

Changes to 2014 H2 Chemistry A Level Question Paper

Dear students,

The TYS you have purchased is based on the 9647 (old) syllabus. You will be sitting for the 9729 (new) syllabus papers. This document will instruct you on the changes you need to make to the TYS questions.

The Planning question for the 9729 syllabus will be in the Paper 4 (Practical).

Some concepts are no longer tested in the 9729 syllabus and the values used for some calculations are now different (e.g. molar volume at s.t.p.) which will affect your choice of the answers.

You are advised to **make the changes** on your question papers **before you attempt it**. Do inform your tutors if you notice any differences which were not highlighted in this document.

Paper 1

14 Not in syllabus

17 Not in syllabus

18 Amend question / option

“Which property **decreases** on descending Group **2** (Mg to Ba)?

Option **D** “the thermal stability of the **carbonate**”

Option **B** is not in syllabus. It is also an incorrect option.

Option **C** is not in syllabus. It is also an incorrect option.

You can decide between **A** and **D**.

39 Not in syllabus

Paper 2

No amendments

Paper 3

1(a)(ii) Change to P_4O_{10}

3(a) Not in syllabus

3(b)(ii) Not in syllabus

4(d) Not in syllabus

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Suggested Solutions to 2014 H2 Chemistry Paper 1 (9647/01)

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

Q1

Amt of ^9Be in 0.09 g = $0.09 / 9 = 0.01$ mol
 There are $9 - 4 = 5$ neutrons in a ^9Be atom.
 No. of neutrons in 0.01 mol of ^9Be
 = $5 \times 0.01 \times L = 0.05L$
 Ans: **B**

Q2

As the reaction is a disproportionation reaction, Cl undergoes both oxidation and reduction.
 Since Cl in ClO_2 has an initial oxidation state of +4, it is reduced when it forms ClO_2^- with oxidation state of +3. Cl must have been oxidised to form Q, so Q must have oxidation state greater than +4 (\Rightarrow answer cannot be **A** or **B**)
 If oxidation state of Cl in Q is +5,
 $2\text{ClO}_2 + 2\text{OH}^- \rightarrow \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O}$
 Equimolar amts of ClO_2 and OH^- are used \Rightarrow Ans: **C**

If oxidation state of Cl in Q is +7,
 $4\text{ClO}_2 + 4\text{OH}^- \rightarrow 3\text{ClO}_2^- + \text{ClO}_4^- + 2\text{H}_2\text{O}$
 Equimolar amts of ClO_2 and OH^- are used \Rightarrow Ans can also be **D**.

Q3

Compound **G** has molecular formula of $\text{C}_7\text{H}_{12}\text{O}_3$.
 $\text{C}_7\text{H}_{12}\text{O}_3 + y\text{O}_2 \rightarrow 7\text{CO}_2 + 6\text{H}_2\text{O}$
 Balancing number of O,
 $3 + 2y = 7 \times 2 + 6 \times 1 = 20$
 $\Rightarrow y = (20 - 3)/2 = 8.5$
 Ans: **A**

Q4

Both H_2O and CH_3OH have H bonded to O
 \Rightarrow strongest intermolecular force in these compounds would be hydrogen bonds
 CH_3OCH_3 does not have H bonded to N, O or F but is polar \Rightarrow strongest intermolecular force is permanent dipoles
 Ans: **A**

Q5

A molecule having a central atom with 2 bond pairs and 2 lone pairs has a non-linear (bent) shape. (**A** is correct and **B** is incorrect)
 A molecule having a central atom with 3 bond pairs and 1 lone pair has a **trigonal pyramidal** shape. (**C** and **D** are incorrect)
 Ans: **A**

Q6

Molecules of *ideal gases* have elastic collisions and have negligible forces of attraction and negligible size. Molecules of *real gases* have inelastic collisions and have significant forces of attraction and size. Molecules of **both real and ideal gases** are in constant random motion.
 Ans: **B**

Q7

$$LE \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

Cs^+ and Na^+ have the same charge of +1; F^- and Cl^- have the same charge of -1 $\Rightarrow |q_+ \times q_-|$ is the same for all 4 compounds.
 Cs^+ is larger than Na^+ and Cl^- is larger than F^- .
 CsCl has the largest value of $|r_+ + r_-|$ and hence the least exothermic lattice energy.
 Ans: **A**

Q8

$$\begin{aligned} \Delta H_{\text{rxn}} &= \sum \Delta H_f(\text{pdt}) - \sum \Delta H_f(\text{rxt}) \\ &= \Delta H_f[\text{C}_6\text{H}_{12}\text{O}_6] - \{6\Delta H_f[\text{CO}_2] + 6\Delta H_f[\text{H}_2\text{O}]\} \\ &= +2807 \text{ kJ mol}^{-1} \text{ (positive)} \end{aligned}$$

Though the reaction consumes and produces the same number of gaseous molecules, 6 mol of liquid H_2O are used up while 1 mol of solid $\text{C}_6\text{H}_{12}\text{O}_6$ is formed.
 There is an decrease in the disorder of the system and hence the **entropy change, ΔS , is negative**.
 Ans: **C**

Q9

For SCN^- to be oxidised by halogen Y_2 ,
 $E^\ominus_{(\text{SCN})_2/\text{SCN}^-} = x < E^\ominus_{\text{Y}_2/\text{Y}^-}$

Y_2	Cl_2	Br_2	I_2
$E^\ominus_{\text{Y}_2/\text{Y}^-}/\text{V}$	+1.36	+1.07	+0.54

Since SCN^- is oxidised by chlorine and bromine but not by iodine, $+0.54 < x < +1.07$
 Ans: **C**

Q10

From information given, rate = $k[P][Q]^2$

For experiment 1, rate₁ = $k[P]_1[Q]_1^2$

For experiment 2, rate₂ = $k[P]_2[Q]_2^2$ -----(1)

Substitute $[P]_2 = 2[P]_1$ and $[Q]_2 = \frac{1}{2}[Q]_1$ in (1)

Rate₂ = $k(2[P]_1)(\frac{1}{2}[Q]_1)^2 = \frac{1}{2} k[P]_1[Q]_1^2 = \frac{1}{2} \text{rate}_1$

The rate of experiment 2 is half that of experiment 1 so the volume of gas produced in 1 minute is half that of experiment 1.

Volume of gas in experiment 2 = $\frac{1}{2} \times 100 = 50 \text{ cm}^3$

Ans: **B**

Q11

Change in pH cannot be used as the reaction is **catalysed** by H^+ , which implies that $[H^+]$ (and hence pH) remains unchanged in the reaction. (Even though ethanoic acid is produced, it remains mostly undissociated in presence of H^+ due to common ion effect so that pH of the reaction mixture remains approximately constant) (**A** is incorrect)

Measuring rate of reaction several times but at a different concentration of ethyl ethanoate each time allows the order of reaction with respect to ethyl ethanoate (but not H^+) to be found. (**B** is incorrect)

Measuring rate of reaction several times but at a different $[H_2SO_4]$ each time allows the order of reaction with respect to H^+ to be found. (**C** is correct)

The removal of samples at various time intervals and titration against standard aq NaOH allows rate of reaction to be found but would not allow the order of reaction with respect to H^+ to be found. (**D** is incorrect)

Ans: **C**

Q12

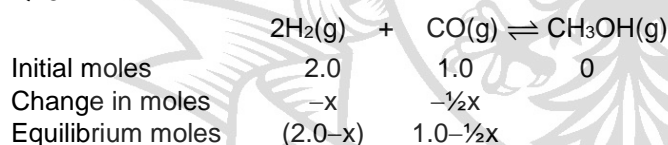
After dilution, the total volume of the dilute nitric acid solution is 100 cm^3 .

$$\text{New } [HNO_3] = \frac{\text{initial vol} \times \text{initial conc}}{\text{final vol}} = \frac{10 \times 0.01}{100} = 0.001 \text{ mol dm}^{-3}$$

Since HNO_3 is a strong acid,

$$[H^+] = [HNO_3] = 0.001 \text{ mol dm}^{-3}, \text{ pH} = -\log [H^+] = 3$$

Ans: **C**

Q13

$$\text{Equilibrium } [CO] = \frac{n_{CO}}{V} = \frac{1.0-x}{0.5}$$

Ans: **B**

Q14

(*Not in syllabus*) Colour of the flame when barium is burned in oxygen is green.

Ans: **B**

Q15

Statements **A**, **C** and **D** are consistent with **Z** being aluminium.

Statement **B** is **not** correct as aluminium has a fixed oxidation state of +3 and does not form a pentachloride with chlorine.

Ans: **B**

Q16

In excess conc. HCl (ligand exchange reaction):



Blue

Yellow

Ans: **D**

Q17

(*Not in syllabus*) In hot $NaOH$ (aq), Cl_2 undergoes disproportionation to Cl^- and ClO_3^- (O.S. of -1 and -5 respectively). Hence the equation:



Ans: **C**

Q18

Charge density of Group 2 cation: Down the group, charge remains at +2, while ionic radii of Group 2 cation increase. Hence, charge density **decreases** down the group (**A** is correct)

Reactivity of Group 2 elements with water involves loss of two valence electrons. Down group 2, the valence electrons are further away from the nucleus and hence are more easily removed. Thus reactivity with water **increases** down the group. (**B** is incorrect)

Solubility of Group 2 oxides in water **increases** down the group. (**C** is incorrect - *Not in syllabus*)

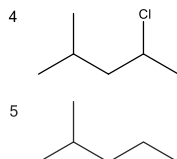
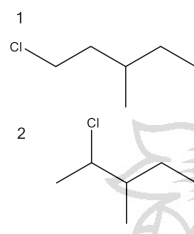
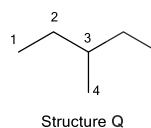
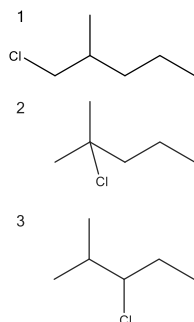
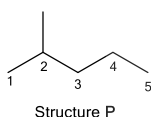
Thermal stability of Group 2 carbonate is dependent on polarising power and hence charge density of the cation. Since charge density and thus polarising power **decreases** down Group 2, thermal stability **increases** down Group 2 (**D** is incorrect).

Ans: **A**

Q19

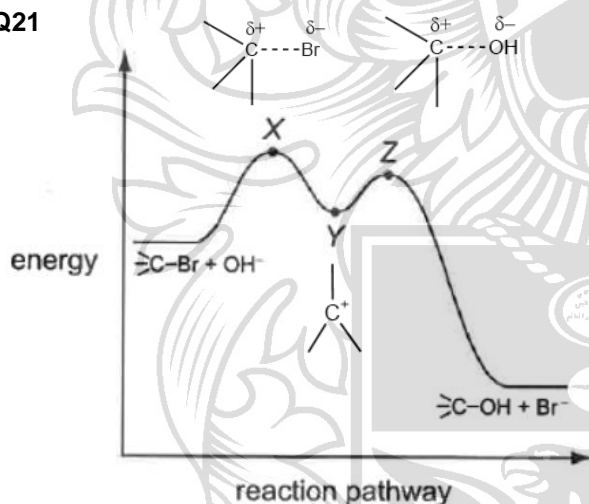
dibasic organic acid	contains 2 $-COOH$ groups
non-cyclic no $C=C$	carbon chain in molecule is <i>aliphatic</i> with a general formula of $-(CH_2)_n-$
M_r of 146	M_r of aliphatic chain $= 146 - 2(12+16+16+1)$ $= 56$ Based on general formula of chain, $M_r = 14n$ Hence, $14n = 56 \Rightarrow n = 4$
	Total number of C atoms = $4 + 2$ (from 2 $-COOH$) = 6
Ans: C	

Q20



Ans: B

Q21



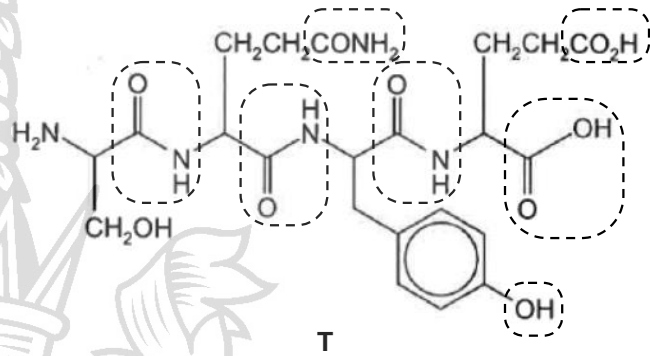
The energy profile diagram showed a 2-step reaction pathway \Rightarrow reaction proceeds via a **S_N1** mechanism.
At position **X** and **Z**: Transition state as shown in diagram above.
At position **Y**: carbocation intermediate
Ans: **A**

Q22

The following functional groups can react with NaOH when heated under reflux:

- Amides (alkaline hydrolysis – 1 mol of NaOH per mol of functional group)
- Carboxylic acids (acid-base reaction)
- Phenols (acid-base reaction)

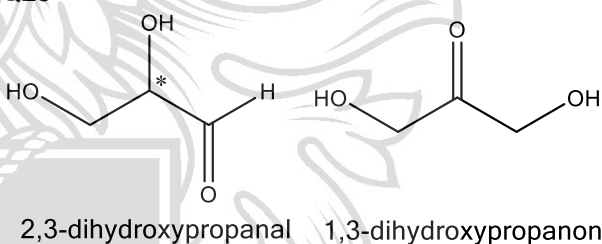
These functional groups are circled as shown below:



Since there are 7 of these functional groups in **T**, 0.1 mol of **T** reacts with 0.7 mol of NaOH completely.

Ans: **D**

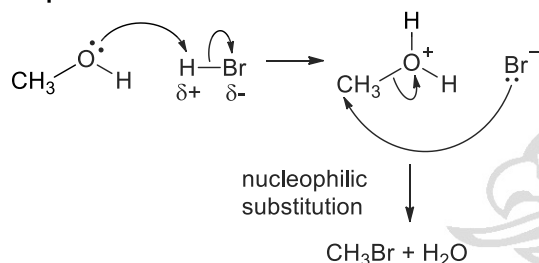
Q23



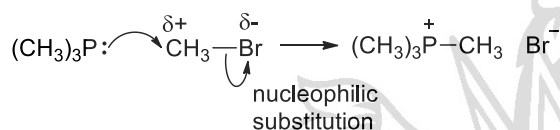
A is incorrect as only 2,3-dihydroxypropanal is chiral.
B is incorrect as only 2,3-dihydroxypropanal gives silver precipitate with Tollens' reagent
C is incorrect as both do not give yellow precipitate with alkaline aqueous iodine
D is correct as both 2,3-dihydroxypropanal and 1,3-dihydroxypropanone have similar empirical formula of C₃H₆O₃
Ans: **D**

Q24

Step 1



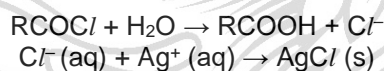
Step 2



Ans: **D**

Q25

Both compounds in **A** and **C** are acid chlorides and will give a white precipitate when shaken with aqueous silver nitrate at room temperature because acid chlorides undergo hydrolysis with water to give carboxylic acids and chloride ions:
i.e.



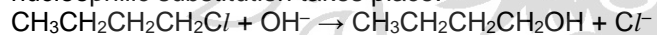
A and **C** are incorrect.

Compound in **B** is a chloroarene and will not give a white precipitate because nucleophilic substitution with OH^- does not take place due to the overlapping unhybridised p-orbital of Cl with the π electron cloud of the benzene ring, resulting in a partial double bond character in the $\text{C}-\text{Cl}$ bond.

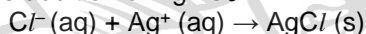


Compound in **D** is a halogenoalkane.

Upon heating 1-chlorobutane with NaOH (aq), nucleophilic substitution takes place:



The free Cl^- ions then form a white ppt of AgCl with Ag^+ upon the addition of AgNO_3 .



Ans: **D**

Q26

ala-gly
lys-ser
ser-gly-ala

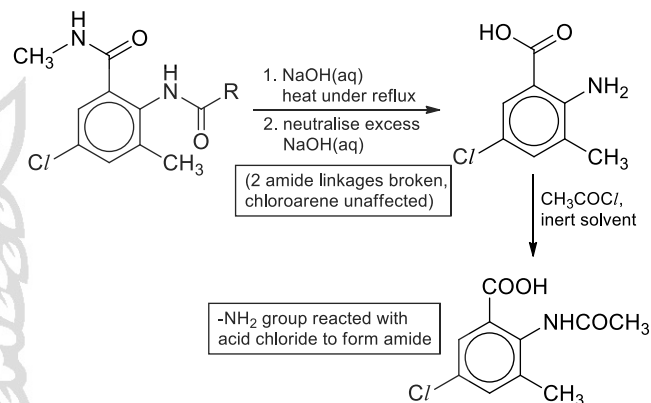
met-ala

gly-lys

met-ala-gly-lys-ser-gly-ala

Ans: **C**

Q27



Ans: **D**

Q28

A: aliphatic aldehyde ($-\text{CH}_2\text{CHO}$) will give a reddish-brown ppt with Fehling's solution

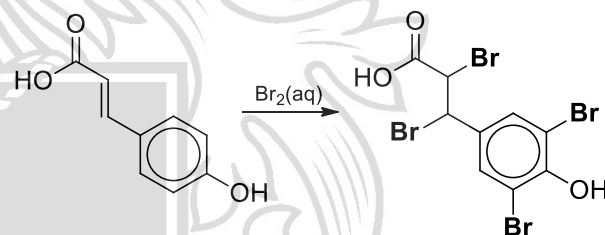
B: alkene ($-\text{CH}=\text{CH}_2$) will decolourise purple KMnO_4

C: phenol (colourless) undergoes acid-base reaction with NaOH (aq) to give the colourless phenoxide (reaction took place with no colour change)

D: phenol will react with nitric acid to form nitrophenol, which is yellow in colour

Ans: **C**

Q29



Alkene and phenol functional groups react with Br_2 (aq) to incorporate **a maximum of 4 bromine atoms**.

Note: the structure drawn is a minor product in which the $\text{C}=\text{C}$ reacts to give the dibromo product, instead of the bromohydrin. Though it is minor, it is still one of the products formed and it gives the **maximum number** of bromine atoms incorporated.

Ans: **B**

Q30

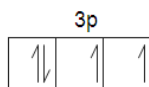
Suggestion 1 is incorrect as the compound does not contain any aliphatic aldehyde group which is necessary to give a ppt with Fehling's solution.

Suggestion 2 is correct as the carbonyl functional group present (ketone) will give an orange ppt with 2,4-DNPH.

Ans: **B**

Q31
 ${}_{16}\text{S} : 1s^2 2s^2 2p^6 3s^2 3p^4$

The sulfur atom at ground state has **2 unpaired e⁻**.



1 Ti: [Ar] $3d^4 4s^2 \Rightarrow$ **2 unpaired electrons**

2 Ni: [Ar] $3d^8 4s^2 \Rightarrow$ **2 unpaired electrons**

3 Co: [Ar] $3d^7 4s^2 \Rightarrow$ 3 unpaired electrons

Options 1 and 2 are correct.

Ans: B

Q32

NH_3 is a weak base and NH_4^+ is its conjugate acid. Hence, they are a conjugate acid/base pair \Rightarrow Statement 1 is **correct**.

NH_3 has a total of 10 electrons (7 from N and 3 from 3H). NH_4^+ also has a total of 10 electrons (7 from N and 3 from 3H and 0 from 1 H^+). \Rightarrow Statement 2 is **correct**.

NH_3 can act as a ligand but NH_4^+ cannot act as a ligand as there is no available lone pair of electrons on N for donation.

(NH_4^+ is formed by NH_3 forming a dative bond with H^+)

\Rightarrow Statement 3 is **incorrect**.

Ans: B

Q33

Solubility of a Group 2 sulfate, MSO_4 , is affected by its enthalpy change of solution, $\Delta H_{\text{soln}}[\text{MSO}_4(\text{s})]$.

In general, the more exothermic the $\Delta H_{\text{soln}}[\text{MSO}_4(\text{s})]$, the greater is the solubility of MSO_4 .

$\Delta H_{\text{soln}} = \Delta H_{\text{hyd}} - \text{LE}$

Since ΔH_{soln} is dependent on hydration energies of $\text{M}^{2+}(\text{g})$ and $\text{SO}_4^{2-}(\text{g})$ and LE of $\text{MSO}_4(\text{s})$, factors 1 and 2 are correct.

Factor 3 is incorrect as MSO_4 already contains M^{2+} so that 1st and 2nd IE of M does not affect $\Delta H_{\text{soln}}[\text{MSO}_4(\text{s})]$.

Ans: B

Q34

Label 1 is **not correct** as a temperature of 298 K (25°C) is required, not 273 K (0°C).

Label 2 is **not correct** as $1.00 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ gives $[\text{H}^+] = 2.00 \text{ mol dm}^{-3}$ instead of $[\text{H}^+] = 1.00 \text{ mol dm}^{-3}$.

Label 3 is correct.

Recall: A standard hydrogen electrode consists of

- a **platinum electrode** coated with finely divided platinum (called platinum black),
- immersed in an aqueous solution of H^+ where $[\text{H}^+] = 1 \text{ mol dm}^{-3}$,
- with hydrogen gas bubbling in at a pressure of **1 bar**,
- at a temperature of **298 K (25 °C)**.

Ans: B

Q35

Scandium only forms Sc^{3+} , which has an electronic configuration of [Ar], having no partially filled 3d orbitals.

Statement 1 is **correct** as scandium, a metal which is the first of the 3d block of elements, forms ionic chlorides.

Statement 2 is incorrect as scandium only forms ions with +3 oxidation state.

Statement 3 is incorrect as Sc^{3+} , with no partially filled 3d orbitals, is not coloured.

Ans: D

Q36

Atomic number 33

\Rightarrow Belongs to group 15

\Rightarrow Similar properties to phosphorus, P

Since P forms chloride with formula PCl_5 , X is expected to form a chloride with formula $\text{XCl}_5 \Rightarrow$ statement 1 is correct

Since P forms oxide with formula P_4O_6 , X is expected to form an oxide X_2O_3 (same empirical formula to oxide of P) \Rightarrow statement 2 is correct

(Reaction of P_4O_6 with water/NaOH is not in syllabus)

Since oxides of P are acidic, oxide of X is expected to be acidic and react with alkali to form salt \Rightarrow statement 3 is correct

Ans: A

Q37

Alkyl halide undergoes nucleophilic substitution with NH_3 in ethanol to give the corresponding amine. \Rightarrow 1 is correct

Alkyl halide undergoes nucleophilic substitution with CN^- in ethanol to form the corresponding nitrile \Rightarrow 2 is correct

Alkyl halide undergoes elimination with NaOH in ethanol to give an alkene. The product shown in 3 is the correct elimination product of the reactant given \Rightarrow 3 is correct

Ans: A

Q38

Cars are fitted with reaction catalytic converters in the exhaust system to remove three main pollutants:

Pollutants		Less harmful products
CO	$\xrightarrow{\text{converted to}}$	CO_2
unburnt hydrocarbons		CO_2 and H_2O
NO_x		N_2

Reactions 1 and 2 occur. Reaction 3 does not occur as, in a catalytic converter, CO_2 should not be converted CO and NO should be reduced to N_2 , not oxidised to NO_2 .

Ans: B

Q39

(Not in syllabus)

Primary structure is the sequence of amino acids held together by peptide bonds, not hydrogen bonds

⇒ **1** is incorrect

Secondary structures are usually the alpha-helices or beta-pleated sheets which are stabilised by hydrogen bonds.

⇒ **2** is correct

The tertiary structure is the 3D arrangement of protein due to R-group interactions, one of which is hydrogen bonding.

⇒ **3** is correct

Ans: **C**

Q40

Formula of E: $C_{12}H_{10}N_2O_2$

Formula of F: $C_{12}H_{10}N_2O_2$

Formula of G: C_6H_5NO

The molecular formula of E is $(C_6H_5NO)_2$, hence E and G have the same empirical formula ⇒ **1** is correct

Isomers have the same molecular formula but different arrangement of atoms. Hence, E and F are isomers ⇒ **2** is correct

The molecular formula of F is $(C_6H_5NO)_2$, hence the M_r is twice that of G ⇒ **3** is correct

Ans: **A**

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Suggested Solutions to 2014 H2 Chemistry
Paper 2 (9647/02)



(b) Pre-calculations

Assuming that 20.00 cm^3 of $\text{Ba}(\text{OH})_2$ was used,

$$\text{Amt of OH}^- = \frac{20}{1000} \times 1.00 \times 2$$

$$= 0.04 \text{ mol}$$

Amt of HNO_3 used = 0.04 mol

Assuming $[\text{HNO}_3] = 1.5 \text{ mol dm}^{-3}$,
 volume of HNO_3 required

$$= \frac{0.04}{1.5} = 26.67 \text{ cm}^3$$

(Since extrapolation is required, aim for ≥ 5 points before and after peak to allow for good extrapolation.)

The use of 5 cm^3 portions will allow ~ 5 points before the peak and ending at 50.00 cm^3 will allow ~ 5 points after the peak)

Thus, HNO_3 will be added in 5.00 cm^3 portions until 50.00 cm^3 has been added.

Procedure

- Using a 50.00 cm^3 burette, transfer 20.00 cm^3 of $\text{Ba}(\text{OH})_2$ into a polystyrene cup, supported in a 250 cm^3 beaker.
- Place a thermometer (with divisions of $0.2 \text{ }^\circ\text{C}$) into the polystyrene cup and measure the initial steady temperature of the $\text{Ba}(\text{OH})_2$ solution in the cup.
- Fill a separate 50.00 cm^3 burette with HNO_3 and place the polystyrene cup with the beaker under the burette.
- Add 5.00 cm^3 of HNO_3 from the burette into the polystyrene cup. Stir the mixture with the thermometer. Measure and record the maximum temperature rise, T_{max} , attained and record it in the following table.

Volume of HNO_3 added / cm^3	Total volume of HNO_3 added / cm^3	T_{max} / $^\circ\text{C}$
--	0.00	
5.00	5.00	
5.00	10.00	
5.00	15.00	
5.00	20.00	
5.00	25.00	
5.00	30.00	
5.00	35.00	
5.00	40.00	
5.00	45.00	
5.00	50.00	

5. Repeat step 4 until a total of 50.00 cm^3 of HNO_3 has been added.

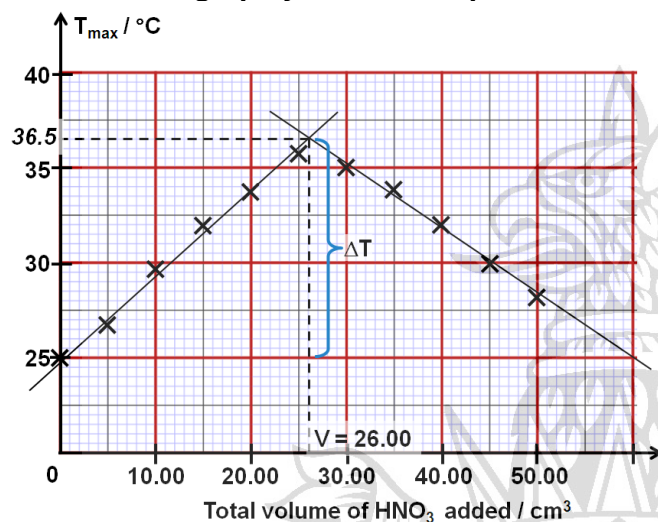
6. Plot a graph of $T_{\text{max}} / ^\circ\text{C}$ against volume of $\text{HNO}_3 / \text{cm}^3$. Draw best-fit lines for the points before and after the maximum T_{max} has been reached and extend them until they intersect. The point at which the two best-fit lines meet corresponds to the volume of HNO_3 required for neutralisation and the maximum T_{max} .

How you would recognise that the equivalence-point has been passed

Neutralisation is an exothermic reaction and the maximum temperature is reached at the end-point.

If equivalence point has been passed, the temperature will decrease as no further reaction will take place and the further addition of acid distributes the heat evolved over a larger volume of liquid.

Sketch of the graph you would expect



Note the following:

1. In reality, the points would look like they form a curve.
2. A grid was provided, therefore
 - rough plots (X) must be drawn on the grid
 - axes on your graph should show values of T and volumes consistent with your own plan (e.g. one "X" every 5 cm³)
3. Temperature change (from initial T to highest T) is given to be 10–12 °C in the question. The temperature difference (ΔT)
 - must be shown on your plot,
 - between initial T and highest T should be 10–12 °C (11.5 °C in the diagram shown above).

An explanation of the shape of your graph

Between 0.00 cm³ to 26.00 cm³ of HNO₃ added: Ba(OH)₂ is in excess while HNO₃ is limiting. As more HNO₃ is added, more Ba(OH)₂ is reacted, more heat is given off and the temperature rises.

From 26.00 cm³ to 50.00 cm³ of HNO₃ added: HNO₃ is in excess and Ba(OH)₂ has been completely reacted. No further reaction takes place with the addition of more HNO₃, hence no additional heat is given off. The addition of HNO₃ distributes the energy released from the reaction over a larger volume, causing the temperature to decrease.

Treatment of data to find [HNO₃] and value of ΔH_n

Let V cm³ be the volume of HNO₃ required to reach end-point and T °C be the corresponding maximum temperature rise obtained. Assuming initial T was 25 °C.

Amt of OH⁻ = 0.04 mol (from pre-calculations)

Amt of HNO₃ to neutralise Ba(OH)₂

= 0.04 mol

$$[\text{HNO}_3] = \frac{0.04}{\frac{V}{1000}} = \frac{40}{V} \text{ mol dm}^{-3}$$

$$\text{Heat evolved} = (V+20)(4.18)(36.5-25) \text{ J}$$

$$\Delta H_{\text{neut}} = \frac{(V+20)(4.18)(36.5-25)}{0.04 \times 1000}$$

$$= (1.20V + 23.0) \text{ kJ mol}^{-1}$$

(c) The maximum temp rise will remain unchanged.

Heat released = Total volume of solution x specific heat capacity x temp change

When the volume of each solution used is doubled, the number of moles of water formed will double and the heat released will also be doubled. However, the total volume of solution is doubled too. So, the maximum temperature change is thus the same.

OR

$$\Delta H_{\text{neut}} = \frac{mc\Delta T}{n_{\text{H}_2\text{O}}}$$

$$\Rightarrow \Delta T = \left(\frac{\Delta H_{\text{neut}}}{c} \right) \left(\frac{n_{\text{H}_2\text{O}}}{m} \right)$$

c is a constant and the value of ΔH_{neut} for this reaction has a fixed value. Hence, $\left(\frac{\Delta H_{\text{neut}}}{c} \right)$ is a constant.

When the volume of each solution used is doubled,

- $n_{\text{H}_2\text{O}}$ is doubled (as double the water is produced with double the reactants)
- total mass (m) of the solution will be doubled.

$$\Rightarrow \frac{n_{\text{H}_2\text{O}}}{m} \text{ is also a constant.}$$

Hence, ΔT remains unchanged

Question 2

(a)(i) Mg^{2+} and SO_4^{2-}

(a)(ii) Fe^{2+} , Mn^{2+} , Cu^{2+} (common mistake: Zn^{2+} is not a transition metal ion)

(b) $[\text{H}^+]$ in normal seawater
 $= 10^{-7.8} = 1.58 \times 10^{-8} \text{ mol dm}^{-3}$

$[\text{H}^+]$ in hydrothermal vent water
 $= 10^{-4.3} = 5.01 \times 10^{-5} \text{ mol dm}^{-3}$

(c) $10\text{H}^+ + 8\text{e}^- + \text{SO}_4^{2-} \longrightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$

(d)(i) oxidised: sulfur
 reduced: hydrogen

(d)(ii) $\left[\begin{array}{c} \cdot \cdot \\ \cdot \cdot \end{array} \text{S} \times \begin{array}{c} \times \times \\ \times \times \end{array} \right]^{2-}$

(iii) Electronic configuration of Fe^{2+} : $[\text{Ar}]3\text{d}^6$
 The presence of ligands causes the splitting of the originally degenerate five 3d orbitals in Fe^{2+} into two sets of slightly different energy levels.

Since the 3d subshell in Fe^{2+} are partially filled, electrons from the lower-energy d orbitals can get promoted to the higher-energy d orbitals (d-d transitions) with the absorption of energy corresponding to certain wavelengths from the visible spectrum.

The yellow colour observed is the complement of the colour absorbed, violet.

(e)(i) Relative atomic mass is defined as the **average mass** of one atom of the element divided by 1/12 of the mass of an atom of the ^{12}C isotope.

(e)(ii) Let proportion of ^3He in the mixture be x.
 4.0025959

$$= x(3.0160293) + (1-x)(4.0026033)$$

Solving for x,

$$x = 0.00000750$$

$$\text{percentage of } ^3\text{He} = 7.50 \times 10^{-4} \%$$

OR

Let percentage of ^3He in the mixture be x.

$$(100)(4.0025959)$$

$$= x(3.0160293) + (100-x)(4.0026033)$$

$$\Rightarrow x = 0.000750$$

$$\text{Percentage of } ^3\text{He} = 7.50 \times 10^{-4} \%$$

Question 3

3 (a) $pV = nRT$
 $n/V = p/RT$
 $[\text{CO}_2] = 250 \times 10^3 / (8.31)(298)$
 $= 100.95 \text{ mol m}^{-3} = 0.101 \text{ mol dm}^{-3}$

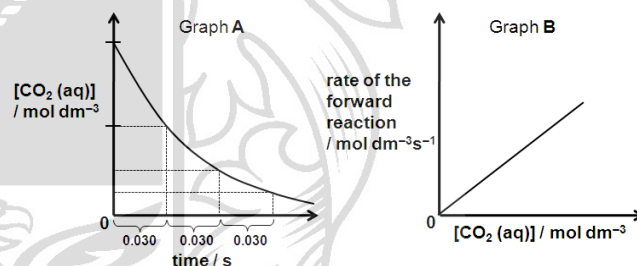
(b)(i) $K_c = [\text{H}_2\text{CO}_3] / [\text{CO}_2]$
 $[\text{H}_2\text{CO}_3] = K_c[\text{CO}_2] = 1.70 \times 10^{-3} \times 0.084$
 $= 1.43 \times 10^{-4} \text{ mol dm}^{-3}$

(ii) When the bottle is opened, the gas pressure is decreased to atmospheric pressure (101.325 kPa). Thus, position of eqm 1 shifts to the left to produce more $\text{CO}_2(\text{g})$, which causes $[\text{CO}_2(\text{aq})]$ to decrease.

This in turn causes position of eqm 2 to shift to the left to produce more $\text{CO}_2(\text{aq})$, causing $[\text{H}_2\text{CO}_3(\text{aq})]$ to decrease.

The decrease in $[\text{H}_2\text{CO}_3(\text{aq})]$ causes position of eqm 3 to shift to the left to produce more $\text{H}_2\text{CO}_3(\text{aq})$, which reduces $[\text{H}^+(\text{aq})]$, thereby causing the pH to increase.

(c)(i)



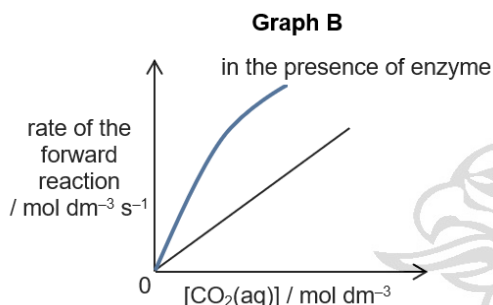
(ii) $k = \ln 2 / 0.030 = 23.1 \text{ s}^{-1}$
 units = s^{-1}

(iii) $0 \rightarrow 50 \rightarrow 75 \rightarrow 87.5 \rightarrow 93.75 \rightarrow 96.875$
 $\rightarrow 98.4375 \rightarrow 99.21875$

7 half-lives are required for carbonic acid to reach 99% of its equilibrium conc.

$$\text{Time taken} \approx 7 \times 0.030 = 0.210 \text{ s}$$

(d)(i)



- (ii) At low concentrations of CO_2 , the active sites on the surface of the enzyme catalyst are not saturated with CO_2 molecules. As the reaction is sped up by the presence of the enzyme, the gradient of the line representing the enzyme-catalysed reaction is greater than the gradient of the line representing the uncatalysed reaction.

At moderate or high concentrations of CO_2 , most, if not all, of the active sites present on the surface of the enzyme are taken up by CO_2 molecules. As the enzyme is saturated with CO_2 , the gradient of the line representing the enzyme-catalysed reaction is now slightly smaller.

[Note: The rate of the enzyme-catalysed reaction (even when the enzyme is saturated) is greater than the rate of the uncatalysed reaction.]

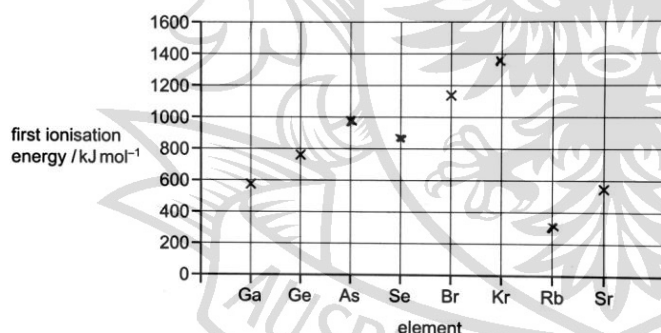
- (b) The first ionisation energy of As is higher than that of Ge because As has one more proton and hence has a **higher nuclear charge** than Ge. Though As also has one more electron than Ge, the **increase in shielding effect is minimal** since this additional electron occupies the outermost shell. Consequently, the valence electrons in As experience a **higher effective nuclear charge** and are more strongly attracted by the nucleus.

The first ionisation energy of As is **higher** than that of Se. In this case, the valence electron to be removed from As is an **unpaired electron** while that to be removed from Se is a **paired electron**. The paired electron in Se experiences inter-electron **repulsion**, which facilitates its removal and hence requires less energy for ionisation.

The first ionisation energy of Kr is higher than that of Br for the same reason given above (as to why the first ionisation energy of As is higher than that of Ge).

The first ionisation energy of Kr is higher than that of Rb. In this case, Rb has a **greater number of electron shells** than Kr. Hence, the **distance between Rb's nucleus and valence (5s) electron is greater** than that between Kr's nucleus and valence (4p) electron. Consequently, the 4p electron in Kr is **more strongly attracted** by the nucleus and requires **more energy** to be removed compared to the 5s electron in Rb.

4 (a)



5 5(a) $\text{C}_6\text{H}_5\text{NO}_2 + 6[\text{H}] \longrightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}$

- (b) The reaction takes place under highly acidic conditions, forming $\text{C}_6\text{H}_5\text{NH}_3^+$ as the product. By making the solution alkaline, $\text{C}_6\text{H}_5\text{NH}_3^+$ reacts with the OH^- present to liberate phenylamine.

- (c) Amt of nitrobenzene used
= $4.84/123$
= 0.0393 mol

Amt of phenylamine produced
= $2.64/93$
= 0.0284 mol

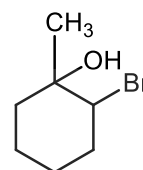
Percentage yield
= $(0.0284/0.0393) \times 100\%$
= 72.2%

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- (d) Add $\text{Br}_2(\text{aq})$ to the mixture at room temperature.

