1 (a) [1]

Halogen (X_2)	***E*$^⦵$ / V**
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

Down the Group, $\underline{E^⦵}_{X_2/X^-}$ becomes <u>less positive</u>. Hence, decreasing tendency for X_2 to be reduced to X^-. The <u>oxidising power</u> of halogens <u>decreases</u> from <u>F_2 to I_2</u>. [1]

(b) (i) $2HX \longrightarrow H_2 + X_2$ [1]

where X = F, C*l*, Br, I

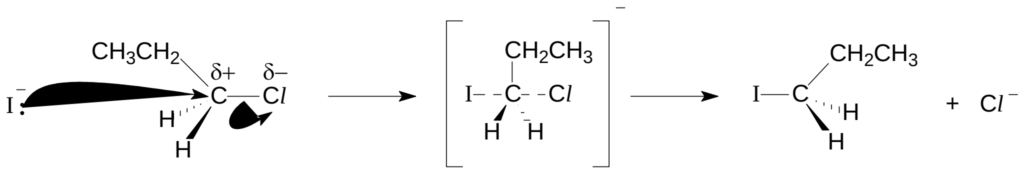
(ii) Thermal stability of HX <u>decreases</u> down the Group. [1]
(Order of thermal Stability: HF > HC*l* > HBr > HI)

<u>HF and HC*l*</u> are stable to heat and hence <u>do not decompose</u>.
<u>HBr</u> decomposes <u>slightly on heating</u>, brown fumes of Br_2 observed.
<u>HI</u> decomposes <u>easily</u>, gives out dense purple fumes of I_2 <u>on gentle heating</u>.

This is because down the Group, ~~the atomic radius of the halogen (X) increases. Consequently, the bonding electrons are less strongly attracted to the nuclei of H and X and~~ the <u>H–X bond</u> becomes <u>weaker</u> and so, is more easily broken. [1]

<u>Comments</u>
Most students knew the trend in stabilities of the hydrogen halides. Some wrote a significant amount of irrelevant, factually correct material concerning bond lengths, electronegativities and ionisation energies. A number of students wrote about van der Waals' interactions, confusing thermal stability with volatility.

(c) (i) Nucleophilic substitution (S_N2) [2]



[1m] for correct curly arrows, lone pair of electrons on I and partial charges
[1m] for transition state & inverted final product.

<u>Comments</u>
A significant number of students drew the attacking species as Na–I (covalent). Several omitted the important lone pair on the iodide ion. Most depicted the partial charges of the $C^{\delta+}-Cl^{\delta-}$ bond, but their curly arrows were not always clearly drawn from the I^- lone pair to the δ+ carbon, or from the C–Cl bond to the chlorine.

(ii) As <u>NaC*l* is almost insoluble</u> in propanone (organic solvent), NaC*l* formed will be precipitated and the <u>concentration of Cl^- decreases</u>, causing the <u>position of *equilibrium 1* to shift right</u>. Hence, the reaction goes almost to completion. [1]

(iii)

Evidence	**Deduction (type of reaction & functional group present)**	
A (bromoalkane) when warmed with NaOH(aq) produces alcohol **B**	nucleophilic substitution	
Alcohol **B** when heated with excess $Na_2Cr_2O_7/H^+$ gives neutral compound **C**.	**B** undergoes <u>oxidation</u> to give **C.** <u>C is a ketone</u> since it is neutral and it is a product of the oxidation of an alcohol. <u>B is a 2° alcoho</u>l. $\therefore$ <u>**A** is a 2° bromoalkane</u>.	[1]
A when heated with NaI in propanone, iodoalkane **D** is formed.	nucleophilic substitution	
M_r of **D** is 38.2% larger than M_r of **A**.	General formula of **A**: $C_xH_{2x+1}Br$ M_r of **A** $= 12x + 2x + 1 + 79.9$ $= 14x + 80.9$ General formula of **D**: $C_xH_{2x+1}I$ M_r of **D** $= 12x + 2x + 1 + 127 = 14x + 128$ $\frac{(14x+128)-(14x+80.9)}{(14x+80.9)} = 0.382$ $x = 3$ $\therefore$ **A** is a 2° bromoalkane with <u>3 carbon atoms</u>. *OR* Let M_r of **A** be y $\frac{127-79.9}{y} = 0.382$ $y = 123.3$ $\therefore$ M_r of alkyl group in **A** $= 123.3 - 79.9$ $= 43.4 \approx 43$ $\therefore$ **A** is a 2° bromoalkane with <u>3 carbon atoms</u>.	[1]

