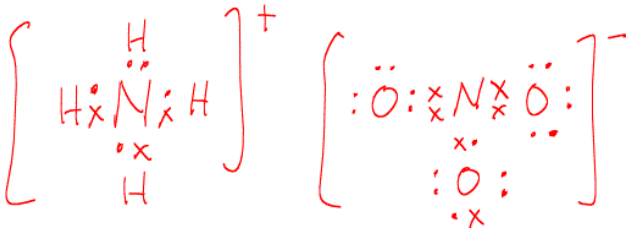
2017 H2 Chemistry Prelim Answers

Paper 1 Answer Key

1	**B**	6	**D**	11	**A**	16	**D**	21	**D**	26	**C**
2	**D**	7	**B**	12	**C**	17	**A**	22	**B**	27	**A**
3	**C**	8	**A**	13	**C**	18	**B**	23	**A**	28	**A**
4	**C**	9	**A**	14	**D**	19	**D**	24	**C**	29	**A**
5	**C**	10	**A**	15	**D**	20	**B**	25	**B**	30	**D**

Paper 2 Answers

1 (a) (i)



Shape of ammonium ion: tetrahedral
Shape of nitrate ion: trigonal planar

(ii) ΔH_{sol} = -(-Lattice Energies) + ($-\Delta H_{hyd}$) = |L.E.| - | ΔH_{hyd} |

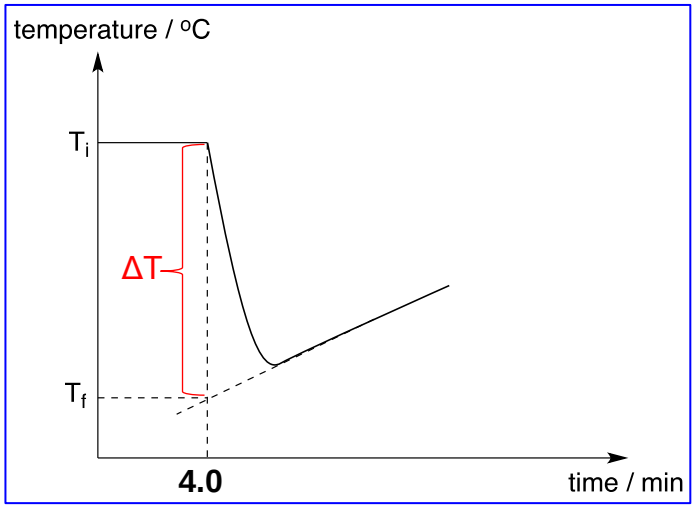
$|L.E.| \propto \frac{|q^+q^-|}{r^+ + r^-}$

$|\Delta H_{hyd}| \propto \frac{|q|}{r}$

Anionic radius of nitrate ion is larger than chloride, therefore the decrease in | ΔH_{hyd} | of nitrate ion is larger than the decrease in |L.E.|. ΔH_{sol} is expected to be more endothermic.

(b) (i) Assuming a temperature change of 5 ^oC and no heat loss to surroundings,
n(salt) x 15 000 = 100 x 4.3 x 5
n(salt) = 0.1433 mol
minimum mass = 0.1433 x 53.5 = 7.67 g

(ii)



(iii) $\Delta G^o = \Delta H^o - T\Delta S^o$
ΔG^o is negative since reaction is spontaneous and ΔH^o is positive since reaction is endothermic. Therefore sign of ΔS^o is positive as there are more ways to arrange the particles when the solid dissolves in water.

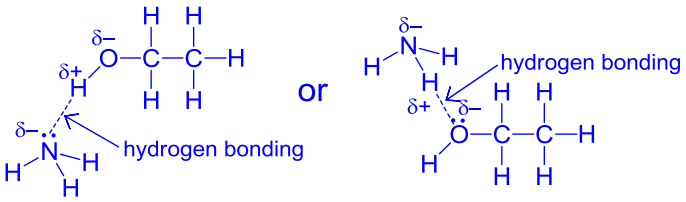
(c) **(i)** Since Zn is oxidised, $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$

Overall equation:
$Zn(s) + 2\ MnO_2(s) + 2\ NH_4Cl(aq) \rightarrow Mn_2O_3(s) + ZnCl_2(aq) + 2NH_3(aq) + H_2O(l)$

(ii) $E°_{cell} = (+0.5) - (-0.76) = +1.26V$

(iii) $\Delta G^o = -\ nFE^o = -\ 2 \times 96500 \times 1.26 = -\ 243\ 000\ J\ mol^{-1}$
$= -\ 243\ kJ\ mol^{-1}$
The sign of ΔG^o is negative and hence the reaction is spontaneous.

2 **(a)**



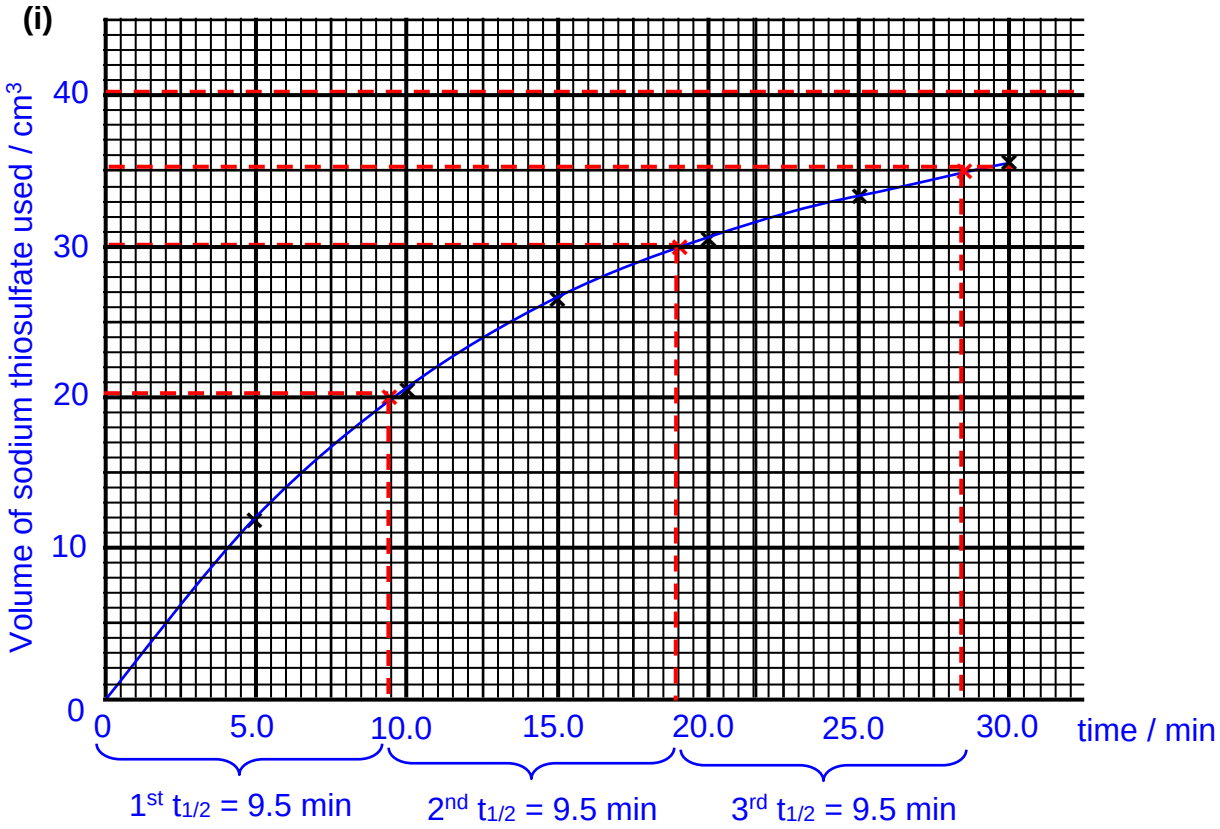
(b) **(i)** Quenching is required to stop or slow down the reaction so as to achieve a more accurate titre value at that time or to find the concentration at that instant.
Quenching agent: large volume of cold water / add large volume of acid to remove the NH_3 (in this question).