There would be decolourisation of orange $\text{Br}_2(\text{aq})$ and the formation of a white precipitate, indicating the presence of phenylamine in the mixture.

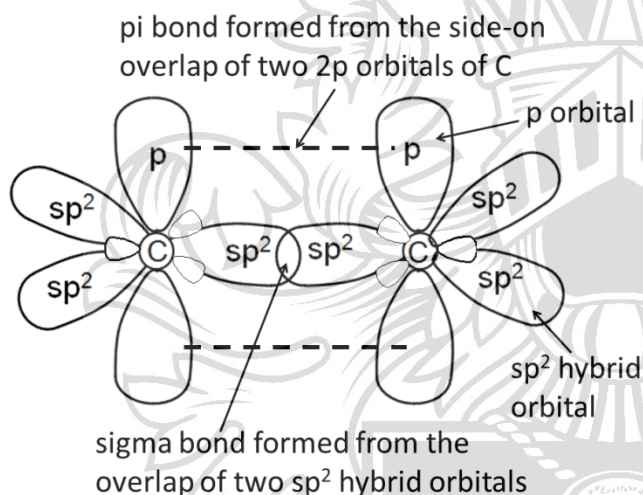
(c)



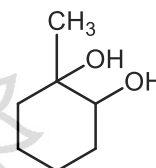
The organic compound is formed from the attack of the **lone pair electrons on O atom** in H_2O which **acts as a nucleophile** on the carbocation formed in the slow step.

- 6 (a) (Students need to understand the requirements of the question carefully. Most students simply drew sp^2 hybrid orbitals which was insufficient, given the requirements of the question)

Type of hybridisation involved is sp^2 hybridization.

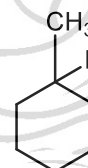


(d)(i)



Step 1: $\text{KMnO}_4(\text{aq})$, $\text{NaOH}(\text{aq})$, cold
Step 2: $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat under reflux

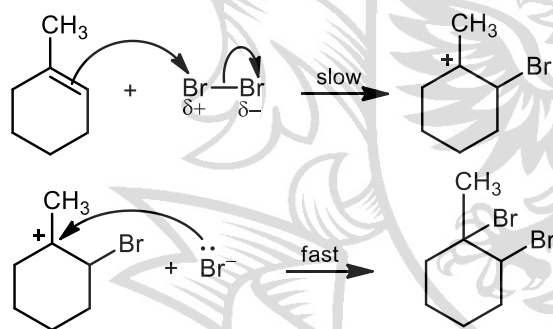
(d)(ii)



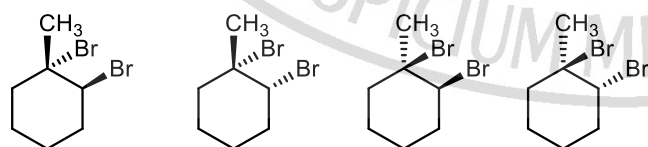
Step 1: $\text{HBr}(\text{g})$
Step 2: excess concentrated NH_3 in ethanol, heat in a sealed tube

(b)(i)

Electrophilic addition



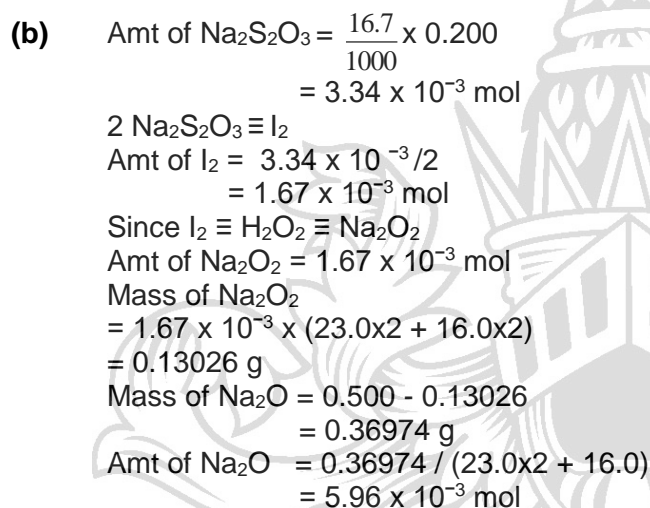
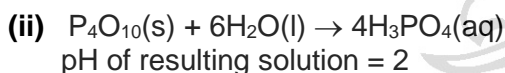
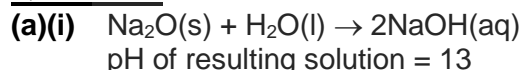
(b)(ii) 2 chiral centres in product \Rightarrow 4 isomers



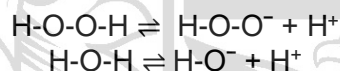
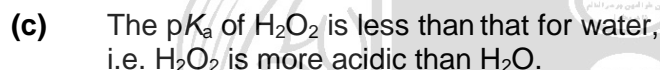
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Suggested Solutions to 2014 H2 Chemistry
Paper 3 (9647/03)

Question 1



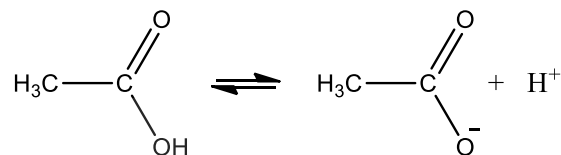
moles of Na_2O / moles of Na_2O_2
 $= 5.96 \times 10^{-3} / 1.67 \times 10^{-3} = 3.57$ (Ans)



The more stable the conjugate base, the stronger the acid.

The electron withdrawing $-\text{OH}$ group bonded to O atom **decreases** the electron density of the negative charge on the $-\text{O}^-$ atom and **disperses** the negative charge on the HOO^- anion to a greater extent. Hence, the HOO^- anion is more stable than HO^- anion and H_2O_2 is more acidic than H_2O . Hence H_2O_2 has a lower $\text{p}K_a$ than water.

The $\text{p}K_a$ of $\text{CH}_3\text{CO}_3\text{H}$ is more than that for $\text{CH}_3\text{CO}_2\text{H}$, i.e. $\text{CH}_3\text{CO}_3\text{H}$ is less acidic than $\text{CH}_3\text{CO}_2\text{H}$.

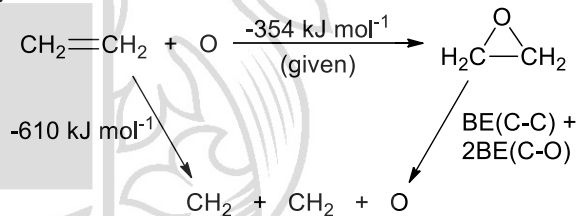


CH_3COO^- forms 2 equivalent resonance structures with delocalisation of the negative charge over 2 highly electronegative O atoms (resonance effect) and hence the conjugate base of $\text{CH}_3\text{CO}_2\text{H}$ is resonance stabilised.

CH_3COOO^- is not stabilised by resonance as the negative charge on O atom cannot be delocalised over the $\text{C}=\text{O}$ group due to the presence of the additional O atom. Hence, it is only stabilised by a weaker electron-withdrawing inductive effect of the CH_3COO^- group. Hence, the CH_3COO^- is more stable than CH_3COOO^- and $\text{CH}_3\text{CO}_2\text{H}$ is a stronger acid than $\text{CH}_3\text{CO}_3\text{H}$. Thus, the $\text{p}K_a$ of $\text{CH}_3\text{CO}_3\text{H}$ is more than that for $\text{CH}_3\text{CO}_2\text{H}$.

(d)(i) $350 + 2(360) = +1070 \text{ kJ mol}^{-1}$

(d)(ii)



$$-354 = 610 - \text{BE}(\text{C}-\text{C} + 2\text{xC}-\text{O})$$

(Assuming that C-H bond energy is the same in ethene and epoxyethane.)

$$\text{BE}(\text{C}-\text{C} + 2\text{xC}-\text{O}) = 610 + 354$$

$$= +964 \text{ kJ mol}^{-1}$$

The actual value of bond energies is smaller than the theoretical value.

In the 3-membered ring, the $\text{C}-\text{O}-\text{C}$ and $\text{O}-\text{C}-\text{C}$ bond angles are about 60° , deviating from the ideal bond angles of 105° and 109.5° respectively.

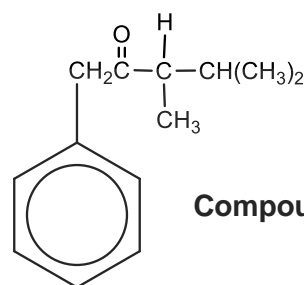
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The smaller-than-ideal bond angles increase the bond pair–bond pair repulsions between the C–C and C–O bonds in the ring, causing it to be less stable.

OR

The smaller-than-ideal bond angles cause the overlap between the orbitals to be less effective, resulting in a weaker bond and smaller bond energies.

(e)(vi)

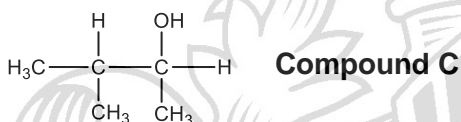


Compound A

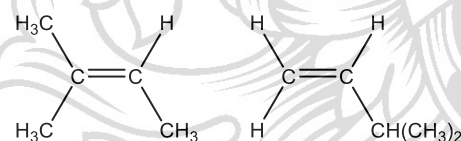
Question 2

(a)

(e)(i)



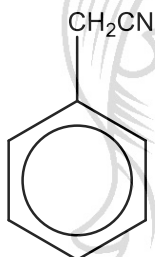
Compound C



alkenes E and F

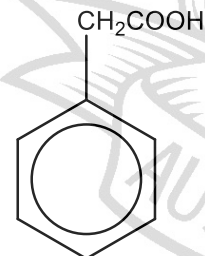
(e)(ii) Reaction I: limiting Cl_2 , uv

(e)(iii)



Compound G

(e)(iv)

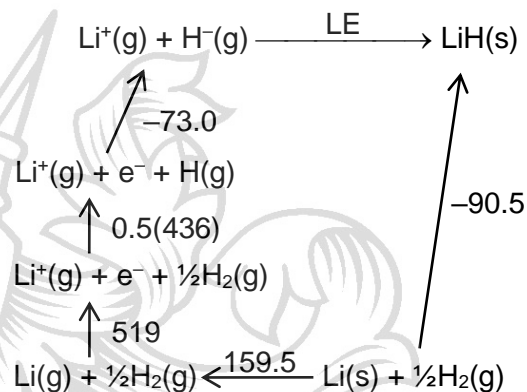


Compound D

(e)(v) Reaction II: NaCN in aq ethanol, heat
Reaction III: $\text{HCl(aq)} / \text{H}_2\text{SO}_4\text{(aq)}$, heat

(c)(ii) Oxidation number of H in LiA/H_4 is -1 .
Oxidation number of A in $\text{Li}_3\text{A/H}_6$ is $+3$.

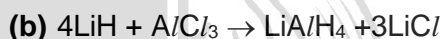
(c)(iii) The shape of A/H_6^{3-} is **octahedral**.



By Hess' Law,

$$\text{LE}[\text{LiH}] = 73.0 - \frac{1}{2}(436) - 519 - 159.5 - 90.5$$

$$\text{LE}[\text{LiH}] = -914 \text{ kJ mol}^{-1}$$



$$\Delta H_{\text{rxn}} = \sum \Delta H_f(\text{pdt}) - \sum \Delta H_f(\text{rxt})$$

$$= \Delta H_f[\text{LiAlH}_4] + 3\Delta H_f[\text{LiCl}] - \{4\Delta H_f[\text{LiH}] + \Delta H_f[\text{AlCl}_3]\}$$

$$\Rightarrow -276 = \Delta H_f[\text{LiAlH}_4] + 3(-408.5) - 4(-90.5) - (-704)$$

$$\Delta H_f[\text{LiAlH}_4] = -116.5 \text{ kJ mol}^{-1}$$

(c)(i) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$$\Delta S^\ominus = (\Delta H^\ominus - \Delta G^\ominus)/T$$

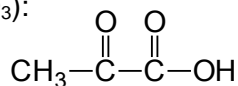
$$= [3.46 - (-27.68)]/298$$

$$= +0.104 \text{ kJ K}^{-1}\text{mol}^{-1}$$

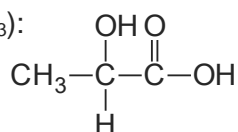
$$= +104 \text{ J K}^{-1}\text{mol}^{-1}$$

The sign of the entropy change is positive and is consistent with the increase in disorder of the system as there is an increase in number of gaseous particles after the reaction, i.e. 3 mol of gaseous H_2 are produced and no gaseous molecules are used up in the reaction.

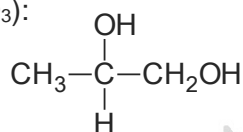
(d)(i) H (C₃H₄O₃):



J (C₃H₆O₃):

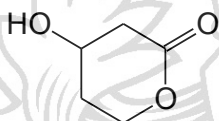


K (C₃H₈O₃):

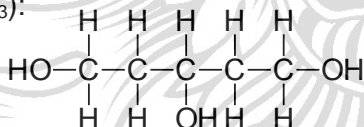


Note: NaBH₄ only reduces carbonyl group to alcohol, but LiAlH₄ reduces both carbonyl and carboxylic acid to alcohol.

(d)(ii) L (C₅H₈O₃):



M (C₅H₁₂O₃):



(Remember to check the molecular formula of your proposed structure against the given one.)

(d)(iii) L is chiral as there are 4 different groups attached to the C bearing –OH group and it has no plane of symmetry in its structure (the carbon at which the –OH group is attached is chiral).

M is non-chiral due to the presence of plane of symmetry in its structure (no chiral C present in M).

(e)(i) Reaction of LiAlH₄ with H₂O:



Reaction of mixture with dilute acid:

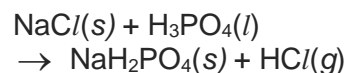
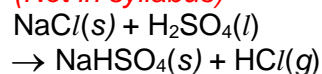


$$(e)(ii) \quad n_{\text{LiAlH}_4} = \frac{2.00}{6.9 + 27.0 + 4 \times 1.0} = 0.05277 \text{ mol}$$

$$n_{\text{H}_2} = 4 n_{\text{LiAlH}_4} = 0.2111 \text{ mol}$$

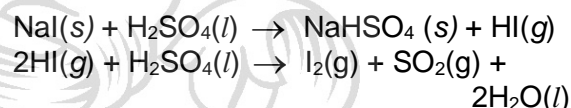
$$\text{At rtp, } V_{\text{H}_2} = 0.2111 \times 24.0 = 5.07 \text{ dm}^3$$

3(a) *(Not in syllabus)*



Pure hydrogen chloride can be made because both H₃PO₄ and H₂SO₄ are not sufficiently strong to oxidise HCl.

H₂SO₄ is a stronger oxidising agent than H₃PO₄. HI can only be prepared with phosphoric acid because it does not oxidise I[–] while sulfuric acid oxidises I[–]. This difference in reactivity also reflects the greater ease of oxidation of I[–] relative to Cl[–].



(b)(i) PCl₃ is prepared by passing excess dry chlorine gas into a sample of phosphorus heated above its melting point.

PCl₃ is purified by simple distillation where PCl₃ collected at 76 °C. (At that temperature, any PCl₅ remains as a solid.)

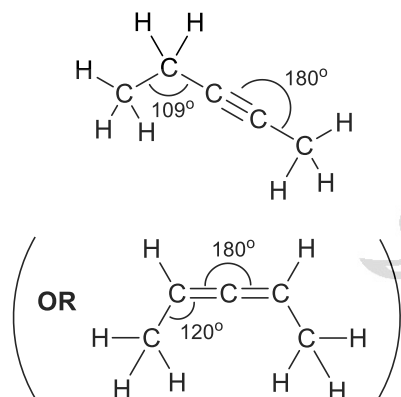
(b)(ii) *(Not in syllabus)* PCl₃ reacts violently with water in an exothermic reaction to produce dense white fumes of hydrogen chloride gas (HCl) and phosphorous acid (H₃PO₃).



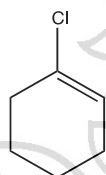
(c)(i) POC_l₃

(c)(ii) CH₃C≡CCH₂CH₃ (or CH₃CH=C=CHCH₃)

(c)(iii)



(c)(iv)



The loss of both Cl atoms does not occur as this will result in the formation of a C≡C bond in a six-membered ring with 2 bond angles of 180° in the linear C-C≡C-C unit. There is severe strain caused in this ring structure and hence the product cannot be formed.

(d)(i)

	P	N	Cl
% by mass	20.5	9.2	70.3
Amt	0.661	0.657	1.980
Ratio	1	1	3

Empirical formula of **S** : PNC_l₃

Molecular formula of **S** : P₂N₂Cl₆

Structural formula of **S** : Cl₃P=N-N=PCl₃

(d)(ii)

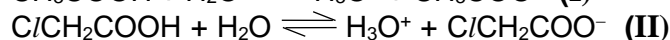
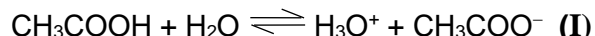


(d)(iii) (H₂N)₃P=N-N=P(NH₂)₃

Question 4

(a)(i)

The acidity of a compound depends on the relative stability of its conjugate base anion. The more stable the conjugate base, the more acidic the compound will be.



The electron-withdrawing Cl group in ClCH₂COO⁻ **decreases** the electron density of the negative charge on the O atom, dispersing the negative charge in ClCH₂COO⁻ to a greater extent than in CH₃COO⁻, hence stabilising the ClCH₂COO⁻ ion to a greater extent.

The position of equilibrium in **(II)** lies further to the right than **(I)** so K_a of ClCH₂COOH is greater than K_a of CH₃COOH, i.e. pK_a(ClCH₂COOH) < pK_a(CH₃COOH).

(a)(ii)

$$\text{pH} = \text{pK}_a + \lg([\text{anion}]/[\text{acid}])$$

$$\lg([\text{anion}]/[\text{acid}]) = \text{pH} - \text{pK}_a$$

$$[\text{anion}]/[\text{acid}] = 10^{(\text{pH} - \text{pK}_a)}$$

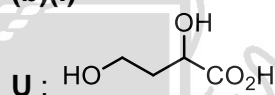
For CH₃COOH,

$$[\text{anion}]/[\text{acid}] = 10^{(3.8 - 4.76)} = 0.110$$

For ClCH₂COOH,

$$[\text{anion}]/[\text{acid}] = 10^{(3.8 - 2.87)} = 8.51$$

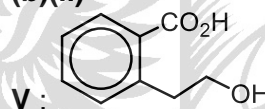
(b)(i)



Step 1: HCl(aq) / H₂SO₄(aq), heat with reflux

Step 2: KMnO₄ (aq), H₂SO₄(aq), heat under reflux

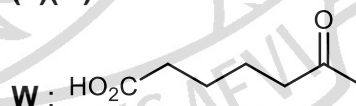
(b)(ii)



Step 1: HCl(aq) / H₂SO₄(aq), heat with reflux

Step 2: KMnO₄ (aq), H₂SO₄(aq), heat under reflux

(b)(iii)

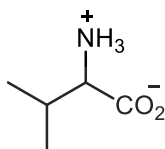


Step 1: KMnO₄ (aq), H₂SO₄(aq), heat under reflux

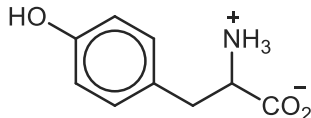
Step 2: I₂(aq), NaOH(aq)/ warm, followed by

HCl(aq) / H₂SO₄(aq)

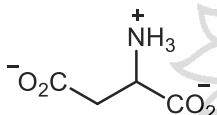
(c)(i)



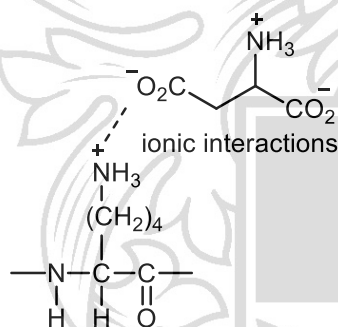
(c)(ii)



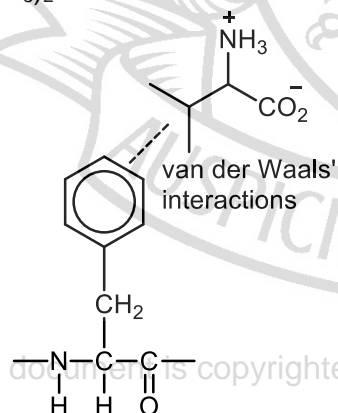
(c)(iii)



(d)(i) *(Not in syllabus)* The amino acid residue will interact with the side chain of aspartic acid via ionic interactions between the -NH_3^+ of amino acid residue and $\text{-O}_2\text{C-}$ of the side chain of aspartic acid.



(d)(ii) *(Not in syllabus)* The amino acid residue will interact with the side chain of valine via van der Waals' interactions between the $\text{-CH}_2\text{-C}_6\text{H}_5$ of amino acid residue and $(\text{CH}_3)_2\text{CH-}$ of the side chain of valine.

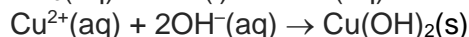
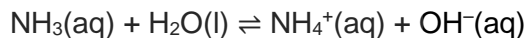


Question 5

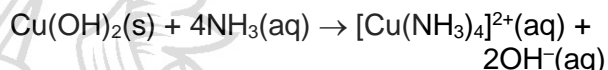
(a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

(b) When $\text{NH}_3(\text{aq})$ is slowly added to $\text{Cu}^{2+}(\text{aq})$, a pale blue ppt of $\text{Cu}(\text{OH})_2(\text{s})$ is formed.



When excess $\text{NH}_3(\text{aq})$ is added, the pale blue ppt dissolves to give a deep blue solution containing the complex, $[\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq})$.



(c) (i) $E^\ominus_{\text{cell}} = E^\ominus_{\text{cat}} - E^\ominus_{\text{anode}}$
 $= +0.34 - (-0.25) = +0.59 \text{ V}$

(ii) $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$ $E^\ominus = -0.25 \text{ V}$
When $[\text{Ni}^{2+}]$ decreases, according to Le Chatelier's Principle, the position of above eqm will shift to the left to increase $[\text{Ni}^{2+}]$ making $E(\text{Ni}^{2+}/\text{Ni})$ more negative. Hence, since $E_{\text{cell}} = E(\text{Cu}^{2+}/\text{Cu}) - E^\ominus(\text{Ni}^{2+}/\text{Ni})$, E_{cell} will become more positive, i.e. greater than +0.59V.

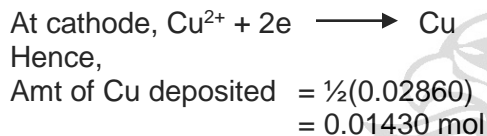
(d) $E^\ominus(\text{Ag}^+/\text{Ag}) = +0.80 \text{ V}$
 $E^\ominus(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$
 $E^\ominus(\text{Ni}^{2+}/\text{Ni}) = -0.25 \text{ V}$

At the anode, since the $E^\ominus(\text{Ni}^{2+}/\text{Ni})$ is less positive than $E^\ominus(\text{Cu}^{2+}/\text{Cu})$, Ni is preferentially oxidised and goes into the solution (as Ni^{2+} ions) first, followed by Cu.

However, since the $E^\ominus(\text{Ag}^+/\text{Ag})$ is more positive than $E^\ominus(\text{Cu}^{2+}/\text{Cu})$, Ag impurities will not be oxidised and they fall to the bottom as 'sludge'.

At the cathode, the Ni^{2+} ions are not reduced to form Ni metal since $E^\ominus(\text{Ni}^{2+}/\text{Ni})$ is negative and is less easily reduced than Cu^{2+} which has a positive value of $E^\ominus(\text{Cu}^{2+}/\text{Cu})$. Hence, nickel remains in solution as $\text{Ni}^{2+}(\text{aq})$.

(e) (i) $Q = It = nF$
 $n = It / F$
 $= (2.00)(23)(60) / 96500$
 $= 0.02860 \text{ mol}$



Expected increase in mass of cathode
 $= \text{Mass of Cu deposited}$
 $= 0.01430 \times 63.5 = \mathbf{0.908 \text{ g}}$

(ii) Actual mass of Ag deposited = **0.0500 g**

Molar mass of $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$
 $= 288.7 \text{ g mol}^{-1}$
Amt of $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2 = \text{Amt of Ni}^{2+}$
 $= \text{Amt of Ni} = 0.492 / 288.7$
 $= 1.704 \times 10^{-3} \text{ mol}$

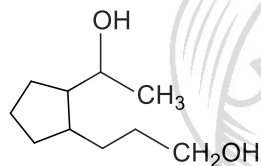
Actual mass of Ni removed from alloy
 $= 1.704 \times 10^{-3} \times 58.7 = \mathbf{0.100 \text{ g}}$

Actual mass of Cu removed from alloy
 $= 0.950 - 0.050 - 0.100 = \mathbf{0.800 \text{ g}}$

Evidence	Deduction
X and Y do not react with 2,4-DNPH	No condensation reaction with 2,4-DNPH. - X and Y do not contain the carbonyl compounds.
X and Y do not react with aqueous bromine	No electrophilic addition with $\text{Br}_2(\text{aq})$ - Both X and Y do not contain $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$.
Z and Ω reacts with Na_2CO_3	Acid-carbonate reaction between $-\text{COOH}$ group in Z and Ω with carbonate. - $-\text{COOH}$ group present in Z and Ω
Z and Ω form salts with HCl	Acid-base reaction with $\text{HCl}(\text{aq})$ - Z and Ω contain basic group - $-\text{CN}$ group is reduced by H_2 to primary amine ($-\text{CH}_2\text{NH}_2$) in Z and Ω .
$M_r(\text{Z}) = 191$ $M_r(\Omega) = 197$	- 6 more H added to Ω than Z - Reduction of benzene ring to cyclohexane occurred.

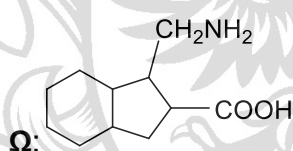
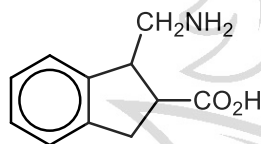
(f)

X:



Y: $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$

Z:



(The following reasoning is not required, but it is provided for you to check your reasoning.)

Evidence	Deduction
X and Y react with Na	X and Y contain $-\text{OH}$ or $-\text{COOH}$ groups - Reduction of carbonyl groups in precursor of X occurred.
Only Y reacts with Na_2CO_3	Y (but not X) contains the $-\text{COOH}$ group - $-\text{COOH}$ group is not reduced by H_2

Changes to 2015 H2 Chemistry A Level Question Paper

Dear students,

The TYS you have purchased is based on the 9647 (old) syllabus. You will be sitting for the 9729 (new) syllabus papers. This document will instruct you on the changes you need to make to the TYS questions.

The Planning question for the 9729 syllabus will be in the Paper 4 (Practical).

Some concepts are no longer tested in the 9729 syllabus and the values used for some calculations are now different (e.g. molar volume at s.t.p.) which will affect your choice of the answers.

You are advised to **make the changes** on your question papers **before you attempt it**. Do inform your tutors if you notice any differences which were not highlighted in this document.

Paper 1

15 Amend question

“Which property generally **increases** down Group **2**?”

Amend Option D

thermal stability of the **carbonate**

Paper 2

3(d) Not in syllabus

Paper 3

1(a)(ii) Amend question

“How many chiral centres are there in the menthol molecule, and how many **enantiomers** are possible?”

2(b) Not in syllabus

3(a)(i) Not in syllabus

3(a)(ii) Not in syllabus - Reaction of calcium oxide with water

3(c)(i) - (ii) Not in syllabus

4(b) Bond energy of C=O in CO₂ in the Data Booklet (for new syllabus) is the same as that given by the question

5(c)(ii) Amend question

“Unlike other Group **1** carbonates,”

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2015 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

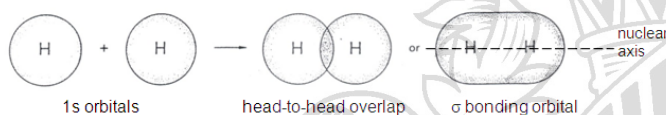
Q1 (B)

A	$1s^2 2s^1 2p^1$	Excited state of Group 2
B	$2s^2 2p^2$	Ground state of Group 14
C	$2s^1 2p^3$	Excited state of Group 14
D	$3p^4$	Excited state

Q2 (B)

σ bonds formed by head-on overlap of either s or p orbitals.

(i) s-s overlap



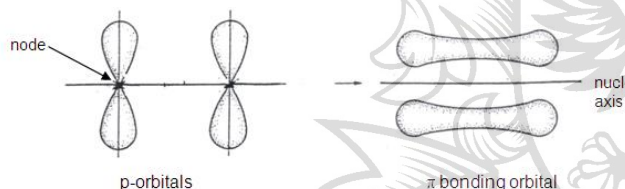
(ii) p-p overlap



(iii) s-p overlap



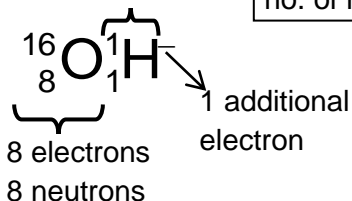
π bonds formed by side-to-side overlap of p-orbitals.



s-orbitals are spherical and thus **cannot** overlap in a way to form π bonds.

Q3 (C)

1 electron
0 neutron



no. of electrons = $8+1+1=10$
no. of neutrons = $8+0=8$

Q4 (C)

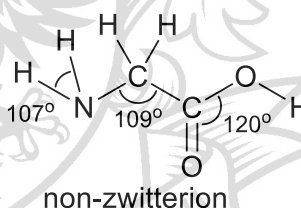
Calcium and sodium are metals. Their melting points depend on the strength of their metallic bonds.

Strength of metallic bonds depend on:

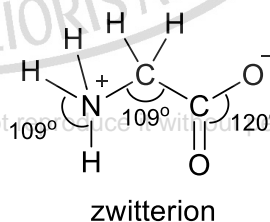
- charge of metal ion
 - size of metal ion
- } charge density
(high charge & small size \Rightarrow high charge density \Rightarrow stronger attraction for delocalised electrons.)
- no. of valence electrons which can be delocalised
(more delocalised electrons \Rightarrow greater attraction between metal cations and delocalised electrons)

A	true, but irrelevant
B	true, but irrelevant
C	Ca^{2+} has a higher charge and hence higher charge density than Na^+ .
D	true, but irrelevant. This option discusses the total no. of electrons <u>in each cation</u> and not the no. of <u>delocalised electrons</u> .

Q5 (B)



90° bond angle
absent



90° bond angle
absent

$-\text{NH}_2 \longrightarrow -\text{NH}_3^+$
107° 109°

90° bond angle absent in both structures
107° bond angle absent only in zwitterion.

Q6 (D)

Lattice energy is the energy released when **one mole** of the **solid ionic compound** [i.e. $\text{Na}_2\text{O(s)}$] is formed from its **constituent gaseous ions** [i.e. $\text{Na}^+(\text{g})$ and $\text{O}^{2-}(\text{g})$] under **standard conditions** of **298 K** and **1 bar**.

D	$2\text{Na}^+(\text{g}) + \text{O}^{2-}(\text{g}) \longrightarrow \text{Na}_2\text{O(s)}$ <div style="display: flex; justify-content: space-around; width: 100%;"> (from gaseous ions) (to 1 mol of solid ionic compound) </div>
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Q7 (B)

Amt of NaOH used
 $= (12.5 / 1000)(0.0500)$
 $= 0.000625 \text{ mol}$
 $= \text{Amt of HCl reacted}$

Amt of HCl remaining
 $= (25/1000)(0.100) - 0.000625$
 $= 0.001875 \text{ mol}$

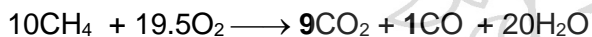
$$[\text{HCl}]_{\text{remaining}} = \frac{0.001875}{(12.5 + 25.0) / 1000} = \underline{\underline{0.0500 \text{ mol dm}^{-3}}}$$

Q8 (C)

"...methane reacted with oxygen to form a mixture of carbon dioxide and carbon monoxide in a mole ratio of 9:1..."



Balance the equation:



At constant pressure and temperature,
 volume of gas \propto amt of gas in mol

$$\text{volume of O}_2 = \frac{19.5}{10}(1) = 1.95 \text{ dm}^3$$

Q9 (A)

CO_2 forms hydrogen bonds with H_2O molecules
 $\Rightarrow \Delta H$ is negative (bond formation is exothermic)

Reaction causes decrease in amount of gaseous particles (1 mol to 0 mol of gaseous particles)
 $\Rightarrow \Delta S$ is negative (increase in order)

Q10 (B)

Standard electrode potential, E^\ominus , is the electromotive force,

- measured at **298 K**
- in which the concentration of any reacting species in solution is 1 mol dm^{-3} , and
- any gaseous species is at a pressure of **1 bar**.

$$\text{Hence, } [\text{HOCl}] = [\text{H}^+] = [\text{Cl}_2] = 1 \text{ mol dm}^{-3}$$

Q11 (D)

	$\text{CH}_3\text{CO}_2\text{H}$	\rightleftharpoons	CH_3CO_2^-	+	H^+
Initial	C		0		0
Change	$-\alpha C$		$+\alpha C$		$+\alpha C$
Eqm	$(1 - \alpha)C$		αC		αC

$$K_c = \frac{(\alpha C)^2}{(1 - \alpha)C} = \frac{\alpha^2 C}{(1 - \alpha)}$$

Q12 (C)

To \uparrow amt of methanol \Rightarrow to favour forward reaction

Exothermic forward reaction is favoured by **decrease in temperature**.

An increased pressure would favour the forward reaction, which reduces amt of gaseous particles.

Q13 (D)

Let x be the eqm amt of H_2 and CO_2 .

	$\text{H}_2\text{O(g)}$	+	CO(g)	\rightleftharpoons	$\text{H}_2\text{(g)}$	+	$\text{CO}_2\text{(g)}$
Initial / mol	1.0		1.0		0		0
Change / mol	$-x$		$-x$		$+x$		$+x$
Eqm /mol	$1.0 - x$		$1.0 - x$		x		x

$$\text{Total amt of gases at eqm} = 2(1.0 - x) + 2(x) = 2 \text{ mol}$$

$$\frac{\text{amt of H}_2}{\text{total amt of gases}} = \frac{x}{2} = 0.333 \Rightarrow x = 0.666$$

$$K_c = \frac{(0.666)^2}{(1 - 0.666)^2} = 3.97 \approx 4$$

Q14 (B)

Given: rate = $k[\text{H}_2][\text{NO}]^2$

From expt 1 to 2, $[\text{H}_2]$ remains the same
when $[\text{NO}] \times \frac{1}{2}$, initial rate $\times (\frac{1}{2})^2 = \frac{1}{4}$
 $\Rightarrow x = \frac{1}{4}(6.0) = 1.5$

From expt 2 to 3, $[\text{NO}]$ remains the same
when $[\text{H}_2] \times 2$, initial rate $\times 2$
 $\Rightarrow y = 2(1.5) = 3.0$

From expt 3 to 4, $[\text{H}_2]$ remains the same and
initial rate $\times \frac{1}{4}$ (from 3.0 to 0.75).
Since rate $\propto [\text{NO}]^2$, $[\text{NO}]$ must have halved from 1.0
to 0.5 mol dm⁻³ $\Rightarrow z = 0.5$

Q16 (D)

Period 3 elements: Na Mg Al Si P S Cl Ar

A	False. Sulfur also forms 2 acidic oxides, i.e. SO_2 and SO_3 .
B	False. First ionisation energy (IE) generally increases across the period. Hence, Ar has the highest first IE. (or refer to IE data from Data Booklet)
C	False. Si forms SiCl_4 , while P forms PCl_3 and PCl_5 , all of which dissolve in water to form acidic solutions. (<i>Reaction of PCl_3 with water in not in syllabus</i>)
D	True. <u>P</u> , S and Cl exist as simple molecules with formula <u>P</u> ₄ , S ₈ and Cl ₂ respectively.

Q15 (D)

A	charge density $\propto \frac{\text{charge}}{\text{radius}}$ Down Group 2, charge of M^{2+} remains the same, but ionic radius increases. \Rightarrow magnitude of charge density decreases down the group.
B	Electronegativity decreases as the number of shells of electrons increases down the group, reducing the attraction by the nucleus for the valence electrons.
C	Elements of Group 2 have the same number of valence electrons i.e. 2.
D	Thermal stability of Group 2 carbonates increase down the group. Down Group 2, <ul style="list-style-type: none"> ionic radii of Group 2 cations increase charge density, and hence polarising power of cations decrease, covalent bonds in carbonate anion are less polarised / weakened to smaller extent, more thermal energy required to break covalent bonds in carbonate anion, thermal stability increases.

Q17 (A)

A✓	$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}\text{SO}_4^{2-}$	dark blue solution
B✗	$[\text{Cu}(\text{NH}_3)_6]^{2+}\text{SO}_4^{2-}$	dark blue precipitate solution
C✗	$\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4$	pale blue solution precipitate <ul style="list-style-type: none"> essentially $\text{Cu}(\text{OH})_2$ which is a precipitate
D✗	$[\text{Cu}(\text{H}_2\text{O})_6]^+\text{Cl}^-$	pale blue colourless solution <ul style="list-style-type: none"> Cu^+ has a fully filled d-subshell and hence no d-d transition can occur $\Rightarrow \text{Cu}^+$ is colourless

Q18 (C)

Atomic radii: $Mg > Al > Si > P$

(increased nuclear charge but approximately constant shielding across period)

⇒ reject option D since atomic radius of P is shown to be higher than Si.

Melting point: $P_4 < Mg < Al < Si$

(melting phosphorus involves overcoming id-id interactions between P_4 molecules, which require significantly less energy than for the metallic bonds in Mg and Al. Si has the highest melting point due to its giant molecular structure)

⇒ reject options A and B.

Q19 (B)

$Y + Cr_2O_7^{2-} + X \rightarrow [Cr(H_2O)_6]^{3+} + \text{organic pdt}$

Oxidation state of Cr decreased from +6 in $Cr_2O_7^{2-}$ to +3 in $[Cr(H_2O)_6]^{3+}$.

⇒ reduction of $Cr_2O_7^{2-}$ occurred

⇒ organic compound Y was oxidised

⇒ Y could be C_2H_5OH (option B) or CH_3CHO (option D)

$Cr_2O_7^{2-}$ is used under acidic conditions

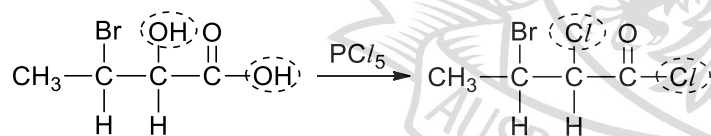
⇒ X is an acid i.e. H_2SO_4 (option B)

Note: $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

In alkaline medium, $Cr_2O_7^{2-}$ changes to CrO_4^{2-} .

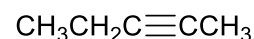
Q20 (A)

PCl_5 reacts with functional groups containing $-OH$ except phenols i.e. it reacts with alcohols ($R-OH$) and carboxylic acids ($RCOOH$). $-OH$ group is substituted by Cl .

