

J2 H2 Chemistry Prelim Answers

Paper 1 Answer Key

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

Paper 1 Worked Solutions

1 (B)

100 g of mixture contains 21.25 g of Mg.

	M_r
MgCl ₂	95.3
Mg(NO ₃) ₂	148.3

Let mass of MgCl₂ present in 100 g of mixture be x.

$$\frac{x}{95.3} \times 24.3 + \frac{100 - x}{148.3} \times 24.3 = 21.25$$

$$x = 53 \text{ g}$$

2 (C)

$$n(\text{M}_2\text{O}_n) = 0.500 \times \frac{10.00}{1000} = 0.00500 \text{ mol}$$

$$n(\text{KMnO}_4) = 0.300 \times \frac{20.00}{1000} = 0.00600 \text{ mol}$$

Given the reduction half equation: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

$n(\text{e}^-)$ involved in the redox = $0.00600 \times 5 = 0.0300 \text{ mol}$

0.00500 mol of M_2O_n contain 0.0100 mol of M^{n+} .

Hence, 0.0100 mol of M^{n+} loses 0.0300 mol of e^- to form M^{6+} .

1 mol of M^{n+} loses 3 mol of e^- to form M^{6+} .

$$n = 3$$

3 (C)

1 st	2 nd	3 rd	4 th	5 th	6 th
660	1267	2218	3313	7863	9500
607		951	1095	4550	1637

Largest increase from 4th I.E. to 5th I.E. indicates that the 5th electron is removed from an inner electron shell.

Element Q is a Group 14 element with 4 valence electrons and reacts with chlorine to form QCl_4 . Other statements cannot be inferred from the data given (while option D is incorrect). Since Q is ns^2np^2 , element preceding it is ns^2np^1 , hence it should follow the general increasing trend).

4 (D)

Statement 1 is incorrect.

van der Waals radius of chlorine is smaller than that of argon. This is because Cl_2 molecules ($M_r = 71.0$) have stronger instantaneous dipole-induced dipole (id-id) interactions than id-id forces between Argon atoms ($A_r = 39.9$).

Statement 2 is incorrect.

CH_3CH_2CHO do not have hydrogen bonds between its molecules.

Statement 3 is correct.

C-C bond length in diamond is longer and weaker than graphite due to the smaller s character of the sp^3-sp^3 overlap in diamond as compared to the sp^2-sp^2 overlap in graphite.

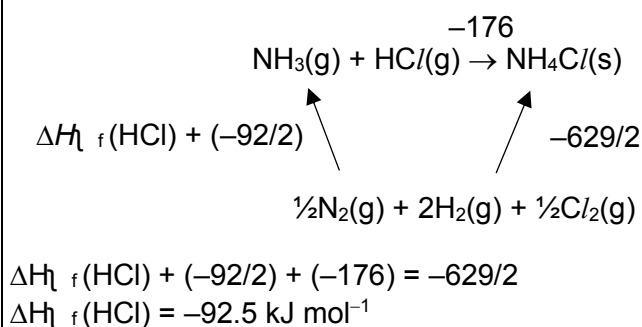
5 (D)

Step 1. Determine R under standard conditions:

$$R = \frac{pV}{nT} = \frac{10^5 \times 22.7 \times 10^{-3}}{1 \times 273}$$

Step 2. Substitute R into the equation

$$P = \frac{\rho RT}{M_r} = \frac{8 \times (300 + 273)}{2.0} \times \frac{10^5 \times 22.7 \times 10^{-3}}{1 \times 273} = \frac{573 \times 4 \times 22.7 \times 100}{273}$$

6 (B)

Alternative:

$$\Delta H_f^\circ(\text{NH}_4\text{Cl}) = -629/2$$

$$\Delta H_f^\circ(\text{NH}_3) = -92/2$$

$$\begin{array}{c}
 -176 \\
 \text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s}) \\
 -176 = -629/2 - (-92/2) - \Delta H_f^\circ(\text{HCl}) \\
 \Delta H_f^\circ(\text{HCl}) = -92.5 \text{ kJ mol}^{-1}
 \end{array}$$

7 (A)

Statement 1 is correct:

$$\begin{aligned}\Delta H_r^\ominus &= \sum n\Delta H_f^\ominus (\text{products}) - \sum m\Delta H_f^\ominus (\text{reactants}) \\ &= -1273 - [6 \times (-394) + 6 \times (-286)] \\ &= +2807 \text{ kJ mol}^{-1}\end{aligned}$$

Statement 2 is correct.

The photosynthesis process has no change in number of particles of gases, but there is a change of state (liquid water in the reactant to solid $\text{C}_6\text{H}_{12}\text{O}_6$ in the product). There is a decrease in overall entropy and thus, ΔS has a negative sign (e.g. less disordered).

Statement 3 is correct.

Since $\Delta G = \Delta H (+ve) - T\Delta S (-ve)$, the ΔG for the reaction will always be positive at all temperatures as ΔH and $-T\Delta S$ is always positive.

8 (D)

$$\begin{aligned}t_{1/2} &= \ln 2/k = \ln 2/7.70 \times 10^{-4} \\ &= 900 \text{ s} = 15 \text{ min}\end{aligned}$$

$$\text{no. of half-lives} = 80 / 15 = 5.33$$

$$\frac{A_t}{A_0} = \left(\frac{1}{2}\right)^n \quad \frac{0.0315}{A_0} = \left(\frac{1}{2}\right)^{5.33}$$

$$\text{Conc} = 1.27 \text{ mol dm}^{-3}$$

9 (D)

Statement 1 is correct.

Comparing Expt 1 and 3, when $[\text{HC}]/$ is halved (0.20/0.10), the rate is halved (0.192/0.096). Hence it is a first order with respect to $\text{HC}]/$.

Comparing Expt 2 and 3, when $[\text{methyl propanoate}]$ is increased 1.5 times (0.15/0.10), the rate increased 1.5 times (0.144/0.096). Hence it is a first order with respect to methyl propanoate.

Since $\text{rate} = k[\text{methyl propanoate}][\text{HC}]/$, when $[\text{methyl propanoate}]$ doubles and $[\text{HC}]/$ increases 1.5 times from expt 2 to expt 4, the rate = $0.144 \times 2 \times 1.5 = 0.432$.

Statement 2 is incorrect as units are incorrect.

$$\begin{aligned}\text{Using Expt 1: } 0.192 &= k(0.10)(0.20) \\ k &= 9.6 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}\end{aligned}$$

Statement 3 is correct.

$$\text{rate} = k[\text{methyl propanoate}][\text{HC}]/$$

$\text{rate} = k'[\text{methyl propanoate}]$ where $k' = k[\text{HC}]/$. Since $\text{HC}]/$ is a catalyst which gets regenerated in the reaction, the $[\text{HC}]/$ remains constant.

$$t_{1/2} = \ln 2/k' = \ln 2/k[\text{HC}]/$$

$$\text{Since } [\text{HC}]/ \text{ is decreased } \frac{0.15}{0.20} = \frac{3}{4}, \text{ the time taken will be } \frac{4}{3} \times 6 = 8 \text{ min.}$$

10 (B)

	N_2O_4	$\rightleftharpoons$	2NO_2	
Initial amt/ mol	x		0	
Change/ mol	-0.5x		+1.0x	
Eqm amt/ mol	0.5x		1.0x	Total amount = 1.5x mol

$$P_{\text{N}_2\text{O}_4} = \left(\frac{0.5x}{1.5x}\right) \times 1 = \frac{1}{3} \text{ atm}$$

$$P_{\text{NO}_2} = \left(\frac{x}{1.5x}\right) \times 1 = \frac{2}{3} \text{ atm}$$

$$K_p \text{ for the reverse reaction} = \frac{P_{\text{N}_2\text{O}_4}}{(P_{\text{NO}_2})^2} = \frac{(\frac{1}{3})}{(\frac{2}{3})^2} = \frac{3}{4} \text{ atm}^{-1}$$

11 (C)

Given $[\text{OH}^-] = 10^{-7}$

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = 1.76 \times 10^{-5}$$

$$\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = \frac{5.681 \times 10^{-3}}{1}$$

$$\frac{[\text{NH}_3]}{[\text{NH}_3] + [\text{NH}_4^+]} = \frac{5.681 \times 10^{-3}}{5.681 \times 10^{-3} + 1} = 5.65 \times 10^{-3}$$

12 (A)

A buffer solution's pH will not change significantly when some alkali is added.

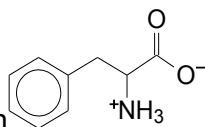
Statement 1 is correct.

When 0.003 mol of CH_3COOH (excess) was mixed with 0.002 mol of KOH (limiting), 0.002 mol of $\text{CH}_3\text{COO}^- \text{Na}^+$ (salt) and 0.001 mol of CH_3COOH (remaining) will be formed at equilibrium. This is a buffer solution.

Statement 2 is correct.

0.0025 mol of HPO_4^{2-} (conjugate base) is mixed with 0.00075 mol of H_2PO_4^- (acid). This is a buffer solution.

Statement 3 is correct.



0.002 mol phenylalanine exist as a zwitterion NH_3^+ . It can act as a buffer as it has both an acidic ($-\text{NH}_3^+$) and a basic ($-\text{COO}^-$) group.

13 (C)

	Highest			Lowest
Melting point	Si	Al	Mg	P
First IE	P	Si	Mg	Al

14 (D)

Option A is incorrect. Down the group, the number of electron shell increases, shielding effect increases significantly, hence the outermost electron is further away and is less attracted by the nucleus. Hence first ionisation energies points of elements decreases.

Option B is incorrect. With increasing proton number, cationic radius increases while charge remains the same. Charge density decreases with increasing proton number of Group 2 ions. The acidity of solutions of the chlorides decreases due to the decrease in charge density.

Option C is incorrect. From MgSO_4 to BaSO_4 , the $|\Delta H_{\text{hydration}}|$ of Group 2 sulphates decreases faster than the $|\text{lattice energy}|$ of Group 2 sulphates, hence the solubility decreases down the group. We can also infer that MgSO_4 (soluble salt) while BaSO_4 (insoluble salt).

Option A is correct. The decomposition temperature of carbonates increases since the polarising power of Group 2 cations decreases with decreasing charge density. The C–O bond in carbonates is less weakened.

15 (B)

Statement 1 is incorrect.

The higher the boiling point, the lower its volatility.

