**, **B**, **C** and **D** ≈ 1:1 - Contains a benzene ring Compound **A** undergo oxidative esterification: - **A** has an aldehyde group / phenol / alcohol group. - **B** has an ester group (also accept **B** being ester due to neutral nature) Compound **B** undergo (alkaline) hydrolysis to form the sodium salt of C - B is a cyclic ester - **C** has a carboxylic acid and alcohol / phenol group. **A**, **B** and **C** undergo reduction to form **D** - **D** contains 2 –OH group, of which one is a primary alcohol. **A**, **B** and **D** can undergo electrophilic substitution with Br_2(aq) - **A**, **B** and **D** contains a phenol	**[7]**

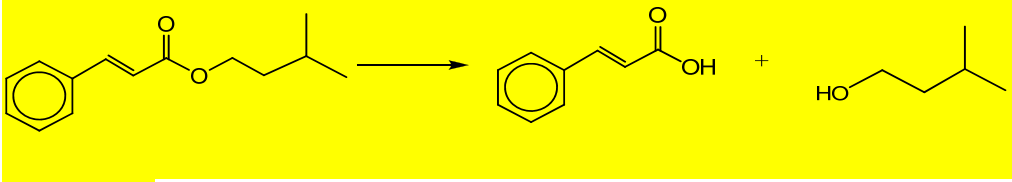
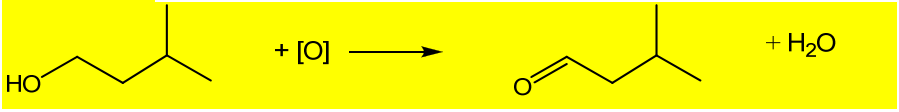
						
			A	**B**		
						
			C	**D**		
						[Total: 20]

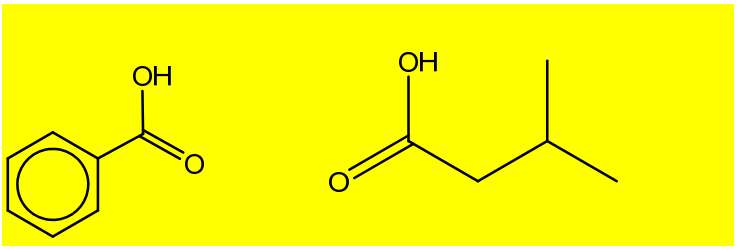
Section B

Answer **one** question from this section.

4	**(a)**	**(i)**	Base	**[1]**
		(ii)	S_N2 nucleophilic substitution 	**[3]**
		(iii)	Phenylamine is a weaker base. The lone pairs of electrons on the $–NH_2$ group is delocalised into the benzene ring, this makes the lone pair less available for protonation.	**[1]**
		(iv)	Step 2: ethanal Step 4: Acidified $K_2Cr_2O_7$, heat (under reflux)	**[2]**
		(v)	 The C=C is electron rich hence C=C does not attract CN^- nucleophiles. The carbonyl C in C=O is electron-deficient (or electrophilic) as it is bonded to highly electronegative O atom, attracting CN^- nucleophiles.	**[3]**
	(b)	**(i)**	Lattice energy is the enthalpy change when one mole of the solid ionic compound is formed from its constituent gaseous ions under standard conditions.	**[1]**

		(ii)	 By Hess' Law, − L.E. – (+494) – (+107) – (–78.2) – 2(–241) + 2(+40.8) − 1059 = −210 L.E. = − 808 kJ mol^{-1}	[5]
	(c)	(i)	$Q = It = nF$ $n = \frac{It}{F} = \frac{0.12 \times 60}{96500} = 7.4611 \times 10^{-5}\ mol$ $n_{ethanol} = \frac{1}{4} \times 7.4611 \times 10^{-5} = 1.87 \times 10^{-5}\ mol$ Mass of alcohol per breath = $1.87 \times 10^{-5} \times 46.0 = 8.58 \times 10^{-4}\ g$	[3]
		(ii)	Amount of ethanol per cm^3 of blood = $\frac{2100}{65} \times 1.87 \times 10^{-5}$ $= 6.04 \times 10^{-4}\ mol$	[1]
				[Total: 20]