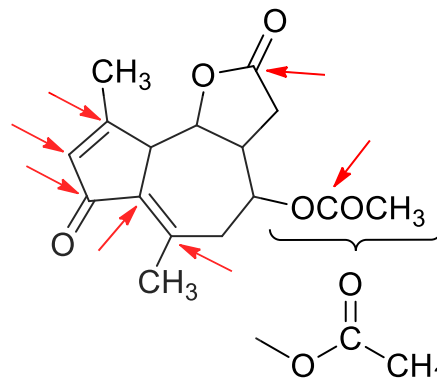
**Q21 (B)**

Information from the question:

1. non-cyclic hydrocarbon
2. general formula: C_nH_{2n-2}
3. one carbon-carbon triple bond per molecule

**Q22 (D)**

sp^2 -hybridised carbon atoms are indicated with an arrow. The structure of the $-OCOCH_3$ group has been expanded and shows that it contains a sp^2 carbon as well.

**Q23 (B)**

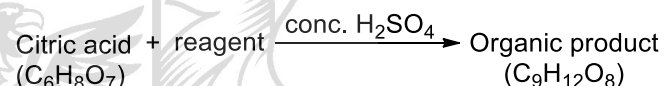
$NaBH_4$ only reduces ketones and aldehydes.

$CH_2=CHCH_2CHO$ contains

- an alkene (not reduced by $NaBH_4$)
- an aldehyde (reduced by $NaBH_4$: $RCHO \rightarrow RCH_2OH$)

**Q24 (A)**

Rough working (equation is not balanced):



- Increase in 3 C, 4H and 1O from citric acid to product
- Options contain carboxylic acids and alcohols
- Together with the use of conc. H_2SO_4 , it is likely that the organic product contains ester functional group(s).

A	Forms ester with tertiary alcohol of citric acid to form ester with formula $C_9H_{12}O_8$.
B	Reject, since $C_3H_7CO_2H$ contains 4 C's.
C	Assuming 1 mol of C_3H_7OH reacts with 1 mol of citric acid (i.e. 1 $-COOH$ of citric acid reacted with C_3H_7OH), the resultant ester has molecular formula $C_9H_{14}O_7$.
D	Assuming 3 mol of CH_3OH reacts with 1 mol of citric acid (i.e. all 3 $-COOH$ of citric acid reacted with CH_3OH), the resultant ester has molecular formula $C_9H_{14}O_7$.

Q25 (D)

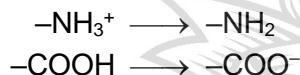
This question deals with the relative ease of hydrolysis of various chloroalkanes to produce the corresponding organic product and Cl^- . The Cl^- ion reacts with Ag^+ to give AgCl .

The ease of hydrolysis increases in the following order: $\text{Ph-Cl} < \text{R-Cl} < \text{RCOCl}$. Hence, ethanoyl chloride (CH_3COCl) hydrolyses most easily and gives a white precipitate of AgCl most rapidly.

A	Large $-\text{Cl}$ atoms hinder the approach of the water nucleophile to the central carbon atom / C does not have low-lying vacant orbitals to accept an electron pair from H_2O form a pentavalent intermediate, $\text{H}_2\text{O} \rightarrow \text{CCl}_4$. Hence, no hydrolysis occurs, no ppt is formed.
B	Partial double bond character strengthens the C-Cl bond, making hydrolysis difficult.
C	Hydrolysis of ethanoyl chloride occurs more readily than 2-chlorobutane due to <ul style="list-style-type: none"> the C atom in $-\text{COCl}$ being more electron deficient due to the presence of 2 highly electronegative atoms, compared to 1 such atom in 2-chlorobutane
D	<ul style="list-style-type: none"> trigonal planar geometry around C atom in $-\text{COCl}$ allows the water nucleophile to attack the C atom more easily than in the case of 2-chlorobutane where the water nucleophile attacks a more hindered sp^3 C atom with tetrahedral geometry.

Q26 (D)

At a highly alkaline pH of 11, the acidic functional groups of an amino acid would be deprotonated i.e.



In the case of aspartic acid, the two $-\text{COOH}$ groups will be deprotonated to $-\text{COO}^-$.

Q27 (D)

Information from question

- Q is oxidised to form R
- $M_r(\text{R}) = M_r(\text{Q}) + 14$

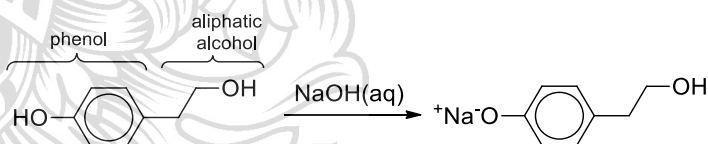
	Q → R	
A	$\text{RCHO} \rightarrow \text{RCOOH}$	$M_r(\text{R}) = M_r(\text{Q}) + 16$
B	Reaction does not happen	
C	$\text{RCH}_2\text{OH} \rightarrow \text{RCHO}$	$M_r(\text{R}) = M_r(\text{Q}) - 2$
D	$\text{RCH}_2\text{OH} \rightarrow \text{RCOOH}$	$M_r(\text{R}) = M_r(\text{Q}) + 14$

Q28 (C)

This question discusses the different reactivity of aliphatic alcohols and phenols with NaOH(aq) .

The following table summarizes the reactivities of aliphatic alcohols, phenols and carboxylic acids with Na, NaOH and Na_2CO_3 .

	Na(s)	NaOH(aq)	Na₂CO₃(aq)
Aliphatic alcohols (ROH)	✓ to form RO^-Na^+ & $\text{H}_2(\text{g})$	✗	✗
Phenols (PhOH)	✓ to form PhO^-Na^+ & $\text{H}_2(\text{g})$	✓ to form PhO^-Na^+ & H_2O	✗
Carboxylic acids (RCOOH)	✓ to form RCOO^-Na^+ & $\text{H}_2(\text{g})$	✓ to form RCOO^-Na^+ & H_2O	✓ to form RCOO^-Na^+ , H_2O , CO_2

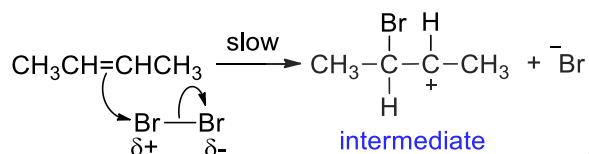
**Q29 (B)**

A	AlBr_3 is used as a catalyst in the electrophilic substitution of benzene rings. However, it must be used together with Br_2 as a reagent, and not just on its own.
B	Polysubstitution on benzene ring of phenols, e.g. bisphenol A, requires the use of $\text{Br}_2(\text{aq})$.
C	This combination does not produce the required electrophile (Br^+) for reaction with the phenols; $\text{HBr} + \text{AlCl}_3 \rightarrow \text{H}^+ + [\text{BrAlCl}_3]^-$.
D	Br_2 may be produced by the reaction of NaBr with hot concentrated H_2SO_4 , but not with dilute H_2SO_4 .

Q30 (A)

The reaction between the alkene and Br₂(aq) proceeds via an electrophilic addition reaction.

The alkene first attacks the bromine molecule in the slow step to form a carbocation **intermediate**.



In the fast step, H₂O acts as a nucleophile and attacks the carbocation intermediate to generate a bromohydrin as the major product.

Q33 (C)

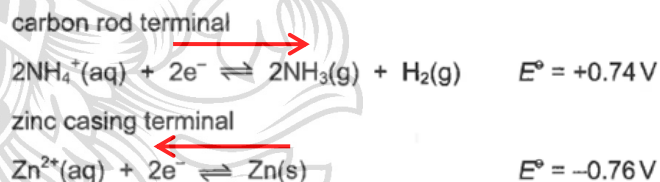
1	Molecules of an ideal gas have a finite mass i.e. they have non-zero masses.
2	Molecules of ideal gas are in constant random motion – this is one of the assumptions.
3	Molecules of ideal gas have no volume – this is one of the assumptions. It is more properly stated as “molecules of an ideal gas have negligible volume compared to the volume of the container”

Other assumptions are:

1. Molecules of ideal gas exert negligible forces of attraction on each other.
2. The collisions between ideal gas molecules are perfectly elastic.

Q31 (D)

	Ion	Electronic Configuration	Remarks
1	Mn ²⁺	[Ar] 3d ⁵	no paired 3d e ⁻
2	Fe ²⁺	[Ar] 3d ⁶	2 e ⁻ are paired in a d-orbital
3	Co ³⁺	[Ar] 3d ⁶	2 e ⁻ are paired in a d-orbital

Q34 (A)

Reduction occurs at the carbon terminal and oxidation occurs at the zinc terminal since $E^\ominus(\text{reaction at the carbon rod terminal}) > E^\ominus(\text{reaction at zinc terminal})$

Q32 (A)

1	Si and Ge are elements of Group 14 which tend to form halides that are covalent in nature. Their low boiling points confirm that these are simple covalent molecules with weak intermolecular forces of attraction between the molecules.
2	Students should draw a parallel to AlCl ₃ . AlCl ₃ is covalent in nature due to significant polarisation of the electron cloud of Cl ⁻ by the small and highly charged Al ³⁺ .
3	Br ⁻ is larger and its electron cloud is more easily polarised than that of Cl ⁻ , causing stronger covalent character in AlBr ₃ . Hence, AlBr ₃ is covalent.

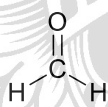
1	$E^\ominus = +0.74 - (-0.76) = +1.50 \text{ V}$
2	reduction: $2\text{NH}_4^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{NH}_3(\text{g}) + \text{H}_2(\text{g})$ oxidation: $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$ combining the above equations, $2\text{NH}_4^+(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{NH}_3(\text{g}) + \text{H}_2(\text{g})$
3	Since the zinc electrode is oxidised to Zn ²⁺ (aq), the zinc casing becomes thinner.

Q35 (B)

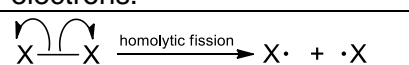
Rate constant, k , depends on temperature and the use of a catalyst. (Arrhenius equation: $k = Ae^{-E_a/RT}$)

1	Introduction of a catalyst provides an alternative pathway of lower E_a . The E_a of both the forward and backward reactions are lowered and hence both k_f and k_b are increased.
2	Heating the equilibrium mixture increases the rate of both the forward and backward reactions by increasing both k_f and k_b .
3	Increasing the concentration of the reactants increases reaction rate, but does not increase the value of k_f and k_b .

Q36 (A)

1	The C atom is sp^2 hybridised and hence the molecule is planar around the C atom.  \Rightarrow the 3 atoms around the C atom lie in the same plane as the C atom \Rightarrow all 4 atoms lie in the same plane
2	Since electronegativity (EN) of C > H, H has an oxidation state of +1. Since $EN(O) > EN(C)$, O has an oxidation state of -2. Let x be the oxidation state of C atom. Since methanal has an overall charge of 0, then $2(+1) + (-2) + x = 0 \Rightarrow x = 0$.
3	Complete combustion of methanal gives CO_2 and H_2O as products. Writing the balanced equation gives $HCHO + O_2 \rightarrow CO_2 + H_2O$, i.e. complete combustion of 1 mol of methanal requires 1 mol of oxygen gas.

Q37 (C)

1	$H\cdot$ is a radical which does not have any lone pair of electrons \Rightarrow this statement is not true.
2	A free radical is a species with unpaired electrons.
3	 In homolytic fission of a covalent bond, each atom takes 1 electron, resulting in the formation of free radicals.

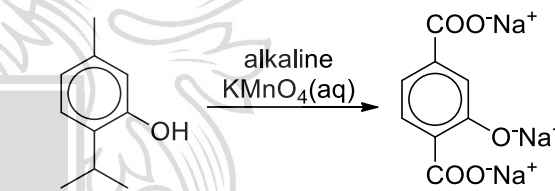
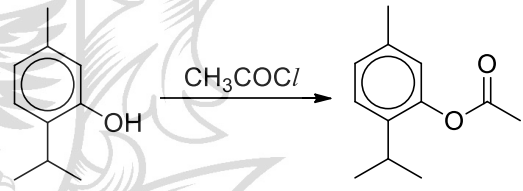
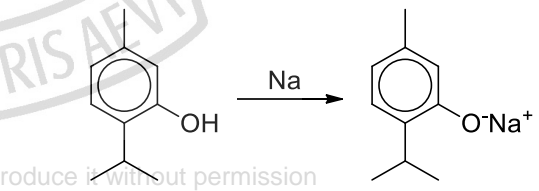
Q38 (C)

One criterion for displaying cis-trans isomerism is that each C atom of the $C=C$ should bear different atoms / groups of atoms.

Regardless of the identities of **X** and **Z**, the alkenes containing atoms **X** and **Z** cannot display cis-trans isomerism. This is because the alkene containing atom **X** is such that one of the C atoms of the $C=C$ contains 2 -H, while the alkene containing atom **Z** is such that one of the C atoms of the $C=C$ contains 2 -CH₃.

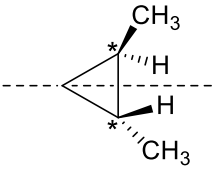
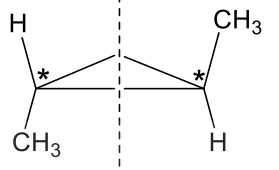
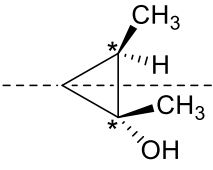
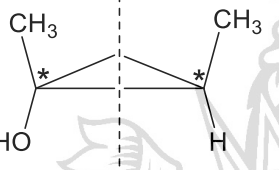
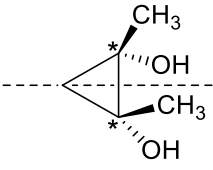
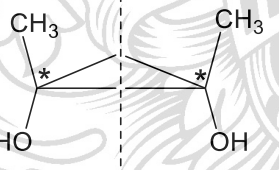
In order for the molecule to display cis-trans isomerism, **Y** cannot be H i.e. **reject option 1**. Options 2 and 3 allow the molecule to display cis-trans isomerism.

Q39 (A)

1	Oxidation of side chains of benzene and acid-base reaction of phenol occurred. 
2	Condensation reaction with phenol occurred. 
3	Redox reaction with phenol occurred (see suggested solutions for Q28). 

Q40 (B)

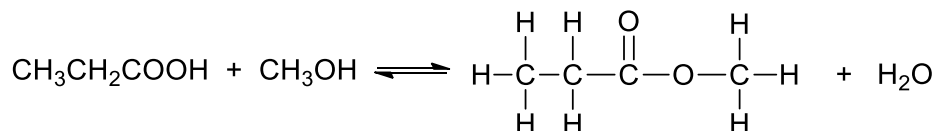
Molecules with no internal plane of symmetry are optically active.

1	<div><div><p>top view</p></div><div><p>side view</p></div></div> <p>No internal plane of symmetry \Rightarrow optically active</p>
2	<div><div><p>top view</p></div><div><p>side view</p></div></div> <p>No internal plane of symmetry \Rightarrow optically active</p>
3	<div><div><p>top view</p></div><div><p>side view</p></div></div> <p>Internal plane of symmetry exists (meso compound) \Rightarrow optically inactive</p>

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Q1 Planning

(a)

(b) Determine concentration of hydrochloric acidPre-calculations (to determine volume of HCl(aq) to be used for titration)

Since $[\text{HCl(aq)}] \sim 3 \times [\text{NaOH(aq)}]$, 10 cm^3 of HCl would react completely with $\sim 30 \text{ cm}^3$ of NaOH.

$\Rightarrow 10.0 \text{ cm}^3$ of HCl(aq) can be pipetted into a conical flask and be titrated against NaOH(aq) placed in a 50.00 cm^3 burette.

Procedure

- Using a 10.0 cm^3 pipette, transfer 10.0 cm^3 of $\sim 3 \text{ mol dm}^{-3}$ HCl(aq) into a 100 cm^3 conical flask.
- Add 2–3 drops of thymolphthalein indicator.
- Titrate HCl(aq) against 1.00 mol dm^{-3} NaOH(aq), placed in 50.00 cm^3 burette, adding NaOH(aq) dropwise near the endpoint. The endpoint is reached when the solution changes from colourless to blue. Record your results in an appropriate table.
- Repeat titrations until at least 2 consistent results (i.e. within $\pm 0.10 \text{ cm}^3$ of each other) are obtained.
- Calculate the average titre value, $V_1 \text{ cm}^3$, used.

Calculations

$$[\text{HCl(aq)}] = \frac{V_1}{10} \times \frac{1.00}{1000} = 0.1 V_1 \text{ mol dm}^{-3}.$$

Preparation of reaction mixturesPre-calculations

The mixture at equilibrium will be titrated against 1.00 mol dm^{-3} NaOH(aq) which reacts with **both the** HCl catalyst and $\text{CH}_3\text{CH}_2\text{COOH}$ present at equilibrium.

\Rightarrow amt of NaOH used = amt of propanoic acid at eqm + amt of HCl

Note to student:

Important instructions from question:

“...**whole mixture is titrated** against a standard solution of sodium hydroxide.

This allows the **total amount of acid** in the mixture to be found. This total amount of acid is made up of **the strong acid and the carboxylic acid present** in the equilibrium mixture.”

Maximum amt of NaOH used occurs if there is a lot of propanoic acid left at eqm, i.e. negligible amt of propanoic acid was reacted. This maximum amt of NaOH cannot exceed the capacity of the burette (50.00 cm^3).

$$\begin{aligned}\text{Maximum amt of NaOH used} &= \frac{50}{1000}(1.00) \\ &= 0.05 \text{ mol}\end{aligned}$$

Assuming 1 cm³ of 3 mol dm⁻³ HCl was used, then

0.05 = amt of propanoic acid at eqm + amt of HCl

$$0.05 = \text{amt of propanoic acid at eqm} + \frac{1}{1000}(3.00)$$

amt of propanoic acid at eqm = 0.047 mol

Initial mixture A (mole ratio of acid to alcohol = ~1:1)

mass of propanoic acid used = 0.047(74.0) = 3.48 g

mass of methanol used = 0.047(32.0) = 1.50 g

Initial mixture B (mole ratio of acid to alcohol = ~1:2)

mass of propanoic acid used = 3.48 g

mass of methanol used = 3.00 g

Procedure

1. Place a clean, dry 100 cm³ conical flask on an electronic balance and tare the balance.
2. Weigh accurately about 3.4 g of propanoic acid in the conical flask, using a glass dropper to transfer the acid. Record the accurate mass of propanoic acid used, m₁ g.
3. Tare the balance and weigh accurately about 1.5 g of methanol into the same conical flask, using a different glass dropper to transfer the methanol. Record the accurate mass of methanol used, m₂ g.
4. Using a 50.00 cm³ burette, transfer 1.00 cm³ of HCl(aq) into the same conical flask.
5. Stopper the conical flask with a rubber bung and swirl the mixture to obtain a homogeneous solution. Label the flask as mixture **A** and leave it to stand at room temperature for a week.
6. Repeat steps 1 to 5, weighing accurately about 3.4 g of propanoic acid and 3.0 g of methanol. Label this flask as mixture **B**.

Titration of equilibrium mixtures

Procedure

1. Using a 50 cm³ measuring cylinder, add 30 cm³ of cold deionised water into the conical flask containing mixture **A**.
2. Add 2–3 drops of thymolphthalein indicator
3. Titrate the mixture quickly against 1.00 mol dm⁻³ NaOH(aq), placed in a 50.00 cm³ burette, adding NaOH(aq) dropwise near the endpoint. The endpoint is reached when the mixture turns from colourless to blue.
4. Record your results in an appropriate table and calculate the titre value, V₂ cm³.
5. Repeat steps 1 to 4 for mixture **B** to obtain titre value, V₃ cm³.

Note to student:

1. Instruction from question is to titrate the entire mixture i.e. this titration can only be carried out once for each mixture.
2. The endpoint we want to observe is that of the reaction between propanoic acid (weak acid) and sodium hydroxide (strong base) where the endpoint pH > 7. Thymolphthalein is a suitable indicator, but not (screened) methyl orange.

Details of how results are used

Initial amounts of substances present

$$\begin{aligned}\text{amt of propanoic acid} &= \frac{m_1}{74.0} \text{ mol} \\ \text{amt of methanol} &= \frac{m_2}{32.0} \text{ mol} \\ \text{amt of ester} &= 0 \text{ mol} \\ \text{amt of water from } 1 \text{ cm}^3 \text{ of HCl (aq)} &= \frac{1.00}{18} \\ &= 0.0556 \text{ mol}\end{aligned}$$

Note to student:

H₂O is not a solvent in this reaction and is produced as a by-product. Its concentration needs to be accounted for.

In addition, account for the water contributed by the use of HCl(aq). A hint was given in the question:

“... you may assume that 1.00 cm³ of HCl(aq) contains 1.00 cm³ of water and that the density of water is 1 g cm⁻³.”

Amount of propanoic acid at eqm

Using results from mixture **A**,

amt of NaOH used = amt of propanoic acid at eqm
+ amt of HCl

$$\frac{V_2(1.00)}{1000} = \text{amt of propanoic acid at eqm} + \frac{1.00(0.1 V_1)}{1000}$$

where [HCl] = 0.1 V₁ mol dm⁻³

amt of propanoic acid at eqm
= (0.001 V₂ – 0.0001 V₁) mol

Let amt of propanoic acid at eqm = (0.001 V₂ – 0.0001 V₁) mol = x mol and V_T be the total volume of the mixture.

	CH ₃ CH ₂ COOH	+	CH ₃ OH	⇌	CH ₃ CH ₂ COOCH ₃	+	H ₂ O
initial conc / mol dm ⁻³	$\frac{m_1}{74.0}$		$\frac{m_2}{32.0}$		0		$\frac{0.0556}{V_T}$
Δ conc / mol dm ⁻³	$-\left(\frac{m_1}{74.0} - x\right)$		$-\left(\frac{m_1}{74.0} - x\right)$		$+\left(\frac{m_1}{74.0} - x\right)$		$+\left(\frac{m_1}{74.0} - x\right)$
eqm conc / mol dm ⁻³	$\frac{x}{V_T}$		$\frac{m_2}{32.0} - \frac{m_1}{74.0} + x$		$\left(\frac{m_1}{74.0} - x\right)$		$\frac{0.0556 + \frac{m_1}{74.0} - x}{V_T}$

The equilibrium constant, K_c, can be calculated from the data in the above table.

Safety precautions

1. Propanoic acid is corrosive and methanol is toxic. Therefore, gloves, safety goggles and lab coats should be worn to prevent direct contact of the chemicals with our skin.
2. Methanol is volatile and toxic. The experiment should be carried out in a fumehood to prevent inhalation of methanol vapours.

Question 2

(a)(i) It is the **energy released** when **one mole** of a **substance** is **completely** burnt in excess oxygen **under standard conditions of 298 K and 1 bar**.

(a)(ii) Petrol is a **mixture of hydrocarbons** with no fixed composition. Hence, ΔH_c^\ominus cannot be accurately determined.

(b)(i) Since energy released per dm^3 at 25 °C & 101 kPa is $0.0358 \text{ MJ dm}^{-3}$,
energy released per dm^3 at 25°C & 24.8 MPa
$$= \frac{24.8 \times 10^6}{101 \times 10^3} \times 0.0358$$
$$= 8.79 \text{ MJ dm}^{-3}$$

(Note: there is no need to use ideal gas equation to solve this problem if you choose the correct data from the table)

(b)(ii) The **combustion of methane releases CO_2** , a **greenhouse gas** which can have a **negative impact** on the environment, while the **combustion of H_2 releases H_2O** , which is (generally) **harmless** to the environment.

(c) 1. A molecule of methanol has **more electrons** than a molecule of methane, so methanol has a **larger and more polarisable electron cloud**. Hence, methanol has **stronger instantaneous dipole – induced dipole interactions** than methane.

2. Methanol forms **intermolecular hydrogen bonds**, which are absent in methane.

More energy is required to overcome the intermolecular forces in methanol, which are stronger than those in methane. Hence, methanol has a **higher boiling point** than methane.

(d)(i)
$$\Delta H^\ominus = \sum n\Delta H_c^\ominus(\text{rxnts}) - \sum m\Delta H_c^\ominus(\text{pdtts})$$
$$= -726 - [2(-286) + (-283)]$$
$$= +129 \text{ kJ mol}^{-1}$$

(d)(ii) For reaction to be spontaneous, $\Delta G^\ominus < 0$

$$\Rightarrow \Delta H^\ominus - T\Delta S^\ominus < 0$$

$$\Rightarrow 129 - T \left(\frac{332}{1000} \right) < 0 \Rightarrow T > 388.6 \text{ K}$$

Min. T for rxn to be spontaneous = 389 K

(e) Both O_2 and CO (where the C atom in CO is the donor atom) form **dative covalent bonds to the Fe(II) centre** in haemoglobin.

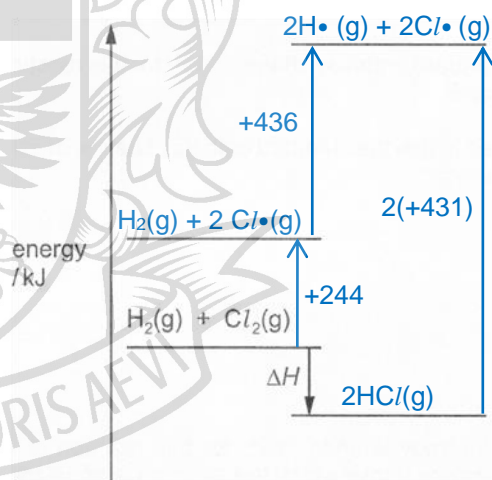
C is less electronegative than O, i.e. the **lone pair of electrons on C in CO are less tightly held** than the lone pair of electrons on O in O_2 . **CO is more likely to form dative covalent bond** with the Fe(II) centre than O_2 , preventing O_2 from being transported on the haemoglobin. The bond formed between CO and Fe is also stronger than the bond formed between O_2 and Fe.

(Note to student: Do not discuss this from a biological point of view; you should discuss this “in terms of the bonding involved”.)

Question 3

(a)(i)
$$\Delta H^\ominus = 436 + 244 - 2(431)$$
$$= -182 \text{ kJ mol}^{-1}$$

(a)(ii)



Notes to student:

1. Since bond energies are positive values, the arrows point upward.
2. The height of each arrow is proportional to magnitude of each enthalpy change. This is why the shorter upward arrow corresponds to +244 and the longer one corresponds to +431.

3. State symbols must be shown for each chemical species because each enthalpy change is defined for certain physical states.

(b)(i) UV light **provided the energy** to break the **Cl–Cl bond**, forming $\text{Cl}\cdot$ radicals for reaction.

(b)(ii) Type of reaction: Free radical substitution



(b)(iii) Once initiated, the $\text{Cl}\cdot$ radicals react with H_2 . In the **propagation steps**, the $\text{Cl}\cdot$ radicals **are regenerated**, allowing the reaction to continue despite the brief exposure to light.

The overall **reaction is exothermic**, causing the **temperature of the system to rise** as the reaction proceeds, leading to an **increasing rate as the reaction proceeds**.

Note: There are 2 main points to explain:

- why the reaction **continues** after brief exposure to light,
- why it proceeds with **increasing rate**.

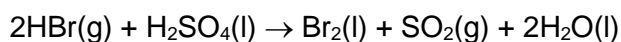
(c) $\Delta H^\ominus = \text{BE}(\text{H-H}) + \text{BE}(\text{X-X}) - 2\text{BE}(\text{H-X})$

	$\text{BE}(\text{H-H}) + \text{BE}(\text{X-X})$		$2\text{BE}(\text{H-X})$
$\text{X} = \text{Cl}$	436	+ 244	2(431)
$\text{X} = \text{Br}$	436	+ 193	2(366)

Since $\text{BE}(\text{H-Br}) < \text{BE}(\text{H-Cl})$, the **energy released from the formation of H–Br is less than that of H–Cl**. This causes the **overall enthalpy change of the reaction to be less exothermic in the case of H–Br** than for H–Cl **despite the lower energy required to break the Br–Br bond** (193 kJ mol^{-1}) compared to the Cl–Cl bond (244 kJ mol^{-1}).

(d)(i) $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{HCl} + \text{NaHSO}_4$
(Not in syllabus)

(d)(ii) (Not in syllabus) The initial reaction between NaBr and conc. H_2SO_4 forms **HBr, which is a stronger reducing agent than HCl**. Therefore, HBr reduces conc. H_2SO_4 while itself being **oxidised to Br_2** . This method will not generate significant amounts of HBr.



(e) **Test:**

To separate samples of $\text{HCl}(\text{aq})$ and $\text{HBr}(\text{aq})$, add $\text{Cl}_2(\text{aq})$ dropwise until in excess.

Observations:

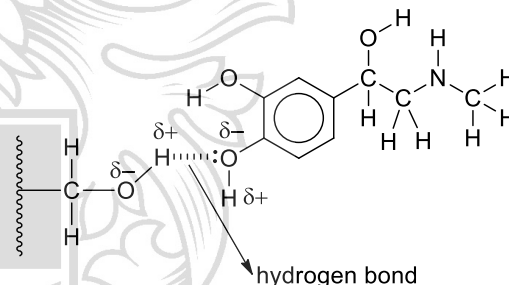
An orange solution of $\text{Br}_2(\text{aq})$ will be observed for $\text{HBr}(\text{aq})$. The solution of $\text{HCl}(\text{aq})$ remains colourless.

Notes to student:

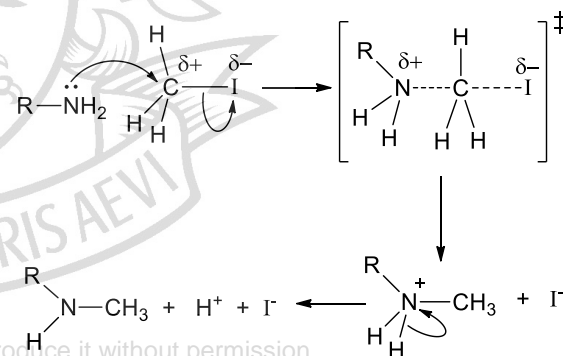
- It was the “**aqueous solutions** of these two gases” that needed distinguishing.
- (Not in syllabus) Many students incorrectly suggested the use of concentrated H_2SO_4 to distinguish between the compounds. The addition of concentrated H_2SO_4 to an aqueous solution dilutes the concentrated acid, which will no longer act as an effective oxidising agent.

Question 4

(a)



(b)(i) **Nucleophilic substitution ($\text{S}_\text{N}2$)**



Notes to student:

- all partial charges must be clearly shown
- all curly arrows must be shown, **including the curly arrow which shows the breaking of the N–H bond in RNH_3^+** .

- (b)(ii) If the reaction proceeded via an **S_N1 mechanism**, the **CH₃⁺ carbocation** formed will be **highly unstable** as it does not have **electron-donating groups** to stabilise the positive charge. Hence it is more likely for the reaction to proceed via an **S_N2 mechanism**, where no carbocation intermediates are involved.

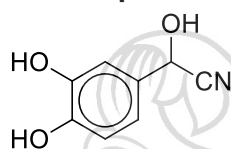
Also, there is **little steric hindrance** around the central C atom due to the **small size of the H atoms around the central C atom**.

This allows the nucleophile to attack the electrophilic central C atom easily.

- (c)(i) **Step 1:** HCN(aq) with trace KCN, 10 – 20 °C

Step 2: LiAlH₄ in dry ether, room temp.

Intermediate compound:



- (c)(ii) Due to the **trigonal planar** shape of the carbonyl carbon, the **CN⁻ can attack the carbonyl carbon from above or below the plane** of the molecule with **equal probability**, leading to a **1:1 mixture** of both enantiomers of noradrenaline. Since only **1 of the 2 enantiomers of noradrenaline can bind** to the active sites on the proteins in the body, only 50% of the drug synthesised is likely to be active.



(d)(ii) amt of adrenaline = $\left(\frac{50}{1000}\right)(3.0 \times 10^{-3})$
 $= 0.0015 \text{ mol}$

Mole ratio of Ag₂O : adrenaline = 2 : 1

Amt of Ag₂O = 0.0015 x 2 = 0.0030 mol

Mass of Ag₂O = 0.0030[2(108) + 16]
 $= 0.0696 \text{ g}$

Question 5

- (a) **X and Y are chlorobenzenes.**

The **p-orbital containing the lone pair of electrons on Cl** overlaps with the **π electron cloud of benzene**, thereby allowing the lone pair of electrons to delocalise into the ring. As a result, the **C–Cl bond is strengthened**. The **partial double bond character in the C–Cl bond** makes it difficult to cleave the bond under the experimental conditions described in the question.

- (b)(i) Assuming a 100g sample of compound **X**,

	C	H	Cl
mass / g	49.0	2.7	48.3
amt / mol	$\frac{49.0}{12} = 4.08$	$\frac{2.7}{1} = 2.7$	$\frac{48.3}{35.5} = 1.36$
mole ratio	3	2	1

Empirical formula = **C₃H₂Cl**

- (b)(ii) $pV = nRT$

$$M_r = \frac{\text{mass}(RT)}{pV}$$

$$= \frac{(0.344)(8.31)(181 + 273)}{(101000)(87.4 \times 10^{-6})}$$

$$= 147.0$$

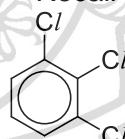
Let molecular formula of **X** be C_{3n}H_{2n}Cl_n

$$3n(12) + 2n(1) + n(35.5) = 147.0$$

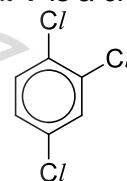
$$n = 2$$

Molecular formula of **X** = **C₆H₄Cl**

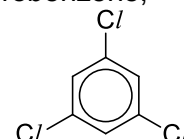
- (c) Recall from (a) that **Y** is a chlorobenzene,



1,2,3-trichlorobenzene

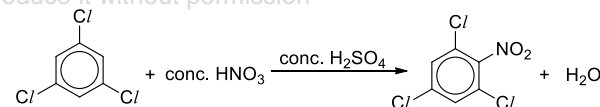


1,2,4-trichlorobenzene

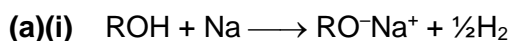


1,3,5-trichlorobenzene

- (d) **Y is 1,3,5-trichlorobenzene.**



Compound **Y**

Question 1

Mole ratio of ROH : H_2 = 2 : 1

Amt of ROH = $2(1.32 \times 10^{-2}) = 2.64 \times 10^{-2}$ mol

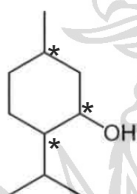
M_r of menthol = $10(12) + 20(1) + 16 = 156$

Mass of ROH = $(2.64 \times 10^{-2})(156) = 4.118\text{g}$

Percentage by mass of menthol

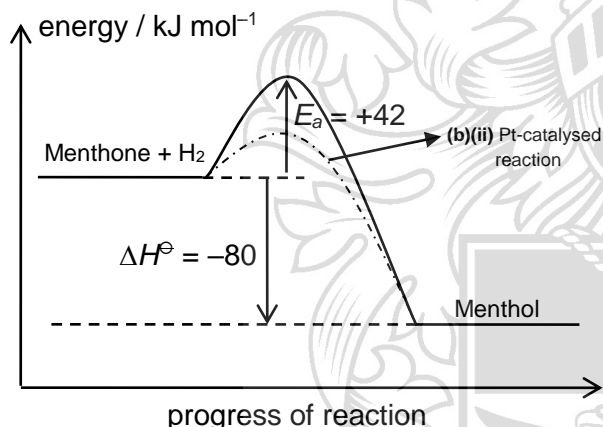
$$= \frac{4.118}{10.0} \times 100$$

$$= 41.2\%$$



- (a)(ii) No. of chiral centres = 3
No. of enantiomers = $2^3 = 8$

(b)(i) & (ii)



(b)(iii)

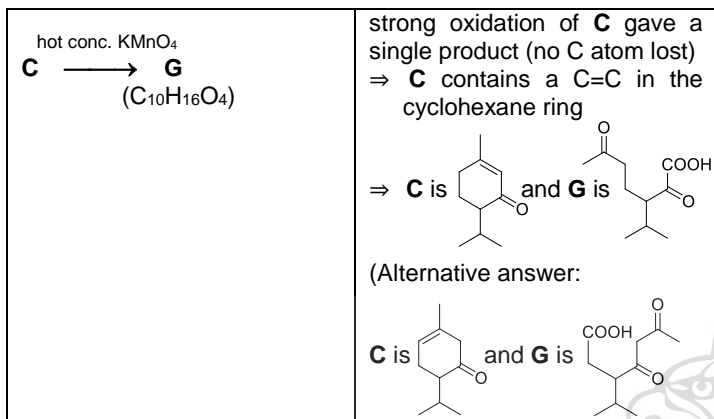
The nickel or platinum metal acts as a **heterogeneous catalyst** which allows menthone and hydrogen gas molecules to **adsorb** on the catalyst by forming **weak interactions** with the metal surface. The **activation energy of the reduction is lowered** as the bonds within the reactants are weakened through the adsorption and the reactants **are brought closer together (with the correct orientation)**, thereby increasing the **frequency of effective collisions**. After reaction takes place on the metal surface, the products **desorb from the catalyst**, freeing up active sites for other reactant molecules to adsorb.

(b)(iv) Pd. As it is in the same group as Ni and Pt, it will have similar physical and chemical properties, e.g. it has partially filled d subshell which allow for the ready exchange of electron pairs to and from

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reactant molecules, making it suitable to be a heterogeneous metal catalyst.

(c) Evidence	Deductions
A, B and C are isomers • with molecular formula $\text{C}_{10}\text{H}_{16}\text{O}$, and • are reduced to menthol ($\text{C}_{10}\text{H}_{20}\text{O}$)	Reduction caused a gain in $2 \text{ H}_2 \Rightarrow$ presence of 2 double bonds ($\text{C}=\text{C}$ or $\text{C}=\text{O}$) A, B and C contain the same carbon skeleton as menthol (contains a cyclohexane ring)
A, B and C decolourise bromine water.	Electrophilic addition reaction occurred. \Rightarrow A, B and C contain $\text{C}=\text{C}$ bond / alkene
A, B and C give orange ppt with 2,4-DNPH but do not reduce Fehling's solution.	A, B and C undergo condensation reaction with 2,4-DNPH but does not reduce Fehling's solution. \Rightarrow does not contain aliphatic aldehyde \Rightarrow contains 1 ketone \Rightarrow contains 1 $\text{C}=\text{C}$ (since there are only 2 double bonds present)
A, B and C react with hot concentrated KMnO_4 .	Strong oxidation occurred. \Rightarrow $\text{C}=\text{C}$ bond in A, B and C is cleaved.
D, F and G give a yellow ppt with alkaline aqueous iodine.	Positive iodoform test to give a yellow ppt of CHI_3 . \Rightarrow $-\text{COCH}_3$ group present (no $-\text{CH}(\text{OH})\text{CH}_3$ group present because these are products of strong oxidation and the alcohol would have been oxidised)
$\text{A} \xrightarrow{\text{hot conc. KMnO}_4} \text{D} + \text{E}$ $(\text{C}_3\text{H}_6\text{O}) \quad (\text{C}_7\text{H}_{10}\text{O}_2)$	D is \Rightarrow A contains group \Rightarrow A is and E is
$\text{B} \xrightarrow{\text{hot conc. KMnO}_4} \text{CO}_2 + \text{F}$ $(\text{C}_9\text{H}_{14}\text{O}_2)$	Strong oxidation of B gave CO_2 \Rightarrow B contains $=\text{CH}_2$ group \Rightarrow B is and F is (NOT and) (–ve iodoform test)



(d) The reaction of silver nitrate with chloride ions gives a white ppt of AgCl , which dissolves in aqueous ammonia to give a colourless solution of $[\text{Ag}(\text{NH}_3)_2]\text{Cl}(\text{aq})$.