A is <u>$CH_3CHBrCH_3$</u>. [1]

(d) **(i)** $K_c = \dfrac{[I_3^-]}{[I_2][I^-]}$ [1]

units = $\underline{mol^{-1}\ dm^3}$ [1]

(ii) No. of moles of I_2 = 2.54 / (127 x 2) = 0.0100 mol

Concentration of aq. I_2 = 0.0100 / (100 / 1000) = 0.100 mol dm^{-3}

	$I_2(aq)$	+	$I^-(aq)$	$\rightleftharpoons$	I_3^-
Initial conc.	0.100		1.00		0
Change	–x		–x		+x
Final conc.	0.100 – x		1 – x		x

Since $[I_3^-(aq)]$ at equilibrium = 9.98×10^{-2} mol dm^{-3}, x = 9.98×10^{-2}

Eqm $[I_2(aq)]$ = 0.100 – 9.98×10^{-2} = $\underline{2.00 \times 10^{-4}\ mol\ dm^{-3}}$ [1]

Eqm $[I^-(aq)]$ = 1 – 9.98×10^{-2} = $\underline{0.900\ mol\ dm^{-3}}$

$$K_c = \frac{(9.98 \times 10^{-2})}{(2.00 \times 10^{-4})(0.900)} = \underline{554}$$ [1]

(iii) $K_c = \dfrac{[I_3^-]}{[I_2][I^-]}$

$$554 = \frac{(1.00)}{[I_2](1.00)}$$

$[I_2(aq)]$ = $\underline{1.81 \times 10^{-3}\ mol\ dm^{-3}}$ [1]

(iv) *(2 immiscible layers will be observed)*

Since I_2 is much more soluble in hexane than it is in water, $[I_2(aq)]$ decreases as it dissolves in hexane (and is removed from the aqueous layer). Hence, by Le Chatelier's Principle, the position of *equilibrium 2* shifts left. $[I_3^-(aq)]$ decreases and $[I^-(aq)]$ increases. [1] [1]

$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$ ——— (2)

Comments

Most students correctly predicted that the effect of hexane on $[I_2(aq)]$. Some erroneously thought that I_2 reacts with hexane, rather than dissolving in it. Some also thought that I^- or I_3^- dissolved in the hexane and came up with incorrect predictions. A significant number did not apply Le Chatelier's principle correctly, stating that the $[I_2(aq)]$ would increase to make up for the iodine that had dissolved in the hexane.

(v) $E^{\ominus}_{cell} = E^{\ominus}_{red}(I_3^-/I^-) - E^{\ominus}_{ox}(Cu^{2+}/Cu) = 0.536 - 0.34 = +0.196$ V

On addition of hexane to the I_3^-/I^- half cell, the $[I_3^-(aq)]$ decreases and $[I^-(aq)]$ increases as deduced from part **(iv)**.

$I_3^-(aq) + 2e^- \rightleftharpoons 3I^-(aq)$

By Le Chatelier's Principle, the position of the above equilibrium shifts left. [1]
Hence, the reduction potential for the I_3^-/I^- half cell becomes less positive (than +0.536 V).

Therefore, the cell potential will become less positive. [1]

Comments
Students had to consider two equilibria. It was not always clear from some answers which of the two equilibria students were referring to. Some students suggested there would be no change, as neither I_3^- nor I^- are soluble in hexane.

2 **(a)** **(i)** A *Bronsted–Lowry base* is a proton acceptor. [1]

A *conjugate acid–base pair* contains a pair of *Bronsted–Lowry* acid and base which differ by the presence or absence of a proton. [1]

For example, NH_4^+ and NH_3 is a conjugate acid–base pair, while NH_3 is a Bronsted–Lowry base.