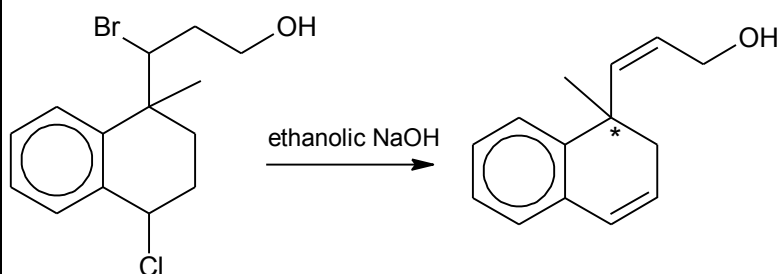
HF has the highest boiling point as most energy is needed to overcome the strong hydrogen bonds between HF molecules. Boiling point of $\text{HI} > \text{HBr} > \text{HCl}$. Down the group, the size of electron cloud of hydrogen halides increases and become more polarisable. More energy needed to overcome the stronger instantaneous dipole – induced dipole interactions between molecules.

Statement 2 is incorrect.

The thermal stability of the hydrogen halides decreases down the group. This is due to the decreasing strength of the H–X bond. The weaker the bond, the lesser the energy required for decomposition.

Statement 3 is correct.

Reducing strength of halide ions increases down the group. $E^\ominus(\text{X}_2/\text{X}^-)$ becomes less positive, hence X^- is more likely to be oxidised.

16 (B)

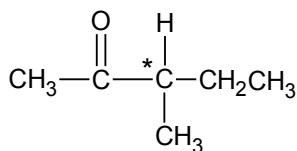
There is only 1 chiral centre (marked with *), and 1 C=C that can exhibit cis-trans isomerism. Note that the C=C in the ring cannot exhibit cis-trans isomerism.

Hence, total number of stereoisomers $\rightarrow 2^2 = 4$

17 (C)

A ketone must contain a C=O between two C atoms. $\text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array} \text{C}$.

For a chiral centre to be present, one C present must be bonded to 4 different groups and the 4 different groups are (CH_3CO , H, CH_3 and CH_2CH_3).



i.e. Hence compound must contain at least 6 C atoms (the compound could contain 6 or 7 carbon atoms).

18 (A)

Statement 1 is correct.

Maleic acid is the cis isomer because it has a lower $\text{p}K_{\text{a}1}$ and a higher $\text{p}K_{\text{a}2}$ value. A lower $\text{p}K_{\text{a}1}$ would suggest that maleic acid is more acidic as it has a more stable monoanion due to the intramolecular hydrogen bonding. It has a higher $\text{p}K_{\text{a}2}$ value because the dianion experiences repulsion between the 2 $-\text{COO}^-$ groups, hence making the conjugate base unstable.

Statement 2 is incorrect.

Boiling point of fumaric acid is higher as it does not have intramolecular hydrogen bonding between the $-\text{COOH}$ groups and thus forms more extensive intermolecular hydrogen bonding. Hence more energy is required to overcome the stronger intermolecular forces.

Statement 3 is correct.

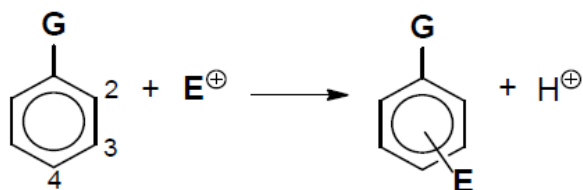
$\text{CH}(\text{OH})(\text{CO}_2\text{H})\text{CH}(\text{Br})\text{CO}_2\text{H}$ is formed when fumaric acid reacts with aqueous Br_2 .

Statement 4 is incorrect.

$\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$ reacts with alkaline KMnO_4 to form 4 moles of CO_3^{2-} .

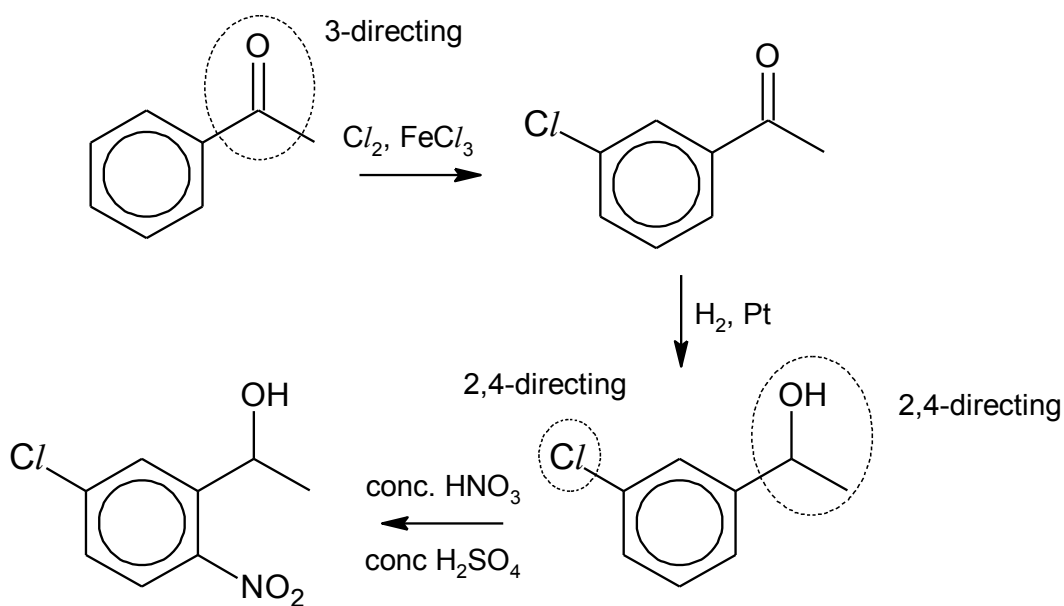
Note: $(\text{COOH})_2$ can be further $[\text{O}]$ by KMnO_4 .

19 (B)



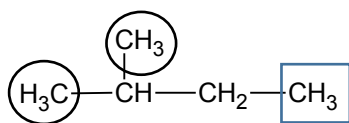
G	-alkyl -OH or -OR -NH₂, -NHR or -NR₂ -NHCOR	-Cl , -Br, -I	-CHO, -COR -CO₂H, -CO₂R -NH₃⁺ -NO₂ , -CN
Reactivity of ring (compared to benzene)	Activated	Deactivated	Deactivated
Position of E (relative to position of G)	2- and/or 4-	2- and/or 4-	3-

The directing effects of the circled substituents will decide the sequence of substituent entering the ring.



20 (B)

Statement 1 is correct.



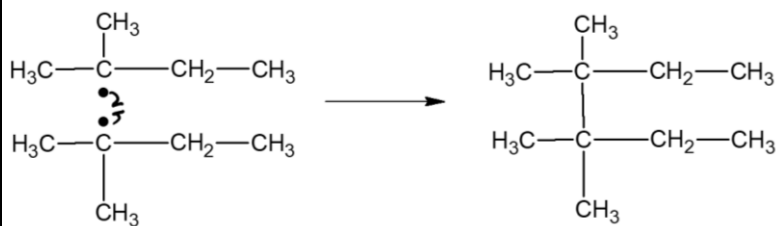
There are 6 H atoms that will give $\text{H}_3\text{C}-\overset{\text{CH}_2\text{Cl}}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{CH}_3$ and 3 H atoms that will give

$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{CH}_2\text{Cl}$. Hence ratio is 2 : 1.

Statement 2 is incorrect.

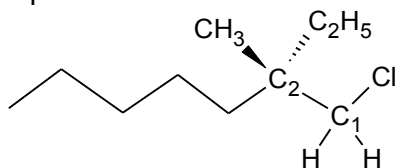
Homolytic fission occurs in both the initiation and propagation steps.

Statement 3 is correct.



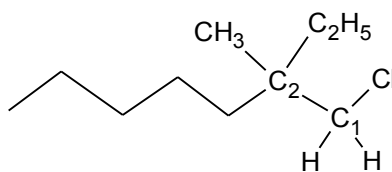
21 (A)

Option A is correct.



The 1° chloroalkane (at C₁) undergoes S_N2 reaction resulting in an inversion of configuration. However there is no chiral C at C₁ (as it contains 2H) so there are no enantiomers present for C₁.

There is a chiral C at C₂. However as the 3D structure is shown, only one of the enantiomers is shown/used in reactant. There is no change at C₂ during reaction, the same enantiomer remain after reaction and no mixture of enantiomers will be formed.

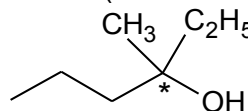


[NOTE: If 3D structure not used e.g.

, it would represent two enantiomers]

Option B is incorrect. The 3° chloroalkane undergoes S_N1 reaction, forming a carbocation

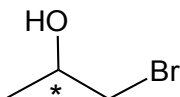
intermediate. The OH⁻ can then attack the carbocation intermediate () forming



the product where there is a chiral centre (marked with *), i.e.

Option C is incorrect. Nucleophilic addition of ketone results in formation of two enantiomers (in equal amounts).

Option D is incorrect. The alkene undergoes electrophilic addition, forming intermediate. H₂O can then attack the carbocation intermediate, forming the product where there is



a chiral centre (marked with *), i.e.

⇒ Options B, C & D will result in formation of two enantiomers.

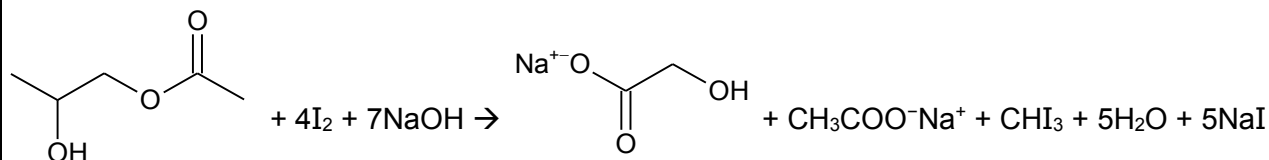
22 (A)

Positive test with [Ag(NH₃)₂]⁺ (Tollens' Reagent): Presence of either aliphatic or aromatic aldehyde
 Negative test with alkaline Cu(II) complex (Fehling's Solution): Absence of aliphatic aldehyde (e.g. Presence of benzaldehyde)

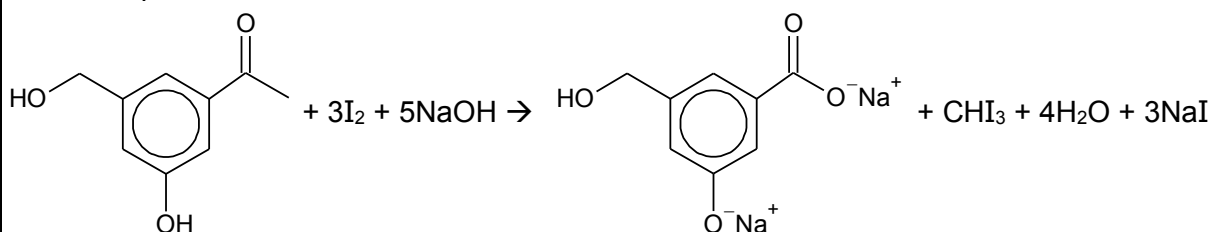
Positive test with PCl₅: Presence of –OH group in either alcohol or carboxylic acid functional group.
 Phenol does not react with PCl₅.