(ii) $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$

(iii) $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

(iv) Starch indicator is added when the solution turns pale yellow.
The end-point can be recognised when one drop of sodium thiosulfate added cause the dark blue solution to permanently turn colourless.

(c) (i)



(ii) [2-iodobutane] = 0.20 / 2 = 0.10 mol dm^{-3}

n(2-iodobutane) : $n(I^-)$: $n(S_2O_3^{2-})$ = 1 : 1 : 1

$n(\text{2-iodobutane}) = n(S_2O_3^{2-}) = \frac{10}{1000} \times 0.10 = 0.001000$ mol

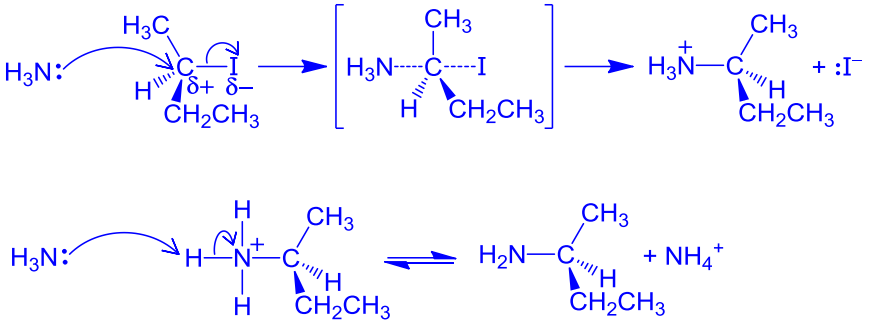
$V(S_2O_3^{2-})$ required when all 2-iodobutane reacted $= \frac{0.001000}{0.0250} = 0.04000$ $dm^3 = 40.00$ cm^3

When volume of sodium thiosulfate increases from 0 to 20 cm^3,
1^{st} $t_{1/2}$ = 9.5 min .
When volume of sodium thiosulfate increases from 20 to 30 cm^3
2^{nd} $t_{1/2}$ = 9.5 min.
Since the 1^{st} $t_{1/2}$ is approximately equal to 2^{nd} $t_{1/2}$, it is 1^{st} order with respect to 2-iodobutane.

(iii) Since the rate for 2.00 mol dm^{-3} of ethanolic ammonia reaction is half the rate for 4.00 mol dm^{-3} of ethanolic ammonia reaction, it is 1^{st} order with respect to ethanolic ammonia.

(iv) rate = k [2-iodobutane][ethanolic ammonia]

(v) Nucleophilic Substitution (S_N2)



(vi) After mixing equal volume of 0.20 mol dm^{-3} 2-iodobutane and 4.00 mol dm^{-3} ethanolic ammonia, [2-iodobutane] = 0.10 mol dm^{-3} and [ethanolic ammonia] = 2.00 mol dm^{-3}.

Since [ethanolic ammonia] is in large excess,
rate = k' [2-iodobutane], where k' = k [ethanolic ammonia]

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k\ [\text{ethanolic ammonia}]}$$

$$9.5 = \frac{\ln 2}{k\ (2.00)}$$

$k = 0.0365$ [1] $mol^{-1}\ dm^3\ min^{-1}$

(vii) I. 2-iodobutane is replaced with 2-chlorobutane.

BE(C−C*l*) = 340 kJ mol^{-1} BE(C−I) = 240 kJ mol^{-1}

As <u>more energy is required to overcome the stronger C−C*l* bond</u>, the rate of reaction <u>decreases</u>.

II. ethanolic ammonia is replaced with ethanolic ethylamine.

<u>Electron donating ethyl group increases the electron density</u> around the nitrogen atom of ethylamine, making the <u>lone pair of electrons more available</u> (or make the nitrogen <u>more nucleophilic</u>) to attack the electrophilic carbon. Hence, rate of reaction <u>increases</u>.

3 (a) From Cr to Co,

- number of protons increases, nuclear charge increases
- additional electron is added to the penultimate 3d subshell.
- Hence, screening/shielding effect also increases as presence of the 3d orbital shields the 4s electrons from the nuclear attraction.
- The effective nuclear charge experience by the outer 4s electrons increases only very gradually.
- Energy required to remove the 4s electron is relatively invariant.

(b) (i) $K_{sp} = [Cr^{3+}][OH^-]^3$
$6.3 \times 10^{-31} = (0.010/2)[OH^-]^3$
$[OH^-] = 5.013 \times 10^{-10}$ mol dm^{-3}

(ii) $K_{sp} = [Fe^{3+}][OH^-]^3$
$4 \times 10^{-38} = [Fe^{3+}](5.013 \times 10^{-10})^3$
$[Fe^{3+}] = 3.174 \times 10^{-10}$ mol dm^{-3} << 0.005 mol dm^{-3} hence effective

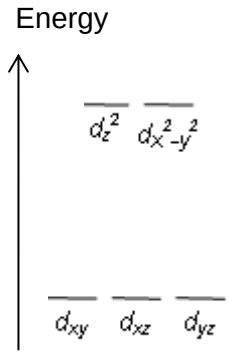
(iii) To the solution of Cr^{3+} and Fe^{3+} ions, add sodium hydroxide until excess. $Cr(OH)_3$ ppt forms and is soluble in excess.

$Cr^{3+} + OH^- \rightarrow Cr(OH)_3$
$Cr(OH)_3 + 3OH^- \rightarrow [Cr(OH)_6]^{3-}$

$Fe(OH)_3$ ppt is insoluble in excess sodium hydroxide.
$Fe^{3+} + OH^- \rightarrow Fe(OH)_3$

Filter the mixture and $Fe(OH)_3$ is the residue and $[Cr(OH)_6]^{3-}$ is the filtrate.

(c) (i) The electrons in orbitals that lie along the same axes as the ligands experiences greater repulsion, hence the energy is raised.



(ii) In the presence of ligands, the 3d orbitals split into 2 groups with an energy gap. When visible light passes through the iron complex, the violet wavelength of light corresponding to the energy gap is absorbed by the 3d electron in the lower energy level. This electron is promoted to a vacant 3d orbital at the higher energy level. The complementary colour, corresponding to unabsorbed wavelengths is observed.

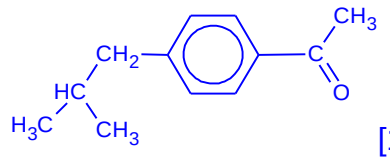
4 **(a)** At low pressure, when volume increases, pressure of chloromethane falls more than that of ideal gas as <u>permanent dipole-permanent dipole interaction</u> between CH_3Cl molecules hold the particles closer together, hence they strike the walls of the container with less force, resulting in lower pressure.

OR

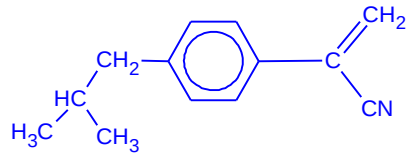
At low pressure, volume of chloromethane gas is lower/decreases more than ideal gas for a given pressure as <u>permanent dipole-permanent dipole interaction</u> between molecules is significant and the molecules are attracted closer to each other.

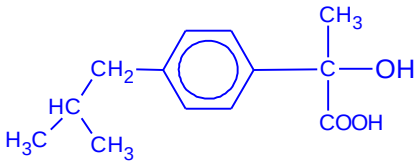
(b) **(i)** Electrophilic Substitution.