The reaction of silver nitrate with iodide ions gives a yellow ppt of AgI , which does not dissolve when aqueous ammonia is added.

(e)(i) The value of pV remains constant for an ideal gas at constant temperature.

(e)(ii)

$$V = \frac{(0.40)(8.31)(300)}{12.0 \times 10^5} = 0.000831 \text{ m}^3 = 0.831 \text{ dm}^3$$

(e)(iii)

p / Pa	V / dm^3	$pV / \text{Pa dm}^3$
5.0×10^5	1.924	9.62×10^5
10.0×10^5	0.926	9.26×10^5
15.0×10^5	0.592	8.88×10^5

Estimated value of pV when $p = 12.0 \times 10^5 \text{ Pa}$

$$= \left[9.26 - \frac{2}{5}(9.26 - 8.88) \right] \times 10^5$$

$$= 9.11 \times 10^5 \text{ Pa dm}^3$$

Value of V when $p = 12.0 \times 10^5 \text{ Pa}$

$$= \frac{9.11 \times 10^5}{12.0 \times 10^5} = 0.759 \text{ dm}^3$$

(e)(iv) The measured volume (0.759 dm^3) is smaller than the volume calculated from the ideal gas equation (0.831 dm^3).

This is due to the **permanent dipole – permanent dipole interactions** between the molecules of H-Cl which cause the gas to **behave non-ideally** at $12.0 \times 10^5 \text{ Pa}$. The **attractive forces** cause the **gas particles to be closer together on average**, taking up a smaller volume than expected in an ideal gas, which is assumed to have negligible intermolecular forces of attraction.

Question 2

(a) The volatilities of the halogens decrease from chlorine to iodine.

From chlorine to iodine, the **total number of electrons per molecule increases**. As the **increase in the size and polarisability of the electron cloud** increases the **strength of instantaneous dipole – induced dipole interactions (id-id)** from chlorine to iodine, **more thermal energy is needed to overcome** the stronger id-id interactions, and thus, leading to decreasing volatility.

(b) *(Not in syllabus)*



Oxidation state of Cl

- decreases from 0 in Cl_2 to -1 in Cl^- .
- increases from 0 in Cl_2 to $+5$ in ClO_3^- .

(c)(i) The breaking of the H-F bond is one of the steps in the dissociation to its aqueous ions. As the bond energy of the **H-F bond ($+562 \text{ kJ mol}^{-1}$) is much greater** than the bond energies of HCl , HBr and HI , **significantly more thermal energy is needed** for HF to dissociate to its aqueous ions.

(c)(ii) Since HCl is a strong acid,
 $[\text{H}^+] = [\text{HCl}] = 0.50 \text{ mol dm}^{-3}$
 $\Rightarrow \text{pH} = -\lg(0.50) = 0.3$

Since HF is a weak acid, it only undergoes partial dissociation.

$$[\text{H}^+] = \sqrt{(0.5)(5.6 \times 10^{-4})} = 0.01679 \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg(0.01679) = 1.77$$

(f)(i) $\Delta G = \Delta H - T\Delta S$

$0.0 = +16.8 - 188(\Delta S)$

$\Delta S = \frac{16.8}{188} = +0.0894 \text{ kJ mol}^{-1} \text{ K}^{-1}$

$\Delta S = +89.4 \text{ J mol}^{-1} \text{ K}^{-1}$

When HCl(l) changes into to HCl(g) , the number of gaseous particles increases, and hence, the disorder in the system increases.

That is why $\Delta S_{\text{vapourisation}}$ is positive.

(f)(ii) $\Delta G = 16.8 - 298(0.0894) = -9.84 \text{ kJ mol}^{-1}$

Since ΔG is negative, the vapourisation of HCl at 298 K is spontaneous (or thermodynamically feasible).

Question 3

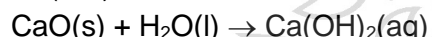
(a)(i) *(Not in syllabus)*

Magnesium burns vigorously in oxygen with a bright white flame and forms a white solid of MgO .

Calcium burns vigorously in oxygen with a brick-red flame and forms a white solid of CaO .

(a)(ii) MgO reacts and dissolves in water very minimally, forming a small amount of Mg(OH)_2 .
 $\text{MgO(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{Mg(OH)}_2\text{(aq)}$

(Not in syllabus) CaO reacts and dissolves readily in water to give a colourless solution of Ca(OH)_2 .



(b)(i) Suggested solubility of Sr(OH)_2
 $= 0.20 \text{ mol dm}^{-3}$ (a suitable value between 0.025 and 0.41 mol dm^{-3})

(b)(ii) $\text{Ca(OH)}_2\text{(aq)} \rightarrow \text{Ca}^{2+}\text{(aq)} + 2\text{OH}^-\text{(aq)}$
 $[\text{OH}^-] = 2(2.5 \times 10^{-2}) = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$
 $\text{pOH} = -\lg(5.0 \times 10^{-2}) = 1.301$
 $\text{pH} = 14 - 1.301 = 12.7$

(b)(iii) $\text{Mg(OH)}_2\text{(s)} \rightleftharpoons \text{Mg}^{2+}\text{(aq)} + 2\text{OH}^-\text{(aq)}$
 $K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2$
 $K_{\text{sp}} = (1.6 \times 10^{-4})[2(1.6 \times 10^{-4})]^2$
 $= 1.64 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$

(b)(iv) At the instant upon mixing, the total volume doubled, so concentrations are halved.

$[\text{Mg}^{2+}] = \frac{1}{2}(1.6 \times 10^{-4}) = 8.0 \times 10^{-5} \text{ mol dm}^{-3}$

$[\text{Ba}^{2+}] = \frac{1}{2}(4.1 \times 10^{-1}) = 2.05 \times 10^{-1} \text{ mol dm}^{-3}$

$[\text{OH}^-] = \frac{2(1.6 \times 10^{-4}) + 2(4.1 \times 10^{-1})}{2}$

$= 0.4102 \text{ mol dm}^{-3}$

IP of $\text{Mg(OH)}_2 = (8.0 \times 10^{-5})(0.4102)^2$

$= 1.34 \times 10^{-5} > K_{\text{sp}} \text{ of } \text{Mg(OH)}_2$

A white ppt of Mg(OH)_2 will be observed.

$K_{\text{sp}} \text{ of } \text{Ba(OH)}_2 = (0.41)[2(0.41)]^2$

$= 0.2757 \text{ mol}^3 \text{ dm}^{-9}$

IP of $\text{Ba(OH)}_2 = (2.05 \times 10^{-1})(0.4102)^2$

$= 0.03449 < K_{\text{sp}} \text{ of } \text{Ba(OH)}_2$

No ppt of Ba(OH)_2 is formed.

(c)(i) *(Not in syllabus)* Aspartic acid and glutamic acid bind to Ca^{2+} via ionic interactions.

(c)(ii) *(Not in syllabus)* α -helix is a right-handed coil which is stabilised by the formation of **intra-chain hydrogen bonds** between the **C=O group of n^{th} amino acid residue and N-H group of $(n+4)^{\text{th}}$ amino acid residue**.

(c)(iii) HCl(aq) , heat under reflux

OR $6 \text{ mol dm}^{-3} \text{ HCl(aq)}$, heat for several hours

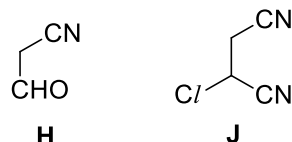
Note to student: Since this is a hydrolysis reaction, water must be present. Thus, terms such as "dilute" or "aqueous" are essential.

(c)(iv)

asp-gly
 gly-asp
 gly-tyr
 ile-ser
 tyr-ile

gly-asp-gly-tyr-ile-ser

(d)(i)



(d)(ii) Step 4: excess concentrated NH_3 in ethanol, heat in sealed tube

Step 5: HCl(aq) or $\text{H}_2\text{SO}_4\text{(aq)}$, heat

Note to student:

A common mistake is to write the slow step as $\text{RCH}_2\text{OH}_2^+ + \text{Cl}^- \longrightarrow \text{RCH}_2\text{Cl} + \text{H}_2\text{O}$. This equation implies that Cl^- participates in the rate-determining step. However, it was given that the rate was independent of $[\text{Cl}^-]$.

Question 4

(a) Step 1: hydrolysis

Step 2: elimination of water / dehydration

(loss of 3 H_2O seen from molecular formula)

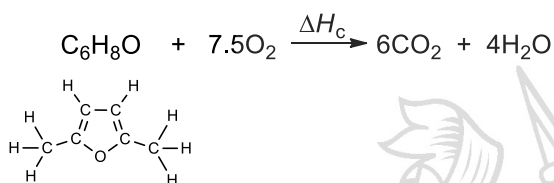
Step 3: reduction

(gain in 2 H and loss of 2 O seen from molecular formula)

(d)(ii) $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{H}_2\text{SO}_4\text{(aq)}$, heat

Note to student: Avoid the use of KMnO_4 as the $\text{C}=\text{C}$ bond in HMF may be ruptured by vigorous oxidation.

(b)



$$\Delta H_c = 3(350) + 2(610) + 2(360) + 8(410) + 7.5(496) - [12(805) + 8(460)] = -3350 \text{ kJ mol}^{-1}$$

(c) total amt of heat evolved

$$= \frac{200(4.18)(32)}{0.8} = 33440 \text{ J}$$

$$\text{amt of DMF} = \frac{1.00}{6(12) + 8(1) + 16} = 0.01042 \text{ mol}$$

$$\begin{aligned} \text{experimental } \Delta H_c &= \frac{-33440}{0.01042} \\ &= -3.209 \times 10^6 \text{ J mol}^{-1} \\ &= -3210 \text{ kJ mol}^{-1} \end{aligned}$$

The experimental ΔH_c is less exothermic than the value calculated in **(b)**, which made use of average bond energy values. In addition, the use of bond energy values assumes that the chemical species involved are in gaseous state. However, DMF is a liquid. The experimental value is less exothermic as it takes into account the energy required to vapourise DMF to a gas.

(e)(i) ester

(e)(ii)



(e)(iii) catalytic amt of concentrated H_2SO_4 , heat

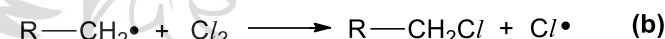
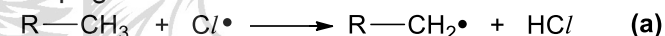
Note to student: Do not write “concentrated $\text{H}_2\text{SO}_4\text{(aq)}$ ”. The “(aq)” implies that H_2SO_4 is dilute.

(f) Free radical substitution

Initiation



Propagation



then **(a)**, **(b)**, **(a)**, **(b)**, ...

Termination



Question 5

(a)(i) Proton number is the **number of protons** in the **nucleus** of an atom.

Nucleon number is the **total number of protons and neutrons** in the **nucleus** of an atom.

(d)(i) rate = $k[\text{RCH}_2\text{OH}][\text{H}^+]$

Step 1: $\text{RCH}_2\text{OH} + \text{H}^+ \longrightarrow \text{RCH}_2\text{OH}_2^+$ (fast)

Step 2: $\text{RCH}_2\text{OH}_2^+ \longrightarrow \text{RCH}_2^+ + \text{H}_2\text{O}$ (slow)

Step 3: $\text{RCH}_2^+ + \text{Cl}^- \longrightarrow \text{RCH}_2\text{Cl}$ (fast)

Step 2 is the rate-determining step.

- (a)(ii) Let x be the % of ${}^6\text{Li}$, so $(100-x)$ is the % of ${}^7\text{Li}$.

$$6.015(x) + 7.016(100-x) = 6.942(100)$$

$$x = 7.39\%$$

% of ${}^6\text{Li} = 7.39\%$ (to 2 dp)

% of ${}^7\text{Li} = (100-7.39) = 92.61\%$ (2 dp)

- (a)(iii) X: ${}^3_2\text{He}$ Y: ${}^7_3\text{Li}$

Note to student: Since the question asks for the **identity** of X and Y, the **identities**, i.e. He and Li, should be written. This is **in addition** to the proton numbers and nucleon numbers.

- (b)(i) metallic bonding

The valence electrons of Li atoms can delocalise and the resultant Li^+ cations attract the delocalised π electron cloud of graphite, similar to how lithium cations attract the sea of delocalised electrons in a metallic lattice.

- (b)(ii) Since O is more electronegative than Co, oxidation state of Co before discharge = +4
oxidation state of Co after discharge = +3

- (b)(iii) BF_4^- has 4 bond pairs and no lone pairs. In order to minimise electrostatic repulsion between the bond pairs, they arrange themselves in a tetrahedral shape, i.e. the shape of BF_4^- is tetrahedral.

- (b)(iv) cold $\text{KMnO}_4(\text{aq})$, $\text{NaOH}(\text{aq})$

- (b)(v) condensation reaction

- (c)(i) $\text{Li}_2\text{O}_2 + \text{CO}_2 \longrightarrow \text{Li}_2\text{CO}_3 + \frac{1}{2}\text{O}_2$

- (c)(ii) Li^+ is a **small cation**. Similar to Mg^{2+} , its **charge density**, and hence **polarising power**, is **high**. The high polarising power **distorts the electron cloud of CO_3^{2-}** and **weakens / further polarises the C–O bond**. Thus, a **smaller amount of energy is needed to break the C–O bond**, accounting for the ease of decomposition of Li_2CO_3 .

- (d)(i)

R–Br	Carbonyl compound
$\text{CH}_3\text{CH}_2\text{Br}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
OR	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	$\text{CH}_3\text{CH}_2\text{CHO}$

- (d)(ii)

R–Br	Carbonyl compound
CH_3Br	$(\text{CH}_3\text{CH}_2)_2\text{C}=\text{O}$
OR	
$\text{CH}_3\text{CH}_2\text{Br}$	$\text{CH}_3\text{CH}_2\text{COCH}_3$

- (e)

Test	Observations
1. To separate test-tubes of each compound, add an equal volume of acidified $\text{K}_2\text{Cr}_2\text{O}_7$ and heat.	Orange $\text{K}_2\text{Cr}_2\text{O}_7$ turns green in test-tubes containing P and Q . Orange $\text{K}_2\text{Cr}_2\text{O}_7$ remains orange in the test-tube containing R .
2. To the two green-coloured solutions from test 1, add 2,4-dinitrophenylhydrazine dropwise until in excess. Filter the mixture if a ppt is formed.	Orange ppt is observed for the test-tube containing Q . No orange ppt is observed for the test-tube containing P .

Note to student:

- After test 1, **P** is oxidised to a carboxylic acid and **Q** is oxidised to a ketone, reducing $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} ; **R**, a tertiary alcohol, will not be oxidised by $\text{Cr}_2\text{O}_7^{2-}$.

In test 2, 2,4-dinitrophenylhydrazine forms an orange ppt with the ketone product from **Q**, which does not happen for the acid product from **P**.

- Aqueous Na_2CO_3 or $\text{PCl}_5(\text{s})$ should **not** be used in test 2. This is because test 2 is carried out on the resultant solutions from test 1, which contain excess acid and water. The excess acid from acidified $\text{K}_2\text{Cr}_2\text{O}_7$ would react with Na_2CO_3 and the water in the aqueous reagents used will react with $\text{PCl}_5(\text{s})$. Hence, both tubes will produce false positive results.

Changes to 2016 H2 Chemistry A Level Question Paper

Dear students,

The TYS you have purchased is based on the 9647 (old) syllabus. You will be sitting for the 9729 (new) syllabus papers. This document will instruct you on the changes you need to make to the TYS questions.

The Planning question for the 9729 syllabus will be in the Paper 4 (Practical).

Some concepts are no longer tested in the 9729 syllabus and the values used for some calculations are now different (e.g. molar volume at s.t.p.) which will affect your choice of the answers.

You are advised to **make the changes** on your question papers **before you attempt it**. Do inform your tutors if you notice any differences which were not highlighted in this document.

Paper 1

17 Amend question

The equation for the thermal decomposition of $\text{Mg}(\text{NO}_3)_2$ is no longer in syllabus. The following equation will help you solve this question:



18 Amend question – Options C & D not in syllabus

C is not true. $\text{Mg}(\text{OH})_2$ is not very soluble in water (QA knowledge)

D is not true. Mg reacts very slowly with cold water.

20 Amend options

- A** Y is in Group **2**.
- B** Y is in Group **13**.
- C** Y is in Group **15**.

Paper 2

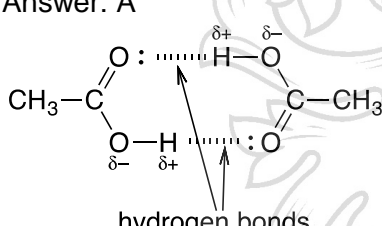
4b(i) Amend question

“... show the feasibility **spontaneity**...”

5(b)(ii) Not in syllabus

Paper 3

No amendments

- 1 Answer: B
Amount of Q = $1.0 \text{ g} \div x \text{ g mol}^{-1} = 1/x \text{ mol}$
Number of molecules = $L \text{ mol}^{-1} \times (1/x) \text{ mol} = L/x$
Number of atoms = $2(L/x) = 2L/x$
- 2 Answer: D
 $2\text{H}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{SO}_2 + 2\text{H}_2\text{O}$
 $\text{CS}_2 + 3\text{O}_2 \rightarrow \text{CO}_2 + 2\text{SO}_2$
Combining both equations: $2\text{H}_2\text{S} + \text{CS}_2 + 6\text{O}_2 \rightarrow 4\text{SO}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$
Mole ratio of $\text{SO}_2 : \text{CO}_2 = 4 : 1$
- 3 Answer: C
 A_r for Cu = $[65(63) + 29(65)] \div (65 + 29) = 63.6$
- 4 Answer: D
 $^{36}\text{S}^{2-}$: 16 protons, 20 neutrons, 18 electrons
 $^{37}\text{Cl}^-$: 17 protons, 20 neutrons, 18 electrons
Option A: The nucleon numbers for S and Cl are 36 and 37 respectively.
Option B: Both ions have an outer electronic configuration of $3s^2 3p^6$.
Option C: Both ions have fewer electrons than neutrons.
Option D: Both ions have 20 neutrons in their nuclei.
- 5 Answer: A

- 6 Answer: C
There are three possible structures.
① $\text{C}^1\text{--C}^2\equiv\text{N}$ (C^1 has 1 lone pair and 1 unpaired electron; N has a lone pair)
② $\text{C}^1=\text{C}^2=\text{N}$ (C^1 has 1 lone pair; N has 1 lone pair and 1 unpaired electron)
③ $\text{C}^1\equiv\text{C}^2\text{--N}$ (C^1 has 1 unpaired electron; N has 2 lone pairs)
All three possible structures have 2 lone pairs of electrons and 1 unpaired electron.
- 7 Answer: C
By conservation of mass, mass of liquid = mass of vapour
 $pV = nRT$
 $(101 \times 10^3)[(78 - 2) \times 10^{-6}] = (0.293/M)(8.31)(97 + 273)$
Molar mass, $M = 117.4 \text{ g mol}^{-1}$
 $M_r \approx 117$
- 8 Answer: D
Lattice energy is the enthalpy change when one mole of ionic compound is formed from its constituent gaseous ions under standard conditions.
Note: Lithium fluoride is a solid under standard conditions.
- 9 Answer: B
 ΔH_f of $\text{KCl} = 90 + \frac{1}{2}(242) + 418 + (-355) + (-710) = -436 \text{ kJ mol}^{-1}$

- 10 Answer: D
 $\Delta G = \Delta H - T\Delta S$

When ΔG is more negative at a higher temperature, ΔS must be positive.

OR

1 mol of gas + 1 mol of solid \rightarrow 2 mol of gases $\Rightarrow \Delta S > 0$ because a gas has greater entropy than a solid

At a lower temperature, when “ $-T\Delta S$ ” is a small negative value, ΔG is positive. This implies that ΔH is positive.

OR

$$+78000 = \Delta H - 378\Delta S$$

Since $\Delta S > 0$, $-378\Delta S < 0$. Thus, ΔH must be positive.

- 11 Answer: C
 $E^\ominus_{\text{cell}} = E^\ominus(\text{Ag}^+/\text{Ag}) - E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+}) = (+0.80) - (+0.77) = +0.03 \text{ V}$
To obtain a cell potential of 0.00 V, $E^\ominus(\text{Ag}^+/\text{Ag})$ needs to become less positive or $E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+})$ needs to become more positive, or both electrode potentials have to be adjusted to the same value.
Option A: Increase in $[\text{Ag}^+]$ will make $E^\ominus(\text{Ag}^+/\text{Ag}) > +0.80 \text{ V}$
Option B: Increase in $[\text{Fe}^{2+}]$ will make $E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+}) < +0.77 \text{ V}$
Option C: Increase in $[\text{Fe}^{3+}]$ will make $E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+}) > +0.77 \text{ V}$ (can be adjusted to +0.80 V)
Option D: Increase in the surface of the electrode does not change the electrode potential.

- 12 Answer: A
Anode reaction: $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$
Amount of electricity passed = $8 \text{ C s}^{-1} \times (100 \times 60) \text{ s} = 48000 \text{ C}$
When $4 \times 96500 \text{ C}$ are passed, 1 mol of O_2 is liberated.
When 48000 C are passed, $48000 / (4 \times 96500) = 0.1244 \text{ mol}$ of O_2 is liberated.
Volume of O_2 liberated at s.t.p. = $0.1244 \times 22.7 = 2.8 \text{ dm}^3$ (1 d.p.)

- 13 Answer: C
X is a saturated solution of ZnF_2 .
 $\text{ZnF}_2(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq}) \quad K_{\text{sp}} = [\text{Zn}^{2+}][\text{F}^{-}]^2 = 3.2 \times 10^{-2} \text{ mol}^3 \text{ dm}^{-9}$
Let $[\text{Zn}^{2+}]$ be $y \text{ mol dm}^{-3}$ and $[\text{F}^{-}]$ be $2y \text{ mol dm}^{-3}$.
 $y(2y)^2 = 3.2 \times 10^{-2}$
 $[\text{F}^{-}] = 2y = 4 \times 10^{-1} \text{ mol dm}^{-3}$
When BaF_2 just precipitates, $[\text{Ba}^{2+}][\text{F}^{-}]^2 = 1.6 \times 10^{-7} \text{ mol}^3 \text{ dm}^{-9}$
Since $[\text{F}^{-}] = 4 \times 10^{-1} \text{ mol dm}^{-3}$, $[\text{Ba}^{2+}] = 1.6 \times 10^{-7} \div (4 \times 10^{-1})^2 = 1 \times 10^{-6} \text{ mol dm}^{-3}$

- 14 Answer: B
 $\text{Al}(\text{H}_2\text{O})_6^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}(\text{aq}) + \text{H}_3\text{O}^{+}(\text{aq})$
 $[\text{H}^{+}] = \sqrt{(1.0 \times 10^{-5} \times 0.1)} = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$
 $\text{pH} = -\log(1.0 \times 10^{-3}) = 3.0$

- 15 Answer: D
 $y = k(\text{a})(\text{a})^2(\text{a})^2$
Hence, $k = y/\text{a}^5$
 $\text{rate} = (y/\text{a}^5)(\text{a}/2)(2\text{a})^2(3\text{a})^2 = 18y$

- 16 Answer: A
Magnesium oxide, though having a giant ionic lattice, has less covalent character than aluminium oxide. Phosphorus pentoxide and silicon dioxide are predominantly covalent, so they do not exist as giant ionic lattices.

- 17 Answer: A
 $\text{Mg}(\text{NO}_3)_2(\text{s}) \rightarrow \text{MgO}(\text{s}) + 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$
 Amount of $\text{Mg}(\text{NO}_3)_2 = 10.4 / 148.3 = 0.07013 \text{ mol}$
 Amount of O_2 (neutral gas) = $\frac{1}{2} (0.07013) = 0.03507 \text{ mol}$
 Mass of O_2 (neutral gas) = $0.03507 \times 32.0 = 1.12 \text{ g}$
- 18 Answer: A
 Option B: Magnesium (m.p. 650°C) has a higher melting point than sulfur (m.p. 115.2°C) because the energy needed to overcome the metallic bonds in the giant metallic lattice of magnesium is greater than that needed to overcome the id-id interactions between S_8 molecules in the simple molecular lattice of sulfur.
 Option C: Magnesium hydroxide is only sparingly soluble in water.
 Option D: Magnesium reacts slowly with cold water.
- 19 Answer: D
 White silver chloride formed dissolves in concentrated aqueous ammonia to give a colourless solution.
 Cream silver bromide formed dissolves in concentrated aqueous ammonia to give a colourless solution.
 Yellow silver iodide formed is insoluble in concentrated aqueous ammonia.
- 20 Answer: D
 Element Y is vanadium.
- 21 Answer: B
 $2\text{VO}_2^+ + \text{SO}_2 \rightarrow 2\text{VO}^{2+} + \text{SO}_4^{2-}$ $E^\ominus_{\text{cell}} = 1.00 - 0.17 = +0.83 \text{ V}$ (feasible)
 $2\text{VO}^{2+} + \text{SO}_2 \rightarrow 2\text{V}^{3+} + \text{SO}_4^{2-}$ $E^\ominus_{\text{cell}} = 0.34 - 0.17 = +0.17 \text{ V}$ (feasible)
 $2\text{V}^{3+} + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{V}^{2+} + \text{SO}_4^{2-} + 4\text{H}^+$ $E^\ominus_{\text{cell}} = -0.26 - 0.17 = -0.43 \text{ V}$ (not feasible)
- 22 Answer: B
 NH_3 ligand has no charge, while Cl^- ligand has a charge of 1^- .
 Let the number of NH_3 ligands be $6 - n$ and the number of Cl^- ligands be n .
 Charge on cation in platinum(IV) compound = $(+4) + (6 - n)(0) + n(-1) = 2$
 Solving, $n = 2$, i.e. there are 2 Cl^- ligands. Hence, there are 4 NH_3 ligands.
 $\text{PtCl}_4 + 4\text{NH}_3 \rightarrow [\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+} + 2\text{Cl}^-$
 Option A: The cation, $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+$, has a $1+$ charge.
 Option C: The oxidation state of platinum in $[\text{Pt}(\text{NH}_3)_6]^{2+}$ is $+2$.
 Option D: The cation, $[\text{Pt}(\text{NH}_3)_6]^{4+}$, has a $4+$ charge.
- 23 Answer: B
 There are 2 π bonds found in the $\text{C}\equiv\text{C}$ bond.
 Both C atoms in the $\text{C}\equiv\text{C}$ bond are sp hybridised.
 The remaining C in CH_3 is sp^3 hybridised.
- 24 Answer: A
 A termination step involves the collision of 2 free radicals. Hence, option B is incorrect.
 An $\text{H}\bullet$ free radical is not formed, so options C and D are incorrect.
- 25 Answer: D
 The rate-determining step of this $\text{S}_\text{N}1$ mechanism involves the breaking of the $\text{C}-\text{Br}$ or $\text{C}-\text{Cl}$ bond.
 Since the $\text{C}-\text{Br}$ bond is weaker, reaction 1 is faster.
- 26 Answer: C
 Na reacts with the phenolic group (ROH) in compound C.
 $\text{ROH} + \text{Na} \rightarrow \text{RO}^-\text{Na}^+ + \frac{1}{2}\text{H}_2$

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27 Answer: A
 Option B shows a compound which does not have the empirical formula CH_2O .
 Option C and option D show compounds which do not produce yellow CHI_3 in the iodoform test because they are neither methyl alcohols nor methyl ketones. In addition, neither one is ethanal.

28 Answer: B
 When 3-bromo-4-hydroxycinnamic acid is dissolved in water, its phenolic and carboxylic acid groups will readily ionise to release H^+ . The resulting conjugate bases may remove a D^+ ion from D_2O .



29 Answer: B

- As X is a carbonyl compound which can be reduced by NaBH_4 , it could be either a ketone or an aldehyde.
- As X does not react with alkaline aqueous iodine or with Tollens' reagent, it is neither a methyl ketone (RCOCH_3) nor an aldehyde.

Hence, X must be a ketone which does not have the $-\text{COCH}_3$ functional group.

The reduction of X will give a secondary alcohol which does not have the $-\text{CH}(\text{OH})\text{CH}_3$ functional group.

Option A shows a tertiary alcohol.

Option C shows a secondary alcohol with a $-\text{CH}(\text{OH})\text{CH}_3$ functional group.

Option D shows a primary alcohol.

30 Answer: B
 Option A and option D show the hydrolysis of esters, a relatively slow reaction which usually requires heating and the use of a catalyst such as dilute H_2SO_4 .

Option B shows the hydrolysis of an acyl chloride, which occurs readily at room temperature because the electron-rich O atom in water can readily attack the highly electron-deficient, sp^2 C atom in the acyl group.

Option C shows the hydrolysis of an amide, a reaction which requires prolonged heating in an acid.

31 Answer: B (1 and 2 only)

Option 1

Isotope	^4He	^{12}C	^{24}Mg
No. of protons	2	6	12
No. of neutrons	2	6	12

Option 2

Isotope	^{14}N	^{20}Ne	^{30}P
No. of protons	7	10	15
No. of neutrons	7	10	15

Option 3

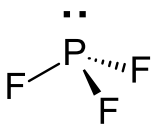
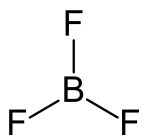
Isotope	^{28}Si	^{34}S	^{40}Ca
No. of protons	14	16	20
No. of neutrons	14	18	20

32 Answer: A (1, 2 and 3)

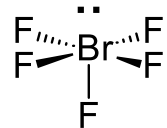
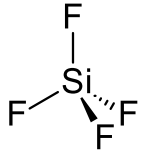
Option 1

Molecule	SO_2	CO_2
Structure	$\begin{array}{c} \cdot\cdot \\ \text{O}=\text{S}=\text{O} \end{array}$	$\text{O}=\text{C}=\text{O}$
Net dipole	Yes	No

Option 2

Molecule	PF ₃	BF ₃
Structure		
Net dipole	Yes	No

Option 3

Molecule	BrF ₅	SiF ₄
Structure		
Net dipole	Yes	No

- 33 Answer: C (2 and 3 only)
 Brønsted-Lowry acid: H⁺ donor
 Brønsted-Lowry base: H⁺ acceptor
 Option 1: NH₃ is a nucleophile, while CH₃Cl is an electrophile.
 Option 2: CH₃OH accepted an H⁺ ion, while HC/O₄ donated an H⁺ ion.
 Option 3: HNO₃ accepted an H⁺ ion, while H₂SO₄ donated an H⁺ ion.
- 34 Answer: D (1 only)
 The ethoxide ion, C₂H₅O⁻, is a nucleophile and it attacks the primary iodoalkane, CH₃I, in a nucleophilic substitution reaction.
 From experiments 1 and 3, when [C₂H₅ONa] is doubled and [CH₃I] is kept constant, the relative initial rate of reaction is doubled. Hence, the reaction is first order with respect to [C₂H₅ONa]. So, option 1 is correct.
 From experiments 2 and 3, when [C₂H₅ONa] is kept constant and [CH₃I] is halved, the relative initial rate of reaction is halved. Hence, the reaction is first order with respect to [CH₃I]. So, option 3 is incorrect.
 The overall order reaction is 1 + 1 = 2. So, option 2 is incorrect.
- 35 Answer: C (2 and 3 only)
 Brønsted-Lowry acid: H⁺ donor
 Option 1: BeCl₂ did not donate any H⁺ ions, so it is not a Brønsted-Lowry acid.
 Option 2: Be(H₂O)₄²⁺ donated 2 H⁺ ions to 2 Cl⁻ ions, so Be(H₂O)₄²⁺ is a Brønsted-Lowry acid.
 Option 3: Be(H₂O)₂(OH)₂ donated 2 H⁺ ions to 2 OH⁻ ions, so Be(H₂O)₂(OH)₂ is a Brønsted-Lowry acid.
- 36 Answer: B (1 and 2 only)
 oxidation no.
- 0

Cl₂

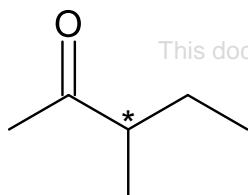
reactant

-1

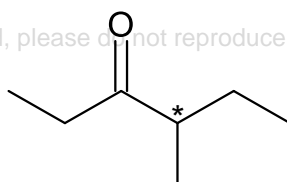
NaCl

+5

NaClO₃
- products
- 37 Answer: C (2 and 3)
 There is no such molecule with x = 5.
 When x = 6

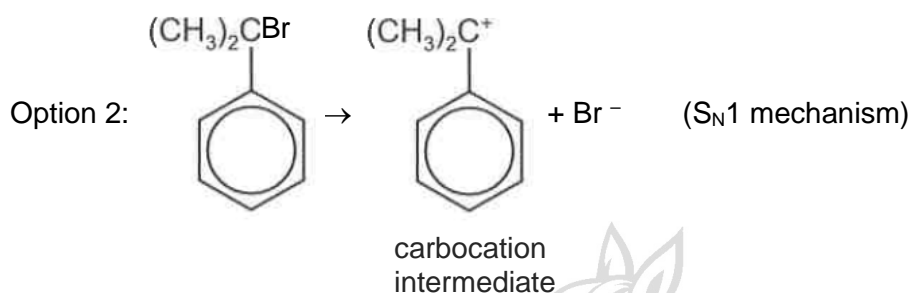


E.g. 3-methyl-pentan-2-one

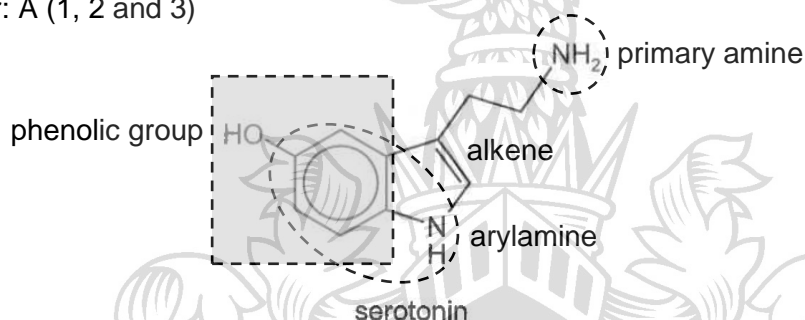


E.g. 4-methyl-hexan-3-one

- 38 Answer: B (1 and 2 only)
 Option 1: $\text{OH}^- + \text{CH}_3\text{Cl} \rightarrow [\text{HO} \cdots \text{CH}_3 \cdots \text{Cl}]^-$ (S_N2 mechanism)
 transition state



- 39 Option 3: This cationic species is not formed in a nucleophilic substitution reaction.
 Answer: A (1, 2 and 3)



- Option 1: CH_3COCl reacts with the phenolic group to give an ester. It also reacts with the primary amine and the arylamine to give amides.
 Option 2: HCl neutralises the amines to give salts. It also undergoes addition with the alkene.
 Option 3: NaOH neutralises the acidic phenolic group to give a phenoxide salt.

- 40 Answer: C (2 and 3 only)

The polypeptide given is glycine–cysteine–lysine–glycine–lysine (N terminus on the left and C-terminus on the right).

Action of trypsin: glycine–cysteine–lysine–glycine–lysine

Possible fragments: glycine–cysteine–lysine, glycine–lysine

Q1 Planning

- (a) Effervescence would be seen; colourless gas which forms a white ppt with $\text{Ca(OH)}_2(\text{aq})$ would be evolved.

The deep blue azurite would dissolve completely to give a blue solution.

- (b) **Calculation of a suitable mass of powdered rock to react with about 75% of the acid in the conical flask**



Amt of H_2SO_4 in $50.00 \text{ cm}^3 = 1.00 \times 50.00 \times 10^{-3} = 0.0500 \text{ mol}$

Amt of azurite that reacts with 75% of $\text{H}_2\text{SO}_4 = \frac{1}{3} \times 0.75 \times 0.0500 = 0.0125 \text{ mol}$

Mass of azurite in $0.0125 \text{ mol} = 0.0125 \times 344.5 = 4.306 \text{ g}$

Mass of powered rock to be used $= \frac{4.306}{0.90} = 4.78 \text{ g}$

Dilution and Volume of unreacted sulfuric acid required for titration

Amt of excess H_2SO_4 in reaction mixture $= 0.25 \times 0.0500 = 0.0125 \text{ mol}$

Assume that **average** volume of NaOH required for titration is 25.00 cm^3

Amt of excess H_2SO_4 used for titration $= \frac{1}{2} \times 0.100 \times 25 \times 10^{-3} = 0.00125 \text{ mol}$ (ie 10% of 0.0125 mol)

Hence, 10% of excess H_2SO_4 is needed for titration with $\text{NaOH}(\text{aq})$.

So, the final reaction mixture can be diluted to 250 cm^3 and 25.0 cm^3 (ie 10% of 250 cm^3) will be pipetted for titration with NaOH.

Procedure

- Using an electronic balance, weigh out accurately about 4.78 g of the powdered rock in a clean and dry weighing bottle. Record the mass of the weighing bottle and powdered rock.
- Transfer the powdered rock sample into the 250 cm^3 conical flask containing 50.00 cm^3 of sulfuric acid and swirl the contents. Place a glass filter funnel on the mouth of the conical flask to prevent acid spray.
- Reweigh the emptied weighing bottle and record its mass.
- When effervescence has ended and all the powdered rock has dissolved, transfer the final reaction mixture quantitatively into a 250 cm^3 graduated flask with the aid of a funnel and a glass rod. Rinse the conical flask and the glass filter funnel a few times with small volumes of deionised water each time and transfer all the washings into the graduated flask.
- Fill the graduated flask to the 250 cm^3 mark with more deionised water. Use a teat pipette (or dropper) to add the deionised water drop by drop when nearing the mark.
- Stopper the graduated flask and shake the solution thoroughly to ensure that it is homogeneous. Label the solution **FA 3**.
- Pipette 25.0 cm^3 of **FA 3** into a 250 cm^3 conical flask. Add 2 drops of phenolphthalein indicator.
- Fill the burette with the $0.100 \text{ mol dm}^{-3}$ $\text{NaOH}(\text{aq})$ provided. Titrate the solution in the conical flask with the standard dilute $\text{NaOH}(\text{aq})$ placed in the burette.

8. Stop the titration when one drop of the NaOH(aq) added changes the colour of the solution in the conical flask from blue to light purple.
9. Repeat the titration until at least two consistent results are obtained, i.e. the two titre volumes do not differ by more than 0.10 cm³.

Calculations

Let that the **average** values of two consistent titres be 1000b cm³ or b dm³.
and

mass of powdered rock sample and weighing bottle / g = d

mass of emptied weighing bottle / g = e

mass of powdered rock sample /g = d – e = c

Amt of excess sulfuric acid in 25.0 cm³ of **FA3** = $\frac{1}{2} \times b \times 0.100 = 0.0500b$ mol

Amt of excess sulfuric in reaction mixture = $0.0500b \times \frac{250}{25.0} = 0.500b$ mol

Amt of sulfuric acid reacted with azurite = $0.0500 - 0.500b$ mol

Amt of pure azurite present in the powdered rock sample = $\frac{1}{3} \times (0.0500 - 0.500b)$ mol

Mass of pure azurite present in the powdered rock sample = $\frac{1}{3} \times (0.0500 - 0.500b) \times 344.5$
= $114.8 \times (0.0500 - 0.500b)$ g

Percentage by mass of pure azurite present in the powdered rock sample
= $\frac{114.8 \times (0.0500 - 0.500b)}{c} \times 100 \%$

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Question 2

(a)(i) Individual fatty acids have intermolecular hydrogen bonds which are stronger than the permanent dipole-permanent dipole intermolecular forces between triester. Fatty acids have higher boiling points than triester as more energy is needed to overcome the strong hydrogen bonding between fatty acid molecules, resulting in its higher boiling point.