23 (D)

For Compound S, the ester requires 1 mole of NaOH for alkaline hydrolysis while the methyl alcohol requires 6 moles of NaOH for oxidation.



For Compound T, the phenol requires 1 mole of NaOH for acid base reaction while the methyl ketone requires 4 moles of NaOH for oxidation.

**24 (C)**

All three species are conjugate bases of weak acids. Since the same amount of each substance is dissolved separately in the same volume of water, the higher the pH of the resultant solution, the stronger the base.

Note: The weaker the acid, the stronger its conjugate base.

In the conjugate base, $\text{CH}_2=\text{CHCOO}^-$, the p orbital of O overlaps with the π electron cloud of the $-\text{C}=\text{O}$ bond and the $\text{C}=\text{C}$ bond. The lone pair of electrons on the oxygen atom delocalises into the $-\text{C}=\text{O}$ and the $\text{C}=\text{C}$ bond. The negative charge is dispersed to a larger extent than CH_3COO^- , stabilising the $\text{CH}_2=\text{CHCOO}^-$ ion.

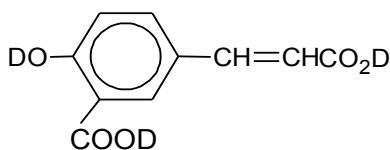
Strength of acid: $\text{CH}_2=\text{CHCOOH} > \text{CH}_3\text{COOH} > \text{C}_6\text{H}_5\text{OH}$

Strength of conjugate base: $\text{CH}_2=\text{CHCOO}^- < \text{CH}_3\text{COO}^- < \text{C}_6\text{H}_5\text{O}^-$
lowest pH $\longrightarrow$ highest pH

25 (C)

When compound V is dissolved in D_2O , the following will take place:

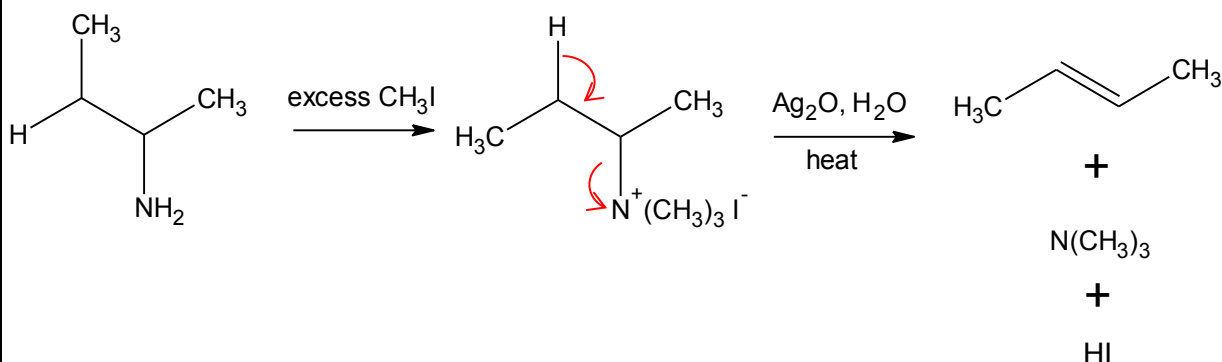
- proton exchange of the 2 acidic functional groups (phenol and carboxylic acid) and
- hydrolysis of acyl chloride $\text{RCOCl} + \text{D}_2\text{O} \rightarrow \text{RCOOD} + \text{DCl}$



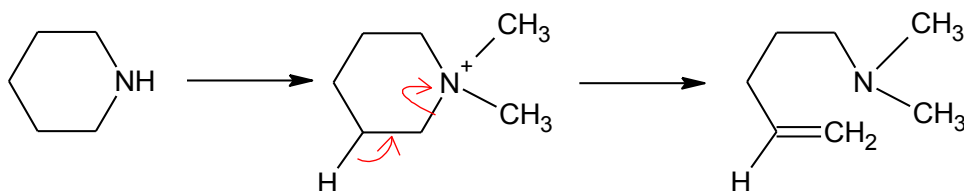
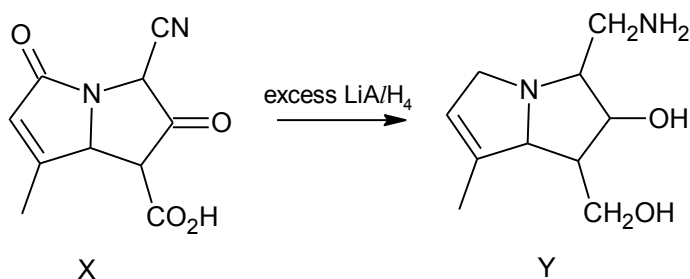
Compound W

26 (A)

For given reaction, observe arrow movement



Similarly for piperidine

**27 (B)**

Option A is not correct.

Five moles of HBr is required (one mole for acid-base reaction with each amine group, one mole for electrophilic addition with alkene group and 2 moles for substitution with each alcohol group).

Option B is correct.

Two moles of SOCl_2 is required (one mole for nucleophilic substitution with each alcohol group).

Option C is not correct.

Three moles of CH_3COCl is required (one mole for condensation with each alcohol group, one mole for condensation with primary amine)

(Note: tertiary amines cannot form amides with CH_3COCl .)

Option D not correct.

One mole of H_2 gas is produced (Each alcohol group will react and the mole ratio of alcohol : H_2 = 1 : $\frac{1}{2}$).

28 (C)

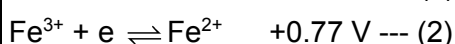
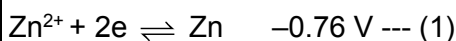
Using the mass and M_r , the amount and hence mole ratio of the amino acids can be calculated.

aspartic acid : glutamine : proline
 = 2 : 1 : 1

Z is a tetrapeptide with 3 amide linkages

Hence, M_r of the polypeptide

$$= (2 \times 133 + 146 + 115) - (3 \times 18) = 473$$

29 (D)

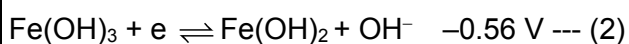
$$E^\ominus_{\text{cell}} = (+0.77) - (-0.76) = +1.53 \text{ V} \quad [E^\ominus_{\text{cell}} \text{ measured is less positive than expected.}]$$

Option A is incorrect. When water is added to the Zn^{2+}/Zn half-cell, $[\text{Zn}^{2+}]$ decreases. The position of equilibrium (1) shifts to left. $E^\ominus_{\text{oxd}}$ becomes more negative which results in a more positive $E^\ominus_{\text{cell}}$.

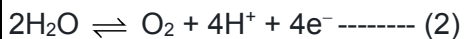
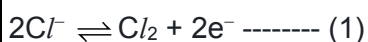
Option B is incorrect. When water is added to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell, $[\text{Fe}^{3+}]$ and $[\text{Fe}^{2+}]$ decreases to the same extent. The position of equilibrium (2) does not shift. $E^\ominus_{\text{cell}}$ will not change.

Option C is incorrect. The size of the Zn electrode does not affect the values of $E^\ominus_{\text{oxd}}$, hence $E^\ominus_{\text{cell}}$ will not change.

Option D is correct. When a small amount of OH^- is added, the $E^\ominus_{\text{red}}$ will change.



$E^\ominus_{\text{red}}$ becomes less positive. This results in a less positive $E^\ominus_{\text{cell}}$.

30 (C)

Since volume of oxygen collected is 1.5 times as much as the volume of chlorine gas, amount of oxygen collected is also 1.5 times as much as the volume of chlorine gas.

$$n(\text{O}_2) = 1.5n(\text{Cl}_2)$$

$$\text{Since } Q = nzF = It, I = nzF/t$$

$$Q \text{ for (1)} = 2n(\text{Cl}_2) F, Q \text{ for (2)} = 4n(\text{O}_2)F = 4 \times 1.5n(\text{Cl}_2) \times F = 6n(\text{Cl}_2) F$$

$$Q \text{ for (1)} : Q \text{ for (2)}$$

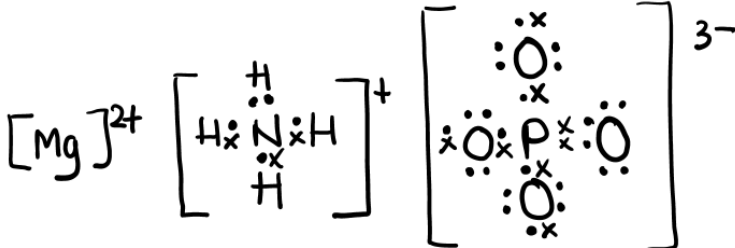
$$2n(\text{Cl}_2) F : 6n(\text{Cl}_2) F = 1 : 3$$