(ii)

A: 

[1]

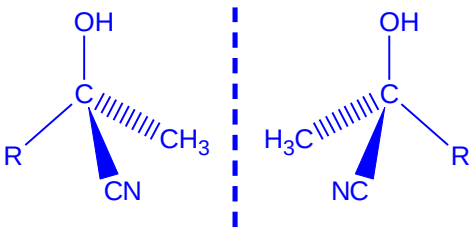
B: 

or 

(iii)

	Reagents and conditions	
Step I	anhydrous $AlCl_3$,$(CH_3)_2CHCH_2Cl$, room temperature	
Step IV	Al_2O_3, heat at 350 ^oC (OR conc H_2SO , 170 ^oC less preferred as hydrolysis of nitrile may occur)	Any dilute acid, heat under reflux
Step VI	H_2, Ni catalyst, heat **OR** H_2, Pt / Pd catalyst, room temp.	

(iv)



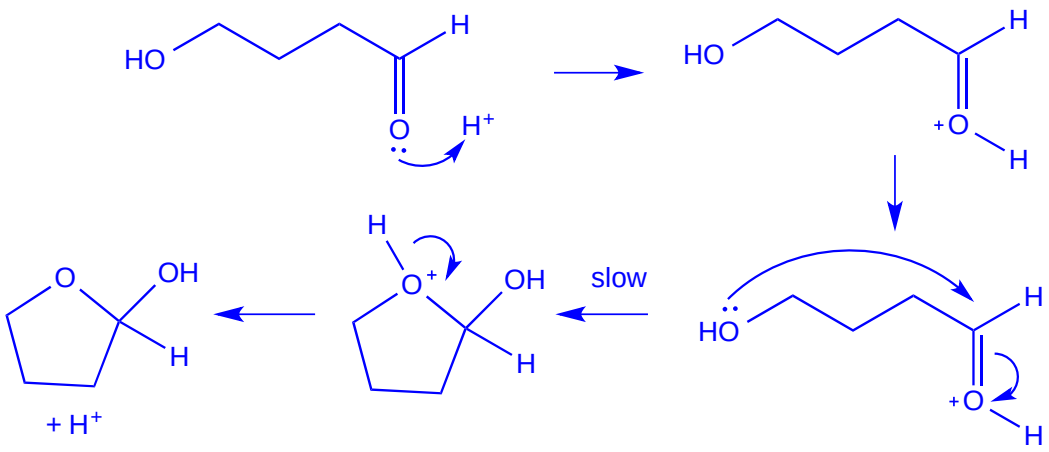
The CN^- <u>nucleophile</u> can approach the trigonal <u>planar carbonyl carbon from the top or bottom of the plane</u> **with equal probability** to <u>give the 2 enantiomers</u> **in equal amounts**.

(v) The sp^3 chiral carbon formed in step III eventually became sp^2 hybridised after elimination in step V (or IV) hence the two enatiomers will form the same alkene (which doesn't exhibit cis-trans isomerism).

(c) The relative strength of an acid depends on the stability of its conjugate base formed. Methoxyphenol has a lower pK_a, thus has a higher K_a value and is a stronger acid than methylphenol.
The $-OCH_3$ group is slightly more electronegative than CH_3 group [1] thus decreases the electron density of the conjugate base and disperses the negative charge on the phenoxide O atom to the OCH_3 group [1] hence has greater stability than the methylphenoxide.

Alternatively:
The relative strength of an acid depends on the stability of its conjugate base formed. Methoxyphenol has a lower pK_a, thus has a higher K_a value and is a stronger acid than methylphenol.
The p orbital of O in OCH_3 group overlaps with the π orbital of the phenoxide ion, thus there is greater dispersion of the negative charge over a larger volume [1] hence methoxyphenol has greater stability than the methylphenoxide.

5 (a) (i) Nucleophilic Addition

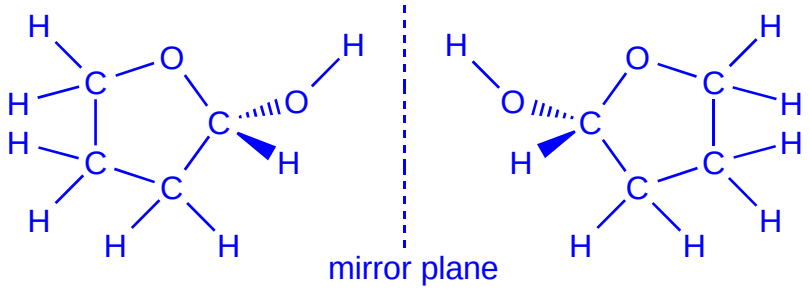


(ii) Add 2,4-DNPH, warm (Accept Fehling's solution OR Tollens' reagent)

When an orange precipitate seen, 4-hydroxyaldehyde is present. The formation of the cyclic hemiacetal is reversible.

No orange precipitate seen, 4-hydroxyaldehyde is absent. The formation of cyclic hemiacetal is irreversible.

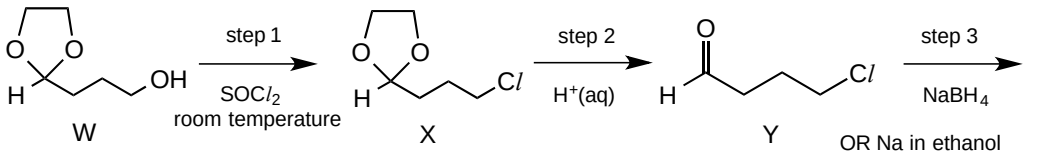
(iii)



(b) **(i)** The <u>electron donating –OCH_3</u> in ester <u>disperses the partial positive charge</u> on the carbonyl carbon, making it <u>less electrophilic</u>. Hence less susceptible to attack by hydride.

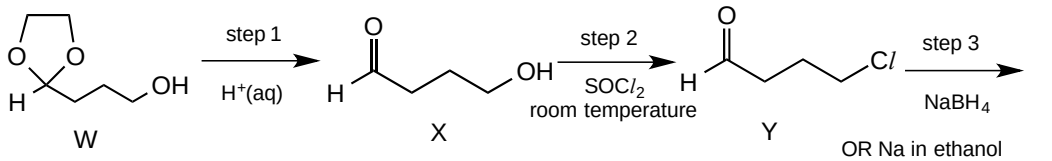
(ii) Possible Synthetic route 1:

(iii)

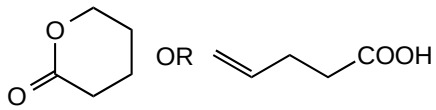


OR Na in ethanol
OR $LiAlH_4$ in dry ether
OR H_2, Ni, heat

Possible Synthetic route 2:



OR Na in ethanol
OR $LiAlH_4$ in dry ether
OR H_2, Ni, heat



Z

(iv) step 4: nucleophilic substitution
step 5: acid hydrolysis or hydrolysis

Paper 3 Answers

1 (a) (i) MgO and Al_2O_3 have giant ionic structures consisting of cations and anions held together by strong ionic bonds, requiring large amount of energy to break the strong bonds.

Al^{3+} in Al_2O_3 has a smaller ionic radius than Mg^{2+} but has a higher ionic charge of 3+ thus have a high charge density and high polarising power.

It is able to cause some polarisation of the O^{2-} ion electron cloud, giving rise to some covalent character / weakening the ionic bond.

SO_3 has a simple molecular structure consisting of SO_3 molecules held together by weak dispersion forces thus require small amount of energy to break the bonds.

(ii) Large electronegativity difference in Mg and O cause the bonds in MgO to be ionic and a basic oxide is obtained.

Smaller electronegativity difference in P and O causes the bond in P_4O_{10} to be covalent hence acidic oxide is obtained.

(b) (i) Al_2O_3 (s) + $2OH^-$ (aq) + $3H_2O$ (l) → $2[Al(OH)_4]^-$ (aq)

P_4O_{10} (s) + $12OH^-$ (aq) → $4PO_4^{3-}$ (aq) + $6H_2O$ (l)

(ii) In Sample 1: 7 moles of **C** (Na_2O) (in Sample 1) dissolved in water to produce 14 mol of OH^- ions which reacted with 12 mol of H^+ from dissolution of 1 mol of P_4O_{10} and 1 mol of Al_2O_3 to give a neutral solution.