(ii) stearic acid has longer hydrocarbon chain (2 more carbon atoms) than palmitic acid. As the chain length of alkyl group, R, increases, the instantaneous dipole-induced dipole forces between RCO_2H molecules become stronger. More energy is needed to overcome these forces.

(iii) The presence of $\text{C}=\text{C}$ bonds in fatty acids with the same number of carbon atoms lowers the melting point of the fatty acids. [m.p. of linolenic acid < linoleic acid < oleic acid < stearic acid]

(b)(i) Electrophilic addition

(b)(ii) Mass of iodine that would react with 100g of olive oil = $(100/0.256) \times 0.237 = 92.6 \text{ g}$

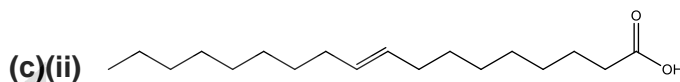
(b)(iii) Amt of iodine in 92.6 g = $92.6 / 254 = 0.3646 \text{ mol}$
Amt of $\text{C}=\text{C}$ bonds in olive oil = 0.3646 mol
Amt of olive oil in 100 g = $100/782 = 0.1279 \text{ mol}$
Average number of $\text{C}=\text{C}$ bonds = $0.3646/0.1279 = 2.85$

(b)(iv) Triesters containing 3 oleic acids contain 3 $\text{C}=\text{C}$ bonds per molecule.

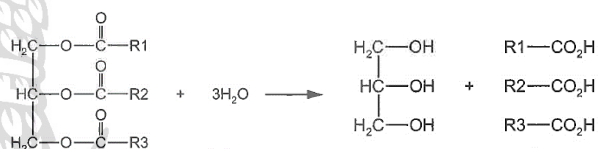
As the average number of $\text{C}=\text{C}$ bond in each molecule of olive oil is 2.85 which is less than 3 and triesters of olive oil are mainly formed from oleic acid, olive oil should contain triesters of palmitic acid and/or stearic acid as the other significant component. Since the average Mr of olive oil is smaller than that of triester of oleic acid ($\text{Mr} = 282 \times 3 + 12 \times 3 + 2 = 884$), the other

major component of olive oil should be triester of palmitic acid which has a lower Mr than that of stearic acid.

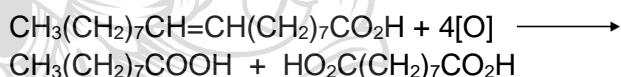
(c)(i) H_2 , Ni catalyst, heat



(d) ester undergoes hydrolysis



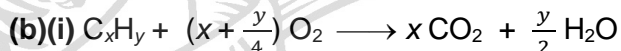
alkene($\text{C}=\text{C}$) undergoes oxidative cleavage



Question 3

(a) Silicon carbide has a giant molecular structure.

Each silicon atom is covalently bonded to four other carbon atoms arranged tetrahedrally around it. Each carbon atom is also covalently bonded to four other silicon atoms. This tetrahedral arrangement is repeated throughout the whole molecule. Melting requires a lot of energy to break the strong covalent bonds between all atoms, hence silicon carbide has very high melting point.



(b) (ii) Heterogeneous catalyst is used, whereby the catalyst and the reactants are in different phases.

For heterogeneous catalysis to occur, the reactant molecules need to be readily adsorbed onto the catalyst surface. The adsorption of the reactant molecules at the catalyst surface increases the reaction rate because it

1. weakens the covalent bonds within the reactant molecules, thereby reducing the activation energy for the reaction.

2. increases the concentration of reactant molecules at the catalyst surface and allows the reactant molecules to come into close contact with proper orientation for reaction.

(c) (i) N(-3) in NH_3 to N(0) in N_2

N(+4) in NO_2 to N(0) in N_2



(d) (i) $\text{NO}_2 + \text{SO}_2 \longrightarrow \text{SO}_3 + \text{NO}$ (I)



Homogeneous catalyst; oxidizes SO_2 to SO_3 , and is regenerated (II)

(ii) Cause breathing difficulties; form acid rain, corrodes buildings

(iii) $K_p = \frac{p_{\text{N}_2\text{O}_4}}{p_{\text{NO}_2}^2} = \frac{p_{\text{N}_2\text{O}_4}}{(1.5 \times 10^{-3})^2}$
 $= 6.25 \times 10^{-5} \text{ Pa}^{-1}$
 $p_{\text{N}_2\text{O}_4} = 1.41 \times 10^{-10} \text{ Pa}$

Question 4

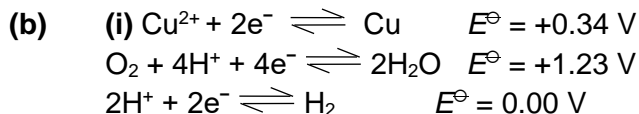
(a) (i) K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
 Cu: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$



First ionisation energy of K is $+418 \text{ kJ mol}^{-1}$ while that for Cu is $+745 \text{ kJ mol}^{-1}$. Much more energy is required to remove an electron from Cu than K. *(Not in syllabus: Cu has a higher nuclear charge than K and there is a minimal increase in shielding effect from K to Cu. This causes the valence electron in Cu to be more strongly attracted to the nucleus and less easily removed.)*

From both the standard reduction potential and ionisation energies, it can be seen that it

is much easier for K to lose an electron than for Cu to lose an electron. Hence Cu is much less reactive than potassium.



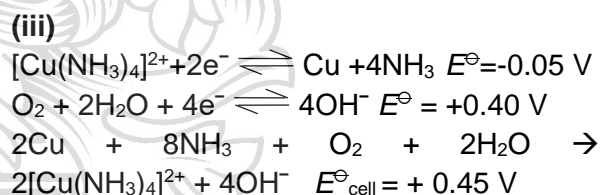
In acid without O_2 ,

$E^\ominus_{\text{cell}} = 0 - 0.34 = -0.34 \text{ V} < 0$ (not spontaneous)

In acid with O_2 ,

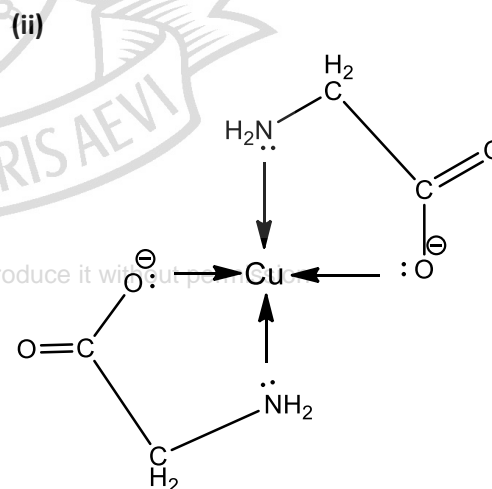
$E^\ominus_{\text{cell}} = 1.23 - 0.34 = +0.89 \text{ V} > 0$ (spontaneous)

(ii) Even though the reaction is spontaneous/thermodynamically feasible, the activation energy is high and hence the rate of reaction is slow.



(c)

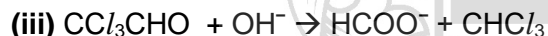
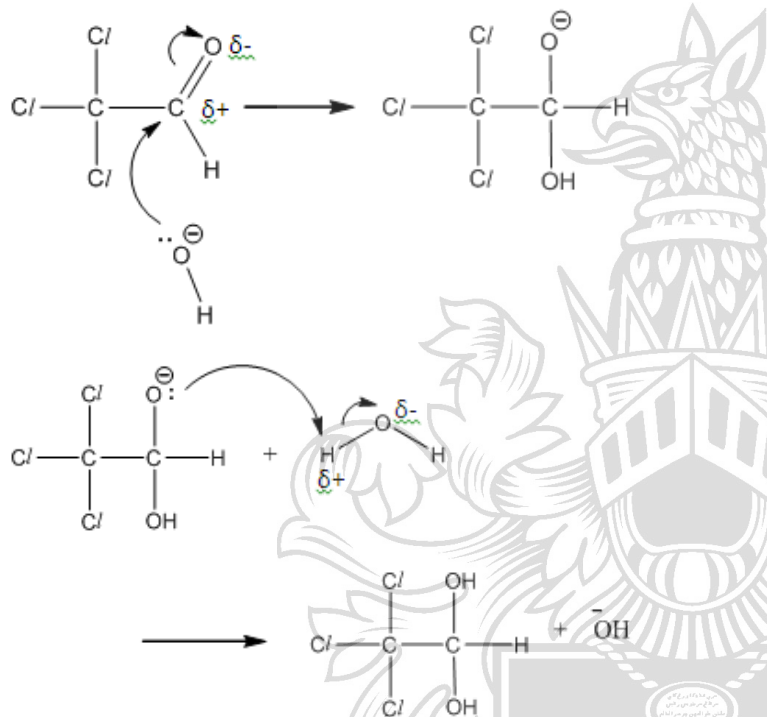
(i) A ligand is an ion or a molecule which contains at least one atom bearing a lone pair of electrons which can be donated into a low-lying vacant orbital of a central metal atom or ion forming a co-ordinate bond (or dative covalent bond), and resulting in the formation of a complex.



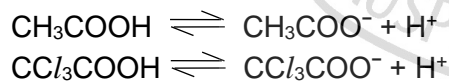
Question 5

- (a) (i) Add 2,4-dinitrophenylhydrazine to the mixture. If orange precipitate is seen, there is some remaining trichloroethanal.

(ii)

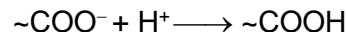


- (b) (i) The acidity of a compound depends on the relative stability of its conjugate base anion (A^-). The more stable the conjugate base, the more acidic the compound will be. The anion may be stabilized by dispersal of negative charge.

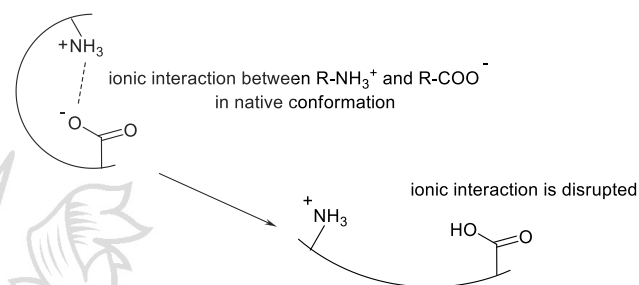


The conjugate base of trichloroethanoic acid is more stable than that of ethanoic acid as the negative charge can be dispersed over 3 electronegative Cl atoms which are electron withdrawing.

- (ii) (*Not in syllabus*) Acids disrupt ionic interactions by protonating ionic side chain R groups containing carboxylate anions:



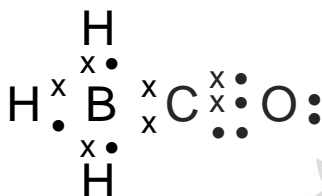
The protonated carboxyl groups are then unable to participate in ionic interactions with side chains containing -NH_3^+ , bringing about denaturation of the protein.



Question 1

- (a) Carbon monoxide bonds strongly (almost irreversibly), via a dative covalent bond, to the iron in haemoglobin. CO is a stronger ligand than O₂ and its presence destroys the O₂ carrying capacity of haemoglobin. Thus, CO is poisonous.

(b)



(f)(i)

$$K_p = \frac{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}{P_{\text{CO}} (P_{\text{H}_2})^3}$$

Units: atm⁻²

(f)(ii)

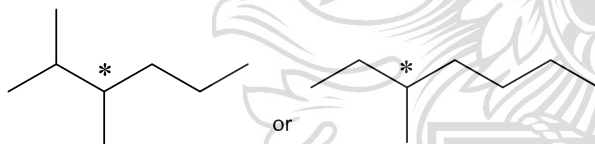
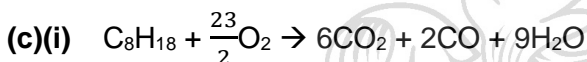
$$P_{\text{CO}} = 0.19 \times 32 = 6.08 \text{ atm}$$

$$P_{\text{CH}_4} = 0.12 \times 32 = 3.84 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = P_{\text{CH}_4} = 3.84 \text{ atm}$$

$$P_{\text{H}_2} = 32 - 6.08 - 3.84 - 3.84 = 18.24 \text{ atm}$$

$$(\text{or } P_{\text{H}_2} = 3 P_{\text{CO}} = 3 \times 6.08 = 18.24 \text{ atm})$$



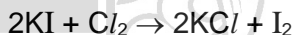
(f)(iii)

$$K_p = \frac{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}{P_{\text{CO}} (P_{\text{H}_2})^3} = 3.9965 \times 10^{-4} \text{ atm}^{-2}$$

$$= 4.00 \times 10^{-4} \text{ atm}^{-2}$$

Question 2

- (a) When aq KI is added to aq Cl₂, the colour of the solution changes from colourless to brown due a redox reaction between KI and Cl₂:



$E^\ominus_{\text{cell}} = E^\ominus_{\text{Cl}_2/\text{Cl}^-} - E^\ominus_{\text{I}_2/\text{I}^-} = 1.36 - 0.54 = +0.82\text{V} > 0$
so that the reaction is spontaneous under standard conditions.

When aq KCl is added to aq Br₂, no reaction occurs as Cl⁻ is not able to reduce Br₂ to Br⁻ as predicted by the negative E^\ominus_{cell} :

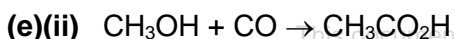
$$E^\ominus_{\text{cell}} = E^\ominus_{\text{Br}_2/\text{Br}^-} - E^\ominus_{\text{Cl}_2/\text{Cl}^-} = 1.07 - 1.36 = -0.29 \text{ V} < 0$$

When aq KBr is added to aq I₂, no reaction occurs as Br⁻ is not able to reduce I₂ to I⁻ as predicted by the negative E^\ominus_{cell} :

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{I}_2/\text{I}^-} - E^\ominus_{\text{Br}_2/\text{Br}^-} = 0.54 - 1.07 = -0.53 \text{ V} < 0$$

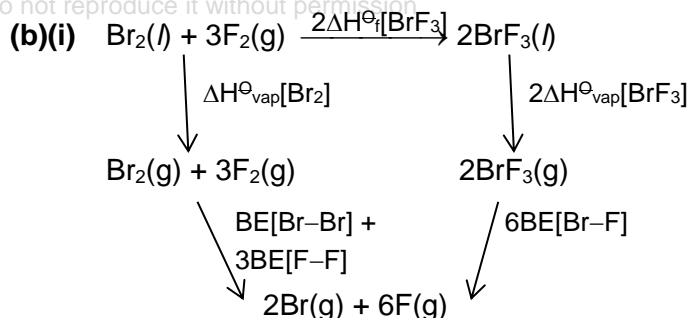
- (e)(i) Homogeneous catalysis.

The catalyst is in the same phase as the reactants.



- (e)(iii) Steps 3 & 5.

- (e)(iv) A is a catalyst as it is consumed in step 1 but regenerated in step 6, showing that it is not chemically changed in the reaction.



$$2\Delta H^\ominus_f[\text{BrF}_3] = \Delta H^\ominus_{\text{vap}}[\text{Br}_2] + \text{BE}[\text{Br}-\text{Br}] + 3\text{BE}[\text{F}-\text{F}]$$

$$- 6\text{BE}[\text{Br}-\text{F}] - 2\Delta H^\ominus_{\text{vap}}[\text{BrF}_3]$$

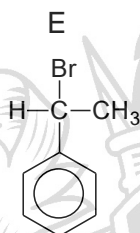
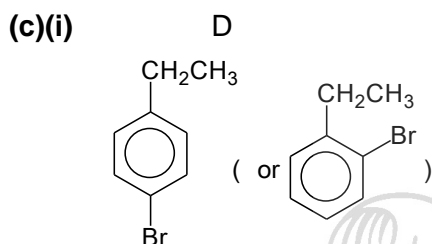
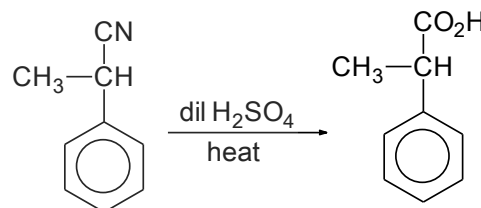
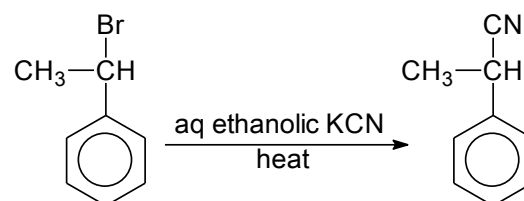
$$2(-301) = 31 + 193 + 3(158) - 6\text{BE}[\text{Br}-\text{F}] - 2(44)$$

$$6\text{BE}[\text{Br}-\text{F}] = 1212$$

$$\text{BE}[\text{Br}-\text{F}] = 1212/6 = +202 \text{ kJ mol}^{-1}$$

(b)(ii) $\Delta G^\ominus_f = \Delta H^\ominus_f - T\Delta S^\ominus_f$
 $-241 = -301 - 298(\Delta S^\ominus_f)$
 $\Delta S^\ominus_f = \frac{-301+241}{298} = -0.201 \text{ kJ mol}^{-1} \text{ K}^{-1}$

ΔS^\ominus_f is negative which is expected as the reaction results in a decrease in the number of moles of gas, which reduces entropy.

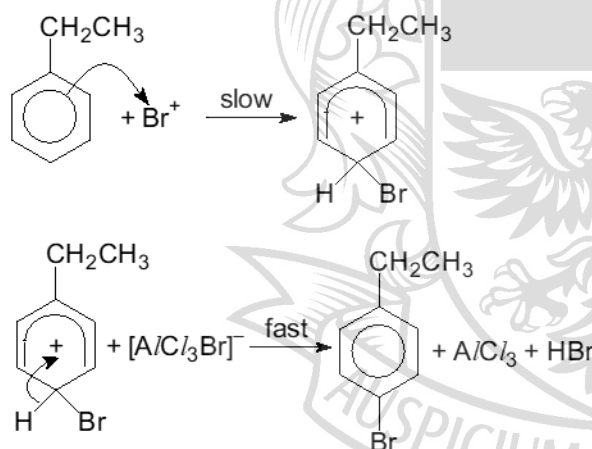
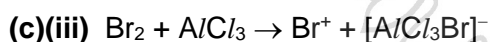


Question 3

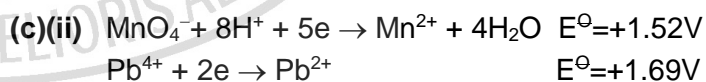
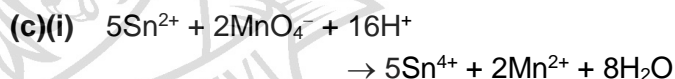
(a)(i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

(a)(ii) MnO_2 . $|LE| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$. Since O^{2-} has a smaller anionic radius than S^{2-} , MnO_2 has a more exothermic lattice energy than MnS_2 .

(c)(ii) Mechanism for reaction 1 is electrophilic substitution while mechanism for reaction 2 is free radical substitution.



(b)(ii) Mn^{4+} (Oxidation number +4) undergoes reduction to gain 2 electrons to form Mn^{2+} (oxidation number +2).
 Each S^{2-} (oxidation number -2) undergoes oxidation and loses an electron each, to form S_2^{2-} (oxidation number of each S is -1).



$$E^\ominus_{\text{cell}} = 1.52 - 1.69 = -0.17 \text{ V} < 0 \text{ V}$$

Hence the reaction is not spontaneous/thermodynamically feasible.

(c)(iv) Compound E is suitable for the synthesis.

Step 1:

Reagent: Aqueous ethanolic KCN

Conditions: Heat with reflux

Step 2:

Reagent: Dil H_2SO_4 (or dil HCl)

Conditions: Heat with reflux

(c)(iii) Colourless solution turns pale pink.

(c)(iv) Amt of $\text{KMnO}_4 = 0.0225 \times 0.0200$
 $= 4.50 \times 10^{-4} \text{ mol}$

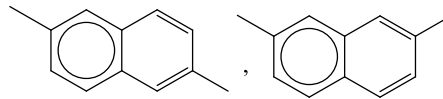
$$\begin{aligned}\text{Amt of Sn}^{2+} \text{ oxidised} &= 5/2 \times 4.5 \times 10^{-4} \\ &= 1.125 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Amt of Sn}^{2+} \text{ in } 250 \text{ cm}^3 &= 1.125 \times 10^{-3} \times 10 \\ &= 0.01125 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Mass of Sn}^{2+} \text{ in sample} &= 0.01125 \times 118.7 \\ &= 1.335 \text{ g}\end{aligned}$$

$$\begin{aligned}\% \text{ by mass in sample} &= 1.335 / 3.00 \times 100\% \\ &= 44.5\%\end{aligned}$$

(d)(iv)



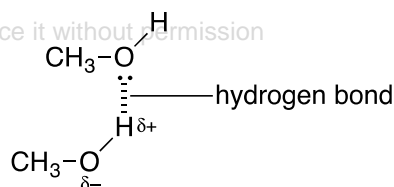
(Other structures are also possible.)
constitutional (or structural) isomerism

Question 4

(a)

Ethane and methane are both non-polar hydrocarbons with instantaneous dipole-induced dipole (id-id) interactions between their molecules. Electrons are constantly moving and at any given moment, the electron density of a molecule can be unsymmetrical, resulting in an instantaneous dipole, which induces a short-lived dipole in a neighbouring molecule. Id-id interactions become stronger when the electron cloud increases in size and becomes more easily distorted. Ethane is a larger molecule with more electrons and thus a larger electron cloud size. As a result, ethane experiences stronger id-id interactions which require a higher energy to overcome and therefore its boiling point is higher.

A methanol molecule contains an –OH group with H covalently bonded to O. Since O is highly electronegative, it attracts the bonding electrons that it shares with H strongly to itself so that H is partially positive. Since H does not have inner shell electrons, its proton is exposed and interacts strongly with a lone-pair of electrons on O in a nearby methanol molecule. The interaction between the partially positive H atom attached to O and lone pair of electrons on O of another methanol molecule gives rise to hydrogen bond as shown below:



(d)(i) Compound **F** contains a tertiary alcohol group which cannot be oxidised by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ but will undergo acid-metal/redox reaction with a reactive metal like Na. **F** cannot be a carboxylic acid as it contains only one O and **F** cannot be a phenol as it does not have a benzene ring.

(d)(ii)

F		G	
H		I	
J		K	
L			

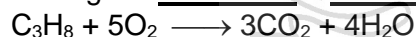
(d)(iii) enantiomerism and cis-trans isomerism
 $2^2 = 4$ stereoisomers

Since the M_r of ethane and methanol do not differ much, the number of electrons of ethane and methanol are similar, so that they have similar id-id interactions. However, relatively stronger hydrogen bonding exist between methanol molecules but are absent in ethane molecules. Thus, more energy is required to overcome the stronger intermolecular forces of attraction in methanol and its boiling point is higher.

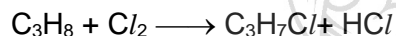
4(b)(i) Alkanes are unreactive because

- ① Alkanes are **saturated** and **non-polar**. They do not contain any region of high or low electron density and thus do not attract electrophiles or nucleophiles respectively.
- ② The strong C-C and C-H bonds in alkanes further contribute to the lack of reactivity of alkanes.

4(b)(ii) When **heated** with **oxygen**, propane undergoes **oxidation** or **combustion**:

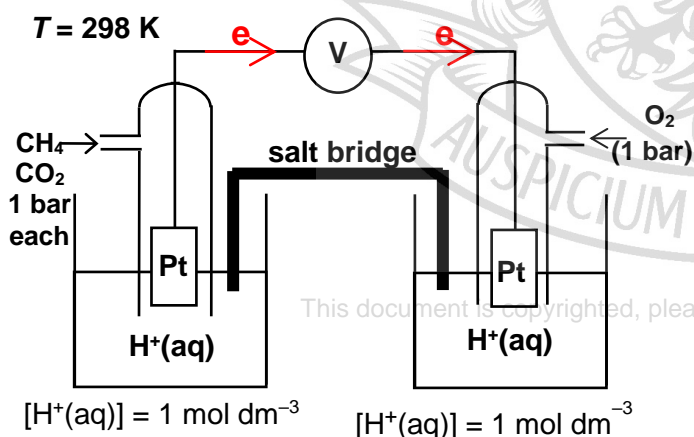


In the presence of **uv light**, propane undergoes **free radical substitution** with chlorine:

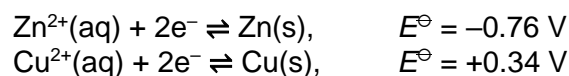


(c)(i) $E^\ominus_{\text{cell}} = 1.23 - 0.17 = +1.06 \text{ V}$

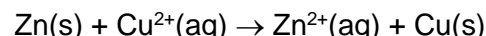
(c)(ii)



(d)(i) Use E^\ominus_{cell} values from the Data Booklet,



Overall redox reaction:

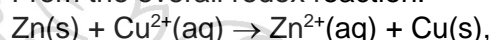


For each pair of zinc and copper discs,
 $E^\ominus_{\text{cell}} = +0.34 - (-0.76) = +1.10 \text{ V}$

As the voltage pile contains 5 pairs of zinc and copper discs connected in series,
 total voltage = $5 \times E^\ominus_{\text{cell}} = 5.50 \text{ V}$

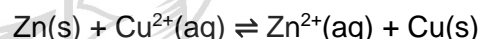
(d)(ii) The mass of the copper discs will have increased while the mass of zinc discs will have decreased.

From the overall redox reaction:



it can be seen that zinc is a reactant and as the reaction progresses, zinc is used up resulting in a decrease in mass of zinc discs. Copper is produced in the reaction and results in an increase in the mass of the copper discs.

The voltage decreases as the concentration of Zn^{2+} increases while the concentration of Cu^{2+} decreases as the reaction progresses:

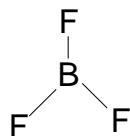


By Le Chatelier's Principle, the position of equilibrium of the above reaction will shift to **left** and hence $E < +5.50 \text{ V}$ (i.e. $E_{\text{cell}} < E_{\text{cell}}^\ominus$).

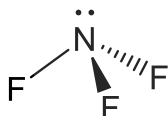
Question 5

(a)(i) VSEPR states that electron pairs (bond pairs and lone pairs) in the **valence/outer** shell of the central atom are arranged as far apart as possible in space, to minimise their mutual repulsion. Lone pair-lone pair repulsion > lone pair-bond pair repulsion > bond pair-bond pair repulsion.

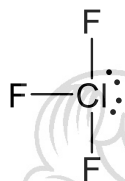
(a)(ii) BF_3 has 3 bond pairs and no lone pairs around B. Hence its electron pair geometry and molecular shape are both **trigonal planar**.



NF₃ has 3 bond pairs and 1 lone pair around N. Hence its electron pair geometry is tetrahedral and its molecular shape is trigonal pyramidal.



ClF₃ has 3 bond pairs and 2 lone pairs around Cl. Hence its electron pair geometry is trigonal bipyramidal and its molecular shape is T-shaped.



(b)(i) React the alcohol with either PCl₅ or SOCl₂ at room temperature to convert the alcohol to its corresponding chloroalkane.

(b)(ii) *Reactivity (Ease of hydrolysis):*
ethanoyl chloride > chloroethane > chlorobenzene

Ethanoyl chloride reacts the most readily due to the **higher δ⁺ charge on C** (bonded to 2 highly electronegative atoms, O and Cl), hence attracting nucleophile more strongly. Also, the sp² hybridised trigonal planar C=O carbon poses **less steric hindrance** for nucleophilic attack. The **highly polarised C–Cl bond cleaves easily** without heating when ethanoyl chloride is reacted with water.

Chloroethane has a lower **δ⁺ charge on C** (bonded to 1 electronegative Cl atom), hence attracts nucleophile less strongly than ethanoyl chloride. Also, the sp³ hybridised tetrahedral carbon (that is bonded to the Cl atom) poses **more steric hindrance** to nucleophilic attack. The **C–Cl bond cleaves**

only with heating when reacted with aq NaOH.

The p-orbital on Cl atom of chlorobenzene overlaps with π-electron cloud of the benzene ring so that the **C–Cl bond** has **partial double bond** character. Thus, no cleavage occurs due to strengthening of the C-Cl bond and chlorobenzene does not react even when heated with aq NaOH.

(c)(i) Phenol can react with either aqueous chlorine or chlorine in CCl₄ at room temperature.

(c)(ii) The acidity of phenols depends on the stability of the phenoxide ion PhO[−] as shown in the equation:



For the chlorinated phenol, as chlorine is an electron withdrawing group, it enhances the delocalisation of the negative charge on O in PhO[−] into the benzene ring. Due to better charge dispersal, the chlorinated phenoxide ion is more stabilised than the phenoxide ion, causing chlorophenol to dissociate to a greater extent so that chlorophenol is a stronger acid.

(d)
Step 1

Reagent: aqueous KMnO₄ and dil H₂SO₄

Condition: heat with reflux

Step 2

Reagent: PCl₃, PCl₅ or SOCl₂

Condition: anhydrous

Step 3

Reagent: HCl

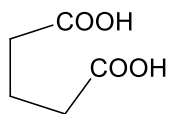
Condition: anhydrous

Step 4

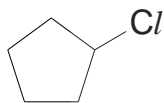
Reagent: Conc NH_3

Condition: in ethanol, heat in a sealed tube

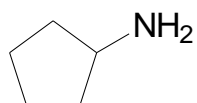
M:



N:



P:



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2017 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

Q1 (C)

Isotope	Abundance / %
^{28}Si	92.23
^{29}Si	x
^{30}Si	$(100 - 92.23 - x) = (7.77 - x)$

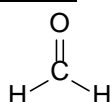
$$28(92.23) + 29(x) + 30(7.77 - x) = 28.10(100)$$

$$x = 5.54\%$$

Q2 (B)

1	Correct. E.g. ^9_4Be has 5 neutrons and 4 protons.
2	Correct. E.g. $^{16}_8\text{O}$ has 8 neutrons and 8 protons.
3	Incorrect. There are no elements from Li to Mg which have more protons than neutrons.

Q3 (D)



3 regions of electron density around C atom of methanal \Rightarrow trigonal planar shape and bond angle of 120°

Q4 (C)

1	Yes. The hydrogen bonds between water molecules are stronger than the id-id interactions between methane, requiring more energy to overcome, resulting in the higher boiling point of water.
2	No. O-H bonds are stronger than C-H bonds. However, boiling does not involve breaking the O-H and C-H bonds. It involves overcoming their intermolecular forces of attraction.
3	No. Water ($10 e^-$) contains more 2 electrons than methane ($8 e^-$). With a slightly larger electron cloud, water has slightly stronger id-id interactions. However, this does not account for the much higher boiling point of water, which can only be attributed to hydrogen bonding between water molecules.

Q5 (D)

A	Incorrect. A change in pressure has no effect on temperature of a gas.
B	Incorrect. The kinetic energy of gas molecules depends on the temperature, not the pressure.
C	Incorrect. Pressure has no effect on the size of the molecules.
D	Correct. Increasing pressure moves the molecules closer, increasing the intermolecular forces of attraction so significantly that the gas becomes liquid.

Q6 (B)

Recall: Lewis base is an electron pair donor. Bronsted-Lowry acid is a proton donor.

A	Incorrect. H^+ does not have electron pairs and cannot be a Lewis base.
B	Correct. Electron pairs on O atom of H_2O allow water to act as a Lewis base. H_2O can donate a H^+ ($\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+$) and acts as a Bronsted-Lowry acid.
C	Incorrect. O^{2-} is unable to donate H^+ .
D	Incorrect. Electron pairs on O atom of OH^- allow it to act as a Lewis base. OH^- can donate a H^+ ($\text{OH}^- \rightarrow \text{O}^{2-} + \text{H}^+$) and acts as a Bronsted-Lowry acid.

Q7 (B)

Mg, Al, Si and P are consecutive elements in Period 3. From the data booklet, the following information about their atomic radii can be obtained:

- atomic radius of $\text{Mg} > \text{Al} > \text{Si} > \text{P}$.
 - atomic radius of Si is closer to that of P than of Al.
- Since atomic radius is the x-axis, going from left to right, the elements should be in the order P, Si, Al, Mg, and Si is closer to P than Al (i.e. more like option **B** than **D**).

Electronegativity increases across the period: $\text{Mg} < \text{Al} < \text{Si} < \text{P}$. Since electronegativity is the y-axis, going from bottom-up, the elements should be in the order Mg, Al, Si, P.

Q8 (B)

From R to S, the difference in 5th IE is extremely large. This is because the 5th IE of R involves removing an electron from R⁴⁺ which has a Group 18 electronic configuration (i.e. ns² np⁶). This also means that element R has 4 valence electrons and element Q would have 3 valence electrons i.e. Q belongs to group 13. Hence, the chloride of Q has the formula QCl₃.

Q9 (C)

The metal ions with the highest polarizing power will form the least stable peroxide. Polarizing power is proportional to charge density which is proportional to $\frac{\text{charge}}{\text{radius}}$.

The charge of Mg²⁺ and Ba²⁺ is greater than that of Cs⁺ and Na⁺ (eliminate options **B** and **D**). The ionic radius of Mg²⁺ is smaller than that of Ba²⁺. Hence, Mg²⁺ has the greatest charge density and polarizing power, and forms the least stable peroxide.

Q10 (B)

	Is statement correct?	Does statement explain why diamond does not change into graphite?
1	Yes and yes. Despite the reaction being spontaneous (see option 2), diamond does not change into graphite due to high E _a which results in a small rate constant.	
2	Yes. $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ $= -1900 - 298(3.4)$ $= -2913 \text{ J mol}^{-1}$ $= -2.9 \text{ kJ mol}^{-1}$	No. The negative ΔG^\ominus implies that diamond should convert into graphite as it predicts the reaction to be thermodynamically feasible.
3	No. Since ΔG^\ominus of forward reaction is -2.9 kJ mol^{-1} , ΔG^\ominus of reverse reaction is $+2.9 \text{ kJ mol}^{-1} > 0$ i.e. reverse reaction is not spontaneous.	No. This does not explain the phenomenon.

Q11 (A)

	X ₂	→	2 X	Pressure
Initial amt / mol	1		0	p
Amt after 1 t _{1/2} / mol	0.5		1	1.5p
Amt after 2 t _{1/2} / mol	0.25		1.5	1.75p

When 75% of X₂ has been converted to X, 25% (i.e. 0.25 mol) of X₂ remains. This happens after 2 half-lives.

1	Time elapsed = 2(30) = 60 min.
2	0.75 mol of X ₂ has reacted. Hence, the amt of X formed = 2(0.75) = 1.5 mol.
3	Total amt of gases after 2 half-lives = 0.25 + 1.5 = 1.75 mol At constant T and V, 1 mol of gas has a pressure of p, 1.75 mol of gas has a pressure of 1.75 p (i.e. 7p / 4)

Q12 (A)

The overall rate equation can be determined from the slow step.

For option **A**, the slow step involves 2 NO and 1 H₂. The rate equation is rate = k[NO]²[H₂] which agrees with the rate equation provided.

Q13 (D)

$$\begin{aligned}\text{Density of water} &= 0.997 \text{ g cm}^{-3} \\ &= (1000)(0.997) \text{ g dm}^{-3} \\ &= 997 \text{ g dm}^{-3}\end{aligned}$$

$$\begin{aligned}[\text{H}_2\text{O}] &= (997/18) \text{ mol dm}^{-3} \\ \text{In pure water, } [\text{H}_3\text{O}^+] &= [\text{OH}^-]. \text{ Hence,}\end{aligned}$$

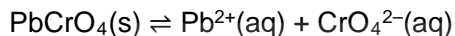
$$K_c = \frac{[\text{H}_3\text{O}^+]^2}{[\text{H}_2\text{O}]^2}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_c [\text{H}_2\text{O}]^2} = \sqrt{K_c} \frac{997}{18}$$

$$\begin{aligned}\text{no. of H}_3\text{O}^+ \text{ in } 1.00 \text{ dm}^3 &= \sqrt{K_c} \frac{997}{18} (1.00)(L) \\ &= \frac{997}{18} L \sqrt{K_c}\end{aligned}$$

Q14 (D)

For $[H_2]_{eqm} > [H_2O]_{eqm}$, the position of equilibrium lies to the right when occurs when $\Delta G^\ominus < 0$ i.e. at points 3 and 4.

Q15 (A)

Eqm conc / mol dm ⁻³	–	1.3×10^{-7}	1.3×10^{-7}
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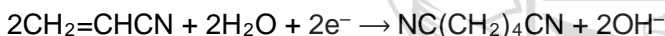
Since solubility = 1.3×10^{-7} mol dm⁻³, the solubility product = $(1.3 \times 10^{-7})^2 = 1.7 \times 10^{-14}$ mol² dm⁻⁶.

Q16 (B)

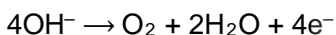
1	Same 2-aminopropane, CH ₃ CH(NH ₂)CH ₃ , has 9 H. 2-bromo-2-methylpropane, (CH ₃) ₃ CBr, has 9 H.
2	Same Ethylpropanoate, CH ₃ CH ₂ CO ₂ CH ₂ CH ₃ , has 10H. Butane-1,2-diol, HOCH ₂ CH(OH)CH ₂ CH ₃ , has 10H.
3	Different Butanenitrile, CH ₃ CH ₂ CH ₂ CN, has 7 H. 2-methylpropanal, CH ₃ CH(CH ₃)CHO, has 8 H.

Q17 (A)

Reduction at cathode



Oxidation at anode

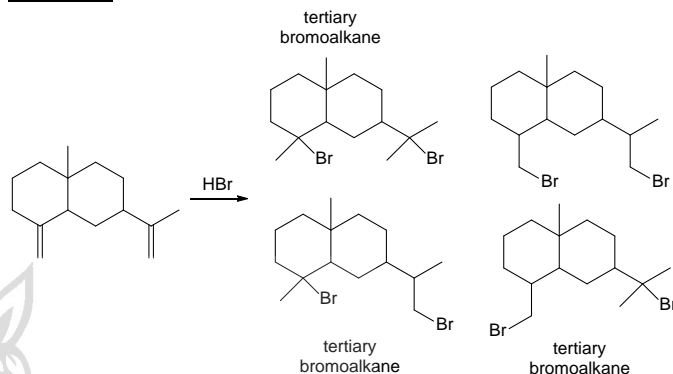


No of mol of acrylonitrile = 0.01 mol

No of mol of e⁻ taken in by acrylonitrile during reduction = 0.01 mol = no of mole of e⁻ released from oxidation.

No of mol of O₂ = 0.01 / 4 = 0.0025 mol

Volume of O₂ released = 0.0025(24) = 0.06 dm³
= 60 cm³

Q18 (D)

When reacted with β -selinene, HBr adds across both C=C to give a mixture of products with molecular formula C₁₅H₂₆Br₂, three of which are tertiary bromoalkanes.