Since $Q = It$ and $t = 5 \text{ min}$ for both experiments,

$$I \text{ for (1)} : I \text{ for (2)} = 1 : 3$$

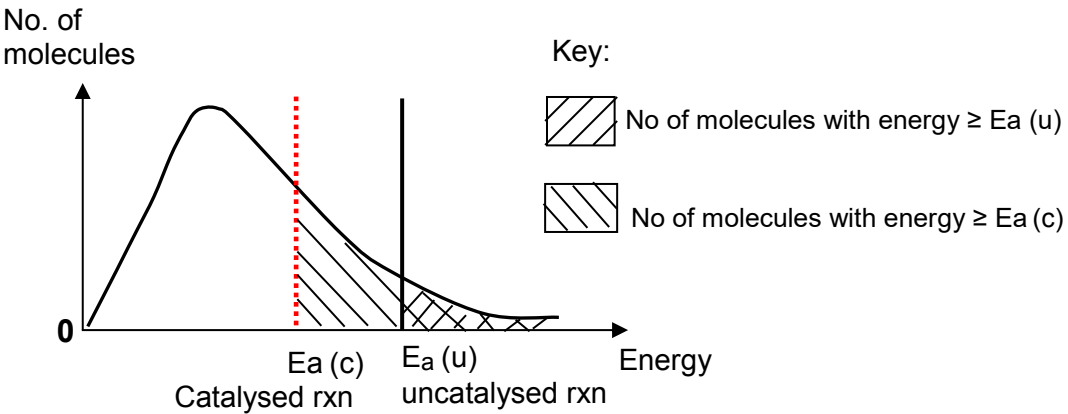
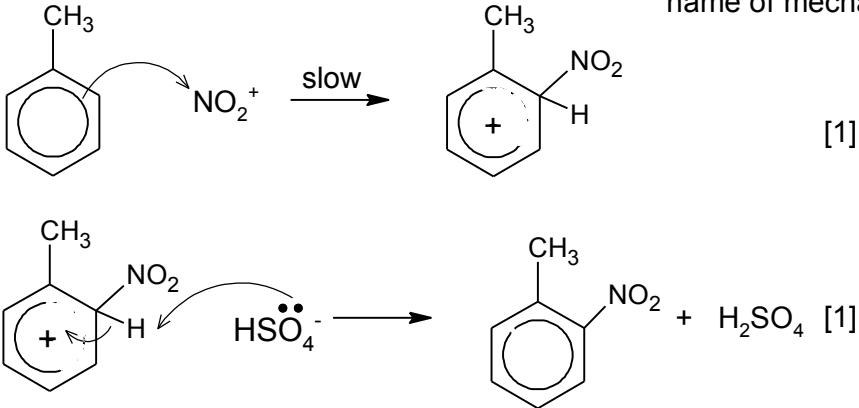
Current used for electrolysis 2 (aqueous sulfuric acid) = $3I$

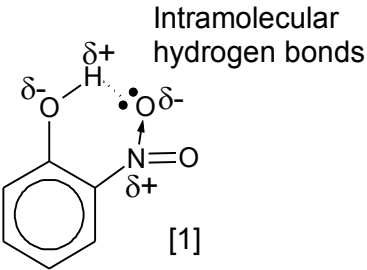
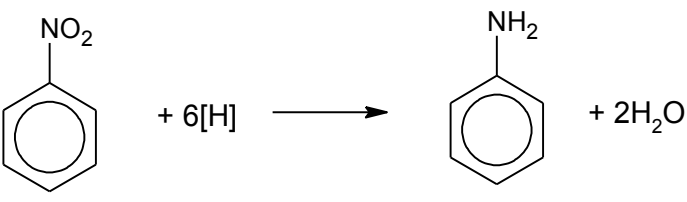
Paper 2 Answers

1	(a)	(i)	 1 mark for 2 correct 2 marks for all 3 correct
		(ii)	The energy released from the formation of ion-dipole interactions between ions in MgNH_4PO_4 and water molecules is insufficient to overcome the energy required to break ionic bonds between oppositely charged ions in MgNH_4PO_4 (and hydrogen bonds between water molecules). [1]
		(iii)	$2\text{MgNH}_4\text{PO}_4(\text{s}) \rightarrow \text{Mg}_2\text{P}_2\text{O}_7(\text{s}) + 2\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$ [1]
	(b)	(i)	$3\text{Mg}^{2+}(\text{g}) + 2\text{PO}_4^{3-}(\text{g}) \rightarrow \text{Mg}_3(\text{PO}_4)_2(\text{s})$ [1] It is the energy evolved when one mole of an ionic solid, $\text{Mg}_3(\text{PO}_4)_2$, is formed from gaseous Mg^{2+} and PO_4^{3-} ions under standard conditions. [1]
		(ii)	- Magnesium chloride and magnesium phosphate have giant ionic structure, with strong electrostatic forces of attraction (ionic bonds) between oppositely charged ions. Cl^- is singly charged while PO_4^{3-} is triply charged. PO_4^{3-} has a larger ionic radius than Cl^-. $LE \propto \frac{ z_+ \cdot z_- }{r_+ + r_-}$. The lattice energy of $\text{Mg}_3(\text{PO}_4)_2$ is more exothermic than MgCl_2. - Contribution of ionic radius to lattice energy is less significant than that of ionic charges. - More <u>energy</u> is needed to break the stronger ionic bonds between Mg^{2+} and PO_4^{3-} in $\text{Mg}_3(\text{PO}_4)_2$. 1 mark for any 3 points 2 marks for all 5 points
		(iii)	$K_{\text{sp}} = [\text{Mg}^{2+}]^3 [\text{PO}_4^{3-}]^2$ units: $\text{mol}^5 \text{dm}^{-15}$
		(iv)	Let x be the solubility of $\text{Mg}_3(\text{PO}_4)_2$ $\text{Mg}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3\text{Mg}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq})$ x 3x 2x $K_{\text{sp}} = [\text{Mg}^{2+}]^3 [\text{PO}_4^{3-}]^2$ $4.0 \times 10^{-25} = (3x)^3 (2x)^2 = (27x^3) (4x^2)$ $108 x^5 = 4.0 \times 10^{-25}$ [1] $x = 5.172 \times 10^{-6}$ $[\text{Mg}^{2+}] = 3x = 1.551 \times 10^{-5} \text{mol dm}^{-3}$ $= 1.6 \times 10^{-5} \text{mol dm}^{-3}$ [1]

		(v)	$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$ $1.8 \times 10^{-11} = [\text{Mg}^{2+}]_{\min}(0.15)^2$ $[\text{Mg}^{2+}]_{\min} = 4.4 \times 10^{-10} \text{ mol dm}^{-3}$ $K_{sp} = [\text{Mg}^{2+}]^3[\text{PO}_4^{3-}]^2$ $4.0 \times 10^{-25} = [\text{Mg}^{2+}]_{\min}^3(0.32)^2$ $[\text{Mg}^{2+}]_{\min} = 1.6 \times 10^{-8} \text{ mol dm}^{-3}$ [1] for $[\text{Mg}^{2+}]_{\min}$ for $\text{Mg}_3(\text{PO}_4)_2$ When the first trace of $\text{Mg}_3(\text{PO}_4)_2$ appears, $[\text{Mg}^{2+}] = 1.6 \times 10^{-8} \text{ mol dm}^{-3}$ To calculate the $[\text{OH}^-]$ present: $K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2$ $1.6 \times 10^{-8} [\text{OH}^-]^2 = 1.8 \times 10^{-11}$ $[\text{OH}^-] = 3.4 \times 10^{-2} \text{ mol dm}^{-3}$ [1] for final answer [1] for 2 sf presentation for both (iv) and (v).
2	(a)	(i)	NO_2 functions as a homogeneous catalyst as it is in the same phase as the gaseous reactants and products. The presence of small amounts of NO_2 (g) provides an alternative mechanism of lower E_a to catalyse the oxidation of gaseous SO_2(g) to SO_3(g). [1] $\text{SO}_2 + \text{NO}_2 \rightarrow \text{SO}_3 + \text{NO}$ $\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2$ [1]
		(ii)	Nitrogen dioxide is a pollutant that is often produced in car engine, when N_2 reacts with O_2 at high temperature condition. The Circuit Breaker of 2020 resulted in reduced usage of cars, and hence reduced production of NO_2. [1]
		(iii)	Circuit Breaker of 2020 resulted in less vehicles on the road but did not reduce as significantly usage of electricity as work from home became a necessity. Since sources of PM_{10} and $\text{PM}_{2.5}$ include power plants and industries, formation of PM_{10} and $\text{PM}_{2.5}$ did not decrease by the same extent as NO_2. [1]
	(b)		$2\text{NO}_2 + \text{HSO}_3^- + \text{H}_2\text{O} \rightarrow 3\text{H}^+ + 2\text{NO}_2^- + \text{SO}_4^{2-}$ [1]
	(c)	(i)	The order of reaction with respect to a given reactant/catalyst is the power to which the concentration of that reactant/catalyst is raised in the experimentally determined rate equation. [1] The rate constant, k, is the proportionality constant in the rate equation. [1] Or In general, for any reaction, $a\text{A} + b\text{B} \longrightarrow m\text{M} + n\text{N}$ The general rate equation can be written in the form $\text{rate} = k[\text{A}]^x [\text{B}]^y$

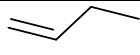
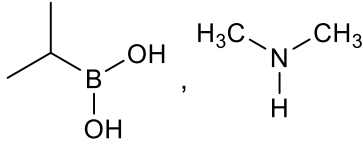
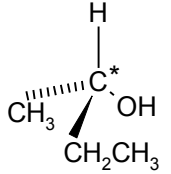
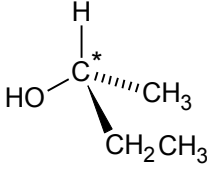
		where	k is called the rate constant , a proportionality constant [1] x is the order of the reaction with respect to reactant A, y is the order of the reaction with respect to reactant B . [1]
		(ii)	This is to ensure that the concentration of NO remains approximately constant so that within an experiment, the rate of reaction will be independent of the concentration of NO/any change in rate is due to decrease in [O ₂] only. Hence the shape of the graph can be used to determine order with respect to O ₂ (using continuous method / conc – time graph). [1]
		(iii)	Using Expt 1, first $t_{1/2} \approx$ second $t_{1/2} \approx 7$ min (with clear working shown in graph). The half-lives of O₂ are approximately constant at 7 min, hence the reaction is first order with respect to O₂. [1] Using Expt 2 & 3, let rate = $k[\text{NO}]^n[\text{O}_2]^1$ $\frac{\text{expt2}}{\text{expt3}} = \frac{5.55 \times 10^{-10}}{3.33 \times 10^{-9}} = \frac{k(0.001)^n(0.002)^1}{k(0.002)^n(0.003)^1}$ $\frac{(0.001)^n}{(0.002)^n} = \frac{1}{4} \rightarrow n = 2$ Therefore second order with respect to NO. [1] Using Expt 2 (or expt 3), $5.55 \times 10^{-10} = k(0.001)^2(0.002)$ $k = 0.2775 = 0.278 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ [1]
		(iv)	rate of formation of NO₂ $= k[\text{NO}]^2[\text{O}_2]$ $= 0.2775 (0.002)^2(0.002)$ $= 2.22 \times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$ [1] rate of depletion of O₂ $= \frac{1}{2} \times \text{rate of formation of NO}_2$ $= \frac{1}{2} \times 2.22 \times 10^{-9}$ $= 1.11 \times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$ [1]