(b)

Ammonia reacting as:	Explanation	
(i) a base	NH_3 accepts a proton from H_2O forming NH_4^+ and OH^-.	[1]
(ii) a reducing agent	The oxidation state of N increases from –3 in NH_3 to 0 in N_2, i.e. NH_3 acts as a reducing agent and is itself oxidised in the process. *Note: Reaction **(ii)** is an example of a comproportionation reaction.*	[1]
(iii) an acid	NH_3 donates a proton to H^- forming NH_2^- and H_2 in the process.	[1]
(iv) a reducing agent	The oxidation state of N increases from –3 in NH_3 to –2 in N_2H_4, i.e. NH_3 acts as a reducing agent and is itself oxidised in the process.	[1]
(v) a nucleophile	NH_3 possesses a lone pair of electrons which can be donated to the electron deficient (δ+) (acyl) carbon, thereby undergoing nucleophilic (acyl) substitution with the acyl chloride functional group.	[1]

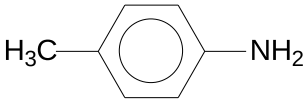
(c) Order of basicity: ethylamine > NH_3 > phenylamine [1]

Ethyl group is electron–donating, thus increasing the electron density on N atom, making the lone pair of electrons on N atom more readily available to accept a proton. Hence, ethylamine is a stronger base than NH_3. [1]

The lone pair of electrons on N atom is delocalised into the π–electron cloud of the benzene ring, making the lone pair less readily available to accept a proton, thus phenylamine is a weaker base than NH_3. [1]

Note: Basicity of amines depends on the availability of the lone pair of electrons on N to accept a proton, H^+.

(d) **(i)** 4–methylphenylamine is a stronger base than phenylamine. [1]



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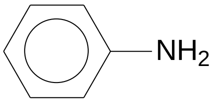
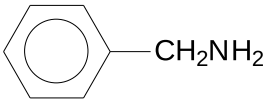


The methyl group is an electron–donating group, thus there is a lesser extent of delocalisation of the lone pair of electrons on N atom into the π–electron cloud of the benzene ring. The lone pair is more readily available to accept a proton, making 4–methylphenylamine a stronger base than phenylamine. [1]

Ethylamine is a stronger base than benzylamine. [1]

$CH_3CH_2NH_2$ >

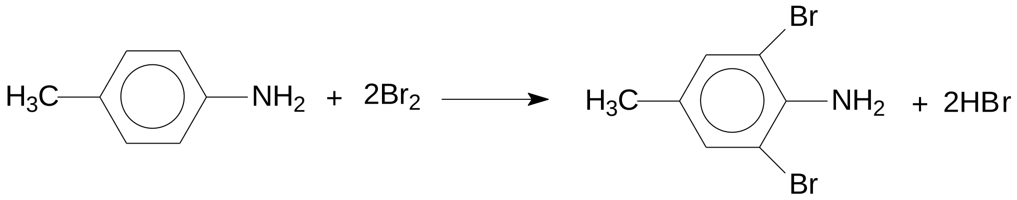


The electron–donating effect of the ethyl group is stronger than that of the benzyl group ($C_6H_5CH_2$–). The lone pair of electrons on N atom in ethylamine is thus more readily available to accept a proton. Hence, ethylamine is a stronger base than benzylamine. [1]

Comments
The most common error in the second comparison was to describe the weaker basicity of benzylamine (compared to ethylamine) as being due to the delocalisation of the lone pair on N over the benzene ring. Since the –NH_2 group is separated from the ring by a –CH_2 group, no delocalisation can occur.

(ii) 4–methylphenylamine decolourises orange Br_2(aq) and a white precipitate is produced. [1]

Orange Br_2(aq) remains for benzylamine.