5	**(a)**		MgO(s) <u>reacts with acid</u> to form neutral salt and water. $MgO(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l)$ $P_4O_6(s)$ **(**or $P_4O_{10}(s)$) <u>react violently/vigorously with alkali</u> to form salt and water. $P_4O_{10}(s) + 12OH^-(aq) \rightarrow 4PO_4^{3-}(aq) + 6H_2O(l)$ $P_4O_6(s) + 8OH^-(aq) \rightarrow 4HPO_3^{2-}(aq) + 2H_2O(l)$ $P_4O_6(s)$ **(**or $P_4O_{10}(s)$) reactions with alkali is too exothermic (could burn the roots of the plant), OR produces conjugate base which makes the soil alkaline.	**[3]**
	(b)	**(i)**	$Mg(NO_3)_2(s) \rightarrow MgO(s) + 2NO_2(g) + ½O_2(g)$ $Ca(NO_3)_2(s) \rightarrow CaO(s) + 2NO_2(g) + ½O_2(g)$	**[1]**
		(ii)	$Mg(NO_3)_2$ decomposed at 575 K but not $Ca(NO_3)_2$. Both $Mg(NO_3)_2$ and $Ca(NO_3)_2$ decomposed at 949 K. Mg^{2+} has a <u>smaller ionic radius</u> than Ca^{2+} while their ionic charges are the same. <u>Charge density of Mg^{2+} is higher</u> and hence has higher polarising power than Ca^{2+}. Mg^{2+} is able to <u>polarise / distort the electron cloud of NO_3^{2-} and weaken the covalent bonds in NO_3^{2-} to larger extent.</u> Since the mole ratio of $Mg(NO_3)_2$ and $Ca(NO_3)_2$ in the samples is 2:1, Sample at 575 K lost x g from $Mg(NO_3)_2$ Sample at 949 K lost x g from $Mg(NO_3)_2$ and $2x$ g from $Ca(NO_3)_2$ ($3x$ g in total).	**[3]**
	(c)	**(i)**	To <u>condense the product</u> formed so that it can be collected.	**[1]**
		(ii)	Hydrolysis:  Oxidation: 	**[2]**
		(iii)	3-methylbutanal (lowest b.p. compared to the isoamyl cinnamate, cinnamic acid and 3-methylbutanol, deduce using chem bonding knowledge)	**[1]**

		(iv)		**[2]**
	(d)	**(i)**	Total amount of gallic acid (GA) = $\frac{1.00}{170}$ = 0.005882 mol GA ≡ 4NaOH Amount of GA in 100 cm^3 aqueous layer = $\frac{20.25}{1000} \times 0.180 \times \frac{1}{4} \times 5$ = 4.556×10^{-3} mol Amount of GA in 50 cm^3 organic layer = $0.005882 - 4.556 \times 10^{-3}$ = 1.326×10^{-3} mol $K_{partition} = \frac{\left(\frac{4.556 \times 10^{-3}}{0.100}\right)}{\left(\frac{1.326 \times 10^{-3}}{0.050}\right)} = 1.72$	**[3]**
		(ii)	Add (100 cm^3 of / an excess of) aqueous NaOH and the (50 cm^3 of) diethyl ether containing both gallic acid and 3,4,5-trimethylgallic acid to a separatory funnel. Shake the two layers to ensure all the gallic acid are neutralised by NaOH. Vent the separatory funnel periodically to prevent pressure build up. Salt of gallic acid much more soluble in aqueous layer than diethyl ether layer as it can form more ion-dipole interaction with water molecules. Thus, mainly 3,4,5-trimethylgallic acid is left in the diethyl ether layer. **modification:** use of aqueous NaOH to neutralise the gallic acid and its derivatives **explanation:** explain why mainly 3,4,5-trimethoxygallic acid is left in diethyl ether layer gallic acid forms anion with more charge (+4) than anion from 3,4,5-trimethoxygallic acid, therefore more ion-dipole interaction bulky 3,4,5-trimethoxybenzyl group hinders the formation of ion-dipole, thus anion from 3,4,5-trimethoxygallic acid form significant pd-pd with diethyl ether	**[2]**
		(iii)	Test: Add acidified $KMnO_4$, heat. Bubble gaseous product into limewater. For methyl gallate, purple $KMnO_4$ is decolourised and a colourless, odourless gas evolved gives white ppt in limewater. For gallic acid, $KMnO_4$ remained purple.	**[2]**
				[Total: 20]