(d)	The catalytic converter act as a (heterogenous) catalyst by providing an alternative reaction pathway with a lower activation energy, E_a (c) compared to the uncatalysed reaction, E_a (u). More molecules will possess energy greater or equal to this lowered activation energy. [1] The frequency of effective collisions increases. Hence, according to the Collision Theory, the rate of reaction increases and NO_2 is converted to harmless N_2 and O_2 more quickly. [1]  [1]
3 (a)	Relative Brønsted-Lowry acidity: Phenol < nitrophenol < ethanoic acid (most acidic) In phenoxide ion, the p orbital of O atom overlaps with the π electron cloud of benzene. The lone pair of electrons on O atom delocalises into the benzene ring. The negative charge on O atom is dispersed over the benzene ring, hence stabilising the phenoxide ion. [1] However, nitrophenol is more acidic than phenol. The electron withdrawing nitro group further delocalises the lone pair of electrons on O atom into the benzene ring. The negative charge on O atom is dispersed to a greater extent, hence the nitrophenoxide ion is more stable. [1] Ethanoic acid is most acidic. In ethanoate ion, the p orbital of the O atom overlaps with the π electron cloud of the $-\text{C}=\text{O}$ bond. The lone pair of electrons on the O atom delocalises into the $-\text{C}=\text{O}$ bond. The negative charge is dispersed most effectively over the carbon atom and the two electronegative O atoms, hence stabilising the ethanoate ion to the largest extent. [1]
(b) (i)	Electrophilic Substitution $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+$ [1] Balanced equation + name of mechanism 

		(ii)	The -OH group in phenol has a greater electron donating effect than -CH_3 in methylbenzene. The lone pair of electrons on O atom in phenol delocalised into the benzene ring, increasing the electron density to a larger extent. Hence, phenol is more susceptible to electrophilic substitution. [1] It is not needed to add conc. H_2SO_4 to generate a stronger electrophile NO_2^+. [1]
		(iii)	The electron donating -O-H group increases electron density in the ring at position 2 and 4 with respect to it, hence these positions are more susceptible to electrophilic attack. [1]
		(iv)	Both 2-nitrophenol and 4-nitrophenol have a simple molecular structure with hydrogen bonds between molecules. The -OH and -NO_2 groups in 2-nitrophenol are in close proximity, hence can form intramolecular hydrogen bonds. Less energy needed to overcome the less extensive intermolecular hydrogen bonds between 2-nitrophenol molecules. 2-nitrophenol has a lower boiling point than 4-nitrophenol. [1]  [1]
(c)	(i)		Nitrogen atom is reduced as the oxidation number decreases from +3 in nitrobenzene to -3 in phenylamine. [1]
	(ii)		 [1]

		(iii)	[1] include slow step + H^+ [1] 2nd and 3rd step
		(iv)	[1] The overall rate of reaction is not affected as the nucleophile is not involved in the rate determining step (slow step) of the $\text{S}_{\text{N}}1$ mechanism. [1]
	(d)	(i)	trans-isomer cis-isomer [1] for correct azo compound [1] for showing and labelling cis and trans isomer.
		(ii)	Two bulky benzene groups in cis-azobenzene are closer together, resulting in larger steric strain or repulsion. [1]
4	(a)	(i)	$K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3}, \text{ atm}^{-2} \text{ [1]}$

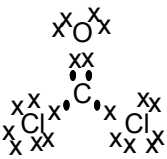
	(ii)	<table><tr><td>n</td><td>N₂(g)</td><td>+</td><td>3H₂(g)</td><td>⇌</td><td>2NH₃(g)</td></tr><tr><td>Initial / mol</td><td>1</td><td></td><td>3</td><td></td><td>0</td></tr><tr><td>Change / mol</td><td>- 0.15</td><td></td><td>- 0.45</td><td></td><td>+ 0.30</td></tr><tr><td>Equilibrium / mol</td><td>0.85</td><td></td><td>2.55</td><td></td><td>0.30</td></tr></table> Total amount at eqm = 0.85 + 2.55 + 0.30 = 3.70 mol $p_{\text{N}_2} = \frac{0.85}{3.70} \times 197 = 45.25 \text{ atm}$ $p_{\text{H}_2} = \frac{2.55}{3.70} \times 197 = 135.7 \text{ atm}$ $p_{\text{NH}_3} = \frac{0.30}{3.70} \times 197 = 15.97 \text{ atm}$ [1] equilibrium partial pressure $K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{N}_2})(p_{\text{H}_2})^3} = \frac{15.97^2}{(45.25)(135.7)^3} = 2.25 \times 10^{-6} \text{ atm}^{-2} \text{ [1] } K_p \text{ value (allow ecf)}$	n	N ₂ (g)	+	3H ₂ (g)	⇌	2NH ₃ (g)	Initial / mol	1		3		0	Change / mol	- 0.15		- 0.45		+ 0.30	Equilibrium / mol	0.85		2.55		0.30
n	N ₂ (g)	+	3H ₂ (g)	⇌	2NH ₃ (g)																					
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Change / mol	- 0.15		- 0.45		+ 0.30																					
Equilibrium / mol	0.85		2.55		0.30																					
	(iii)	All three gases have simple molecular structure. The hydrogen bonds between the NH₃ molecules are stronger and more significant than the instantaneous dipole-induced dipole (id-id) interactions between N₂ molecules and H₂ molecules respectively. Hence, NH₃ deviates the most from ideal gas behaviour. [1] N₂ has a larger M_r, greater number of electrons, hence larger electron cloud that is more polarisable. Hence, the id-id interactions between N₂ molecules is stronger. So, N₂ behaves less ideally than H₂ molecules. [1]																								
	(iv)	amount / mol 1 0.85 N₂ 0.3 NH₃ t time [1]																								
	(v)	Effect on yield of ammonia: Decreasing the volume of container increases the total pressure. By Le Chatelier's Principle, the forward reaction is favoured to reduce the pressure by producing lesser amount of gas particles. Hence the position of equilibrium will shift to the right, increasing the yield of ammonia. [1] Effect on the value of K_p: Since there is no change in temperature, K_p remains constant. [1]																								

	(b)	(i)	G:  [1]
		(ii)	step 1: LiAlH_4 in dry ether, room temp or NaBH_4, room temp or $\text{H}_2(\text{g})$, Ni catalyst, heat or $\text{H}_2(\text{g})$, Pt or Pd catalyst, room temp [1] step 2: excess concentrated H_2SO_4, $170\text{ }^\circ\text{C}$ or Al_2O_3, $350\text{ }^\circ\text{C}$ [1] step 3: steam, concentrated H_3PO_4, $300\text{ }^\circ\text{C}$, 60 atm or concentrated H_2SO_4, room temp followed by $\text{H}_2\text{O}(\text{l})$, heat [1] step 5:  , room temp [1]
		(iii)	type of stereoisomerism: Enantiomerism [1]  mirror  [1] must show 3D representation

(c) (i)	$\text{CH}_3\text{CH}_2\text{CHO} + \text{H}^+ \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}^+\text{OH}$ (step 1) $\text{CH}_3\text{CH}_2\text{CH}^+\text{OH} + \text{H}_3\text{C}-\text{NH}_2 \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}(\text{OH})(\text{NH}_2^+\text{CH}_3)$ (step 2) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})(\text{NH}_2^+\text{CH}_3) \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}(\text{OH}^+\text{H})(\text{NHCH}_3)$ (step 3) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH}^+\text{H})(\text{NHCH}_3) \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}=\text{N}^+\text{CH}_3 + \text{H}_2\text{O}$ (step 4) $\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+\text{CH}_3 + \text{NaBH}_3\text{CN} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3$ (step 5) iminium ion [1] every two correct steps
(ii)	type of stereoisomerism: cis-trans isomerism side way overlap of p orbitals: π bond p orbital of C p orbital of N sp^2 orbital of C sp^2 orbital of N head on overlap of sp^2 orbitals: σ bond • correct type of stereoisomerism • correct orbitals used for overlapping