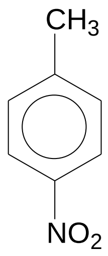


[1]

(iii) ROUTE 1:

Step 1: concentrated HNO_3 and concentrated H_2SO_4~~, 30 °C~~ [1]
Step 2: tin and excess concentrated HCl, heat,
followed by NaOH(aq)

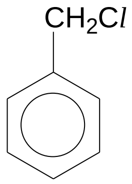
Intermediate:



[1]

ROUTE 2:
Step 1: Cl_2(g), uv light [1]
Step 2: excess conc. NH_3 in ethanol, heat in a sealed tube

Intermediate:



[1]

3 **(a)** Al_2O_3 is insoluble in water. Hence, when added to water, the pH of the solution is 7. [1]

P_4O_6 hydrolyses / reacts vigorously in water, producing a strongly acidic solution of pH 2. [1]

[1]

$$P_4O_6(s) + 6H_2O(l) \longrightarrow 4H_3PO_3(aq)$$

Revised LO: “Candidates should be able to: describe the reactions of the oxides with water (for Na_2O; MgO; Al_2O_3; SiO_2; P_4O_{10}; SO_3)”

(b) **W** has a giant ionic structure with strong electrostatic forces of attraction between the oppositely charged ions, which require a large amount of energy to overcome. Thus, **W** has a high melting point and is only sparingly soluble in water, producing a weakly alkaline solution. Presence of mobile ions allows it to conduct electricity in the molten state., it [1]

X has a giant covalent structure with strong and extensive covalent bonds between its atoms, which require a large amount of energy to overcome. Thus, **X** has a high melting point and is insoluble in water (resulting pH of 7). Absence of mobile ions or delocalised electrons in molten **X** makes it a poor electrical conductor. [1]

As **Y** has a high melting point and is a good conductor in the molten state, it has a giant ionic structure with strong electrostatic forces of attraction between the oppositely charged ions, similar to **W**. However, **Y** ~~readily dissolves in water, and~~ reacts completely and vigorously with water to form a strongly alkaline solution of pH 14. [1]

Z has a simple covalent structure. Small amount of energy is needed to overcome the weak intermolecular forces of attraction between the discrete molecules, thus accounting for its relatively low melting point. Absence of mobile ions or delocalised electrons in molten **Z** makes it a poor electrical conductor. **Z** ~~dissolves readily in water and~~ reacts completely and vigorously in water to form a strongly acidic solution of pH 1. [1]

*(Note: **W**, **X**, **Y**, **Z** are most probably MgO, SiO_2, Na_2O and P_4O_{10} respectively. Question does not require you to identify the compounds.)*

Comments
*Many students could assign the correct structures to the four oxides but merely repeated the properties in the question. Students needed to explain, for example, why giant covalent compounds had high melting points, or why giant ionic compounds conduct electricity when molten. Some students used descriptions other than the four key words simple, giant, covalent and ionic. They described **X** as being giant molecular, without stating that it was a covalent compound. Others described **W** as being giant metallic. The description of **Y** as simple ionic was a common incorrect response.*

(c) **(i)** From *Data Booklet*,

$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$ [1]

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$\mathbf{2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+}$ [1]

(ii) SO_2(aq) is colourless.

At the end–point, the solution turns from colourless to (first permanent) pink colour when one excess drop of aq. $KMnO_4$ is added from the burette. [1]

(iii) No. of moles of $KMnO_4$ required = $20.5 \times 10^{-3} \times 0.0200 = 4.10 \times 10^{-4}$ mol

No. of moles of SO_2 = $5/2 \times 4.10 \times 10^{-4} = 1.025 \times 10^{-3}$ mol [1]

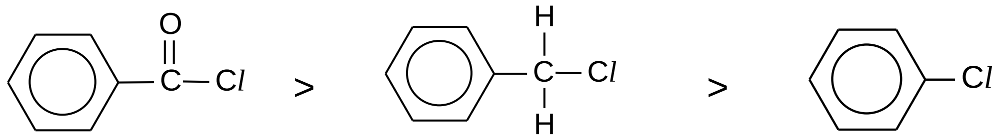
$[SO_2] = 1.025 \times 10^{-3} / (25.0 \times 10^{-3}) = \underline{4.10 \times 10^{-2} \text{ mol dm}^{-3}}$ [1]