In Sample 2: 1 mol of **A** (P_4O_{10}) reacts with water to produce 12 mol of H^+, 6 mol of which reacted with 1 mol of Al_2O_3 and 2 mol with 2 mol NaOH formed, with 4 mol of H^+ still remaining in solution.

A & B: Al_2O_3 & P_4O_{10} **C**: Na_2O

(c) (i) $CaMg(CO_3)_2$ (s) → $CaCO_3$(s) + MgO(s) + CO_2(g)

(ii) Mg^{2+} has a smaller ionic radius than Ca^{2+} while their ionic charges are the same. Charge density of Mg^{2+} is higher and hence has higher polarising power than Ca^{2+}. Mg^{2+} is able to polarise / distort the electron cloud of CO_3^{2-} causing $MgCO_3$ to be less thermally stable and decompose at 315 ^oC. Both carbonates will decompose at a higher temperature of 530 ^oC hence volume of CO_2 evolved is doubled.

(iii)

$$n_{\text{pure dolomite}} \text{ present} = \frac{0.450 / 44.0}{2} = 5.11 \times 10^{-3} \text{ mol} \quad [1]$$

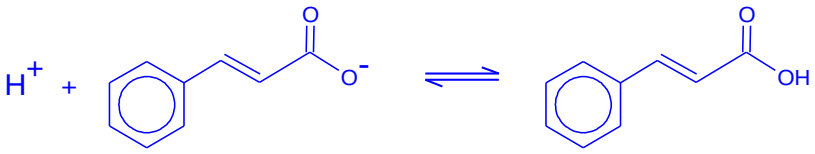
$$\% \text{ purity of dolomite} = \frac{5.11 \times 10^{-3} \times (40.0 + 24.0 + 2(12.0 + 3 \times 16.0))}{1.000} \times 100$$

$$= 94.09 \approx 94.1\% \quad [1]$$

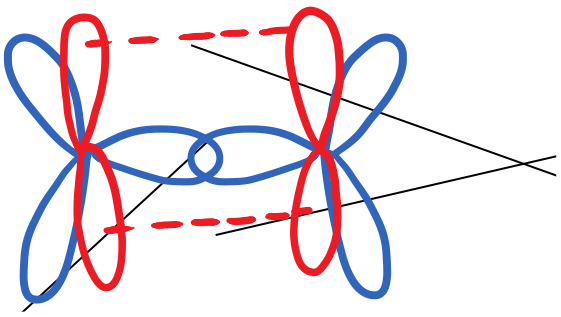
(d) (i) Cinnamic acid will react with aq NaOH first. The p orbital of O atom in cinnamate ion overlaps with the pi orbital of the –C=O, C=C and benzene to form a delocalised electron cloud. The negative charge on O of cinnamate ion is dispersed into the delocalised cloud, stabilising the ion hence is more acidic.

The ethanoate ion has an electron donating methyl group that increases the electron density of the $CH_3CO_2^-$ ion hence destabilising it.

(ii) CO_2 will dissolve in water to form carbonic acid.
$CO_2 + H_2O \rightleftharpoons H_2CO_3$
The carbonic acid is a stronger acid than cinnamic acid thus will dissociate in water to and protonate the cinnamate ion to form back cinnamic acid.
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$



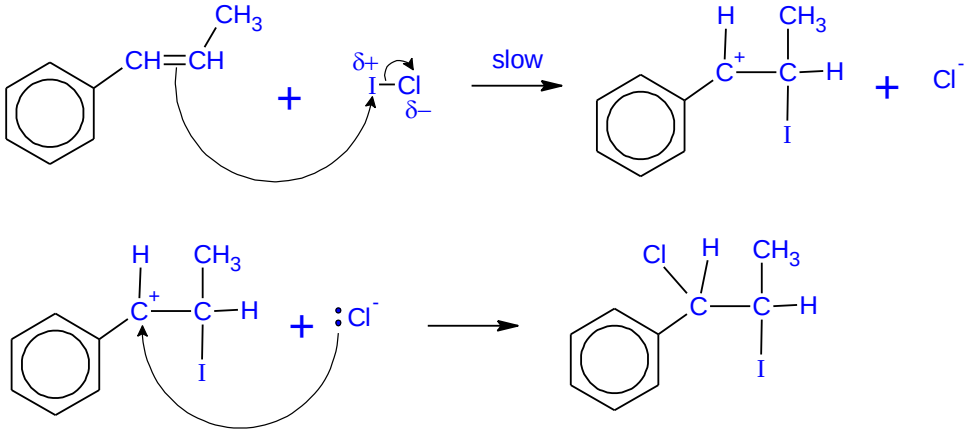
2 (a)



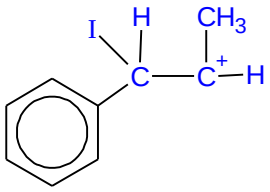
The unhybridised p-orbital overlap sideways to form π bond.

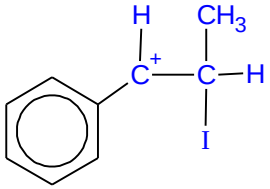
The sp^2 hybrid orbital overlap head on to form σ bond.

(b) (i) Electrophilic Addition

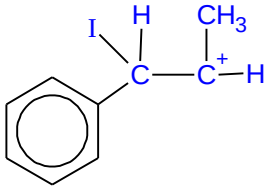


(ii)



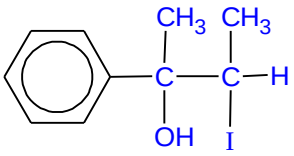


is more stable than



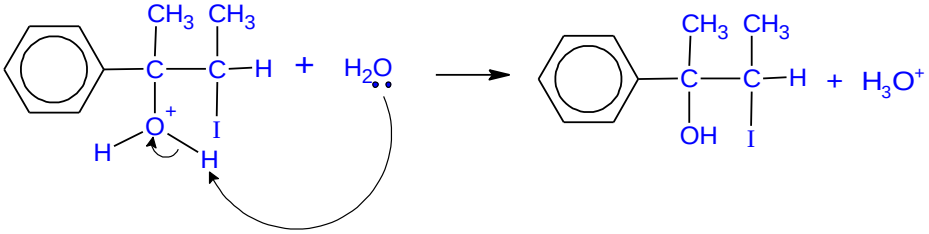
and hence is the preferred carbocation formed. The p orbital of the carbocation centre overlaps with the delocalised π electron cloud of the benzene ring, electrons from the benzene ring delocalises to the carbocation centre. Hence the positive charge can be dispersed into the benzene ring, stabilizing it further.

(iii)



The lone pairs of electrons on O in H_2O acts as competing **nucleophile** in the 2nd step of the mechanism to attack the carbocation intermediate.

Note: A proton will be lost subsequently to form the organic compound as shown in the structure above.



(c)

	$C_6H_5CH_2CH=CH_2$	CO	H_2	⇌	$C_6H_5(CH_2)_3CHO$
Initial pressure / atm	40	40	40		0
Change in pressure / atm	−39.6	−39.6	−39.6		+39.6
Equilibrium pressure / atm	0.4	0.4	0.4		39.6

$$K_p = \frac{(P_{C6H5CH2CH=CH2})}{(P_{C6H5(CH2)3CHO})(P_{CO})(P_{H2})} = \frac{39.6}{(0.4)(0.4)(0.4)} = 619 \text{ atm}^{-2}$$

(d) (i) $C_xH_yOH + Na \downarrow C_xH_yO^-Na^+ + ½ H_2$

amount of H_2, n_{H_2}
$= \frac{10.9 \times 10^{-3}}{22.7}$ = 4.80 x 10^{-4} mol
amount of $C_xH_yOH = 2 \times n_{H_2}$
= 2 x 4.80 x 10^{-3} = 9.60 x 10^{-4} mol

Contraction = initial total volume – final total volume
65 = ($V_{O2\ total}$) – ($V_{O2\ excess}$ + V_{CO2})
$V_{O2\ total} - V_{O2\ excess} = 65 + V_{CO2}$
$V_{O2\ reacted} = 65 + V_{CO2} = 65 + 131 = 195\ cm^3$

OR

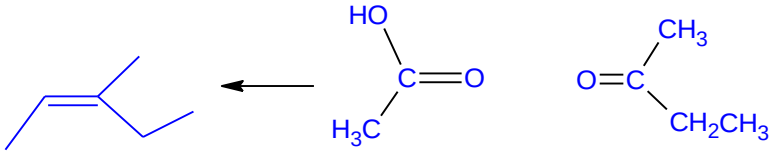
Let initial V_{O2} be z cm^3.