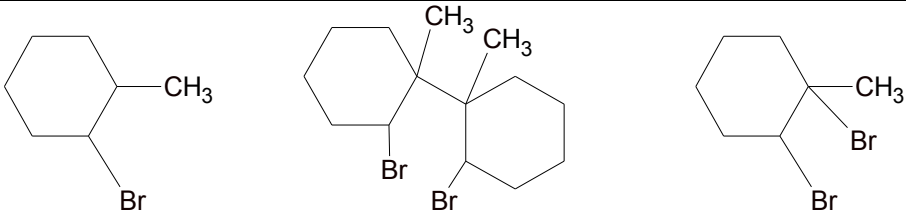
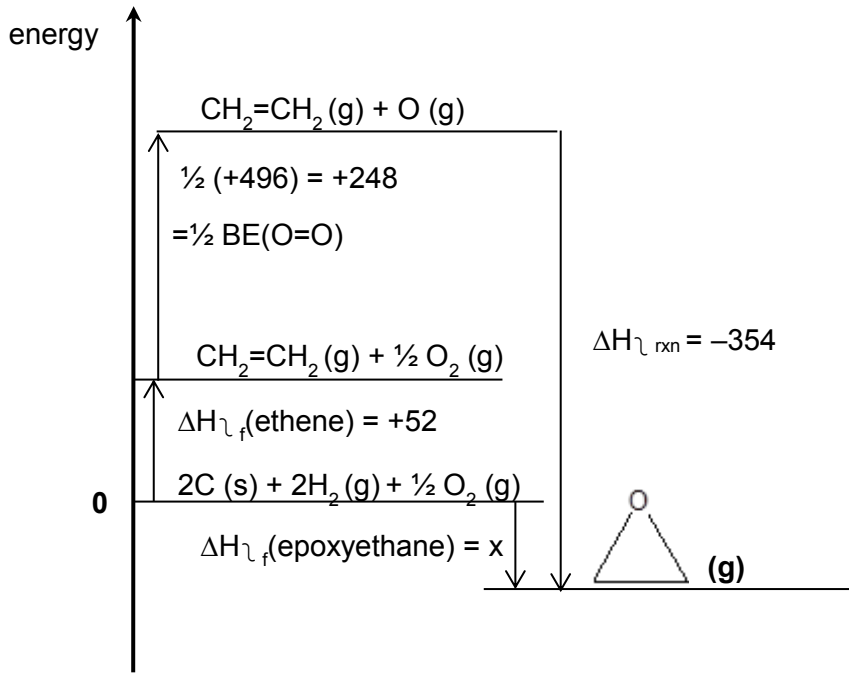
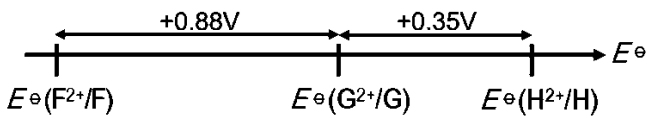
		correct arrangement of orbitals 3 points – 2 marks 2 points – 1 mark There is restricted rotation about C=N bond and two different groups on C and on N atom of the C=N double bond [1]						
	(iii)	test: Add Fehling's solution and warm observations: Ethanal: Brick-red ppt of Cu₂O formed. Benzaldehyde: No brick-red ppt of Cu₂O formed. balanced equation: $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{H} + 2\text{Cu}^{2+} + 5\text{OH}^- \longrightarrow \text{H}_3\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{O}^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$ [1] for test & observation [1] for balanced equation						
(d)	(i)	N-ethylmethylamine and N-methylethanamine are Lewis bases as they are <u>electron pair donor</u>. $\text{CH}_3\text{CH}_2\text{NHCH}_3 + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2(\text{CH}_3)\text{NH}_2^+$ or $\text{CH}_3\text{CH}=\text{NCH}_3 + \text{H}^+ \rightarrow \text{CH}_3\text{CH}=\overset{+}{\text{N}}\text{HCH}_3$ [1] Alternative: AlCl₃, BH₃						
	(ii)	<table border="1"><thead><tr><th>Lewis base</th><th>type of hybridisation of N atom</th></tr></thead><tbody><tr><td>$\text{CH}_3\text{CH}_2\text{NHCH}_3$ N-ethylmethylamine</td><td>sp³</td></tr><tr><td>$\text{CH}_3\text{CH}=\text{NCH}_3$ N-methylethanamine</td><td>sp²</td></tr></tbody></table> [1] for both correctly identified type of hybridisation Since the lone pair in the sp³ orbital has lower s character (the lone pairs are further from the nucleus), the lone pair on N atom of N-ethylmethylamine will be less strongly attracted to the nucleus and thus more available for donation into an empty orbital. Or Since the lone pair in the sp³ orbital has higher p character (the lone pairs are further from the nucleus), the lone pair on N atom of N-ethylmethylamine will be less strongly attracted to the nucleus and thus more available for donation into an empty orbital. [1]	Lewis base	type of hybridisation of N atom	$\text{CH}_3\text{CH}_2\text{NHCH}_3$ N-ethylmethylamine	sp ³	$\text{CH}_3\text{CH}=\text{NCH}_3$ N-methylethanamine	sp ²
Lewis base	type of hybridisation of N atom							
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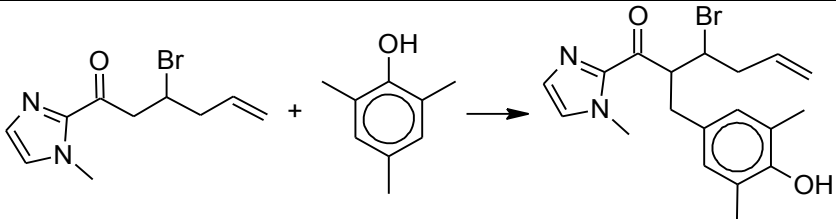
Paper 3 Answers

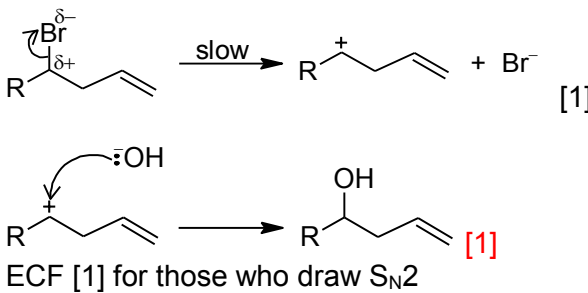
1	(a)	(i)	 [1]
		(ii)	Expected Cl-C-Cl bond angle is 120 ° as there are 3 bond pairs, 0 lone pairs and the three bond pairs will arrange themselves as far apart as possible to minimise repulsion. [1] The actual Cl-C-Cl bond angle is smaller as there is greater repulsion between the C=O bond pair and C-Cl bond pair than that between the two C-Cl bond pairs as there is higher electron density in a double bond. [1]
	(b)		[phosgene] = 1.87 dm³ per 10⁶ dm³ of air = 1.87 / 24 mol per 10⁶ dm³ •convert vol to amt = 0.07791 mol per 10⁶ dm³ = 0.07791 / 10⁶ mol per dm³ •convert per 10⁶ dm³ to per dm³ = 7.791 x 10⁻⁸ mol dm⁻³ = 7.791 x 10⁻⁸ x 99.0 g dm⁻³ •convert mol to g = 7.713 x 10⁻⁶ g dm⁻³ = 7.71 x 10⁻³ mg dm⁻³ •convert g to mg Any 2 • [1], All 4 • (i.e. correct ans) [2]
	(c)	(i)	Urea is a very weak base as p orbital of N overlaps with π electron cloud of C=O hence lone pair of electron on N is delocalised into C=O and hence, less available to form dative bond to accept/with H⁺. [1]
		(ii)	NO₂ is harmful as it catalyses formation of acid rain / forms photochemical smog. [1]
	(d)	(i)	$\Delta H_{\text{reaction}} = +1077 + 244 - (740 + 340(2))$ [1] = - 99 kJ mol⁻¹ [1]
		(ii)	BE (C-Cl) in COCl₂ differs most from than the average value in the data booklet. The C-Cl bond in COCl₂ as it is stronger than average C-Cl bonds as the C is sp² hybridised hence the greater degree of s character give rise to more effective orbital overlap in forming the C-Cl bond. Thus, actual value is more exothermic as more energy is released in forming the stronger C-Cl bond in COCl₂. [1]
		(iii)	ΔS is negative as there is a decrease in number of gaseous particles (2 to 1) during reaction, hence less ways to arrange the particles. Disorder and entropy decreases. [1] ΔH is negative, - TΔS is positive. Since ΔG = ΔH - TΔS, ΔG is more negative at low temperature as - TΔS < ΔH or - TΔS is less positive at low temp. [1] Reaction is thus more feasible at low temperature resulting in greater yield of phosgene. However, rate of reaction is too slow at low temperature hence an optimal temperature of 150 °C and catalyst is used to increase rate. [1]
		(iv)	Rate = k₃[COCl]/[Cl₂] = k₃k₂[Cl]/[CO][Cl₂] = k₃k₂k₁[Cl₂]^{3/2}[CO][Cl₂] Rate = k [CO][Cl₂]^{3/2} [1]