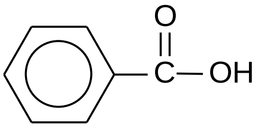
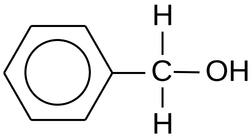
(d) Use $K_a = \dfrac{[H^+][A^-]}{[HA]}$

$[H^+] = (6.3 \times 10^{-5} \times 0.01) / 0.03 = 2.10 \times 10^{-5}$ mol dm^{-3} [1]

pH $= -\log_{10}(2.10 \times 10^{-5}) = \underline{4.68}$ [1]

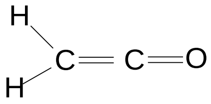
(e) Relative ease of hydrolysis: [3]



• The carbon atom of the acyl group is highly electron–deficient because it is bonded to TWO highly electronegative atoms, oxygen and chlorine. • This makes the carbon very susceptible to attack by nucleophiles, even by weak nucleophile H_2O to form the acid,  *[1m]*	• The carbon atom of C–C*l* group is bonded to only one electronegative atom, chlorine, thus this carbon is less electron–deficient and is less readily attacked by nucleophiles. • A stronger nucleophile like OH^- with heat under reflux conditions is required for hydrolysis to form the alcohol,  *[1m]*	• In chlorobenzene, the lone pair of electrons on C*l* can delocalise into the π electron cloud of the aromatic ring • Hence, the C–C*l* bond has partial double bond character and is stronger and thus not easily cleaved. • Hence, chlorobenzene is not hydrolysed; no reaction with H_2O or NaOH under heat under reflux conditions. *[1m]*

(f) [1]

E :



F : CH_3COCl [1]

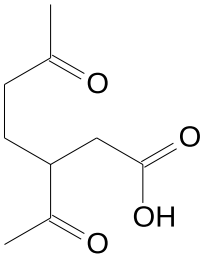
G : CH_3COOH [1]

*Note: Since **G** is weakly acidic, it contains a carboxylic acid. From its formula, it can be deduced that **G** is ethanoic acid. Since acid **G** is formed by reaction of **F** with water, **F** would contain an acyl chloride group, thus **F** is ethanoyl chloride.*
***E** (ketene) contains a C=C as it reacts with aq. Br_2. One can deduce the structure of **E** from its formula and its reactions.*

4 **(a)** Limonene exhibits optical isomerism only. [1]
No. of optical isomers = 2 [1]

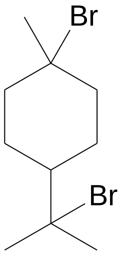
Comments
Most students suggested both cis-trans and optical isomerism, not realising that it is NOT possible for limonene to exhibit cis-trans isomerism.

(b) [1]



CO_2 H_2O [1]

(c) [2]

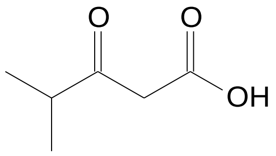


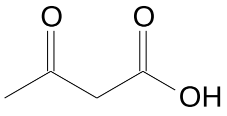
[1m] for the addition of HBr to each C=C based on Markovnikov's rule.

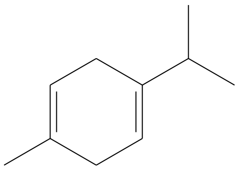
(d) *Since γ–terpinene is an isomer of limonene, it also has a molecular formula of $C_{10}H_{16}$.*

Evidence	Deduction (type of reaction & functional group present)	
On treatment with excess hot conc. MnO_4^-, γ–terpinene forms **H** and **J**.	γ–Terpinene undergoes oxidative cleavage with excess hot conc. MnO_4^- to form **H** and **J** with **no loss of carbon atoms**.	[1]
H and **J** evolve CO_2 with Na_2CO_3(aq).	**H** and **J** undergoes acid–base reaction with Na_2CO_3(aq), evolving CO_2 gas. ⇒ **H** and **J** contain carboxylic acid (–COOH) group.	[1]
H and **J** give orange ppt with 2,4–DNPH.	**H** and **J** undergo condensation reaction with 2,4–dinitrophenylhydrazine to give an orange precipitate. ⇒ **H** and **J** contain ketone functional group since both do not undergo oxidation with Fehling's solution.	[1]
H gives a yellow ppt with alkaline aqueous iodine.	**H** undergoes oxidation reaction (or tri–iodomethane reaction) with alkaline aqueous iodine to give a yellow precipitate. ⇒ **H** contains a methyl ketone (CH_3CO–).	[1]