	C_xH_yOH (l)	$(\frac{4x+y-1}{4})$ O_2 (g)	xCO_2 (g)	$(\frac{y+1}{2})$ H_2O (l)
Initial volume/ cm^3	−	z	0	
After combustion and cooling/ cm^3	0	z – 65		
After reaction with NaOH/ cm^3	0	z – 131 – 65 (leftover O_2)	131 (formed)	

Volume of O_2 used = z – (z– 131 – 65) = 196 cm^3
Amount of O_2 used = $\frac{196 \times 10^{-3}}{22.7}$ = 8.63 x 10^{-3} mol
Volume of CO_2 formed = 131 cm^3
Amount of CO_2 formed = $\frac{131 \times 10^{-3}}{22.7}$ = 5.78 x 10^{-3} mol

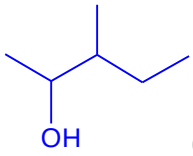
Comparing ratio:
Mole ratio of C_xH_yOH : CO_2 is 1:x.
Hence $\frac{1}{9.60\times10^{-4}} = \frac{x}{5.78\times10^{-3}} \quad \therefore x = \frac{5.78\times10^{-3}}{9.60\times10^{-4}} = 6$
Comparing mole ratio of C_xH_yOH and O_2 = 1 : $\frac{4x+y-1}{4}$
Since x=6, $\frac{1}{9.60\times10^{-4}} = \frac{\frac{4(6)+y-1}{4}}{8.63\times10^{-3}} \quad \therefore y \approx 13$
Hence **D** is $C_6H_{13}OH$.

(ii)

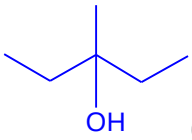
E is 

Alkene **E** is oxidised (•) by hot acidified conc. $KMnO_4$ to give ethanoic acid and butanone.

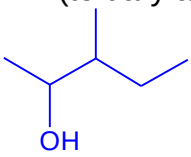
Note: Working backwards, **E** ↓ **D** (via addition of H−OH across the double bond)

D can be 

(secondary alcohol)

or 

(tertiary alcohol)

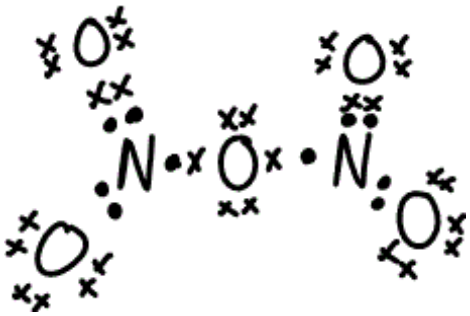
D has to be 

Since **D** can be oxidised (•) by $K_2Cr_2O_7$ it has to be a secondary alcohol.
Alkene **E** can be obtained by the elimination (•) of alcohol **D**.

(iii) Yes. **E** can exhibit cis trans.

There is restricted rotation about the C=C due to the presence of π bonding and there are 2 different groups attached to each of the carbon atom in the C=C.

(e) **(i)**



(ii) $N_2(g) + 5/2\ O_2(g) \downarrow N_2O_5(g)$

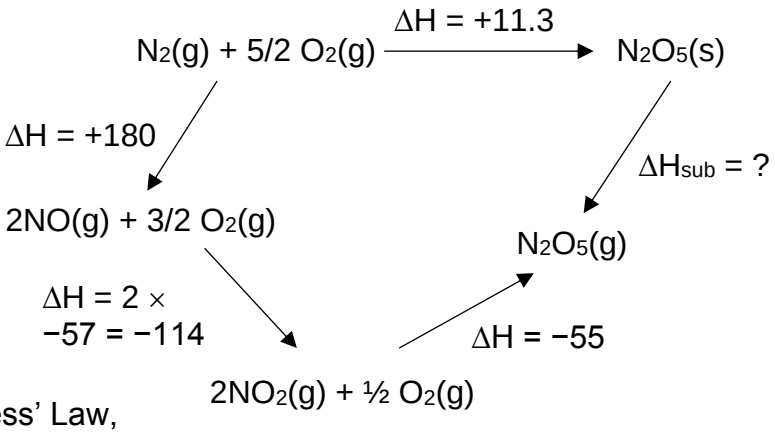
$\Delta H_f\ (N_2O_5) = 180 + 2(-57) - 55 = 11.0\ kJ\ mol^{-1}$

$\Delta H_f\ (N_2O_5) = BE(N{\equiv}N) + 5/2\ BE(O{=}O) - 2BE(N{=}O) - 4BE(N{-}O)$

$+11.0 = 944 + 5/2\ (496) - 2BE(N{=}O) - 4(210)$

$BE(N{=}O) = +666\ kJ\ mol^{-1}$

(iii)



By Hess' Law,

$\Delta Hsub = -11.3 + 180 + (-114) + (-55) = -0.300\ kJ\ mol^{-1}$

3 **(a)** **(i)** $[H^+] = \sqrt{4.57 \times 10^{-3} \times 0.0500} = 0.01511 mol\ dm^{-3}$

$pH = -\lg 0.01511 = 1.82$

(ii) $K_{b(2)} = \dfrac{1.0x10^{-14}}{2.51x10^{-10}} = 3.984 \times 10^{-5}\ mol\ dm^{-3}$

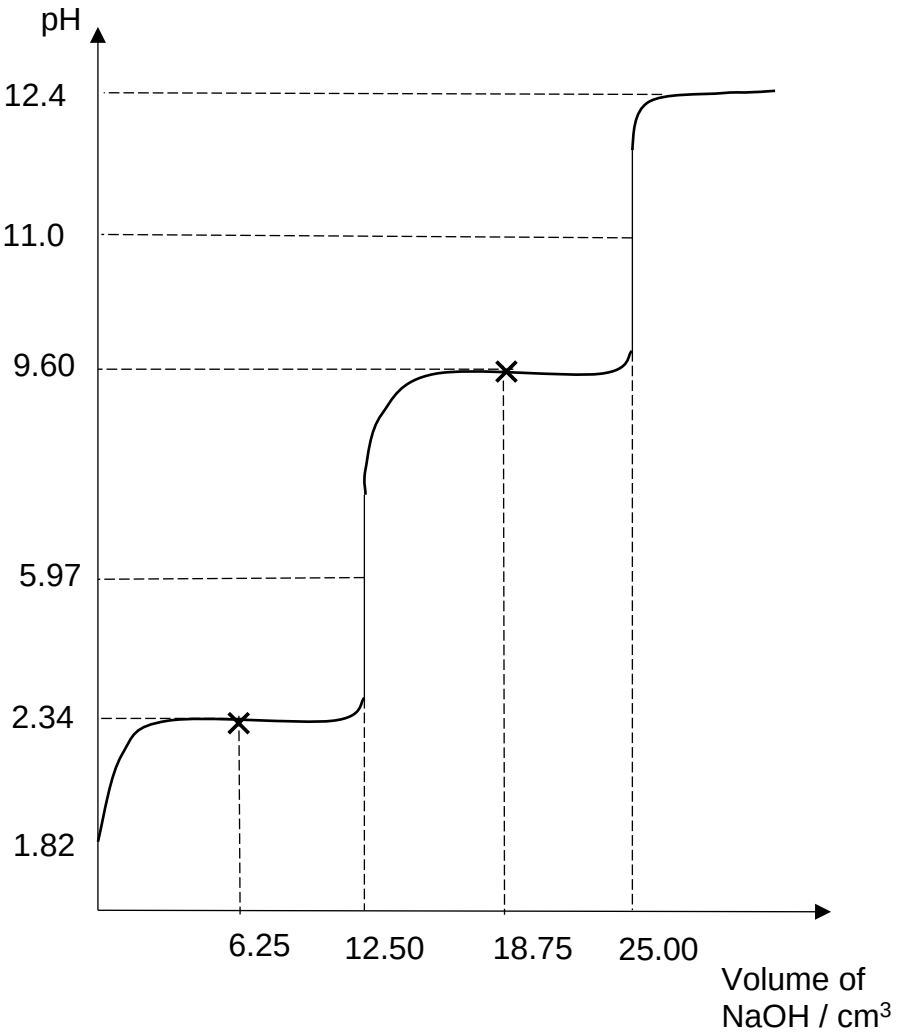
$[NH_2CH_2COO^-] = \dfrac{\frac{25}{1000} x 0.0500}{\frac{50}{1000}} = 0.0250\ mol\ dm^{-3}$