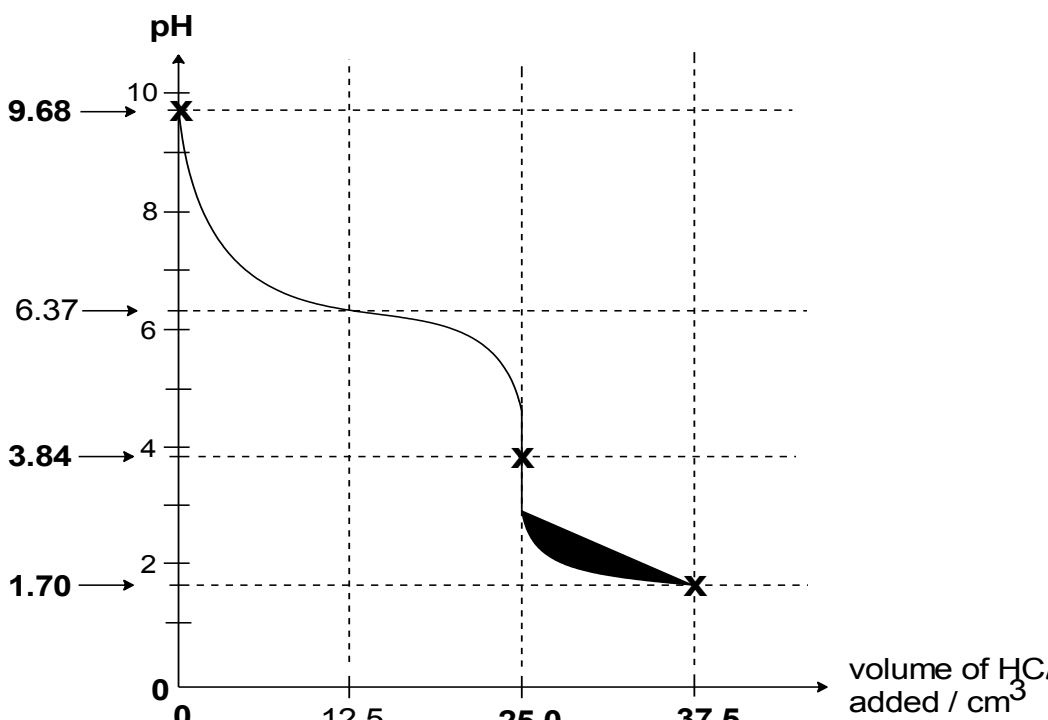
		(v)	It is the energy change when one mole of phosgene liquid COCl_2 (or a cpd) is formed from its constituent elements in their standard states under standard conditions. [1] $\text{C(s)} + \text{Cl}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{COCl}_2(\text{l})$ [1]						
		(vi)	$\Delta H_{\text{reaction}} = \sum \Delta H_{\text{f}}(\text{prdts}) - \sum \Delta H_{\text{f}}(\text{rxt})$ $-107.6 = \Delta H_{\text{f}}(\text{COCl}_2(\text{g})) - (-110.5)$ [1] $\Delta H_{\text{f}}(\text{COCl}_2(\text{g})) = -218.1 \text{ kJ mol}^{-1}$ As energy is lost when COCl_2 condenses from (g) to (l) (or verify using E cycle below). $\begin{array}{ccc} & -218.1 & \\ \text{C(s)} + \text{Cl}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) & \longrightarrow & \text{COCl}_2(\text{g}) \\ & \searrow \quad \nearrow & \\ \Delta H_{\text{f}}(\text{COCl}_2(\text{l})) & & +33.3 \\ & \text{COCl}_2(\text{l}) & \end{array}$ $\Delta H_{\text{f}}(\text{COCl}_2(\text{l})) = \Delta H_{\text{f}}(\text{COCl}_2(\text{g})) - \Delta H_{\text{vap}}(\text{COCl}_2(\text{l}))$ $= -218.1 - (+33.3)$ $= -251.4 \text{ kJ mol}^{-1}$ [1]						
	(e)		Al_2O_3 behaves as an acidic oxide: $\text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} \rightarrow 2\text{NaAl}(\text{OH})_4$ [1] P_4O_{10} behaves as an acidic oxide: $\text{P}_4\text{O}_{10} + 6\text{Ba}(\text{OH})_2 \rightarrow 2\text{Ba}_3(\text{PO}_4)_2 + 6\text{H}_2\text{O}$ [1] Behaviour of P_4O_{10} is expected since P is in Group 15/right of Periodic Table and thus a non-metal which typically forms covalent oxide (as electronegativity difference between P and O is small) that are acidic. Behaviour of Al_2O_3 is not expected as Al is in Group 13/left of Periodic Table and metals typically forms ionic oxide that are basic. (or does not typically form covalent oxide).[1] However, Al_2O_3 is expected to exhibit amphoteric behavior as Al_2O_3 is an ionic oxide with covalent character as it is in Period 3 and has a small size thus high charge density of the Al^{3+} ion which polarises the electron cloud of O^{2-} anion to a large extent, giving some covalent nature to the ionic Al-O interaction. [1]						
2	(a)	(i)	$\begin{array}{lll} \text{Cl}_2 + 2\text{e} \rightleftharpoons 2\text{Cl}^- & E^\circ = +1.36 \text{ V} & E^\circ(\text{Cl}_2/\text{Cl}^-) = +1.36 \text{ V} \\ \text{Br}_2 + 2\text{e} \rightleftharpoons 2\text{Br}^- & E^\circ = +1.07 \text{ V} & \text{OR } E^\circ(\text{Br}_2/\text{Br}^-) = +1.07 \text{ V} \\ \text{I}_2 + 2\text{e} \rightleftharpoons 2\text{I}^- & E^\circ = +0.54 \text{ V} & E^\circ(\text{I}_2/\text{I}^-) = +0.54 \text{ V} \end{array}$ The oxidising power of the halogens decreases down the group [1] as the $E^\circ(\text{X}_2/\text{X}^-)$ become less positive and the halogens are less easily reduced down the group. [1]						
		(ii)	React both Br_2 and I_2 separately with Fe^{2+} . Br_2 is stronger oxidising agent than I_2 and it oxidises Fe^{2+} to Fe^{3+} as $E_{\text{cell}} > 0$, but iodine is unable to do so as $E_{\text{cell}} < 0$. [1]						
	(b)	(i)	$pV = nRT$ $V = \frac{0.40 \times 8.31 \times (25 + 273)}{12 \times 101325} = 8.15 \times 10^{-4} \text{ m}^3 = 0.815 \text{ dm}^3$ [1]						
		(ii)	<table><tr><th>Pressure, p / atm</th><th>V / dm^3</th><th>pressure x volume, pV / atm dm^3</th></tr><tr><td>5</td><td>1.924</td><td>9.62</td></tr></table>	Pressure, p / atm	V / dm^3	pressure x volume, pV / atm dm^3	5	1.924	9.62
Pressure, p / atm	V / dm^3	pressure x volume, pV / atm dm^3							
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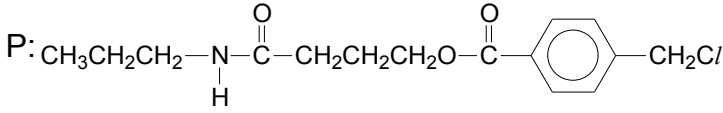
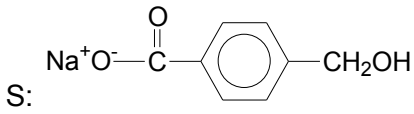
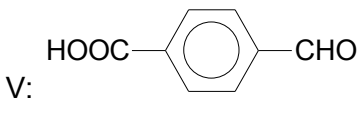
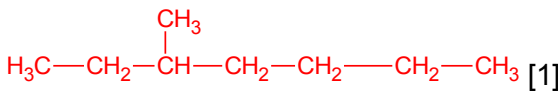
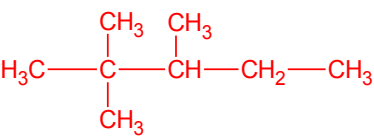
			<table><tr><td>10</td><td>0.926</td><td>9.26</td></tr><tr><td>15</td><td>0.592</td><td>8.88</td></tr></table> [1] Accept any value of x in the range of $8.88 < x < 9.26$: When $p = 12 \text{ atm}$, $pV = 9$ [1] since $pV = 9$, $V = 9 \div 12 = 0.750 \text{ dm}^3$ [1]	10	0.926	9.26	15	0.592	8.88
10	0.926	9.26							
15	0.592	8.88							
	(iii)		HC/ has significant permanent dipole-permanent dipole interactions between its molecules, and its molecules are closer and occupy a smaller volume than an ideal gas. [1]						
(c)	(i)		Propagation $\text{CH}_3\text{CH}=\text{CH}_2 + \cdot\text{Br} \longrightarrow \text{CH}_3\dot{\text{C}}\text{H}-\text{CH}_2\text{Br}$ $\text{CH}_3\dot{\text{C}}\text{H}-\text{CH}_2\text{Br} + \text{H}-\text{Br} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \cdot\text{Br}$ [1] for both propagation steps with arrows Termination $\text{Br}\cdot + \cdot\text{Br} \longrightarrow \text{Br}_2$ $\text{CH}_3\dot{\text{C}}\text{H}-\text{CH}_2\text{Br} + \cdot\text{Br} \longrightarrow \text{CH}_3\text{CHBrCH}_2\text{Br}$ $\text{CH}_3\dot{\text{C}}\text{H}-\text{CH}_2\text{Br} + \cdot\text{CH}_2\text{CH}(\text{CH}_3)-\text{CH}_2\text{Br} \longrightarrow \text{CH}_3\text{CH}(\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Br})\text{CH}_2\text{Br}$ [1] for any 2 correct termination steps with arrows [1] for naming the propagation and termination steps						
	(ii)		The brief exposure to bright lights produces peroxide and Br radicals that initiate the chain reactions of the propagation steps to produce more radicals [1] for reaction to proceed. The exothermic reaction will result in an increase in temperature [1], hence rate of reaction increases.						
	(iii)		The HC/ bond is stronger than the HBr bond, hence the propagation step involving the breaking of the HC/ bond is very slow/requires a high activation energy. [1] OR The HC/ bond is stronger than the HBr bond, hence the propagation step involving the breaking of the HC/ bond is endothermic, and the reaction not favoured. [1]						

		(iv)	 [1] for 1 or 2 correct structures [2] for all 3 structures
	(d)		 $\Delta H_f(\text{epoxyethane}) = x = +52 + \frac{1}{2}(496) - 354 = -54 \text{ kJ mol}^{-1}$ [1] [2] for energy level diagram • Labelling '0' • Labelling all arrows either with value or enthalpy change • All energy states are balanced
3	(a)	(i)	From least positive to most positive: $\mathcal{E}(\text{F}^{2+}/\text{F})$, $\mathcal{E}(\text{G}^{2+}/\text{G})$ and $\mathcal{E}(\text{H}^{2+}/\text{H})$ [1]  In Fig 3.1, when F and G are connected, G is the cathode and F is the anode. Hence, $\mathcal{E}(\text{G}^{2+}/\text{G})$ is more positive than $\mathcal{E}(\text{F}^{2+}/\text{F})$. When G and H are connected, H is the cathode and G is the anode. Hence, $\mathcal{E}(\text{H}^{2+}/\text{H})$ is more positive than $\mathcal{E}(\text{G}^{2+}/\text{G})$. (Explanation not necessary)
		(ii)	$\mathcal{E}_{\text{cell}} = (+0.88) + (+0.35) = +1.23 \text{ V}$ [1] $\text{H}^{2+}(\text{aq}) + \text{F}(\text{s}) \rightarrow \text{H}(\text{s}) + \text{F}^{2+}(\text{aq})$ [1]
		(iii)	$\Delta G = -(2)(96500)(+1.23) = -237390 \text{ J mol}^{-1} = -237 \text{ kJ mol}^{-1}$ [1] allow ecf

	(b) (i)	 [1]
	(ii)	$I = \frac{1.23}{3.62} = 0.340 \text{ A}$ [1] allow ecf
	(iii)	Using $Q = nZF$, $(0.340)(2.5 \times 60 \times 60) = n_{\text{H}_2} \times 2 \times 96500$ $n_{\text{H}_2} = 0.01584 \text{ mol}$ [1] allow ecf $V_{\text{H}_2} = 0.01584 \times 22.7 = 0.3597 \text{ dm}^3 = 360 \text{ cm}^3$ [1] allow ecf
	(c) (i)	• Change electrode T to impure copper • Change electrolyte to aqueous CuSO_4 / $\text{Cu}(\text{NO}_3)_2$ / Cu^{2+} [1] for each change Reject answer that says • change electrode S to pure copper as purification of copper can still be done with inert cathode. • change the electrochemical cell to a battery or regulate the voltage to suit the voltage of purification of copper.
	(ii)	$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag} \quad (+0.80\text{V})$ $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu} \quad (+0.34\text{V})$ $\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn} \quad (-0.76\text{V})$ <u>At electrode T (or anode)</u> Cu is preferentially oxidised to Cu^{2+} and dissolve in the electrolyte. Zn will be oxidised to Zn^{2+} and dissolve in the electrolyte as well since $E^\ominus(\text{Zn}^{2+}/\text{Zn})$ is more negative than $E^\ominus(\text{Cu}^{2+}/\text{Cu})$. [1] Ag will not be oxidised to Ag^+ as $E^\ominus(\text{Ag}^+/\text{Ag})$ is more positive than $E^\ominus(\text{Cu}^{2+}/\text{Cu})$ and will be collected as anode sludge. [1] <u>At electrode S (or cathode)</u> Cu^{2+} is preferentially reduced to Cu and deposited at electrode S as $E^\ominus(\text{Cu}^{2+}/\text{Cu})$ is more positive than $E^\ominus(\text{Zn}^{2+}/\text{Zn})$. Zn^{2+} have less positive $E^\ominus$ than $E^\ominus(\text{Cu}^{2+}/\text{Cu})$, Zn^{2+} will remain dissolve in the electrolyte. [1]
	(d) (i)	Nucleophiles are “electron-rich” species that forms a bond by donating a lone pair of electrons to an electron-deficient species. [1]
	(ii)	$\text{C}_6\text{H}_5\text{ONa} < \text{NaOH} < \text{C}_2\text{H}_5\text{ONa} < \text{C}_2\text{H}_5\text{SNa}$ [1]
	(iii)	rate = $k[\text{N}]$ The relative rate is almost constant. The rate of the reaction is independent of nucleophile. [1]
	(iv)	Nucleophilic Substitution ($\text{S}_{\text{N}}1$)