J can be obtained from oxidation of **K** with hot $Cr_2O_7^{2-}/H^+$. [1]

J is  [1]

H is  [1]



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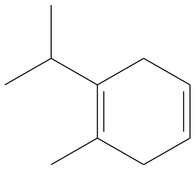
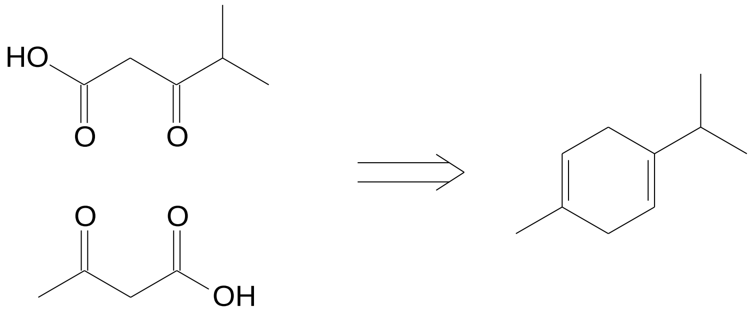


γ–Terpinene

[1]

Thinking process



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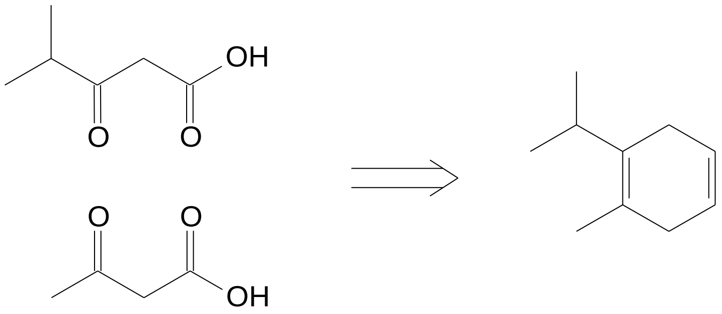


(e) **(i)** $C_{10}H_{16} + 14O_2 \longrightarrow 10CO_2 + 8H_2O$ [1]

(ii) $\Delta H_c = (8BE_{C-C} + 2BE_{C=C} + 16BE_{C-H} + 14BE_{O=O}) - (20BE_{C=O} + 16\,BE_{O-H})$
$= [8(350) + 2(610) + 16(410) + 14(496) - [20(805) + 16(460)]$ [1]
$= -5940 \text{ kJ mol}^{-1}$ [1]

Comments
The most common error was not including the O=O bond energy in the calculation. Other errors were not including the right number of C−C or C=C or C−H bonds.

(iii) Since 1 mol of limonene produces 5936 kJ of energy, 1 g of limonene produces 5936 kJ mol^{-1} / 136 g mol^{-1} = 43.6 kJ of energy. [1]

ΔH_c of limonene = -43.6 kJ g^{-1} [1]

Thus, the enthalpy change of combustion of per gram of limonene is comparable to the conventional diesel fuel. [1]

5 **(a)** **(i)** The covalent radius of silicon can be defined as half the distance between the nuclei of the two covalently bonded silicon atoms in solid silicon lattice. [1]

(ii) Argon is monoatomic. [1]

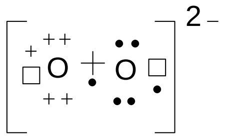
(iii) The van der Waals radius of chlorine should be **smaller** than that of argon. [1]

Chlorine molecule has **larger number of electrons** than argon atom. Hence, the **instantaneous dipole-induced dipole attractions between Cl_2 molecules are stronger** and resulting in a closer approach between the molecules and a smaller van der Waals radius.