$[OH^-] = \sqrt{3.984 \times 10^{-5} \times 0.02500} = 9.980 \times 10^{-4}\ mol\ dm^{-3}$

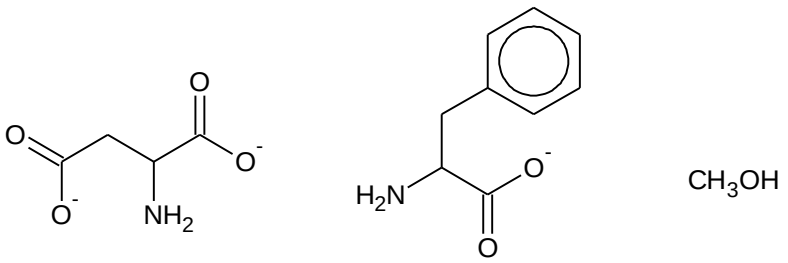
$pOH = -\lg 9.980 \times 10^{-4} = 3.0$

$pH = 14 - 3.0 = 11.0$

(iii) pH at 1st M.B.C. = p$K_{a\,(1)}$ = 2.34
pH at 2nd M.B. C. = p$K_{a\,(2)}$ = 9.60



(b)



(c) **(i)** By Le Chatelier's principle, in the presence of high concentration of H^+, the <u>position of equilibrium shifts left</u> to decrease the concentration of H^+. <u>Iron (II) sulfate dissolves, releasing free Fe^{2+} ions</u> which are mobile and flushed through the intestine without being absorbed into the bloodstream.

(ii) $Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$

$$K_f = \frac{[Fe(CN_6)^{4-}]}{[Fe^{2+}][CN^-]^6}$$

Let the concentration of Fe^{2+} be a mol dm^{-3}

$$10^{35} = \frac{0.65}{(a)(6a)^6}$$

$a = 2.024 \times 10^{-6}$ mol dm^{-3}

$[CN^-] = 6 \times 2.024 \times 10^{-6} = 1.21 \times 10^{-5}$ mol dm^{-3}

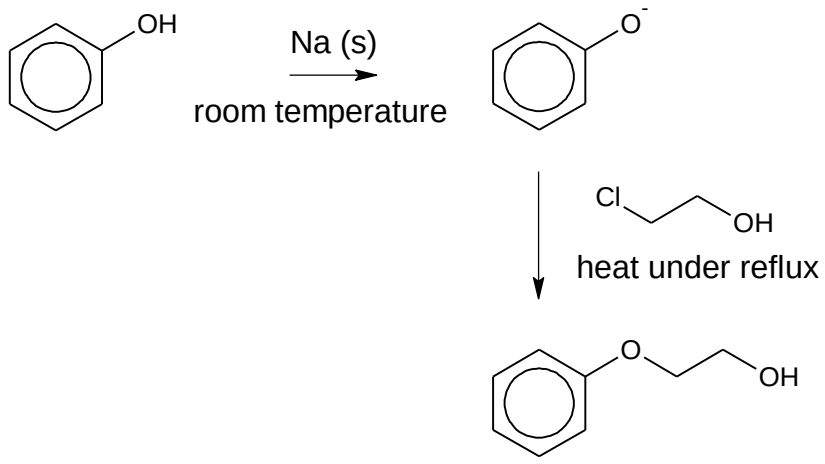
(iii) K_f of complex formed between Fe^{2+} and CN^- is 10^{35} and CN^- binds strongly and reversibly with iron in haemoglobin. They are not easily released and prevent the haemoglobin from carrying oxygen. CN^- cannot be used as a ligand.

Since K_f of complex formed between Hg^{2+} and $edta^{4-}$ is greater than that of complex formed between Hg^{2+} and cysteine ($10^{21} > 10^{14}$), $edta^{4-}$ is able to displace Hg^{2+} from cysteine and forms a more stable complex.

(d) **(i)** 1,5-diaminopentane contain electron donating alkyl groups that increase the electron density on the N atom. This increases the availability of the lone pair of electrons on N atom for bonding with a proton. Hence, 1,5-diaminopentane is a stronger base than ammonia.

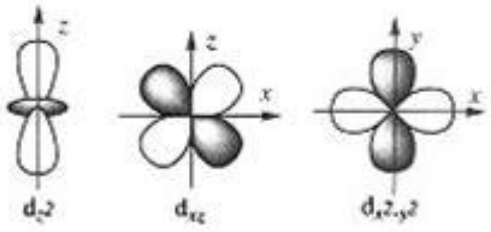
The p-orbital of N atom overlaps with the π-electron cloud of the benzene ring, causing the lone pair on N atom to be delocalised into the benzene ring. This decreases the availability of the lone pair of electrons on N atom for bonding with a proton. Hence, phenylamine is a weaker base than ammonia.

(ii)



4 (a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

(ii)



(b) (i)

			$E_\ominus$/V
(1)	$Ag^+ + e^- \rightleftharpoons$	Ag	+0.80
(2)	$Cu^{2+} + 2e^- \rightleftharpoons$	Cu	+0.34
(3)	$Pb^{2+} + 2e^- \rightleftharpoons$	Pb	–0.13

Reactions at anode:
(The operating voltage is carefully regulated so that it is sufficient for Cu to be oxidised.)

- Since $E_\ominus(Cu^{2+}/Cu)$ is <u>more positive</u> than $E_\ominus(Pb^{2+}/Pb)$, Pb will also be oxidised.
- Both Cu and Pb <u>dissolve</u> into the solution as cations and migrate to the cathode.
- Since $E_\ominus(Ag^+/Ag)$ is <u>more positive</u> than $E_\ominus(Cu^{2+}/Cu)$, Ag will not be oxidised.
- Ag drops off the electrode as the copper around dissolves, and fall to the bottom of the electrolytic tank to form <u>anode sludge</u>.

Reactions at cathode:

- Since $E_\ominus(Cu^{2+}/Cu)$ is <u>more positive</u> than $E_\ominus(Ni^{2+}/Ni)$ for (4), Cu^{2+} is preferentially reduced.
- Pb^{2+} <u>remains</u> in the solution.