			 ECF [1] for those who draw S_N2 [1]
		(v)	The δ⁻ in oxygen atom of water causes an electrostatic repulsion with the π electron cloud of alkene C=C double bond. [1] Hence, alkene double bond cannot attack the oxygen atom of water.
		(vi)	$\Delta H_{\text{reaction 1}} = (610+193) - (350+280) = +173 \text{ kJ mol}^{-1}$ $\Delta H_{\text{reaction 2}} = (610+460) - (350+410) = +310 \text{ kJ mol}^{-1}$ Since $\Delta H_{\text{reaction 1}}$ is less endothermic than $\Delta H_{\text{reaction 2}}$, $\Delta H_{\text{reaction 1}}$ is more spontaneous. [1] or Bond energy of Br–Br = 193 kJ mol⁻¹ Bond energy of O–H = 460 kJ mol⁻¹ Br–Br bonds are weaker and require less energy to break compared to O–H bond. Hence, reaction 1 occurs much faster than reaction 3. [1]
4	(a)	(i)	$K_b \text{ of HCO}_3^- = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} = \frac{y^2}{(0.100)} = 2.34 \times 10^{-8} \text{ mol dm}^{-3}$ $y = (2.34 \times 10^{-9})^{1/2} = 4.84 \times 10^{-5}$ $[\text{OH}^-] = 4.84 \times 10^{-5} \text{ mol dm}^{-3}$ [1] $\text{pOH} = -\lg(4.84 \times 10^{-5}) = 4.32$ $\text{pH} = 14 - 4.32 = 9.68$ [1]
		(ii)	At the equivalence point, the resultant solution contained H₂CO₃(aq). $\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ $K_a \text{ of H}_2\text{CO}_3 = \frac{K_w}{K_b \text{ of HCO}_3^-} = \frac{1.0 \times 10^{-14}}{2.34 \times 10^{-8}} = 4.27 \times 10^{-7} \text{ mol dm}^{-3}$ [1] $K_a \text{ of H}_2\text{CO}_3 = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]} = \frac{w^2}{0.0500} = 4.27 \times 10^{-7} \text{ mol dm}^{-3}$ $\Rightarrow w = 1.46 \times 10^{-4}$ $[\text{H}_3\text{O}^+] = 1.46 \times 10^{-4} \text{ mol dm}^{-3}$ $\text{pH} = -\lg(1.46 \times 10^{-4}) = 3.84$ [1]

	(iii)	Volume of HCl needed to reach equivalence point = 25.0 cm³ Excess volume of HCl added = 37.5 – 25.0 = 12.5 cm³ Amount of H⁺ from HCl(aq) = Amount of HCl = (12.5/1000)(0.100) = 1.25 x 10⁻³ mol Total volume of resultant solution = 25.0 + 37.5 = 62.5 cm³ [1] [H⁺] = 1.25 x 10⁻³/0.0625 = 0.0200 mol dm⁻³ pH = -lg [H⁺] = -lg(0.0200) = 1.70 [1]																
	(iv)	 - Both axes labelled correctly with units for volume - Three points determined from (i), (ii) & (iii) plotted correctly and - connected with smooth curve - Point plotted correctly at MBC [1] for any 3 points [2] for all 6 points																
(b)	(i)	<table border="1"><thead><tr><th>Element</th><th>C</th><th>H</th><th>N</th></tr></thead><tbody><tr><td>Amount/mol</td><td>61.0/12.0</td><td>15.3/1.0</td><td>23.7/14.0</td></tr><tr><td>Mole ratio</td><td>5.08</td><td>15.3</td><td>1.7</td></tr><tr><td>Simplest ratio</td><td>3</td><td>9</td><td>1</td></tr></tbody></table> Hence the empirical formula of Q is C₃H₉N. [1] The M_r of Q is 59. Let Q be (C₃H₉N)_n.	Element	C	H	N	Amount/mol	61.0/12.0	15.3/1.0	23.7/14.0	Mole ratio	5.08	15.3	1.7	Simplest ratio	3	9	1
Element	C	H	N															
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Simplest ratio	3	9	1															

			Then M_r of Q = $(3n)(12.0) + (9n)(1.0) + (n)(14.0) = 59$ $59n = 59$ i.e. $n = 1$ Hence the molecular formula of Q is C_3H_9N. [1]
		(ii)	P:  Q: $CH_3CH_2CH_2NH_2$ R: $Na^+ - O_2C - CH_2CH_2CH_2OH$ S:  T: $[CH_3CH_2CH_2N(CH_3)_3]^+I^-$ U: $HO_2C - CH_2CH_2CH_2OH$ V:  [1] for each correct structure
		(iii)	Solid GABA, 4-aminobutanoic acid, exists as zwitterions in a giant ionic structure with strong ionic bonds between the zwitterions. [1] $H_3N^+ - CH_2CH_2CH_2 - COO^-$ zwitterionic form of GABA (4-aminobutanoic acid) U has a simple molecular structure with intermolecular hydrogen bonds. [1] The ionic bonds in GABA are much stronger than the H-bonds in U. Thus, a larger amount of heat energy is required to melt GABA and hence GABA has a much higher melting point. [1]
5	(a)	(i)	The meso compound has a plane of symmetry in the molecule (or both chiral centres contain the same groups attached to it). The two chiral centres each rotate the plane of polarised light to the same extent but in the opposite direction hence the rotating power cancels out. [1]
		(ii)	isomer A (1 branch)  [1] isomer C: (3 branches)  [1]

		isomer D: (4 branches) $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \quad [1]$															
	(iii)	Isomers A to D are simple molecular structure with weak instantaneous dipole – induced dipole (id-id) interaction between molecules. [1] From isomer A to D, the degree of branching of the molecules increases. The molecules have less surface area of contact, resulting in weaker id-id interaction between molecules. [1] Hence less energy is required to overcome the weaker id-id interaction between molecules, resulting in lower boiling points from isomer A to D.															
	(iv)	<table border="1"> <thead> <tr> <th>Structural formula</th><th>No. of H</th><th>Simplest ratio</th></tr> </thead> <tbody> <tr> <td>$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$</td><td>6</td><td>3</td></tr> <tr> <td>$\begin{array}{c} \text{Cl} \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{H}_3\text{C}-\text{CH}-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$</td><td>4</td><td>2</td></tr> <tr> <td>$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \\ \text{Cl} \end{array}$</td><td>2</td><td>1</td></tr> <tr> <td>$\begin{array}{c} \text{Cl} \\ \\ \text{CH}_2 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$</td><td>6</td><td>3</td></tr> </tbody> </table> structures [1] ratio [1]	Structural formula	No. of H	Simplest ratio	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$	6	3	$\begin{array}{c} \text{Cl} \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{H}_3\text{C}-\text{CH}-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$	4	2	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \\ \text{Cl} \end{array}$	2	1	$\begin{array}{c} \text{Cl} \\ \\ \text{CH}_2 \quad \text{CH}_3 \\ \quad \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$	6	3
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(b)	(i)	- As number of protons increases, nuclear charge increases. - As number of electron shells also increases, shielding effect increases significantly. - The outermost electron is further away from the nucleus. - Hence attraction between the nucleus and outermost electron decreases. - Less energy is required to remove the outermost electron hence ease of losing electrons increases, first ionisation energy decreases. - The reactivity of Group 1 metals increases down the group. [2] 6 points [1] 4-5 points															
	(ii)	All the metals have <u>giant metallic structure</u> with <u>metallic bonds</u> between delocalized <u>sea of valence electrons</u> and <u>metallic cations</u>.															

		Lithium and sodium metals have <u>smaller ionic radius</u>, resulting in stronger electrostatic attraction between the cations and the sea of delocalised valence electrons. More energy needed to break the stronger metallic bonds, hence higher boiling points and <u>can be obtained via electrolysis in molten state</u> even in a high temperature environment. [1] Potassium, rubidium and caesium having <u>larger ionic radius</u> and weaker metallic bonding and <u>vaporises in the high temperature environment</u>. [1]
	(iii)	Down the group, Group 1 ions have <u>larger ionic radii</u> and hence have a <u>lower charge density</u> and <u>polarising power</u> [1] Li^+ has the <u>highest charge density</u> and <u>highest polarising power</u>. It is able to <u>polarise the electron cloud of peroxide or superoxide</u> and <u>weaken the O–O/O=O bond</u> to a large extent. Hence the bond is easily broken to form oxide ion in the final product [1].
(c)	(i)	X CO_2 Y CaCO_3 [1] for X and Y Z $\text{Ca}(\text{HCO}_3)_2$ [1]
	(ii)	$\text{MO} + \text{H}_2\text{O} \rightarrow \text{M}(\text{OH})_2$ $\text{M}(\text{OH})_2 + 2\text{HCl} \rightarrow \text{MCl}_2 + 2\text{H}_2\text{O}$ n_{HCl} for 25.0 cm³ aliquots = $0.0985 \times 20.30/1000 = 0.0020 \text{ mol}$ n_{HCl} reacting with white solid = $0.0020 \times 250/25 = 0.020 \text{ mol}$ [1] $n_{\text{MO}} = n_{\text{M}(\text{OH})_2} = \frac{1}{2} \times 0.020 = 0.010 \text{ mol}$ $M_{\text{w}} = 1.9735 / 0.010 = 197.4$ [1]
	(iii)	W is a carbonate (since gas X CO_2 is evolved upon reaction of W with acid) Hence formula will be MCO₃ Hence Ar of M will be $197.35 - 12.0 - 3(16.0) = \underline{137.35}$ [1] M is <u>Barium</u>.