Note: ***Van der Waals radius*** *is half of the distance between the closest approach of two non-bonded atoms of a given element.*

(FYI: vdW radius of chlorine; 175 pm, argon; 188 pm)

(b) **(i)** [1]



(ii) $Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$ [2]

[1m] for correctly identifying the other product as NaOH
[1m] for correct balanced equation

Comments
(b)(i) *Students need to appreciate that sodium peroxide consists of two ions (Na^+ and O_2^{2-}) and may also make use of the clue from the question that the peroxide anion contains an O–O bond to derive the dot–and–cross diagram. Remember to use the symbol stated in the question to annotate the electrons from different sources.*

(b)(ii) *Students have to infer from the info "… alkaline solution of H_2O_2…" that an alkali is present as product.*

(c) **(i)** Order of reaction with respect to a given reactant is the power to which the concentration of the reactant is raised in the *experimentally determined* rate equation. [1]

Alternatively
For an arbitrary reaction,

$$aA + bB \longrightarrow cC$$

the rate equation takes the general form of rate = k $[\mathbf{A}]^x$ $[\mathbf{B}]^y$, where k is the rate constant. The value of x and y are order of reaction with respect to ***A*** *and* ***B*** *respectively.*

(ii) Half–life of a reaction is the time taken for the concentration of reactant to decrease to half its original concentration. [1]

(d) **(i)** (refer to the plotted graph) [3]

time taken for $[H_2O_2]$ to decrease from 0.0200 to 0.0100 mol dm^{-3}
= 325 s

time taken for $[H_2O_2]$ to decrease from 0.0100 to 0.0050 mol dm^{-3}
= 645 – 325
= 320 s

Since the two $t_{½}$ values are relatively constant, order of reaction w.r.t. H_2O_2 is 1

(Note: The two $t_{½}$ values must not differ by more than 1 small square. Hence, in this case, the two $t_{½}$ values must not differ by more than 10 s.)

[1m] for correct scale and axes used with construction lines (clearly shown)
[1m] for all correctly plotted points
[1m] for correct order of reaction

(ii) [1]

$$\text{gradient of tangent at 0 s} = \frac{(0.0200 - 0.0100)}{(0 - 225)}$$
$$= -\,4.44 \times 10^{-5}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

initial rate = 4.44×10^{-5} mol dm^{-3} s^{-1}

(iii) When initial $[H^+]$ increases 2 times (or doubles) from 0.200 mol dm^{-3} to 0.400 mol dm^{-3} while $[H_2O_2]$ and $[I^-]$ are kept constant, the initial rate also increases ($\frac{8.4 \times 10^{-5}}{4.44 \times 10^{-5}}$) ≈ 2 times (or doubles). Hence, order of reaction with respect to H^+ is 1. [2]

When initial $[I^-]$ increases 2 times (or doubles) from 0.100 mol dm^{-3} to 0.200 mol dm^{-3} while $[H_2O_2]$ and $[H^+]$ are kept constant, the initial rate also increases ($\frac{4.44 \times 10^{-5}}{2.1 \times 10^{-5}}$) ≈ 2 times (or doubles). Hence, order of reaction with respect to I^- is 1.

Alternatively
*It will be good to use the data given in the table to check the conclusion in case your initial rate calculated in **(ii)** is not correct.*

[1m] for each correct order of reaction

(iv) rate = $k\,[H_2O_2]\,[H^+]\,[I^-]$ [3]

$4.44 \times 10^{-5} = k\,(0.0200)(0.200)(0.200)$
$k = \underline{0.0555\ \text{mol}^{-2}\ \text{dm}^{6}\ \text{s}^{-1}}$

[1m] for correct rate equation (including rate constant k)
[1m] for correct rate constant value
[1m] for correct units for k

(e) **(i)** $LiAlH_4$ in dry ether [1]
or $NaBH_4$ in ethanol

(ii) reagents: $K_2Cr_2O_7$, dilute H_2SO_4 (or acidified $K_2Cr_2O_7$) [1]

condition to ensure main product is propanal: warm with immediate distillation [1]

Comments
Use of $KMnO_4$ is not accepted as it will oxidise the propanal formed to propanoic, regardless of reaction conditions. Heating under reflux condition, even with distillation, will also yield only propanoic acid as the product.