Q19 (A)

A	Correct. The CN ⁻ nucleophile attacks the electrophilic carbonyl carbon from above and below the plane with equal probability, resulting in the formation of a mixture of 2 enantiomers.
B	Incorrect. <p>The S_N2 reaction takes place at the –CH₂Cl carbon which is not chiral. The reaction also does not affect the chiral centre indicated. Only one enantiomer is obtained as the product.</p>
C	Incorrect. The reacting tertiary chloroalkane has no chiral centre (note: the carbon bearing the Cl atom has 2 ethyl groups). Since its reaction with OH ⁻ involves substitution of the –Cl for a –OH, the product does not contain any chiral centres i.e. the product mixture does not contain any enantiomers.
D	Incorrect. Reasoning is similar to that of option C. The carbon bearing the Cl atom has 2 methyl groups.

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Q20 (C)

1	Correct. This statement explains the greater acidity of chloroethanoic acid and fluoroethanoic acid as the electronegative F and Cl atoms draw electron density away from the O–H bond of –COOH, weakening the O–H bond, making these acids more acidic.
2	Incorrect. The highly electronegative F and Cl atoms withdraw electron density from the –COO [–] of the respective carboxylate anions, reducing the intensities of the negative charges, stabilising the carboxylate anions.
3	Incorrect. Electron donating groups (such as methyl groups) increase the intensity of the negative charge on the carboxylate anion, destabilizing the carboxylate anion.

Q21 (A)

CH₃CH₂CONHCH₂CH₃ is an amide, Ph–NHCH₂CH₃ is a phenylamine and (CH₃CH₂)₂NH is a secondary amine. An amide is the least basic as the lone pair of electrons on N is delocalized into the C=O bond, making it unavailable for dative bond formation to a proton.

The lone pair of electrons on the N of a phenylamine is partially delocalized into the benzene ring. The lone pair is more available than the N of an amide but less available than the N of the secondary amine for dative bond formation to a proton.

Q22 (A)

The functional groups present on HAA are the carboxylic acid, phenylamine and phenol. Ethanoyl chloride reacts with phenylamine (to form the amide) and phenol (to form the ester), but not the carboxylic acid.

Q23 (D)

W and Y contain halogenobenzenes and do not release their respective halides when heated with ethanolic silver nitrate due to the partial double bond characters in their carbon-halogen bonds. As a result, no silver halide precipitate is formed with W and Y.

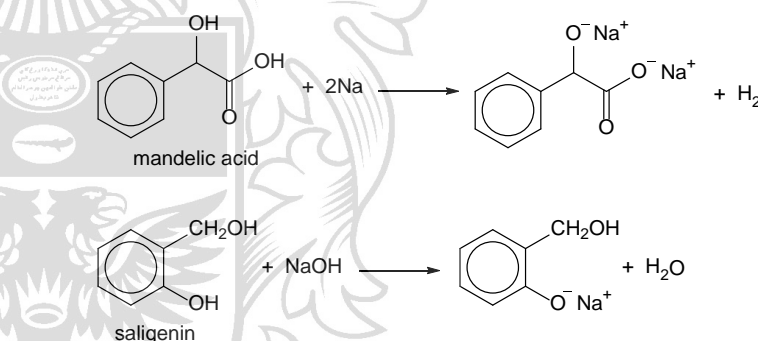
X and Z contain a primary chloroalkane and primary iodoalkane respectively. Since the C–I bond is weaker than the C–Cl bond, the C–I is broken more easily and the **yellow ppt** of AgI is formed the fastest.

Q24 (C)

1	Possible by-product. The presence of NaOH could cause some of the 1-bromopropane to undergo elimination to form prop-1-ene.
2	Not possible. This product is formed when prop-1-ene is mildly oxidized using cold, alkaline KMnO ₄ , which is not present.
3	Not possible. This product is formed when prop-1-ene is hydrated using conc. H ₂ SO ₄ followed by warming with water; or nucleophilic substitution of 2-bromopropane. Neither cases are possible with the given reagents and conditions.

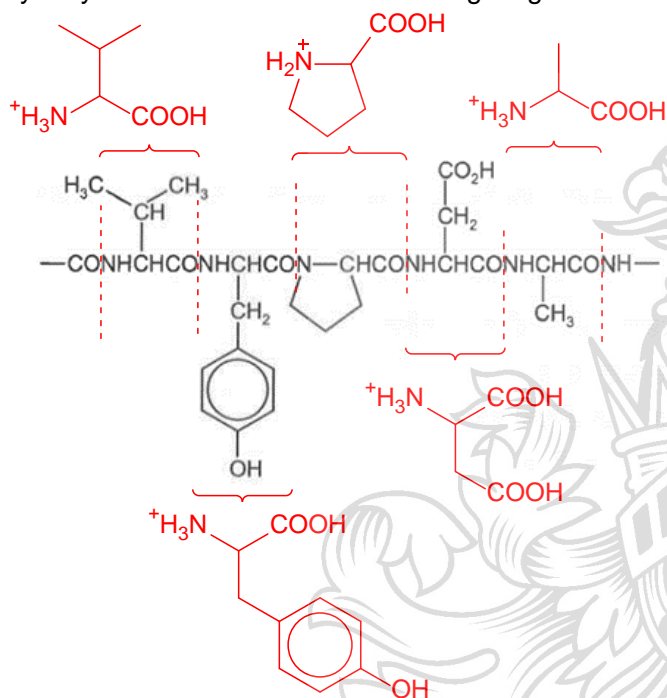
Q25 (D)

Recall: Na metal reacts with alcohols, phenols and carboxylic acids. NaOH(aq) reacts with phenols and carboxylic acids, but **not** alcohols.



Q26 (A)

Under strongly acidic conditions (6 mol dm⁻³ HCl), the amino acids obtained should be fully protonated i.e. option **B** and **C** can be eliminated due to the presence of the –COO⁻ groups. The amino acids obtained after hydrolysis can be seen in the following diagram:

**Q28 (C)**

A	Ethanoic acid dissociates in water to form H ⁺ and CH ₃ CH ₂ COO ⁻ ions. However, since it is a weak acid, [H ⁺] = [CH ₃ CH ₂ COO ⁻] < 1 mol dm ⁻³ .
B	Hydrogen chloride dissociates in water to form H ⁺ and Cl ⁻ ions. Since it is a strong acid, [H ⁺] = [Cl ⁻] = 1 mol dm ⁻³ i.e. it contains more mobile charge carriers than 1 mol dm ⁻³ aqueous ethanoic acid.
C	Does not contain any dissociated H ⁺ and CH ₃ CH ₂ COO ⁻ ions and hence does not contain any mobile charge carriers.
D	Does not contain any dissociated H ⁺ and Cl ⁻ ions and hence does not contain any mobile charge carriers.

Q29 (C)

From Electrochemistry 2 lecture notes:

- Faraday's first law states that mass of substance and/or volume of gas liberated during electrolysis is **directly proportional** to the **amount of charge** that passed through the cell.
- Charge = current x time.**
- The amount of substance formed is **not** dependent on the temperature or concentration.

Q27 (A)

	Is solvent polar?	Are there by-products?
A	Yes	No. Water reacts with the carbocation intermediate to form the same desired product.
B	No	No.
C	Yes	Yes. The lone pair on N of CH ₃ CH ₂ NH ₂ attacks the carbocation intermediate to form (CH ₃ CH ₂) ₃ C–NHCH ₂ CH ₃ as a by-product.
D	Yes	Yes. The lone pair on O of CH ₃ CH ₂ OH attacks the carbocation intermediate to form (CH ₃ CH ₂) ₃ C–OCH ₂ CH ₃ as a by-product.

Q30 (A)

Half-cell X involves H₂, H₂O and NaOH

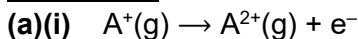


Half-cell Y involves O₂, H₂O and NaOH



(note: the equation with $E^\ominus = +1.23\text{V}$ corresponds to the reaction under acidic medium)

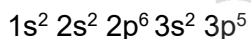
By considering the E^\ominus values, reduction occurs at half-cell Y and oxidation occurs at half-cell X i.e. electrons move from **half-cell X to half-cell Y**.

Question 1

- (a)(ii) In the successive ionization of A, the number of protons remain the same and hence the nuclear charge remains the same. The number of electrons decreases. Hence, the electrostatic attraction between the nucleus and the remaining electrons increases, resulting in an increase in energy required to remove each subsequent electron.

The significant increase in from the 7th to 8th ionization energy is due to the 8th electron being removed from an inner shell which has significantly lower energy. Hence more energy is required to remove the 8th electron compared to the 7th electron.

- (a)(iii) Element **A** is chlorine.



- (b)(i) Hydrogen could be placed on top of Group 1 because the hydrogen atom, like the other Group 1 elements, contain 1 valence electron in the valence s subshell.

- (b)(ii) Hydrogen is not placed at the top of Group 1 because hydrogen exists as simple covalent molecules held by weak instantaneous dipole induced dipole interactions, while Group 1 elements consists of a giant lattice of cations in a sea of delocalized electrons.

As a result of the difference in structure, hydrogen is a gas while Group 1 elements are solids at room temperature. OR hydrogen does not conduct electricity in the solid and liquid state, while Group 1 elements do.

Question 2

(a) $[HCOOH] = 0.0100 / (250/1000)$
 $= 0.0400 \text{ mol dm}^{-3}$

Let $x \text{ mol dm}^{-3}$ be $[H^+]$ at equilibrium.

$$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$$

$$= \frac{(x)(x)}{0.0400 - x} \approx \frac{(x)(x)}{0.0400}$$

since methanoic acid is a weak acid and $[HCOO^-] = [H^+]$ at equilibrium.

$$x = [H^+] = \sqrt{(1.60 \times 10^{-4})(0.0400)}$$

$$= 0.002530 \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg(0.002530) = 2.60$$

- (b) Let $[HCOO^-]$ be $y \text{ mol dm}^{-3}$.

Immediately after mixing,

$$[HCOO^-] = \frac{100y}{100 + 150} = 0.4y \text{ mol dm}^{-3}$$

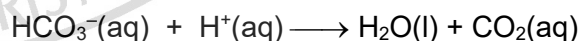
$$[HCOOH] = \frac{150(0.0100)}{100 + 150} = 0.00600 \text{ mol dm}^{-3}$$

$$3.7 = -\lg(1.60 \times 10^{-4}) + \lg \frac{0.4y}{0.00600}$$

$$y = 0.0120 \text{ mol dm}^{-3}$$

- (c)(i) If no buffer were present, the pH of blood will decrease significantly.

- (c)(ii) When a small amount of H^+ ions, from the dissociation of lactic acid, is introduced to blood, the following reaction occurs:



The presence of a large reservoir of HCO_3^- ions in the blood ensures that nearly all the H^+ ions from the dissociation of lactic acid are removed.

Hence $[H^+]$ in the blood changes very little and the pH is kept between 7.35 and 7.45.

Question 3

(a)(i)

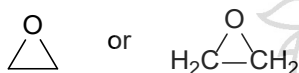
	C	H	O
% by mass	54.5	9.1	36.4
No. of moles in 100g sample	$\frac{54.5}{12.0}$ = 4.542	$\frac{9.1}{1.0}$ = 9.1	$\frac{36.4}{16.0}$ = 2.275
Mole ratio	2 : 4 : 1		

Empirical formula = C₂H₄O

M_r of C₂H₄O = 2(12.0) + 4(1.0) + 16.0 = 44.0

Since M_r of empirical formula = molecular mass of **D**, molecular formula of **D** = C₂H₄O.

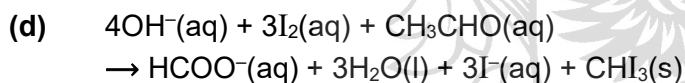
(a)(ii) The third possible isomer of **D**:



(b) Assuming **D** is CH₂=CH(OH)

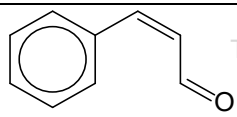
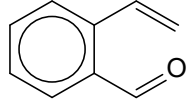
Reagent	Observation
aqueous bromine	Orange Br ₂ is decolourised
aqueous sodium carbonate	No effervescence is observed

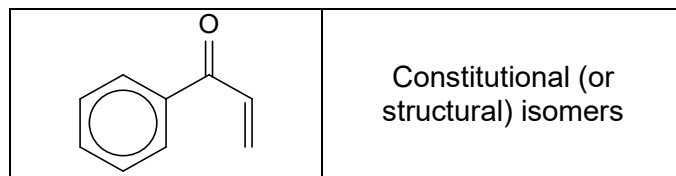
(c) The K_c value is very small and implies that the position of equilibrium lies to the left and the major species is ethanal (CH₃CHO).



Question 4

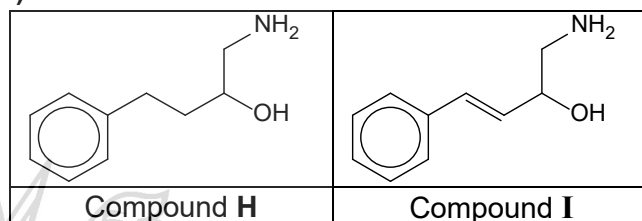
(a) The following structures are possible answers for isomers **E** and **F**. The list is non-exhaustive.

Isomers	Isomeric relationship
	Cis-trans isomers
 (or other positions on benzene ring)	Constitutional (or structural) isomers

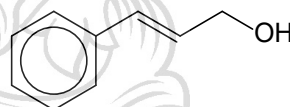


(b)(i) HCN with trace KCN, cold; OR
HCN with trace NaOH, cold; OR
H₂SO₄(aq), KCN(aq).

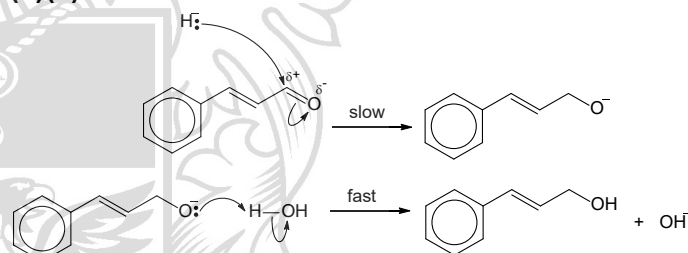
(b)(ii)



(c)(i) Compound **J** (C₉H₁₀O) has the following structure:



(c)(ii)



(Since aqueous NaBH₄ is used, H₂O is the proton donor in the fast step)

(c)(iii) There is a larger difference in electronegativity in A–H than in B–H, which makes the H in A–H more electron rich than in B–H. This allows LiA/H₄ to be a stronger reducing agent.

(d)(i) 1. To a 20 cm³ portion of cinnamaldehyde solution in a beaker, add 6 cm³ of deionized water and 6 cm³ of 2 mol dm^{–3} NaOH(aq) and mix thoroughly until a clear mixture is produced.

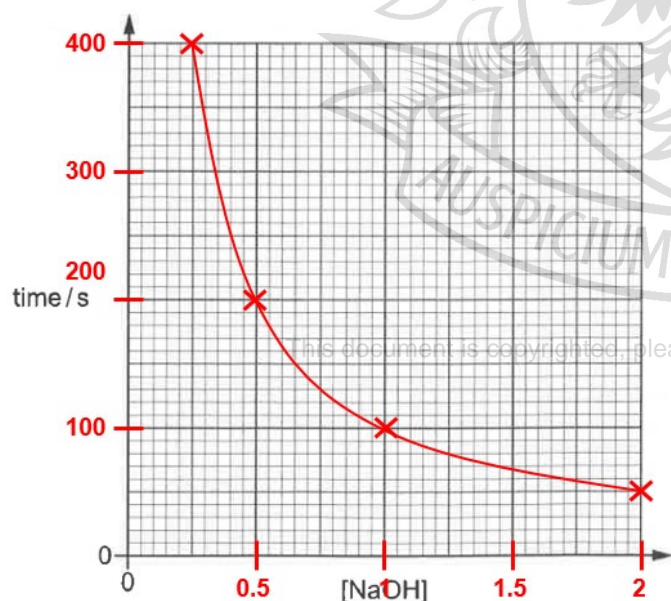
- Add 15 drops of propanone to the mixture in the beaker and start the stopwatch.
- Stir the mixture continuously and stop the stopwatch when a precipitate appears.
- Record the time taken, t , in the following table. Calculate $1/t$ which is proportional to the rate and V_{NaOH} is proportional to $[\text{NaOH}]$.

Expt	$V_{\text{water}} / \text{cm}^3$	$V_{\text{NaOH}} / \text{cm}^3$	Time taken, t / s	$(1/t) / \text{s}^{-1}$
1	0	12	50	
2	6	6		
3	9	3		
4	10.5	1.5		

(d)(ii) In all experiments, [cinnamaldehyde] is kept the same. From the question,

- when $[\text{NaOH}] = 2 \text{ mol dm}^{-3}$, time taken = 50 seconds.
 - rate $\propto [\text{NaOH}]^1$
- Therefore, when $[\text{NaOH}] = 1 \text{ mol dm}^{-3}$, time taken = 100 seconds.

$[\text{NaOH}] / \text{mol dm}^{-3}$	Time taken, t / s
2	50
1	100
0.5	200
0.25	400



Question 5

(a) $E_{\text{cell}}^{\ominus} = +2.01 - (+0.54) = +1.47 \text{ V}$

$$\Delta G^{\ominus} = -nFE_{\text{cell}}^{\ominus}$$

Since 2 mol of e^{-} are transferred in the overall equation,

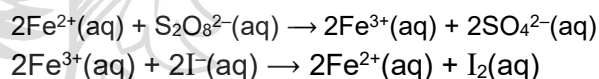
$$\Delta G^{\ominus} = -(2)(96500)(1.47) = -283710 \text{ J mol}^{-1} \\ = -284 \text{ kJ mol}^{-1}$$

Reaction is spontaneous.

(b) When Ag^{+} is added to the I_2/I^{-} half-cell, AgI precipitate is formed, which causes $[\text{I}^{-}]$ to decrease momentarily. The I_2/I^{-} equilibrium shifts to the right to increase $[\text{I}^{-}]$, causing $E(\text{I}_2/\text{I}^{-})$ to become more positive. Hence, $E_{\text{cell}}^{\ominus}$ becomes less positive / smaller than +1.47 V.

(c)(i) Fe^{2+} can be described as a homogeneous catalyst because it is in the same phase (i.e. aqueous) as the reactants, $\text{S}_2\text{O}_8^{2-}$ and I^{-} and provides an alternative pathway of lower activation energy by participating in the mechanism where it is initially consumed and regenerated.

(c)(ii) Transition metals, like iron (II) ions, have variable oxidation states which allows them to act as a catalyst in this reaction.



(d) When the iron (II) and iron (III) ions are coordinated to ligands, their originally degenerated 3d subshell is split into two sets of slightly different energy levels.

One of the H_2O ligands in the solid hydrated iron (III) ions is replaced with an OH^{-} ligand when the aqueous hydrated iron (III) ions are formed. Due to the different ligands around the iron (III) centre, the 3d subshell is split to different extents. This causes the wavelength of light absorbed, and hence the colour observed, to be different.

The solid hydrated iron (II) and iron (III) ions have the same set of ligands but contain different number of d-electrons which repel the electrons of the ligands to different extents, causing the energy gap between the split d-orbitals to be different. This causes the wavelength of light absorbed, and hence the colour observed, to be different.

Question 6

(a)(i) Any one of the following properties of benzoic acid:

- It is readily available in pure form.
- It is stable and does not decompose to other substances on standing.
- It is not hygroscopic (i.e. does not absorb moisture from the air) so its mass can be accurately measured.
- It is not volatile so its mass can be accurately measured.
- It combusts completely to give only CO₂ and H₂O in the calorimeter.
- Its enthalpy change of combustion is accurately known and is easily reproducible.

(source: <https://www.ddscalorimeters.com/the-use-of-benzoic-acid-in-bomb-calorimeters/>)

(a)(ii) The temperature of the water jacket is controlled such that its temperature is the same as the bomb calorimeter. When there is no temperature difference between the bomb and the surroundings i.e. the water jacket, the heat loss to surroundings is minimized.

(b)(i) Burning the first sample produced soot on the surface of the crucible, indicating that the combustion was incomplete. Hence the energy released from the combustion was less than expected and the temperature rise was lower than the other two samples with complete combustion.

(b)(ii) The atmosphere of the steel bomb should be saturated with oxygen gas to ensure there is sufficient oxygen for complete combustion.

(b)(iii) The data from sample 1 is ignored because the combustion was incomplete.

Using data from samples 2 and 3,

$$\Delta T \text{ from sample 2} = 55.3 - 25.0 = 30.3 \text{ }^{\circ}\text{C}$$

$$\Delta T \text{ from sample 3} = 54.7 - 25.0 = 29.7 \text{ }^{\circ}\text{C}$$

$$\text{Average } \Delta T = (30.3 + 29.7) / 2 = 30.0 \text{ }^{\circ}\text{C}$$

Let C be the heat capacity of the calorimeter. (The definition is provided on page 15)

$$-\Delta H_c \times n_{\text{benzoic acid}} = C \Delta T$$

$$3230 \times 10^3 \times \left(\frac{6.10}{7(12.0) + 6(1.0) + 2(16.0)} \right) = C(30.0)$$

$$C = 5383 \text{ J }^{\circ}\text{C}^{-1} = 5.38 \text{ kJ }^{\circ}\text{C}^{-1}$$



(c)(ii) The energy change calculated makes use of data collected from the experiment and the experiment was not conducted at 298 K. Hence, the calculated energy change is slightly different from the standard enthalpy change of combustion.

Question 7

(a)(i) Enthalpy change of hydrogenation of naphthalene = $5(-118) = -590 \text{ kJ mol}^{-1}$

(a)(ii) The actual enthalpy change of hydrogenation of naphthalene is **less exothermic** than the value calculated in (a). This indicates that the **actual structure of naphthalene is more stable** than the structure which contains 5 C=C bonds.

(a)(iii) The carbons in naphthalene are sp² hybridised which contains 3 sp² hybrid orbitals and 1 unhybridised p-orbital. The carbon skeleton of the molecule is formed from the head-on overlap of the sp² hybrid orbitals of adjacent carbon atoms.

The unhybridised p-orbitals of carbon atoms overlap side-on continuously, allowing the delocalization of the pi electrons above and below the plane of the molecule, instead of forming 5 C=C bonds. This resonance stabilizes the molecule.

- (b)(i)** The formula of naphthalene is given as $C_{10}H_8$ in the question on page 18.

$$\text{amt of naphthalene} = \frac{0.32}{10(12.0) + 8(1.0)} = 0.00250 \text{ mol}$$

Let n be the amt of H_2 gas reacted.

$$(101000)(125 \times 10^6) = n(8.31)(30 + 273)$$

$$n = 0.00501 \text{ mol}$$

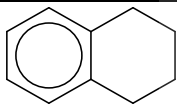
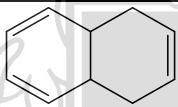
Amt of H_2 : amt of naphthalene

$$= 0.00501 : 0.00250$$

$$\approx 2 : 1$$

Therefore, naphthalene reacts with H_2 gas in a 1: 2 ratio i.e. naphthalene ($C_{10}H_8$) gains 4 H atoms to form $C_{10}H_{12}$.

- (b)(ii)**

	
Compound K , which is aromatic	Compound L , which is not aromatic

- (b)(iii)** Compound **K** is more likely to be formed because of its structure contains a benzene ring which is stabilized by resonance. Such resonance stabilization is absent in **L**.

- (b)(iv)** Excess $H_2(g)$, high pressure (>1 bar), prolonged heating at high temperature (>30 °C) and Ni catalyst.

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Question 1

- (a) Hydrogen chloride is thermally stable. Hydrogen bromide and hydrogen iodide thermally decompose to give hydrogen gas and their respective halogens as shown in the following equation.



The thermal stability of the hydrogen halides is related to the H–X bond strength. Since the bond dissociation energy decreases from H–Cl to H–Br to H–I, the strength of the bonds decreases in the same order. Thus the thermal stability of the hydrogen halides decrease from H–Cl to H–Br to H–I.

- (b)(i) MgCl_2 has a giant ionic lattice held by strong electrostatic forces of attraction between the Mg^{2+} cations and Cl^- anions, while SiCl_4 exists as simple covalent molecules held by instantaneous dipole induced dipole (id-id) interactions. Since the ionic bonds in MgCl_2 are stronger than the id-id interactions in SiCl_4 , MgCl_2 has a higher melting point.

- (b)(ii) Both SiCl_4 and SiF_4 exist as simple covalent molecules held by instantaneous dipole induced dipole (id-id) interactions. SiCl_4 has a larger and more polarizable electron cloud compared to SiF_4 and hence has stronger id-id interactions. Therefore SiCl_4 has a higher melting point than SiF_4 .

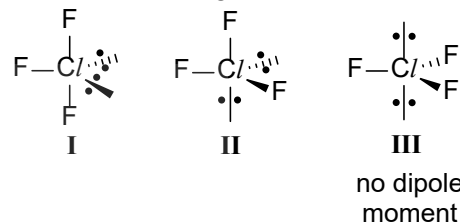
- (b)(iii) Both MgCl_2 and MgF_2 have giant ionic lattices held by strong electrostatic forces of attraction between the Mg^{2+} cations and respective halide anions. Their melting points depend on their lattice energy.

$$|LE| \propto \left| \frac{q_+ q_-}{r_+ + r_-} \right|$$

While q_+ , q_- and r_+ are the same for both compounds, $r_-(\text{Cl}^-) > r_-(\text{F}^-)$. The interionic distance for MgCl_2 is greater and its lattice energy has a smaller magnitude compared

to that of MgF_2 . Hence MgCl_2 has a lower melting point.

- (c)(i) Three possible arrangements:



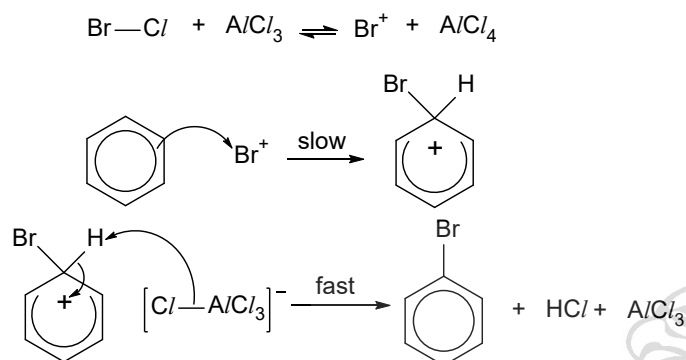
- (c)(ii) The most stable arrangement would minimize the repulsion between electron pairs. In ClF_3 , the 90° electron pair repulsions are the strongest and need to be minimized in the most stable arrangement.

Comparing the 90° electron pair repulsions:

	<p>I</p>	<p>II</p>	<p>III</p>
No. of 90° lone pair lone pair repulsion	0	1	0
No. of 90° lone pair bond pair repulsion	4	3	6

II is the least stable due to the presence of the 90° lone pair-lone pair repulsion which is absent in I and III. Since I has fewer 90° lone pair-bond pair repulsions compared to III, the electron pair repulsions in I are minimized to a greater extent. Hence I is more stable than II and III.

- (d)(i) The product is bromobenzene. Since Cl is more electronegative than Br, Cl attracts the bonding electrons to itself when the Br–Cl bond cleaves heterolytically to react with A/C_3 to form Br^+ and A/C_4^- . Br^+ acts as the electrophile which attacks benzene to form bromobenzene.

(d)(ii) Mechanism: Electrophilic substitution

(e)(i) $K_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})]$; units: $\text{mol}^2 \text{dm}^{-6}$

(e)(ii)

Conc / mol dm^{-3}	$\text{AgCl}(\text{s})$	\rightleftharpoons	$\text{Ag}^+(\text{aq})$	$+$	$\text{Cl}^-(\text{aq})$
Initial	--		0.50		0
Eqm	--		$0.50 + s$		s

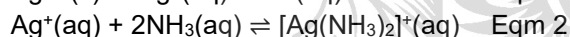
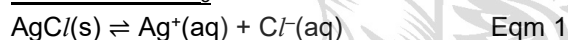
where $s \text{ mol dm}^{-3}$ is the solubility of AgCl .

$$2.0 \times 10^{-10} = (0.50 + s)(s)$$

Since AgCl is a sparingly soluble salt and dissociates to a small extent, s is very small and $(0.50 + s) \approx 0.50$

$$2.0 \times 10^{-10} = 0.50(s)$$

$$s = 4.0 \times 10^{-10} \text{ mol dm}^{-3}$$

(e)(iii) Addition of NH_3 

Upon addition of NH_3 , the $[\text{Ag}(\text{NH}_3)_2]^+$ complex is formed (according to equilibrium 2) which causes $[\text{Ag}^+]$ to decrease. This momentarily causes the ionic product of AgCl to fall below its K_{sp} , which in turn causes the position of equilibrium 1 to shift to the right to increase $[\text{Ag}^+(\text{aq})]$, causing $\text{AgCl}(\text{s})$ to dissolve, increasing the solubility of AgCl .

Addition of $\text{NaCl}(\text{aq})$

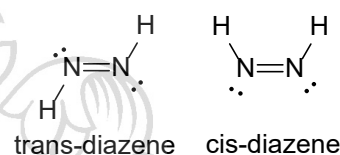
Upon addition NaCl , $[\text{Cl}^-(\text{aq})]$ increases momentarily which causes equilibrium 1 to shift left to reduce $[\text{Cl}^-(\text{aq})]$, producing more $\text{AgCl}(\text{s})$, decreasing the solubility of $\text{AgCl}(\text{s})$.

Question 2

(a)(i) Hydrazine forms an average of 2 hydrogen bonds per molecule while ammonia forms an average of 1 hydrogen per molecule. Hence there is more extensive intermolecular hydrogen bonding in hydrazine than ammonia, which requires more energy to overcome, leading to a higher boiling point.



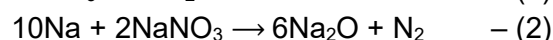
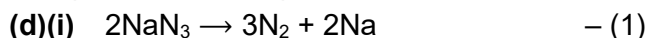
N_2H_4 acts as a base and N_2H_5^+ is its conjugate acid; H_2SO_4 acts as an acid and HSO_4^- is its conjugate base.

(b) Structures of diazene:

With 3 regions of electron density and 1 lone pair, the bond angle could be 117° ($<120^\circ$). Diazene exists as cis-trans isomers due to the restricted rotation around the $\text{N}=\text{N}$ bond and each N atom bearing 2 different groups, namely a H atom and a lone pair of electrons, which allowed for different spatial arrangement of these groups in each molecule.

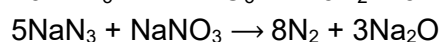
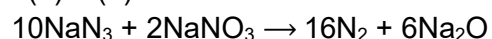
(c) Gaseous mixture: Since moist red litmus paper turns blue, NH_3 is present. Gaseous mixture consists of $\text{NH}_3(\text{g})$ and $\text{HN}_3(\text{g})$.

Aqueous mixture: Since an aqueous solution of A is a good conductor of electricity, ions, which act as mobile charge carriers, are present. Aqueous mixture consists of $\text{NH}_4^+(\text{aq})$ and $\text{N}_3^-(\text{aq})$.



Overall equation does not contain Na.

$5(1) + (2):$



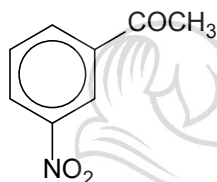
(d)(ii) Amount of NaN_3
 $= 400 / [23.0 + 3(14.0)]$
 $= 6.154 \text{ mol}$

Amount of N_2 produced
 $= (8/5)(6.154) = 9.846 \text{ mol}$

final pressure in airbag, $p = \frac{nRT}{V}$
 $= \frac{(9.846)(8.31)(298)}{100 \times 10^{-3}}$
 $= 243824 \text{ Pa}$
 $= 244 \text{ kPa}$

(e)(i) Amide

(e)(ii) Intermediate **C**:



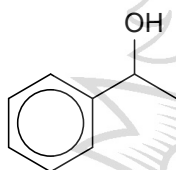
Step 1: conc. HNO_3 , conc. H_2SO_4 , heat

(e)(iii) **Step 3:** $\text{CH}_3\text{CH}_2\text{Cl}$, AlCl_3

Step 4: Cl_2 , uv

(e)(iv) **Step 5:** NaOH(aq) , heat

Intermediate **E**:



(e)(v) NaOH(aq) , heat

(e)(vi) **D** is significantly less basic compared to **F**.

This is because the lone pair of electrons on N of the amide group of **D** is delocalized into the C=O , making it unavailable for dative bond formation to a proton.

Question 3

(a) Copper forms compounds with variable oxidation states, but calcium only forms compound with a +2 oxidation state. This is due to the close similarity in energy between the 3d and 4s electrons of Cu which allows it to use different number of these electrons for bond formation when they form compounds. The 3p and 4s electrons of Ca have a large energy gap. Only the 4s electrons of Ca is used when compounds are formed.

Copper has higher electrical conductivity than calcium. This arises because both of the 3d and 4s electrons of Cu, having similar energies, can contribute to the sea of delocalized electrons; only the 2 4s electrons of Ca can be contributed. Hence, copper has more mobile charge carriers than calcium.

(b)(i) In aqueous solution, both Cu^{2+} and Zn^{2+} as their respective octahedral complexes, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$.

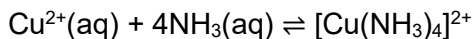
The presence of the H_2O ligands causes the splitting of the five originally degenerate 3d orbitals in the Cu^{2+} and Zn^{2+} ions into two sets of slightly different energy levels.

Since the 3d orbitals of Cu^{2+} are partially filled (Cu^{2+} : $[\text{Ar}] 3d^9$), the electrons from the lower energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d orbitals.

Such d-d transitions are responsible for the colour observed in $\text{Cu}^{2+}(\text{aq})$. The colour observed is the complement of the colour absorbed.

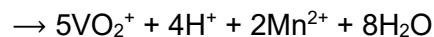
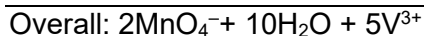
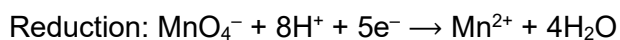
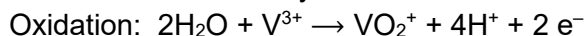
Such d-d transitions are absent in $\text{Zn}^{2+}(\text{aq})$ because the 3d orbitals are fully filled, resulting in a colourless solution.

(b)(ii)



When $\text{Cu}^{2+}(\text{aq})$ ions react with an excess of NH_3 , NH_3 acts as a ligand by donating its lone pair of electrons into the low-lying vacant orbital of the central Cu^{2+} cation forming a co-ordinate bond. In the case of the Cu^{2+} and NH_3 , 4 NH_3 molecules coordinate around the centre Cu^{2+} to form the complex, $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

Oxidation of V^{3+} in **G** by MnO_4^-



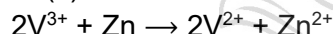
Since amt of MnO_4^- reacted with **G** = 3.28×10^{-5} mol,
amt of V^{3+} = $\frac{5}{2}(3.28 \times 10^{-5}) = 8.20 \times 10^{-5}$ mol

$$[\text{V}^{3+}] \text{ in } \mathbf{G} = (8.20 \times 10^{-5}) / (25.0/1000) \\ = 0.00328 \text{ mol dm}^{-3}$$

(d)

(c)

- G** cannot contain VO_2^+ since it can be oxidized to VO_2^+ .
- G** cannot be V^{2+} because $E^\ominus(\text{V}^{2+}/\text{V}) - E^\ominus(\text{Zn}^{2+}/\text{Zn}) = -1.20 - (-0.76) = -0.44 \text{ V} < 0$ i.e. the reduction of V^{2+} by Zn is not feasible.
- G** contains either V^{3+} or VO^{2+} .
- H** contains V^{2+} since both V^{3+} and VO^{2+} will be reduced to V^{2+} when reacted with excess Zn(s).



$$E^\ominus_{\text{cell}} = -0.26 - (-0.76) = +0.50 \text{ V} > 0$$



$$E^\ominus_{\text{cell}} = +0.34 - (-0.76) = +1.10 \text{ V} > 0$$

(VO^{2+} is first reduced to V^{3+} before being further reduced to V^{2+})

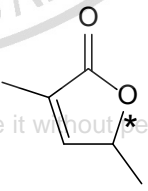
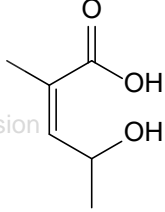
- Amt of MnO_4^- reacted with **G**
= $(2.00 \times 10^{-3})(16.4 \times 10^{-3}) = 3.28 \times 10^{-5}$ mol
Amt of MnO_4^- reacted with **H**
= $(2.00 \times 10^{-3})(24.6 \times 10^{-3}) = 4.92 \times 10^{-5}$ mol
Mole ratio of MnO_4^- reacted with **G** and **H** =
= $3.28 \times 10^{-5} : 4.92 \times 10^{-5}$
= 2 : 3
= mole ratio of electrons lost by **G** and **H**
when oxidized by MnO_4^-

Oxidation of V^{2+} in **H** to VO_2^+ :



Therefore, oxidation of vanadium species in **G** to VO_2^+ would require 2 mol of electrons
i.e. $2\text{H}_2\text{O} + \text{V}^{3+} \rightarrow \text{VO}_2^+ + 4\text{H}^+ + 2\text{e}^-$.

G contains V^{3+} .

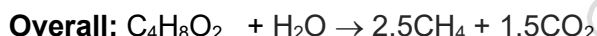
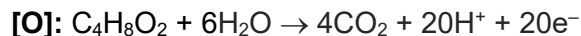
Evidence	Deductions
I ($\text{C}_6\text{H}_8\text{O}_2$) decolourises $\text{Br}_2(\text{aq})$, but does not react with Na(s) or aqueous alkaline I_2 .	I undergoes electrophilic addition with $\text{Br}_2(\text{aq})$ <ul style="list-style-type: none">I contains C=C bonds. I does not undergo acid-metal reaction with Na(s) <ul style="list-style-type: none">Alcohol, phenol and carboxylic acid absent in I. I does not undergo oxidation with aqueous alkaline I_2 . <ul style="list-style-type: none">$-\text{CH}(\text{OH})\text{CH}_3$ and $-\text{COCH}_3$ groups absent in I.
Solution of I is optically active.	I contains at least one chiral centre.
I reacted with $\text{H}_2\text{SO}_4(\text{aq})$ to give J ($\text{C}_6\text{H}_{10}\text{O}_3$)	I gained 1 H_2O to form J <ul style="list-style-type: none">Hydrolysis of ester in I occurred to form J.J contains $-\text{COOH}$ and alcohol group.I contains a cyclic ester since the number of carbons did not change after hydrolysis.
Heating J with acidified KMnO_4 gave K ($\text{C}_3\text{H}_4\text{O}_3$) as the only product.	J undergoes strong oxidation to give K . <ul style="list-style-type: none">Alcohol in J is oxidized.
K reacts with Na metal and aqueous alkaline I_2 .	K undergoes acid metal reaction with Na metal. <ul style="list-style-type: none">Carboxylic acid present in K. K undergoes oxidation with aqueous alkaline iodine. <ul style="list-style-type: none">$-\text{COCH}_3$ present K is $\text{CH}_3\text{COCO}_2\text{H}$
<div><div></div><div></div></div> <div>compound I compound J</div>	

Question 4

- (a)(i) Let x be the average oxidation number of C in butanoic acid.

$$4(x) + 8(+1) + 2(-2) = 0$$
$$x = -1$$

- (a)(ii) [R]: $\text{C}_4\text{H}_8\text{O}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow 4\text{CH}_4 + 2\text{H}_2\text{O}$



- (a)(iii) Bubble the gaseous mixture through aqueous NaOH.