(ii) Q = It C

$I(tx60) = \frac{m_x - m_o}{63.5}$ (2) F [1]

$F = Le = \frac{63.5I(60t)}{2(m_x - m_0)}$

$L = \frac{63.5I(60t)}{2(m_x - m_0)\times 1.6\times 10^{-19}}$

$= \frac{3810It}{3.2\times 10^{-19}(m_x - m_0)} = \frac{1.19\times 10^{22}\, It}{(m_x - m_0)}$ [1]

(c)

Element	Cu	C	H	O
Mass /g	33.55	25.30	1.75	39.40
Amount /mol	0.5283	2.108	1.75	2.462
Ratio	1	3.990	3.31	4.660
Simplest ratio	3	12	10	14

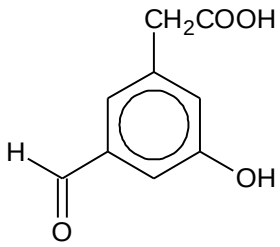
$Cu_3(C_6H_5O_7)_2$
x = 3, y = 6, z = 5

(d) **(i)** It can accept protons.
It can share/donate its lone pair of electrons on O^-.

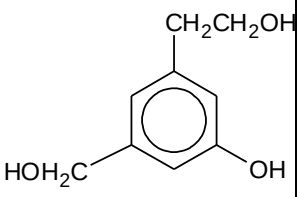
(ii) $HO_2CCO_2H \rightleftharpoons HO_2CCO_2^- + H^+$
$HO_2CCH(OH)CH(OH)CO_2H \rightleftharpoons HO_2CCH(OH)CH(OH)CO_2^- + H^+$
$HO_2CCO_2^-$ is more stable than $HO_2CCH(OH)CH(OH)CO_2^-$ as the negative charge on the O atom can be more effectively dispersed due to 2 electronegative O atoms are beside that carboxylate ion where there is only 1 O atom in the conjugate base of tartaric acid. Dissociation of ethanedioic is more favoured.

(e) **(i)**

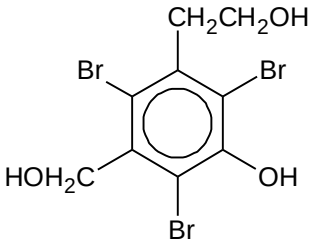
J



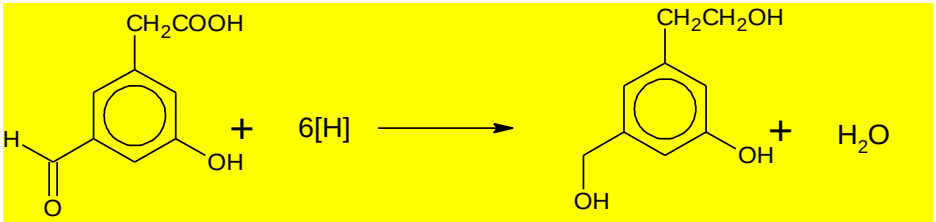
K



L



(ii)



(iii) **2** observations: Orange bromine water decolourises, white ppt forms.

(iv) $LiA/H_4 + 4H_2O \rightarrow LiOH + A/(OH)_3 + 4H_2$

5 (a) (i) The oxidation state of oxygen increases from –2 in CH_3COO^- to –1 in $CH_3COO\bullet$ hence the oxidation reaction took place at the anode.

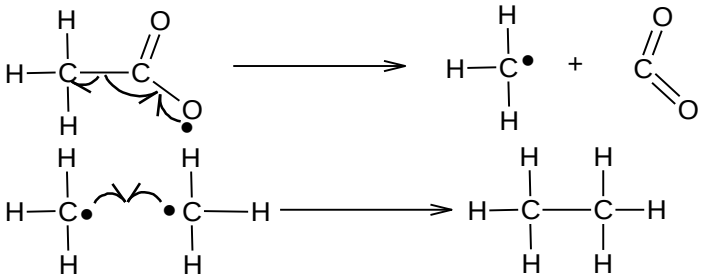
$CH_3COO^- \rightarrow CH_3COO\bullet + e^-$

(ii) $H_2O + 2e^- \rightarrow H_2 + 2OH^-$

$Q = It = 500 \times 10^{-3} \times 20 \times 60 = 600\ C$
$Q = nzF \Rightarrow 600 = n\ (2)(96500)$
$n(H_2) = 3.108 \times 10^{-3}\ mol$

$v(H_2) = 3.108 \times 10^{-3} \times 24 = 0.0746\ dm^3\ (= 74.6\ cm^3)$

(iii)



(b) (i)

$$PV = \frac{m}{M}RT$$
$$M = \frac{mRT}{PV}$$
$$= \frac{(0.30)(8.31)(300)}{(101325) \times (168 \times 10^{-6})}$$
$$= 43.9\ g\ mol^{-1} \Rightarrow M_r = 43.9$$

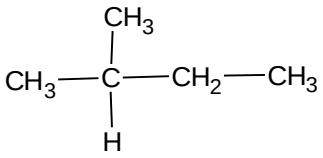
Let molecular formula of X be C_nH_{2n+2} do include this line to introduce what's n.
$12(n) + 2n + 2 = 44$
$n = 3 \Rightarrow$ X is C_3H_8

(ii) Intermolecular forces between the gas particles is negligible/insignificant.
The volume of gas particles is insignificant/negligible compared to volume of container.

(iii) X is C_3H_8 hence its structural formula is $CH_3CH_2CH_3$. Since it is unsymmetrical R–R', it is formed by two different alkyl radicals ($CH_3\bullet$ from ethanoate and another $R\bullet$ from salt of acid A).
Hence, salt of acid W produced $CH_3CH_2\bullet$ in step III.
Alkane **Y** (R'–R') is $CH_3CH_2CH_2CH_3$

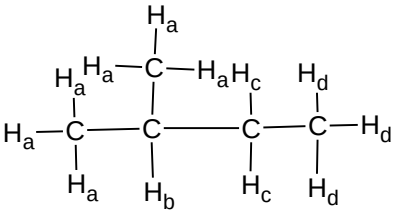
Acid **W** contains an additional COOH (lost during step II decarboxylation) attached to $CH_3CH_2\bullet$ hence it is CH_3CH_2COOH

(c)

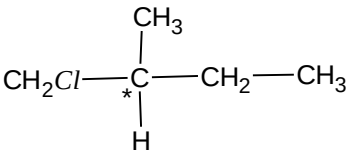


D is

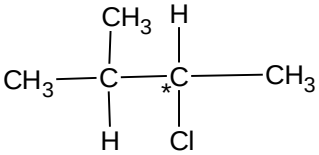
There are four different types of H in different chemical environment in D as shown below.



The 2 chiral products are



and



(d) **(i)** $SiCl_4 + 2H_2O \rightarrow SiO_2\ (s) + HCl\ (g)$

$SiCl_4$ undergoes hydrolysis to form a strongly acidic solution of pH 1-2. The solution turns red.

(ii) $NH_4^+\ (aq) + H_2O\ (l) \rightleftharpoons NH_3\ (aq) + H_3O^+\ (aq)$

Ammonium chloride is an acidic salt. The conjugate acid NH_4^+ hydrolyses in water to form a weakly acidic solution of pH 5 (approx. mid-way of pH change at eq pt for WB-SA titration pH3-7). The solution turns purple/pink.

Paper 4 Answers

1 (a)

Final burette reading / cm^3	
Initial burette reading / cm^3	
Volume of **FA 1** used / cm^3	**V_{FA1}**

(b) (i)

Titration	1	2
Final burette reading / cm^3		
Initial burette reading / cm^3		
Volume of **FA 2** used / cm^3	V1	V2

(ii) $V_{FA2} = \frac{V1 + V2}{2}$ cm^3 (2 d.p)

Correct choices and correct evaluation average titre, correct d.p.

(c) $[FA\ 2] = \frac{3.16}{158.0} = \mathbf{0.0200}$ mol dm^{-3} (3 s.f.)

(d) n_{KMnO_4} reacted during titrtation $= \frac{V_{FA\,2}}{1000} \times \mathbf{0.0200} = \mathbf{Ans\ 2}$ mol (3 s.f.)

(e) $H_2O_2(aq) \rightarrow 2e + O_2(g) + 2H^+(aq)$

$MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$

$[H_2O_2]$ in **FA 4** $= \frac{\mathbf{Ans\ 2} \times \frac{5}{2}}{\frac{25.0}{1000}} = \mathbf{Ans\ 3}$ mol dm^{-3} (3.sf.)