- (a)(iv) pressure of remaining methane

$$= \frac{2.5}{2.5 + 1.5} \times 1.5 \times 10^5$$
$$= 93750$$
$$= 93800 \text{ Pa}$$

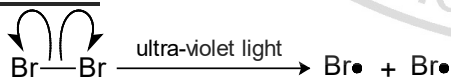
- (b)(i) $\Delta H^\ominus_r = 2.5(-75) + 1.5(-394) - (-534) - (-286)$
 $= +41.5 \text{ kJ mol}^{-1}$

- (b)(ii) $-207 = +41.5 - 298(\Delta S^\ominus_r)$
 $\Delta S^\ominus_r = 0.833 \text{ kJ mol}^{-1} \text{ K}^{-1}$
 $= +833 \text{ J mol}^{-1} \text{ K}^{-1}$

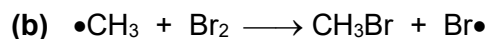
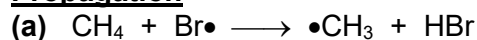
The entropy change is positive due to the formation of large amount of gaseous, highly disordered, products from non-gaseous reactants which are more ordered. With an increase in disorder, the entropy change is positive.

- (c)(i) Free radical substitution

Initiation

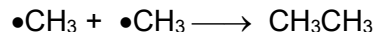


Propagation



Then (a), (b), (a), (b), ...

Termination



- (c)(ii) In the free radical substitution mechanism, the light provides energy to cleave the halogen-halogen bond. The Br-Br bond, being weaker than the Cl-Cl bond, requires less energy to cleave. Hence, cleaving the Br-Br bond only requires lower energy, longer wavelength light.

- (c)(iii) L, M and N are produced in a 1: 6: 9 ratio.

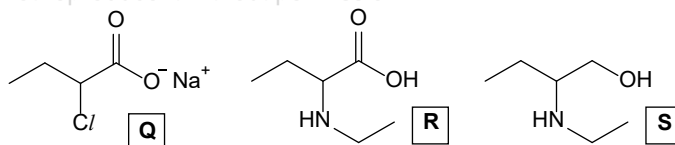
L is produced when the one and only tertiary hydrogen of 3-ethylpentane is substituted. M is produced when one of the 6 secondary hydrogens of 3-ethylpentane is substituted. N is produced when one of the 9 primary hydrogens of 3-ethylpentane is substituted.

- (c)(iv) The overall ratio is dependent on the probability of substitution and the stability of the radical formed.

The probability of substitution is determined in (c)(ii) by considering the number of equivalent hydrogens available to be substituted.

The tertiary free radical produced when the tertiary hydrogen is substituted to form L is significantly more stable than the primary free radical formed when one primary hydrogen is substituted to form N. This resulted in the overall ratio which forms L preferentially over N, despite the probability of substitution.

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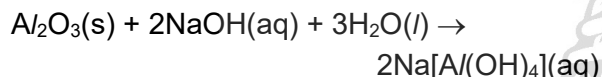
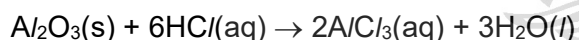
Question 5

- (a) Across Period 3, the oxides of the elements progress from basic to amphoteric to acidic.

Na_2O and MgO are basic oxides which react readily with acids to form the corresponding salts.



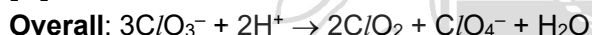
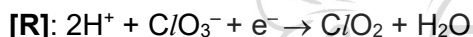
Al_2O_3 is an amphoteric oxide which reacts with both acids and alkalis.



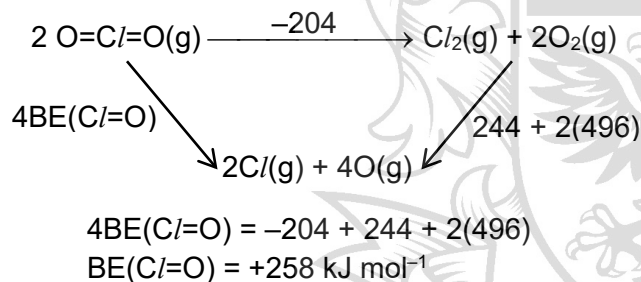
P_4O_{10} and SO_3 are acidic oxides and reacts with alkalis to form the corresponding salts.



- (b)(i) Cl is oxidized from +5 in ClO_3^- to +7 in ClO_4^- ; Cl is reduced from +5 in ClO_3^- to +4 in ClO_2 .



- (b)(ii)



- (b)(iii) ΔS^\ominus is positive since there is an increase in disorder due to the increase in number of gaseous substances from 2 mol in the reactants to 3 mol in the products. This results in $-\text{T}\Delta S^\ominus$ being negative.

Since $\Delta G^\ominus = -204 - \text{T}\Delta S^\ominus$, ΔG^\ominus is negative and will have a greater magnitude compared to ΔH^\ominus .

- (c)(i) Step 3: reduction

Step 4: acid-base reaction

- (c)(ii) Step 1: electrophilic substitution

Step 2: nucleophilic substitution

Step 6: electrophilic addition

- (c)(iii) reagent T: $\text{BrCH}_2\text{CH}=\text{CH}_2$

- (c)(iv) reagent U: $\text{H}_2\text{NCH}(\text{CH}_3)_2$

- (c)(v) In Fig. 5.1, the reaction of Br_2 and the alkene in step 6 produces a secondary carbocation, which is more stable than the primary carbocation produced if the isomer in Fig. 5.2 was formed. Hence, the isomer in Fig. 5.2 was not formed.

2018 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

Q1 (D)

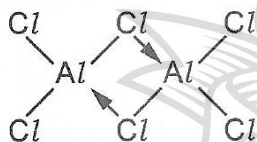
Particle	Direction of deflection	Angle of deflection
proton (positively charged)	towards the <u>negatively</u> charged plate	x° ($x^\circ < y^\circ$)
electron (negatively charged)	towards the <u>positively</u> charged plate	y°

Since angle of deflection $\propto \left| \frac{\text{charge}}{\text{mass}} \right|$, and a proton is heavier than an electron, the angle of deflection for proton is smaller, i.e. $x^\circ < y^\circ$.

Q2 (D)

The high charge density of Al^{3+} causes the distortion of the electron cloud of Cl^- to such an extent that electron sharing becomes predominant. Hence $AlCl_3$ and Al_2Cl_6 are predominantly covalent compounds i.e. they exist as discrete molecules.

Al_2Cl_6 is formed from the dimerisation of $AlCl_3$, in which one Cl atom of each $AlCl_3$ donates a pair of electrons to the vacant, low-lying orbital of the Al atom in the neighbouring $AlCl_3$ to form a dative covalent/coordinate bond (represented by ' \rightarrow ' from the Cl donor atom to the Al acceptor atom).



Q3 (D)

Since the electronegativity of C, Se and Cl are all different, all three molecules contain polar covalent bonds.

Molecule	no. of lp & bp	Shape	Bond dipoles cancel?	Polar?
CSe_2	2 bp	linear	yes	\times
$SeCl_2$	2 bp 2 lp	bent	no	\checkmark
CCl_4	4 bp	tetrahedral	yes	\times

Q4 (B)

Cs^+ , I^- and Xe are isoelectronic species (i.e. with same total number of electrons) \Rightarrow their outermost e^- experience the same shielding effect.

However, nuclear charge of $Cs^+ > Xe > I^-$.

\therefore Effective nuclear charge of $Cs^+ > Xe > I^-$.

Electrostatic attraction between the nucleus and the outermost e^- of $Cs^+ > Xe > I^-$.

\therefore Energy required to remove the outermost e^- decreases in the order: $\Delta H_1 > \Delta H_3 > \Delta H_2$

Q5 (C)

A	Incorrect. (A mole of substance is the amount of that substance which contains as many elementary entities as there are carbon atoms in 12 g of carbon-12.) Since 1 mole of compound (e.g. CO_2) contains more than 1 mole of atoms (e.g. 1 mole of C and 2 moles of O atoms), it will not contain the same number of atoms as there are atoms in 12 g of carbon-12.
B	Incorrect. Relative isotopic mass = $\frac{\text{mass of 1 atom of the isotope}}{\frac{1}{12} \times \text{mass of 1 atom of carbon-12}}$
C	Correct. Relative atomic mass = (weighted) average mass of 1 atom of the element $\frac{1}{12} \times \text{mass of 1 atom of carbon-12}$
D	Incorrect. Relative molecular mass = (weighted) average mass of 1 molecule of the substance $\frac{1}{12} \times \text{mass of 1 atom of carbon-12}$

Q6 (D)

Atomic radius decreases across a period and increases down a group.

	Group		
Period	1	13	17
4	K		Br
5	Rb	In	

\therefore Rb has the largest atomic radius

Q7 (C)

At sea level, $PO_2 = 1/5 \times 1 = 0.2 \text{ bar}$

In the tank,

$PO_2 = 0.2 \text{ bar}$

Total pressure of gas mixture = 4 bar

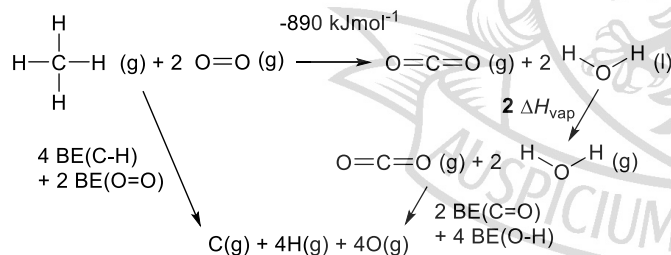
Percentage of $O_2 = 0.2 / 4 \times 100\% = 5\%$

Q8 (C)

A	Incorrect. $2Al^{3+}(g) + 3O^{2-}(g) \rightarrow Al_2O_3(s)$ $\Delta H^\circ_{\text{lattice energy}}(Al_2O_3(s))$ [only 1 mol of $Al_2O_3(s)$ is formed] <i>Recall: Lattice energy (LE) of an ionic compound is the energy released when <u>one mole</u> of the solid ionic compound is formed from its constituent gaseous ions at 298 K and 1 bar.</i>
B	Incorrect. $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ $2\Delta H^\circ_{\text{neutralisation}}$ [2 mol of $H_2O(l)$ are formed] <i>Recall: Standard enthalpy change of neutralisation ($\Delta H^\circ_{\text{neut}}$) is the energy change when an acid and a base react to form <u>one mole</u> of water at 298 K and 1 bar.</i>
C	Correct.
D	$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$ $8\Delta H^\circ_{\text{formation}}(SO_2(g))$ [8 mol of $SO_2(g)$ are formed] <i>Recall: Standard enthalpy change of formation (ΔH°_f) of a substance is the energy change when <u>one mole</u> of the pure substance in a specified state is formed from its constituent elements at 298 K and 1 bar.</i>

Q9 (C)

Recall: Bond energy (BE) of a bond is the average energy absorbed when 1 mole of the bonds are broken in the gaseous state.



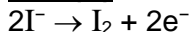
By Hess' law,

$$2\Delta H_{\text{vap}} + (-890) + 2 \text{ BE}(\text{C}=\text{O}) + 4 \text{ BE}(\text{O}-\text{H}) = 4 \text{ BE}(\text{C}-\text{H}) + 2 \text{ BE}(\text{O}=\text{O})$$

$$2\Delta H_{\text{vap}} + (-890) + 2(805) + 4(460) = 4(410) + 2(496)$$

$$2\Delta H_{\text{vap}} = +72 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{vap}} = +72 / 2 = +36 \text{ kJ mol}^{-1}$$

Q10 (B)

$$n(I^-) = n(e^-) = 0.01 \text{ mol}$$

$$n(I_2) \text{ formed from oxide} = 0.006 - \frac{1}{2}(0.01) = 0.001 \text{ mol}$$

0.001 mol of oxide contains $2 \times 0.001 \text{ mol}$ of I

Mole ratio of oxide : I (in oxide): e^-

$$= 0.001 : 2(0.001) : 0.01$$

$$= 1 : 2 : 10$$

$$= 0.5 : 1 : 5$$

1 mol of I (in oxide) accepts 5 mol of e^- to form I_2 .

oxidation number of I (in oxide) + 5 (-1) = 0

\therefore oxidation number of I (in oxide) = +5

Q11 (C)

A	Incorrect. rate = $k[NO_2]$ Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$
B	Incorrect. rate = $k[NO_2]^2$ Overall eqn: $CO + 2NO_2 \rightarrow CO_2 + 2NO + O$
C	Correct. rate = $k[NO_2]^2$ Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$
D	Incorrect. rate = $k[NO_2][CO]$ Overall eqn: $CO + NO_2 \rightarrow CO_2 + NO$

Q12 (D)

For constant temperature and amount (or conc) of catalase (enzyme):

- At low $[H_2O_2]$, not all of the catalase active sites are occupied. Rate $\propto [H_2O_2]$ and reaction is first order wrt H_2O_2 (substrate).
- At high $[H_2O_2]$, the active sites of catalase become saturated with H_2O_2 (substrate). Further increase in $[H_2O_2]$ will not have any effect on the reaction rate. Reaction is zero order wrt H_2O_2 .

Q13 (A)

	Formula	conc. of cation / mol dm ⁻³	charge / radius
A	$Al_2(SO_4)_3$	0.2	$3 / 0.050 = 60.0$
B	$CuSO_4$	0.1	$2 / 0.073 = 27.4$
C	$MgSO_4$	0.1	$2 / 0.065 = 30.8$
D	Na_2SO_4	0.2	$1 / 0.095 = 10.5$

The higher the charge density (charge / radius), the greater the extent of hydrolysis of the cation to form H^+ ions. $Al_2(SO_4)_3$ forms the most acidic solution as it contains the highest concentration of the cation with the greatest charge density.

$$\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$$

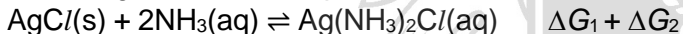
- K_w increases \Rightarrow equilibrium position lies more to the right

- greater extent of self-ionisation of water
- higher conc of H^+ and OH^- (note: $[\text{H}^+]$ is still equal to $[\text{OH}^-]$)
- $\text{pH} \downarrow$ (since $\text{pH} = -\lg [\text{H}^+]$)

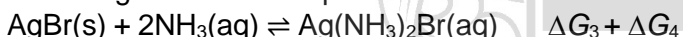
In order to maintain the pH at about 10 (>7), an alkaline buffer consisting of a weak base and its conjugate acid must be used.

A	Correct. Weak base: NH_3 ; Conjugate acid: NH_4^+
B	Incorrect. Weak base: NH_3 ; Strong base: NaOH [conjugate acid of NH_3 , i.e. NH_4^+ , is absent]
C	Incorrect. Strong base: NaOH ; Weak base: CH_3COO^- [conjugate acid of CH_3COO^- , i.e. CH_3COOH , is absent]
D	Incorrect. Only strong base, NaOH , is present

Summing the first two equilibria:



Summing the last two equilibria:



The more negative (or less positive) ΔG is, the more thermodynamically favourable / spontaneous the reaction.

1	Correct. Since AgCl is more soluble in NH_3 than AgBr , $(\Delta G_1 + \Delta G_2) < (\Delta G_3 + \Delta G_4)$
2	Correct. In the aqueous medium, the spectator ions in both the second and fourth equations can be removed to obtain the following ionic equation: $\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(\text{aq})$ $\therefore \Delta G_2 = \Delta G_4$
3	Incorrect. See explanation for option 2.
4	Correct. From options 1 and 2, $(\Delta G_1 + \Delta G_2) < (\Delta G_3 + \Delta G_4)$ and $\Delta G_2 = \Delta G_4$ $\therefore \Delta G_1 < \Delta G_3$ [Values of K_{sp} of $\text{AgCl} = 2.0 \times 10^{-10}$; K_{sp} of $\text{AgBr} = 5.0 \times 10^{-13}$]

If a redox reaction occurs, I^- must be oxidised and H_2O_2 must be reduced.

$$\begin{aligned} E_{\text{cell}}^{\ominus} &= E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus} \\ &= E^{\ominus}(\text{H}_2\text{O}_2/\text{H}_2\text{O}) - E^{\ominus}(\text{I}_2/\text{I}^-) \\ &= +1.77 - (+0.54) \\ &= +1.23 \text{ V} > 0 \text{ (spontaneous)} \end{aligned}$$

$\therefore \text{I}^-$ is oxidised to I_2 (solution turns brown).
No effervescence is observed.

A	Correct. [Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ is the dark blue complex ion formed when excess NH ₃ (aq) is added to Cu ²⁺ (aq).
B	Incorrect. Cu ²⁺ forms the dark blue complex ion, <u>[Cu(NH₃)₄(H₂O)₂]²⁺</u> , with excess NH ₃ . Also, <u>the complex ion is soluble in water (not ppt).</u>
C	Incorrect. Cu(OH) ₂ (H ₂ O) ₄ is the same as Cu(OH) ₂ (s), which is a pale blue <u>ppt.</u>
D	Incorrect. The correct complex ion that gives a pale blue solution is [Cu(H ₂ O) ₆] ²⁺ . [CuCl is a white solid that is sparingly soluble in water.]

A	Incorrect. A <u>redox</u> reaction has occurred. Cu^{2+} in CuCl_2 is reduced to Cu^+ in CuCl_2^- . Cu is oxidised to Cu^+ in CuCl_2^- .
B	Incorrect. A <u>redox</u> reaction has occurred. Cu^{2+} in CuSO_4 is reduced to Cu . Zn is oxidised to Zn^{2+} in ZnSO_4 .
C	Correct. The following ligand exchange reaction has occurred: <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ purple</div> <div>$+ \text{SO}_4^{2-} \rightleftharpoons$</div> <div style="text-align: center;">$[\text{Cr}(\text{H}_2\text{O})_5\text{SO}_4]^+$ green</div> <div>$+ \text{H}_2\text{O}$</div> </div> [oxidation number of Cr remains unchanged]
D	Incorrect. A <u>redox</u> reaction has occurred. Fe^{2+} is oxidised to Fe^{3+} . MnO_4^- is reduced to Mn^{2+} .

Q20 (D)

Transition elements (e.g. V) are generally denser than the s-block elements (e.g. Ca) in the same period due to their smaller atomic size and larger atomic mass.

1	Incorrect. If the outer shell e^- are more shielded in V, the force of attraction between the nucleus and the outer shell e^- will be weaker, resulting in a larger atomic size.
2	Incorrect. Electron configuration of Ca: $[Ar] 4s^2$; V: $[Ar] 3d^3 4s^2$ Both Ca and V have 2 outer shell e^- .
3	Correct. Stronger attraction between the nucleus and outer shell e^- in V will result in smaller atomic radius.

Q21 (C)

A carbocation is a species with a positively charged carbon.

Species	Carbocation?
	✓
	×
	✓
	×

Q22 (A)

Aldehydes, $-CHO$, (both aliphatic and aromatic) can be oxidised by Tollens' reagent.
Only **A** contains an aldehyde group.

Q23 (B)

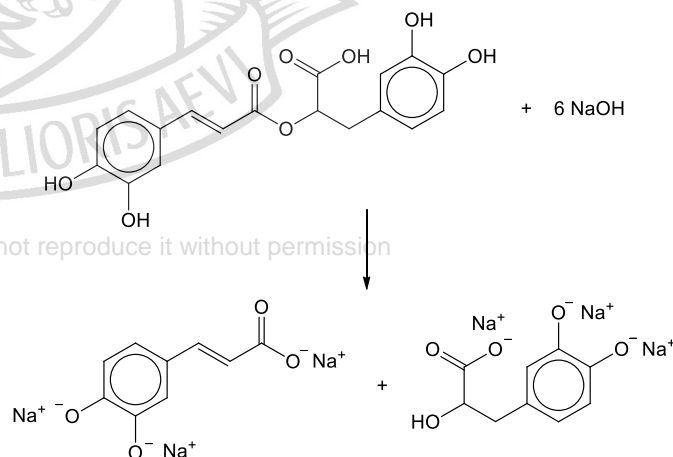
To rotate plane polarised light (i.e. optically active), the molecule cannot have a plane of symmetry.

⇒ A molecule with only one chiral carbon will not have a plane of symmetry and is optically active.

1	Correct. <ul style="list-style-type: none"> Has only one chiral carbon. Absence of plane of symmetry.
2	Correct. <ul style="list-style-type: none"> Has two chiral carbons. Absence of plane of symmetry.
3	Incorrect. <ul style="list-style-type: none"> Has two chiral carbons. Presence of plane of symmetry.
4	Incorrect. [same molecule as option 3] <ul style="list-style-type: none"> Has two chiral carbons. Presence of plane of symmetry.

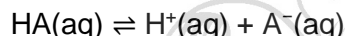
Q24 (D)

The ester group will undergo alkaline hydrolysis while the phenol and carboxylic acid groups will undergo acid-base reaction with NaOH.



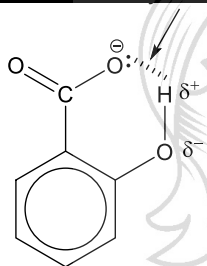
Q25 (A)

1	Correct. In S_N2 , the <u>backside attack</u> of the nucleophile on the chiral C (bonded to Cl) results in the inversion of configuration.
2	Correct. In S_N1 , a carbocation intermediate is formed in the first step. In the second step, the nucleophile attacks the positively charged, <u>trigonal planar sp^2 C</u> from the <u>top and bottom</u> of the plane with <u>equal likelihood</u> , resulting in the formation of equal amounts of a pair of enantiomers (i.e. <u>racemic mixture</u>).
3	Correct. In S_N1 , a carbocation intermediate is formed in the first step. 3° RC/ undergoes S_N1 as the alkyl groups are <u>electron-donating</u> and <u>stabilise the carbocation intermediate</u> .

Q26 (B)

The more stable the conjugate base (A^-), the greater the extent of dissociation of the acid (HA)
 \Rightarrow HA is a stronger acid with $\uparrow K_a$ and $\downarrow pK_a$.

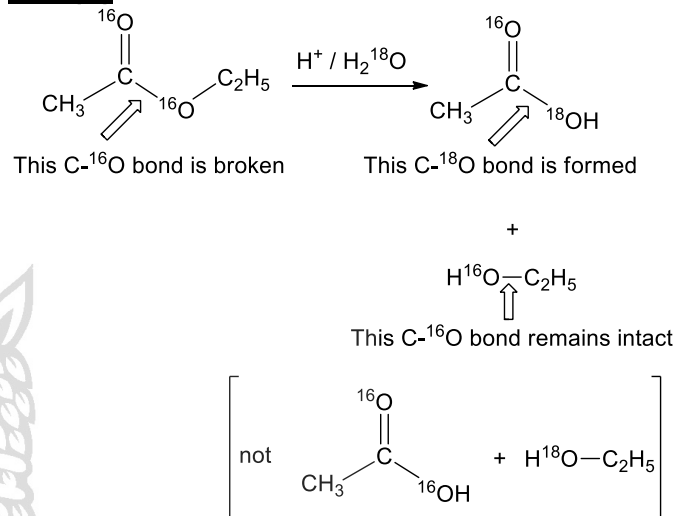
2-hydroxybenzoic acid is much more acidic than 4-hydroxybenzoic acid as its conjugate base is stabilised by intramolecular hydrogen bonding.



Conjugate base of 4-hydroxybenzoic acid has no intramolecular hydrogen bonding as the $-COO^-$ and $-OH$ groups are too far apart.

Q27 (B)

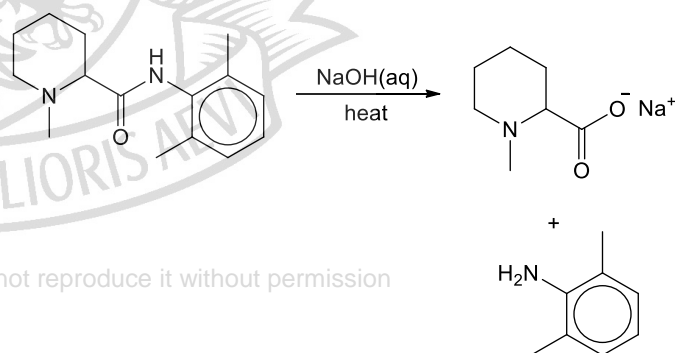
1	Correct. Only alkene group can be reduced to alkane by H_2 , Ni, heat. Carboxylic acid group remains unreacted.
2	Incorrect. Refer to explanation for option 4.
3	Incorrect. Refer to explanation for option 1.
4	Correct. Alkenes cannot be reduced by $LiAlH_4$. The carboxylic acid will be reduced to 1° alcohol by $LiAlH_4$.

Q28 (C)

A	Incorrect. This does not explain why $C_2H_5^{18}OH$ is not formed since its formation also requires the breaking of a C- ^{16}O bond and the formation of a C- ^{18}O bond.
B	Incorrect. Refer to above diagram.
C	Correct. Refer to above diagram.
D	Incorrect. The $H_2^{18}O$ attracts the δ^+ C atom in the <u>$-COO$ group</u> , resulting in the breaking of the C- ^{16}O single bond in the $-COO$ group. [If the $H_2^{18}O$ attracts the δ^+ C atom in the C_2H_5 group, this will result in the breaking of the C- ^{16}O bond in the $O-C_2H_5$ group, which is incorrect based on the products formed.]

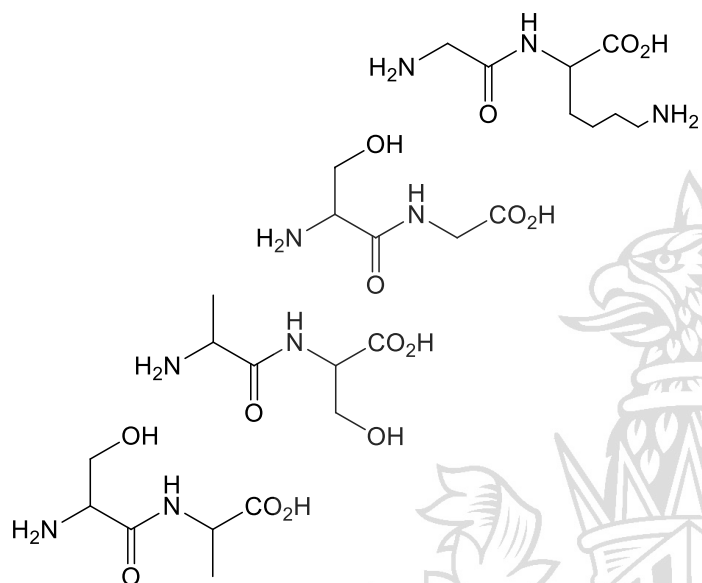
Q29 (D)

When heated with $NaOH(aq)$, the amide group undergoes alkaline hydrolysis to form carboxylate salt and phenylamine.

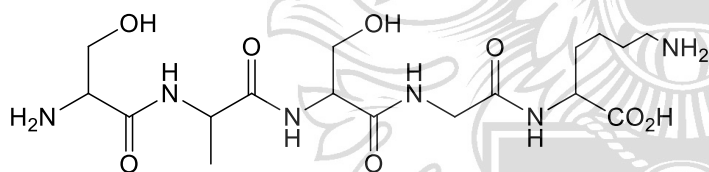


Q30 (D)

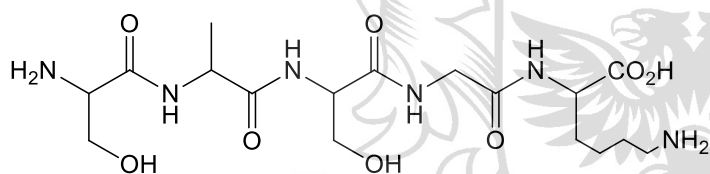
Arranging the overlapping regions of the fragments:



Formula of pentapeptide:



which is the same as **D**



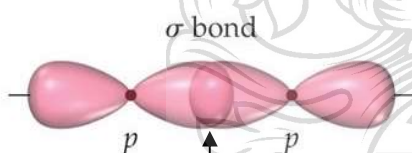
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Question 1

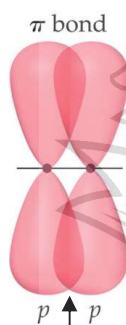
(a)(i)

	similarity	difference
1s & 2s orbital	Both are spherical in shape	2s orbital is larger / more diffuse than 1s orbital
2s & 2p orbital	Both are in the same quantum shell / can accommodate 2 electrons	2s orbital is spherical whereas 2p orbital is dumb-bell in shape.

(a)(ii) Phosgene, $\text{Cl}_2\text{C}=\text{O}$, has 3 bond pairs and 0 lone pairs of electrons around the central C atom. To minimize electronic repulsion between the bond pairs, the shape of the phosgene molecule is trigonal planar.

(a)(iii) σ (sigma) bond

head-on overlap of p orbitals
(show head-on overlap of either s/p orbitals)

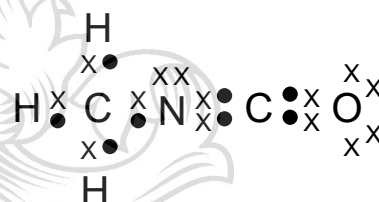
 π (pi) bond

side-to-side overlap of p-orbitals

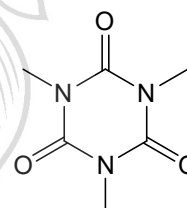
Electrons are constantly moving and at any given moment, the electron density of a phosgene molecule can be unsymmetrical, resulting in an instantaneous dipole, which induces a short-lived dipole in a neighbouring phosgene molecule, hence resulting in id-id interactions.

Phosgene molecules are polar with permanent dipoles in their structures. Pd-pd interactions arise due to the electrostatic attraction between the δ^+ end of one phosgene molecule and the δ^- end of the other phosgene molecule.

(c)(i)



(c)(ii) Possible structure of A



(The above molecule is symmetrical, and hence its dipoles cancel out)

(c)(iii) A (non-polar) has a larger electron cloud than methyl isocyanate (polar). The id-id interactions in A are stronger than the intermolecular forces (id-id and pd-pd) in methyl isocyanate and requires a larger amount of energy to overcome.

(b)(i) Electronegativity is the relative ability of an atom in a molecule to attract bonding/shared electrons.

(b)(ii) Phosgene molecules have intermolecular instantaneous dipole-induced dipole (id-id) and permanent dipole-permanent dipole (pd-pd) interactions.

Question 2

(a) Dynamic equilibrium refers to a state in a reversible system in which the rates of the forward and backward reactions are continuing at the same rate, resulting in no net change in the macroscopic properties (e.g. partial pressure, concentrations) of the reactants and products.

(b)
$$K_p = \frac{P_{\text{NO}}^2}{P_{\text{N}_2}P_{\text{O}_2}}$$

(c) As temperature increases, K_p increases. This shows that the equilibrium position shifts right with increasing temperature to absorb heat energy. Hence, the forward reaction has a positive enthalpy change (i.e. endothermic).

(d)(i) At the instant when the volume of the container is increased 5 times (from 1.0 dm³ to 5.0 dm³), the total pressure of the reaction mixture, as well as the partial pressure of individual gases, is reduced to 1/5 its original value.

However, since the number of gaseous particles on both sides of the equation are the same, the equilibrium position remained unchanged. Therefore, at the new equilibrium, the partial pressure of individual gases remains at 1/5 of its original value and the composition of the reaction mixture is unchanged.

(d)(ii) K_p remains unchanged as temperature is kept constant.

(e) A catalyst lowers the activation energy of both the forward and backward reactions to the same extent. Hence, the rates of both the forward and backward reactions are increased to the same extent, and the equilibrium position and K_p remains unchanged.

(f)(i) ΔG_f^\ominus has a large magnitude and is positive. (Since K_p is very small at 298 K, the equilibrium position lies far left, i.e. forward reaction is negligible/highly non-spontaneous)

(f)(ii) Since $\Delta G_f^\ominus < 0$, forward reaction is spontaneous and equilibrium position lies to the right. Hence the ratio of [products] / [reactants] is greater than 1.

Question 3

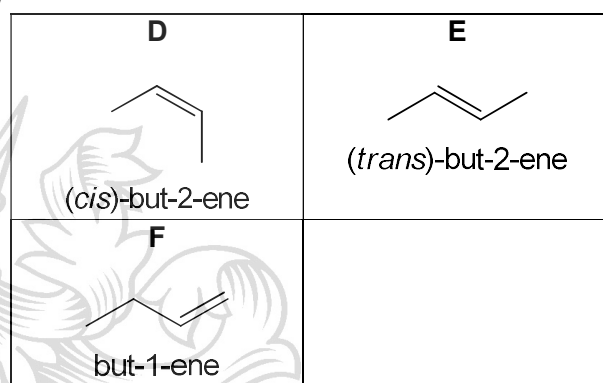
(a)(i) Nucleophilic substitution

(a)(ii) Test: Add NaOH(aq) to **B** and heat. Cool the mixture and acidify with HNO₃(aq). Then add AgNO₃(aq).

Observation: White ppt of AgCl is formed.

(b)(i) reagent: ethanolic NaOH
condition: heat under reflux.

(b)(ii)



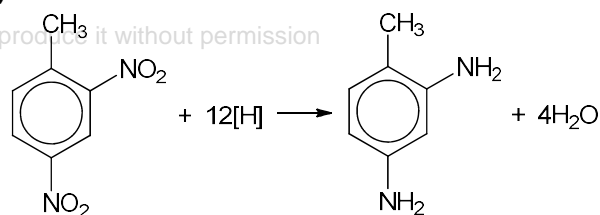
(b)(iii) **D** and **E** are stereoisomers (cis-trans isomers) due to the restricted rotation about the C=C bond and each C atom in the double bond have two different groups/atoms (H and CH₃) attached to it.

Although **F** has a C=C bond, one of the C atoms in the double bond has two identical H atoms bonded to it and hence it does not show stereoisomerism (cis-trans isomerism).

Question 4

(a)(i) Step 1: excess concentrated HNO₃, concentrated H₂SO₄, heat (30°C)
Step 2: Sn, concentrated HCl, heat under reflux, followed by NaOH(aq)

(a)(ii)



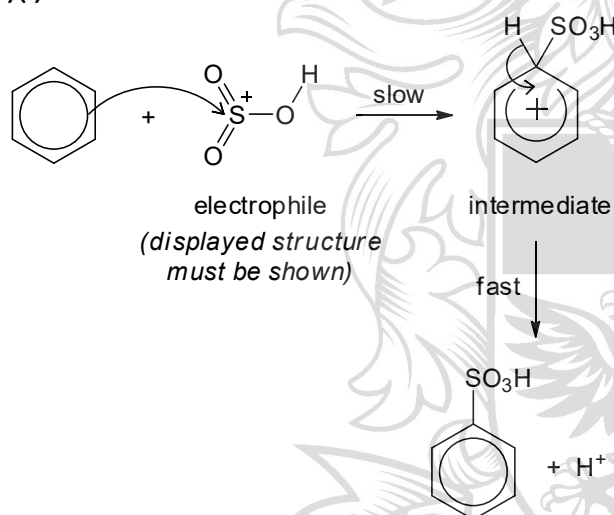
(a)(iii) Constitutional (Structural) isomerism. Compounds with the same molecular formula but different structural formula, i.e. different arrangement of atoms.

(a)(iv) $C_9H_6N_2O_2$

(b)(i) The $-CH_3$ substituent is a 2,4-directing group and directs the substitution of $-SO_3H$ on the ring at the 2 and 4-positions wrt to it. H, however, has the $-SO_3H$ at the 3-position wrt to $-CH_3$.

(b)(ii) The $-CH_3$ group poses steric hindrance to the approach of the electrophile at the 2-position during the reaction. Hence, substitution by $-SO_3H$ at the 2-position wrt to $-CH_3$ occurs less than the 4-position resulting in a lower concentration of **G** than **J**.

(c)(i)



(c)(ii) Benzene does not undergo addition reactions with fuming sulfuric acid as its overall aromatic character will be destroyed, removing the extra stability associated with the delocalisation of the six π electrons.

(c)(iii) The more electron rich the benzene ring, the more reactive it is towards electrophilic substitution with fuming sulfuric acid. The $-CH_3$ group is electron donating whereas the $-COCH_3$ group is electron withdrawing.

Hence, the electron density of the benzene ring in methylbenzene $>$ benzene $>$ **K**.

\therefore Order of reactivity:

methylbenzene $>$ benzene $>$ **K**

Question 5

(a)(i) $E_{cell}^{\ominus} = +1.23 - (-0.22) = +1.45 \text{ V}$

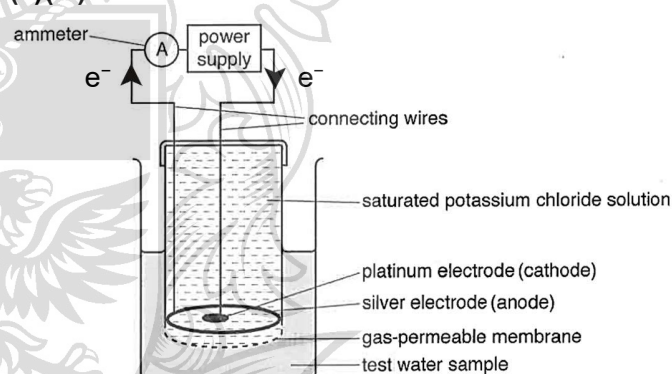
As the cell is operating under non-standard conditions ($[Cl^-]$ and $[O_2]$ are not 1 mol dm^{-3} . $[Cl^-]$ is high due to the saturated KCl solution and $[O_2]$ is low), the $E_{cell} < E_{cell}^{\ominus}$ at 298 K .

When the external voltage of $+1.45 \text{ V}$, which is beyond E_{cell} , is applied, the chemical reaction occurs and current flows, resulting in flow of electrons.

(a)(ii) Type of reaction: reduction

Oxidation state of oxygen decreases from 0 in O_2 to -2 in H_2O .

(a)(iii)



(a)(iv) $n(e^-) = 4 \times n(O_2)$

$$Q = It = n_e F$$

$$\Rightarrow 0.85 \times t = 4 \times n(O_2) \times 96500$$

$$\Rightarrow n(O_2) / t = 0.85 / (4 \times 96500)$$

$$= 2.202 \times 10^{-6} \text{ mol s}^{-1}$$

$$= 2.202 \times 10^{-6} \times 6.02 \times 10^{23} \times 60$$

$$= 7.95 \times 10^{19} \text{ molecules min}^{-1}$$

(a)(v) ΔS is negative as there is a decrease in disorder of the reaction system due to the decrease in number of particles as a large number of particles reacted to form a smaller number of particles.

(a)(vi) To ensure that the dissolved O_2 is homogeneously distributed in the water sample and can diffuse across the gas-permeable membrane.