(f) $[H_2O_2]$ in **FA 1** = **Ans 3** $\times \frac{250}{V_{FA\,1}} =$ **Ans 4** mol dm^{-3}

(g) % error in measurement made by student **A** $= \frac{0.5}{20.90} \times 100 = 2.39$ %

correct working [1]

% error in measurement in original expt $= \frac{0.05 \times 2}{20.90} \times 100 = 0.478$ %

Ratio of percentage error $= \frac{2.39}{0.478} = 5$ Correct answer [1]

(h) Since volume of H_2SO_4 used is in excess, the use of a burette does not affect / increase the reliability of the results.

2 **(a)**

Expt	$V_{FA\ 5}$ / cm^3	V_{H2O} / cm^3	$V_{FA\ 6}$ / cm^3	time / s	$\left(\frac{1000}{time}\right)$ / $s^{-1} \times 10^3$	$lg\left(\frac{1000}{time}\right)$	lg ($V_{FA\ 5}$)
1	60.0	0.0	5.0				
2	50.0	10.0	5.0				
3	40.0	20.0	5.0				
4	30.0	30.0	5.0				
5	20.0	40.0	5.0				

(b) Axes labels + choice of scales to occupy at least half graph paper.

Correctly plotted points to half a square.

Best–fit line (minimal deviation and approx. equal deviation above and below the line)

(c) Points chosen to calculate gradient should be at least half the size of best–fit line.
Constructions lines for gradient shown, read off points accurately to half a square.
Gradient correctly evaluated to whole number with working shown.

(d) Rate of reaction is given by rate= $\frac{\text{amount of sulfur produced}}{\text{time taken}}$.

Since a constant amount of sulfur is produced for every experiment, rate is inversely proportional to time.

(e) 5 cm^3 of **FA 6** was used for every experiment and total volume of solution was kept constant at 65 cm^3 by adding deionised water.

The volume of **FA 5** measured out would be proportional to the concentration of **FA 5** used for each experiment.

(f) Relative rates and concentrations of $S_2O_3^{2-}$ were used in the experiment thus the proportionality constants are not available.
The student should use actual rate and concentrations of $S_2O_3^{2-}$ for the experiment to plot the graph.

(g) Expt 1 (60 cm^3 **FA 5**).
Time taken for the reaction to obscure the printed insert is the smallest leading to a largest percentage error in time measurement.

$$\text{percentage error in time measurement} = \frac{\text{uncertainty in time measurement}}{\text{time taken}} \times 100$$

OR
Expt 5 (20 cm^3 of **FA 6**)
The rate of producing sulfur is the slowest, leading to difficulty in estimating when the printed insert is obscured.

(h) Plan

1. Using a 25 cm^3 measuring cylinder, measure 20 cm^3 of **FA 5** and place it in a boiling tube.
2. Using another 25 cm^3 measuring cylinder, measure 10 cm^3 of **FA 6** into a second boiling tube.
3. Fill a large beaker with some water and warm it to about 75 ^oC
4. Place a 0.2 ^oC division thermometer into each boiling tube and warm the boiling tubes in the water bath (beaker of hot water).
5. Note the exact temperature of each solution and pour both contents into a 100 cm^3 beaker.
6. Start timing and swirl the solution to ensure even mixing before placing it on a printer insert.
7. Note the time taken for the mixture to just obscure the printed insert.
8. Discard the solution and rinse the beaker immediately. Wipe the external wall of the beaker dry.
9. Repeat steps 1 to 8 to obtain 3 other experiments at temperatures of 60, 45, and 30 ^oC.

Table – Temperature and Time

Expt	$T_{FA\ 5}$ / ^oC	$T_{FA\ 6}$ / ^oC	Ave Temp / ^oC	Time taken / s
1				
2				
3				
4				

3

Test	*Observations*
(a) Add sodium hydrogencarbonate to **FA 7**.	• Orange / Yellow-brown / brown ppt formed. • Effervescence. Gas evolved gives white ppt with lime water.
(b) Add, with shaking, aqueous ammonia to **FA 7**, until the aqueous ammonia is in excess. Filter the mixture and add dilute sulfuric acid dropwise to the filtrate.	• Orange / Yellow-brown / brown ppt formed, insoluble in excess aq NH_3. • Colourless filtrate obtained. • White ppt formed, soluble in excess acid to give a colourless solution.
(c) Add dilute sulfuric acid followed by aqueous potassium iodide to **FA 7**. Add starch solution.	• Orange / Yellow-brown / brown solution fades in acid. • Orange / brown solution formed with KI. • Dark blue / black / blue-black solution formed with starch
(d) Add aqueous barium chloride to **FA 7**. Add dilute hydrochloric acid.	• White ppt formed, • insoluble in excess acid.
(e) Add aqueous sodium hydroxide to **FA 7** until the alkali is in excess. Filter the mixture, add a little aluminium powder to the filtrate. Warm cautiously.	• Orange / Yellow-brown / brown ppt formed, insoluble in excess alkali. • Red litmus remained unchanged.

(f) Add aqueous silver nitrate to **FA 7**. Filter the mixture, discarding the filtrate. Wash the residue by pouring distilled water through it. Discard the washings and then pour aqueous ammonia through the residue. Collect the filtrate produced. Add dilute nitric acid dropwise to the filtrate.	• White ppt formed with $AgNO_3$. • Pale yellow filtrate obtained. • White ppt soluble in aq NH_3. • White ppt reformed, insoluble in excess acid.

(g) Possible cation(s): Fe^{3+} and Zn^{2+}

Reason(s)
• Fe^{3+} forms brown ppt of $Fe(OH)_3$ with NaOH and aq NH_3 and ppt is insoluble in excess NaOH and aq NH_3
• sulfuric acid neutralises NH_3 in filtrate to give the zinc ppt ($Zn(OH)_2$) and dissolves in excess acid to form Zn^{2+}

Possible anion(s): Cl^- and SO_4^{2-}

Reason(s)
• Cl^- form white ppt with $AgNO_3$ and is soluble in aq NH_3
• SO_4^{2-} forms white ppt with Ba^{2+} which is insoluble in acid.

(h) **FA 7** behaves as acid

Fe^{3+} has a small size and high charge hence highly polarising. It undergoes hydrolysis with water to produce H^+ ions.

$[Fe(H_2O)_6]^{3+}$ (aq) + H_2O (l) ⇌ $[Fe(H_2O)_5OH]^{2+}$ (aq) + H_3O^+ (aq)

(i)

Test No.	Reagent added	Butanal	Phenyl propan–2–ol	Propanol	Propanone
1	2,4–DNPH		✓		✓
2	aq I_2, NaOH	✓			✓
Other possible tests					
3	Fehling's	✓			
4	Sodium		✓	✓	
5	Tollens'	✓			
6	$KMnO_4$ / H^+	✓	✓	✓	

Plan

1. To 4 separate test–tubes, place 1 cm depth of each unknown solution followed by 2,4–DNPH, shake the mixture and warm. Record the observation.

2. To another set of 4 test–tubes, add 1 cm depth of each unknown solution followed by 1 cm depth of aq I_2. Add NaOH(aq) dropwise to each test–tube till the yellow colour is almost discharged. Warm the test–tubes. Record the observation.

Deduction

- Solution that gives orange ppt with 2,4–DNPH and yellow ppt with alkaline aq I_2 is methyl propapone.
- Solution that gives orange ppt with 2,4–DNPH but does not give yellow ppt with alkaline aq I_2 is butanal.
- Solution that gives yellow ppt with alkaline aq I_2. but does not give orange ppt with 2,4–DNPH is phenylpropan–2–ol.
- Solution that does not give orange ppt with 2,4–DNPH nor yellow ppt with alkaline aq I_2 is propanol