(a)(vii) Electrode: Silver electrode (anode)
White solid: AgCl

(a)(viii)

- The KCl solution is kept saturated to provide an approximately constant concentration of Cl^- ions so that $E(AgCl/Ag)$ remains approximately constant. This will allow the rate of flow of electrons to be only dependent on the concentration of O_2 in the sample.
- If a much lower concentration of KCl is used, the $E(AgCl/Ag)$ will become less negative and E_{cell} (which is equal to $E(O_2/H_2O) - E(AgCl/Ag)$) will become more negative/less positive.

(b)(i) It exhibits variable oxidation states (or ability to act as catalyst) during the reactions, which is typical of a transition element.

(b)(ii) electron configuration of Mn(III) in $Mn(OH)_3$:
 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$

(b)(iii) $n(S_2O_3^{2-}) = 11.20 / 1000 \times 0.0100$
 $= 0.000112 \text{ mol}$

mole ratio of $O_2 : I_2 : S_2O_3^{2-}$
 $= 0.5 : 1 : 2$
 $= 1 : 2 : 4$

$n(O_2) = 0.000112 / 4 = 0.000028 \text{ mol}$
 $[O_2] = 0.000028 / 100 \times 1000$
 $= \underline{2.80 \times 10^{-4} \text{ mol dm}^{-3}}$

(c)(i) Mass of O_2 escaped in 1 dm^3 of sample
 $= 8.24 - 6.93 = 1.31 \text{ mg} = 0.00131 \text{ g}$

$n(O_2) \text{ escaped} = 0.00131 / (2 \times 16.0)$
 $= \underline{4.09 \times 10^{-5} \text{ mol}}$

(c)(ii) $n(O_2) \text{ escaped} = 4.09 \times 10^{-5} \text{ mol}$

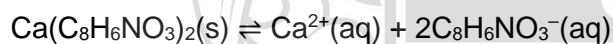
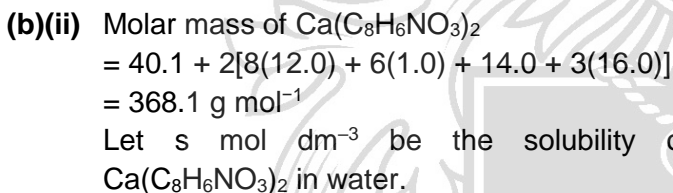
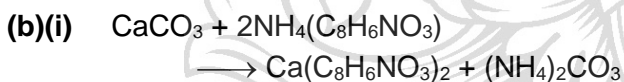
$P_{O_2} \text{ escaped} = \frac{4.09 \times 10^{-5} \times 8.31 \times (35 + 273)}{1 \times 10^{-3}}$
 $= 104.7 \text{ Pa} = 0.1047 \text{ kPa}$

Total P_{O_2} in vessel Y $= 0.1047 + 103.4$
 $= \underline{103.5 \text{ kPa (1 d.p.)}}$

(c)(iii) The O_2 gas present initially in vessel Y suppresses the escape of O_2 from the distilled water (i.e. conversion of $O_2(l)$ to $O_2(g)$). Hence, less O_2 escaped from the distilled water and this resulted in the actual value for pressure to be different from the calculated value.

Question 1**(a)** Down Group 2,

- cationic radius increases, resulting in a lower charge density and weaker polarising power of the cations.
- consequently, there is decreasing extent of distortion of the electron cloud of the CO_3^{2-} anion and hence decreasing extent of weakening of covalent bonds within the CO_3^{2-} anion.
- more heat energy is required to break the covalent bonds within the CO_3^{2-} anion, causing the decomposition temperature to increase.
- hence, thermal stability of the Group 2 carbonates increases.

eqm conc / mol dm^{-3} s $2s$

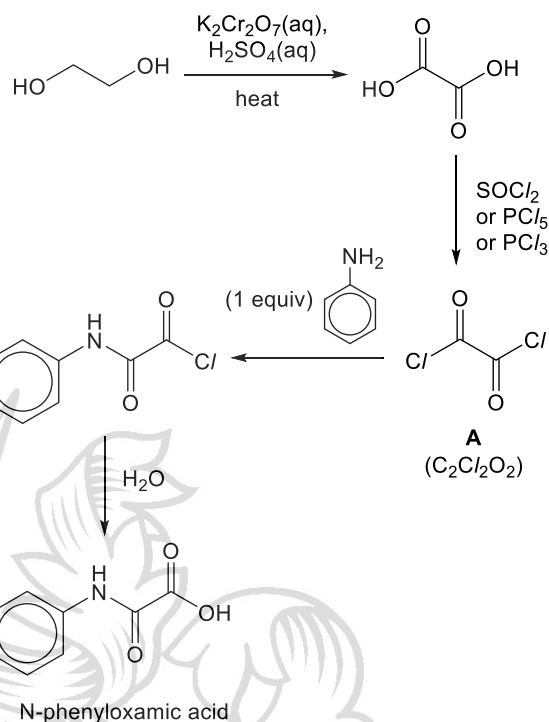
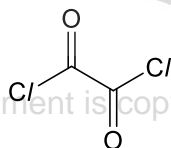
$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_8\text{H}_6\text{NO}_3^{-}]^2 = s(2s)^2$$

$$4s^3 = 1.75 \times 10^{-5}$$

$$s = 0.0164$$

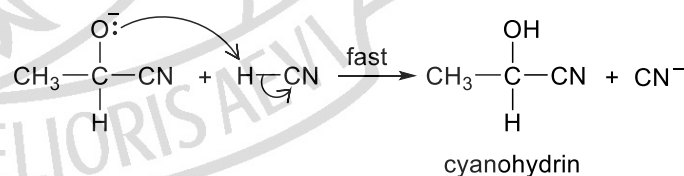
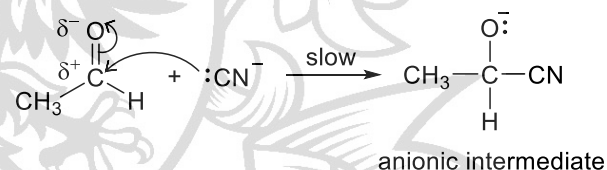
Solubility of $\text{Ca}(\text{C}_8\text{H}_6\text{NO}_3)_2$ in water
 $= 0.0164 \times 368.1 = \underline{6.02 \text{ g dm}^{-3}}$

- (c)** The amide bond in N-phenyloxamic acid must be formed between the $-\text{NH}_2$ group in phenylamine and an acyl chloride. Since the formula of **A** is $\text{C}_2\text{Cl}_2\text{O}_2$, **A** must be



(Note: $\text{KMnO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat cannot be used for first step as ethanedioic acid can be further oxidised to CO_2 and H_2O .)

(d) In amides, RCONH_2 , the lone pair of electrons on N is delocalised into the $\text{C}=\text{O}$ group. Hence, the lone pair of electrons on N is not available for coordination with a proton and amides are neutral.



- (e)(ii) 1,3-butadiene does not undergo nucleophilic addition reaction with HCN due to the absence of electron deficient C to attract the CN^- nucleophile.

(Note: Both $\text{C}=\text{C}$ and $\text{C}=\text{O}$ π bonds are electron rich. Hence it is insufficient to state that the $\text{C}=\text{C}$ π electron cloud repel the nucleophile CN^- as carbonyl with $\text{C}=\text{O}$ group can undergo nucleophilic addition reaction).

In 4-methyl-1-penten-3-one, the p orbitals of the sp^2 C in $\text{C}=\text{C}$ and $\text{C}=\text{O}$ overlap to form a delocalised π electron cloud. Due to the highly electronegative O atom, the delocalised π electron cloud is pulled towards the O atom and the terminal alkene C becomes δ^+ .

As nucleophilic attack on the δ^+ carbonyl C is sterically hindered by the $-\text{CH}(\text{CH}_3)_2$ group, the nucleophile will attack the δ^+ terminal alkene C instead, resulting in the nucleophilic addition occurring at the alkene group to form **C** instead of at the carbonyl group to form **B**.

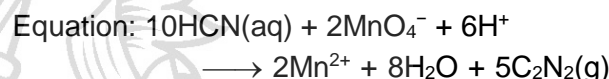
- (a)(iii) The mixture is an acidic buffer consisting of the weak acid HCN and its conjugate base CN^- . For an acidic buffer,

$$\text{pH} = \text{pK}_a + \lg \left(\frac{[\text{CN}^-]}{[\text{HCN}]} \right)$$

$$10.0 = -\lg (7.2 \times 10^{-10}) + \lg \left(\frac{[\text{CN}^-]}{[\text{HCN}]} \right)$$

$$\frac{[\text{CN}^-]}{[\text{HCN}]} = \underline{7.2}$$

- (b)(i) In an acidic solution, a suitable oxidant will be KMnO_4 .



$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}} \\ &= E^\ominus(\text{MnO}_4^-/\text{Mn}^{2+}) - E^\ominus(\text{C}_2\text{N}_2/\text{HCN}) \\ &= +1.52 - (+0.37) \\ &= \underline{+1.15 \text{ V}} \end{aligned}$$

(Other suitable oxidants include $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2O_2 since under acidic medium, the $E^\ominus_{\text{cell}} > 0$ (spontaneous))

- (b)(ii)



hybridisation of C atoms: sp

- (b)(iii) Since N is more electronegative than C, N attracts the bonding electrons more strongly. Hence, the electron density distribution of the $\text{C}\equiv\text{N}$ bond is asymmetrical and the $\text{C}\equiv\text{N}$ bond is polar, with C having δ^+ and N having δ^- .

However, as the cyanogen molecule is linear in shape, the bond dipoles cancel out each other and the molecule is overall non-polar.

- (c)(i) Nucleophilic substitution / hydrolysis

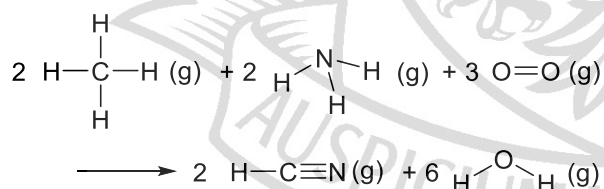
- (c)(ii) (In reaction 2, H_2O is involved in the rate-determining step and order of reaction wrt H_2O is one, i.e. $\text{rate} = k [\text{ClCN}][\text{H}_2\text{O}]$)

Question 2

- (a)(i)

	Reactant	Product
Oxidation number of	C in $\text{CH}_4 = -4$	C in $\text{HCN} = +2$
	N in $\text{NH}_3 = -3$	N in $\text{HCN} = -3$
	O in $\text{O}_2 = 0$	O in $\text{H}_2\text{O} = -2$

- (a)(ii) $\Delta H_r = \Sigma \text{BE of bonds broken in reactants} - \Sigma \text{BE of bonds formed in product}$



$$\begin{aligned} \Delta H_r &= 8(410) + 6(390) + 3(496) \\ &\quad - 2(410) - 2(890) - 12(460) \\ &= \underline{-1012 \text{ kJ mol}^{-1}} \end{aligned}$$

Since H_2O is in excess, $[\text{H}_2\text{O}]$ remains almost constant during the reaction. Hence reaction 2 is a pseudo first-order reaction, i.e. $\text{rate} = k_2[\text{C/CN}]$ and units of k_2 are s^{-1} .

(c)(iii) H_2O acts as a nucleophile as the O atom donates its lone pair of electrons to the electron deficient C in C/CN to form the C-O bond in HO-CN .

(c)(iv) $\text{rate} = k_3 [\text{C/CN}][\text{OH}^-]$

(c)(v) $[\text{C/CN}] = 0.010 / 100 \times 1000$
 $= 0.100 \text{ mol dm}^{-3}$

$$\begin{aligned}\text{rate}_2 &= k_2 [\text{C/CN}] \\ &= 5.1 \times 10^{-7} \times 0.100 \\ &= 5.1 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}\end{aligned}$$

$$\begin{aligned}\text{At pH } 10.0, \\ \text{pOH} &= 14 - 10 = 4 \\ [\text{OH}^-] &= 10^{-4} \text{ mol dm}^{-3}\end{aligned}$$

$$\begin{aligned}\text{rate}_3 &= k_3 [\text{C/CN}][\text{OH}^-] \\ &= 4.2 \times 0.100 \times 10^{-4} \\ &= 4.2 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}\end{aligned}$$

$$\begin{aligned}\text{rate}_2 / \text{rate}_3 &= (5.1 \times 10^{-8}) / (4.2 \times 10^{-5}) \\ &= 1.21 \times 10^{-3}\end{aligned}$$

(d) (Method: sampling, quenching and titrimetric analysis)

Upon adding excess water to a known initial concentration of C/CN, start the stopwatch simultaneously.

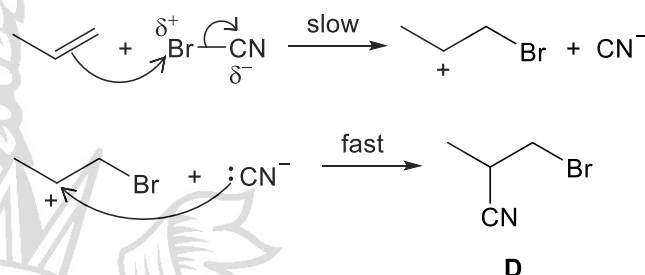
An aliquot is withdrawn from the reaction mixture at suitable time intervals and quenched by adding a large volume of ice-cold water.

Each quenched sample is titrated against a base (e.g. NaOH(aq)) to determine the concentration of the acidic products.

Plot the graph of volume of titrant used (or concentration of products) against time.

Obtain the initial rate by finding the gradient of the tangent drawn to the curve at $t = 0 \text{ s}$, and $k_2 = \text{initial rate}_2 / \text{initial } [\text{C/CN}]$
 [Alternatively, obtain half-life from the curve and $k_2 = \ln 2 / t_{1/2}$]

(e) Mechanism: Electrophilic addition



In step 1, the electrophilic (electron deficient) Br atom bonds to the less substituted C atom in C=C to form the more stable 2° carbocation. Since the 2° carbocation forms faster than the less stable 1° carbocation, **D** is formed preferentially.



Question 3

(a)(i) An amine is a Lewis base as the N atom is an electron-pair donor.

Equation: $(\text{CH}_3)_3\text{N} + \text{BF}_3 \longrightarrow (\text{CH}_3)_3\text{N} \rightarrow \text{BF}_3$
 (Note: An amine, not ammonia, is required for the illustration)

(a)(ii) In the gas phase, basicity of $\text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$

From CH_3NH_2 to $(\text{CH}_3)_2\text{NH}$ to $(\text{CH}_3)_3\text{N}$, there is an increasing number of electron donating alkyl groups.

Hence, the electron density of the N atom increases from CH_3NH_2 to $(\text{CH}_3)_2\text{NH}$ to $(\text{CH}_3)_3\text{N}$, making the lone pair of electrons on the N atom increasingly more available for donation to a Lewis acid.

$$(b)(i) \quad K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]}$$

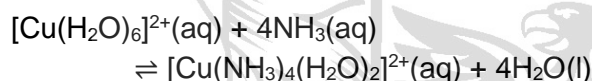
- (b)(ii) The higher the K_b value, the stronger the base and the more available the lone pair of electrons on the N atom for coordination to a proton.

The aromatic amines, phenylamine and 4-chlorophenylamine, are less basic than ammonia and the aliphatic amine, ethylamine, because of the delocalisation of the lone pair of electrons on the N atom into the benzene ring.

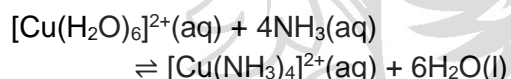
4-chlorophenylamine is less basic than phenylamine because the electron withdrawing –Cl group further decreases the electron density on the N atom and hence further reduces the availability of the lone pair of electrons on the N atom for coordination to a proton.

Ethylamine is a stronger base than ammonia because the alkyl group (–CH₃CH₂) bonded to the N atom is electron donating and this increases the electron density on the N atom, making the lone pair of electrons on the N atom more available for coordination to a proton.

- (c)(i) Ligand exchange reaction

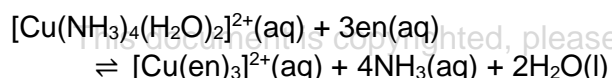


OR

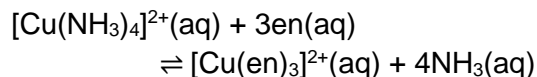


(Both $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ are commonly used and accepted).

- (c)(ii) A ligand exchange reaction occurs as the H₂NCH₂CH₂NH₂ (en) bidentate ligand displaces the NH₃ monodentate ligand. The deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (or $[Cu(NH_3)_4]^{2+}$) changes to the purple $[Cu(en)_3]^{2+}$.



OR



[The above reaction is entropy driven]

Pentane is a non-polar compound with only weak instantaneous dipole-induced dipole (id-id) interactions which requires the least amount of energy to overcome. Hence, it has the lowest m.p.

Propanoic acid and butylamine have higher m.p. than pentane as they are polar compounds with stronger intermolecular forces of id-id, permanent dipole-permanent dipole (pd-pd) interactions and hydrogen bonding. As the O–H bond is more polar than the N–H bond, propanoic acid forms stronger hydrogen bonding which requires a larger amount of energy to overcome. Hence, propanoic acid has a higher m.p. than butylamine.

Glycine has the highest m.p. as it exists as zwitterions held together by strong ionic bonds which requires the largest amount of energy to overcome.

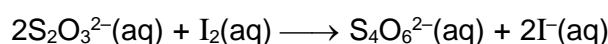
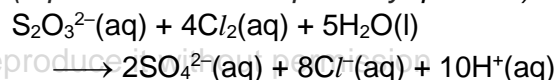
Question 4

- (a)(i) Down Group 17, the value of $E^\ominus(X_2/X^-)$ becomes less positive and the position of equilibrium of the reduction of X_2 to X^- lies increasingly to the left. Hence, down the group, X_2 has less tendency to be reduced and the oxidising power of X_2 decreases.

- (a)(ii) Chlorine, being a stronger oxidising agent, oxidises thiosulfate to sulfate ions, where the average oxidation state of S increases from +2 to +6.

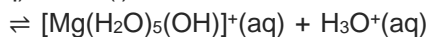
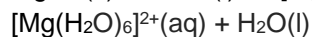
Iodine, being a weaker oxidising agent, oxidises thiosulfate to tetrathionate ions, where the average oxidation state of S only increases from +2 to +2.5.

(equations are not required by question)

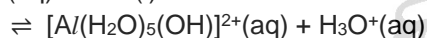
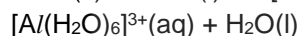
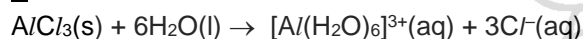


(b)(i) MgCl_2 dissolves readily with slight hydrolysis.

pH of resultant solution is around 6.5.



AlCl_3 dissolves readily with appreciable hydrolysis. pH of resultant solution is around 3.



SiCl_4 dissolves readily and it hydrolyses to produce white fumes of $\text{HCl}(\text{g})$ which dissolves in excess water to give $\text{HCl}(\text{aq})$. pH of resultant solution is around 2.



(b)(ii) MgCl_2 is an ionic compound. When dissolved in water, ion-dipole interactions are formed between water and the ions.

SiCl_4 is a simple covalent molecule. The electron-deficient Si atom is attacked by the lone pairs of electrons on water, leading to the hydrolysis of SiCl_4 .

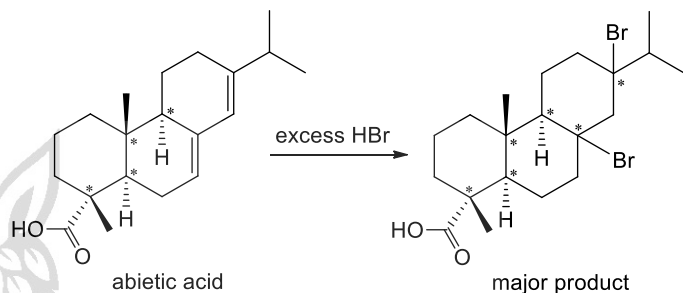
(c)(i) $K_c = \frac{[\text{HXO}][\text{X}^-][\text{H}^+]}{[\text{X}_2]} \text{ mol}^2 \text{ dm}^{-6}$

(c)(ii)

	$\text{I}_2(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightleftharpoons \text{IO}^-(\text{aq}) + \text{I}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$				
Initial conc / mol dm^{-3}	0.10	0.50	0	0	-
Change in conc / mol dm^{-3}	-0.097	-2(0.097)	+0.097	+0.097	-
Eqm conc / mol dm^{-3}	0.003	0.306	0.097	0.097	-

$$K_c = \frac{[\text{IO}^-][\text{I}^-]}{[\text{I}_2][\text{OH}^-]^2} = \frac{(0.097)(0.097)}{(0.003)(0.306)^2} = 33.5 \text{ mol}^{-1} \text{ dm}^3$$

(d)(i)

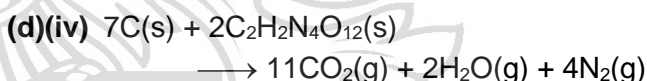


no. of extra chiral centres = 2

(d)(ii) KCl is an ionic compound with strong ionic bonds between the oppositely charged K^+ and Cl^- ions which requires a large amount of energy to overcome. Hence KCl has a high b.p. and is not volatile.

(d)(iii) M_r of tetranitrateoethane
 $= 4(14.0) + 2(12.0) + 12(16.0) + 2(1.0) = 274$

% mass of oxygen
 $= 12(16.0) / 274 \times 100\% = 70.1\%$



(d)(v) ΔS is positive due to the increase in disorder of the system as gaseous products are formed from solid reactants.

ΔS is large due to the large increase in number of gaseous particles, as 17 mol of gaseous products are formed from 9 mol of solid reactants.

Question 5

(a)(i) Due to the presence of ligands in the transition metal complexes, the five 3d orbitals are split into two sets of different energy levels. Since these 3d subshell is often partially filled, electrons from the lower-energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher-energy d orbitals. (d-d transitions). This causes the complexes to be coloured and the colour observed is the complement of the colour absorbed.

(a)(ii) In $V_2(SO_4)_3$, the electronic configuration of vanadium(III) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$. Since the 3d subshell of vanadium(III) is partially filled, d-d transition is possible and $V_2(SO_4)_3$ is coloured.

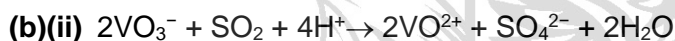
In $NaVO_3$, the electronic configuration of vanadium(V) is $1s^2 2s^2 2p^6 3s^2 3p^6$. Since the 3d subshell of vanadium(V) is vacant, no d-d transition is possible and $NaVO_3$ is colourless.

(b)(i)

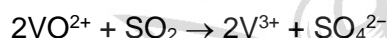


As pH increases ($[H^+]$ decreases), the position of both equilibria (1) and (2) shifts left and both E become less positive. Both VO_2^+ and VO_3^- have less tendency to be reduced and their oxidising power decreases.

Since equilibrium (2) has more H^+ , the position of equilibrium (2) shifts further left than equilibrium (1). This is because the reaction quotient, Q, of equilibrium (2) will increase more than that of equilibrium (1). Hence, equilibrium (2) has a less positive E value than equilibrium (1). VO_2^+ has greater tendency to be reduced than VO_3^- and VO_2^+ is a more powerful oxidant at pH 7.



$$E^\ominus_{\text{cell}} = +1.00 - (+0.17) \\ = +0.83 \text{ V} > 0 \text{ (spontaneous)}$$



$$E^\ominus_{\text{cell}} = +0.34 - (+0.17) \\ = +0.17 \text{ V} > 0 \text{ (spontaneous)}$$

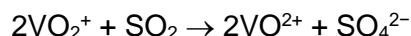
Products: V^{3+} and SO_4^{2-}

Equation:

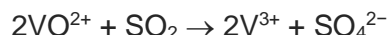


OR

Under acidic conditions, colourless VO_3^- is converted to yellow VO_2^+ .



$$E^\ominus_{\text{cell}} = +1.00 - (+0.17) \\ = +0.83 \text{ V} > 0 \text{ (spontaneous)}$$

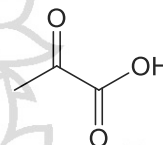


$$E^\ominus_{\text{cell}} = +0.34 - (+0.17) \\ = +0.17 \text{ V} > 0 \text{ (spontaneous)}$$

Products: V^{3+} and SO_4^{2-}

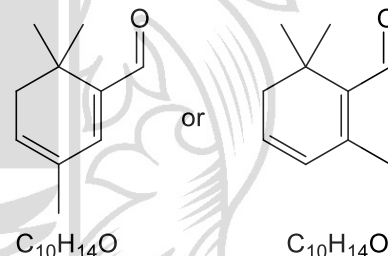


(c)(i) Structure of compound F:



(Since F is a product from the oxidation of safranal, F does not contain $1^\circ/2^\circ$ alcohol or aldehyde groups. Also, since F gives a yellow ppt with alkaline $I_2(aq)$, F contains the $-COCH_3$ group.)

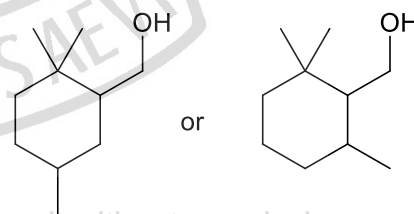
(c)(ii) Two possible structures of safranal:

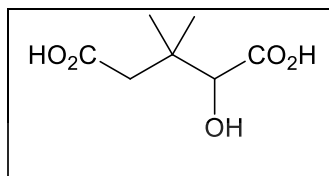


(From its name and molecular formula, safranal contains an aldehyde group, which is oxidised to form a carboxylic acid in G)

(c)(iii) $C_{10}H_{20}O$

(Both the alkene and aldehyde groups in safranal will be reduced by H_2 , Ni, heat to form





(d)(i) Since **J** ($C_7H_{10}N_2O$) is neutral, **J** does not have phenol and amine groups.

Since **J** ($C_7H_{10}N_2O$) does not react with 2,4-DNPH or $Br_2(aq)$, **J** does not have carbonyl, alkene, phenol and phenylamine groups.

Since **J** ($C_7H_{10}N_2O$) reacts with Na, **J** must have one alcohol group and two nitrile groups.

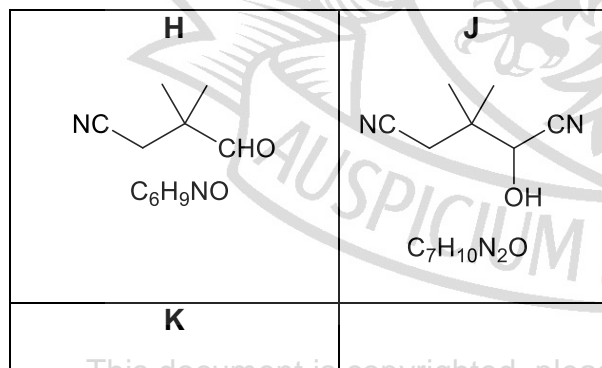
(d)(iii) Step 1: ethanolic KCN, heat
Step 3: $H_2SO_4(aq)$, heat
Step 4: $KMnO_4(aq)$, $H_2SO_4(aq)$, heat

(Note: Oxidation of the 2° $-OH$ by $KMnO_4(aq)$, $H_2SO_4(aq)$, heat cannot be done in step 3 as the hot, acidic conditions will also result in acidic hydrolysis of the nitrile groups to form carboxylic acids)

(detailed elucidation not required by question)

Evidence	Deduction
J ($C_7H_{10}N_2O$) is neutral	J does not contain phenol and amine groups. J contains an amide or nitrile.
J does not react with 2,4-DNPH	J does not undergo condensation with 2,4-DNPH. J does not contain carbonyl group.
J does not react with bromine water	J does not undergo electrophilic substitution and electrophilic addition with $Br_2(aq)$. J does not contain phenol, phenylamine and alkene groups.
J reacts with sodium metal	J undergoes acid-metal reaction with Na. J contains <u>one alcohol</u> group. J must contain <u>two nitrile</u> groups (since it has only 1 O atom present as $-OH$ group and the 2 N atoms must be present in 2 nitrile groups).

(d)(ii)



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

Q1 (B)

$^{84}_{38}\text{Sr}$ has 38 protons, 46 neutrons, 38 e^-

\Rightarrow W, X and Y have 46 neutrons

$^{84}_{38}\text{Sr}^{2+}$ has 38 protons, 46 neutrons, 36 e^-

\Rightarrow W, X^- and Y^{2-} have 36 e^-

\Rightarrow W has 36 e^- , X has 35 e^- and Y have 34 e^-

\Rightarrow W has 36 protons, X has 35 protons and Y have 34 protons

Nucleon no. of W = 46 neutrons + 36 protons = 82

Nucleon no. of X = 46 neutrons + 35 protons = 81

Nucleon no. of Y = 46 neutrons + 34 protons = 80

Q2 (C)

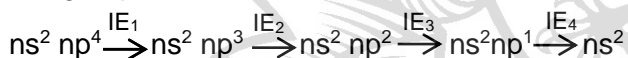
Electrons, being negatively charged, are deflected towards the (+) plate. Protons, being positively charged, are deflected towards the (–) plate.

Electrons, having the same magnitude of charge but lighter than protons, have a higher charge/mass ratio, and are deflected more than protons.

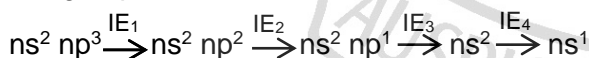
Q3 (B)

The ionization energy (IE) data for As, Sb, Se and Te are not available in the Data Booklet.

For group 16 element,



For group 15 element,



IE_4 of a Group 15 element involves the removal of e^- from the inner ns subshell, requiring a larger than expected amount of energy compared to IE_3 which involves the removal of e^- from the higher energy np subshell.

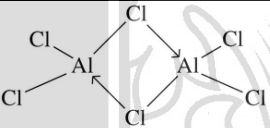
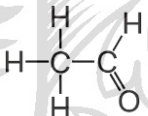
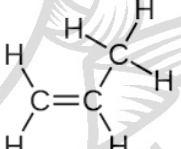
Comparing the values of IE_3 and IE_4 in the options, options A and C have large differences between IE_3 and IE_4 i.e. A and C are group 15 elements.

B and D corresponds to Group 16 elements. Since Tellurium is below Selenium, the IE 's of Tellurium are lower than that of Se since IE 's decrease down the Group. Hence, B is Tellurium.

Q4 (C)

After forming a single bond between the two oxygen atoms, each oxygen will gain one more e^- to achieve octet configuration i.e. peroxide has a 2– charge. Barium, a group 2 element, forms a cation with a 2+ charge.

Q5 (C)

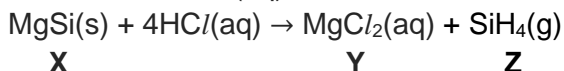
A		All bonds are sigma bonds.
B	$O=C=O$	CO_2 contains two sigma bonds and two pi bonds.
C		CH_3CHO contains six sigma bonds and one pi bond.
D		CH_2CHCH_3 contains eight sigma bonds and 1 pi bond.

$$\underline{pV = nRT}$$

$$pV = \frac{\text{mass}}{M_r} RT$$

react with acids and only reacts with concentrated alkaline solutions.

Note: Gas Z is actually SiH_4 and is formed from the reaction of **X** with HCl(aq) .



A	Electron affinity decreases down the group.
B	Electronegativity decreases down the group.
C	The chemical reactivity of the elements is determined by the valence electrons. The increase in nuclear charge down the group is actually outweighed by the increased distance of the valence electron from the nucleus, resulting in increased ease of loss of their valence electrons. Hence, the increase in nuclear charge does not result in increase in reactivity.
D	Due to the increase in the number of electron shells down the group, the valence electrons are further away from the nucleus, decreasing the attraction of the nucleus for the valence electrons. Hence, down the group, less energy is required for the atoms to lose their valence electrons in a reaction.

$$2\text{NaN}_3(\text{s}) \rightarrow 2\text{Na}(\text{s}) + 3\text{N}_2(\text{g})$$

$$\text{Amount of NaN}_3 \text{ reacted} = \frac{5.00}{23.0 + 3(14.0)} = 0.07692 \text{ mol}$$

$$\text{Amount of N}_2 \text{ gas produced} = (3/2)(0.07692) = 0.1154 \text{ mol}$$

$$\begin{aligned}\text{Volume of N}_2 \text{ gas} &= \frac{nRT}{p} \\ &= \frac{0.1154(8.31)(273 + 30.0)}{9.85 \times 10^4} \\ &= 0.00295 \text{ m}^3 = \mathbf{2.95 \text{ dm}^3}\end{aligned}$$

From the question, Germanium (a period 4, group 14 element) will have similar properties to Silicon (a period 3, group 14 element). Since silicon has high melting point and is a semiconductor, it can be predicted that Germanium has the same properties.

Q9 (D)

From QA notes, solution Y contains Mg^{2+} since, when reacted with NaOH , a white ppt is formed which is insoluble in excess NaOH .

Gas Z contains the other period 3 element, which reacts with air to give water and a white solid that is insoluble in dilute acid or alkali. The oxide of phosphorus, P_4O_6 , is acidic and therefore reacts with alkali. The oxide of silicon, SiO_2 , does not

Q11 (A)

	B ₂ O ₃	PbO
mass in 100g of solder glass / g	16	84
amount / mol	$\frac{16}{2(10.8)+3(16.0)}$ = 0.2299	$\frac{84}{207.2+16.0}$ = 0.3763

Amount of Pb = 0.3763 mol

Since 1 mol of B_2O_3 contains 2 mol of B,
amount of B = $2(0.2299) = 0.4598$ mol.

$$\text{Mole ratio of Pb/B} = \frac{0.3763}{0.4598} = 0.818 \approx 0.82$$

Q12 (B)

A	The equation for ΔH_1 shows <i>gaseous</i> H_2O being formed as the product of combustion. For the <i>standard</i> enthalpy change of combustion (i.e. at 298 K and 1 bar), <i>liquid</i> H_2O should be produced.
B	The equation for ΔH_2 correctly shows the <i>standard</i> enthalpy change of formation of liquid C_6H_{12} from the corresponding elements in their standard states i.e. $C_{\text{graphite}}(s)$ and $H_2(g)$.
C	The <i>standard</i> enthalpy change of atomisation of $H_2(g)$ is the energy required to form 1 mole of $H(g)$ from $H_2(g)$ under standard conditions i.e. $\frac{1}{2} H_2(g) \rightarrow H(g)$. Since ΔH_3 involves $6H_2(g) \rightarrow 12 H(g)$, $\Delta H_3 = 12 \times \Delta H_{\text{atomisation of } H_2(g)}$.
D	This option used the standard enthalpy of formation which involves the formation of the required substance <u>from the corresponding elements in their standard states</u> . The standard state of hydrogen is $H_2(g)$ and not $H(g)$. For the option to be correct, the reaction should read $6C_{\text{graphite}}(s) + 6H_2(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$.

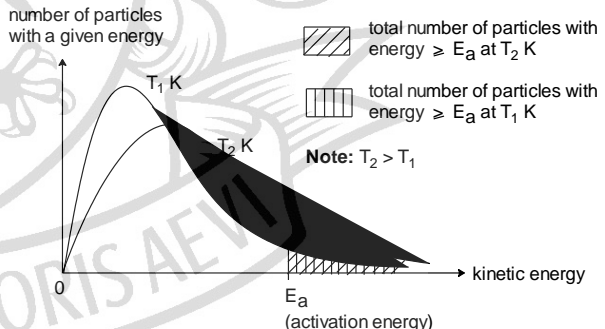
Q13 (D)

1	Incorrect. The reaction involves an increase in entropy due to the formation of a gaseous product (which is more disordered) from non-gaseous reactants (which are less disordered) i.e. $\Delta S > 0$. Since $\Delta H < 0$ and $\Delta S > 0$, $\Delta G = \Delta H - T\Delta S < 0$ for all temperatures i.e. ΔG is negative at 20 °C.
2	Correct. It can be deduced from the information provided that the given decomposition reaction occurs very slowly at room temperature, meaning that the reaction has very high activation energy.
3	Incorrect. See explanation of option 1.

Q14 (D)

1	Incorrect. As can be seen from the graph, if [substrate] is increased beyond x, the graph is a horizontal line. This means that the value of initial rate does not change when [substrate] is increased beyond x.
2	Incorrect. When [substrate] is increased beyond x, the initial rate does not change i.e. the reaction has become zero order with respect to the substrate.
3	Correct. When [substrate] is sufficiently high (at x and beyond), all the active sites of the enzyme are occupied. There are no active sites available to catalyse the reaction

Q15 (D)

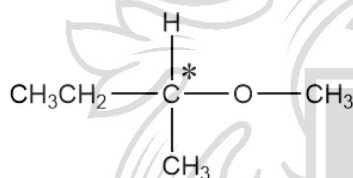
1	Incorrect. Changing the concentration of the reactants has no effect on the rate constant.
2	Incorrect. Increasing the concentration increases the number (or amount) of particles having energy greater than activation energy. The proportion remains the same. This is because the total number of particles is greater and the number of particles with energy greater than activation energy will be proportionally greater i.e. the proportion remains the same.
3	Correct. Increasing the temperature increases the rate constant. The Arrhenius equation (shown in Reaction Kinetics lecture notes) shows this relationship, but students are not required to memorise the equation.
4	Correct. This is evident from how the Boltzmann distribution changes at higher temperatures.  <p>number of particles with a given energy</p> <p>total number of particles with energy $\geq E_a$ at T_2 K</p> <p>total number of particles with energy $\geq E_a$ at T_1 K</p> <p>Note: $T_2 > T_1$</p> <p>kinetic energy</p> <p>E_a (activation energy)</p>

Q16 (A)

A	$\text{H}-\text{C}\equiv\text{C}-\text{H}$	Each of the two C atoms have 2 regions of electron density \Rightarrow 2 sp -hybridised atoms.
B	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	Each of the two C atoms have 3 regions of electron density \Rightarrow 2 sp ² -hybridised atoms.
C	$\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$	Each of the four C atoms have 2 regions of electron density \Rightarrow 4 sp -hybridised atoms.
D	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	Each of the four C atoms have 3 regions of electron density \Rightarrow 4 sp ² -hybridised atoms.

Q17 (B)

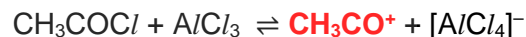
R₁ and R₂ should only contain C and H atoms since they are hydrocarbons. The structure of an ether with the smallest number of C atoms and 1 chiral carbon is shown below. It contains 5 carbon atoms.

**Q18 (A)**

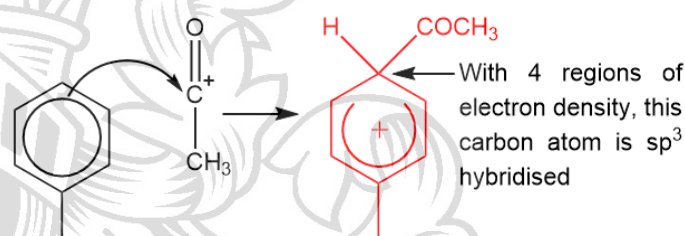
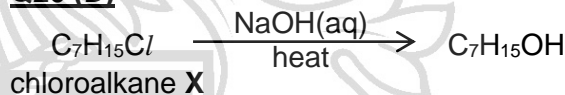
1	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ is one of the mono-substituted products of the free radical substitution reaction between propane and chlorine.
2	$\text{CH}_2\text{ClCH}_2\text{CH}_2\text{Cl}$ is one of the di-substituted products of the free radical substitution reaction between propane and chlorine.
3	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ is formed when the following radicals react in the termination step. $\text{CH}_3\text{CH}_2\text{CH}_2\bullet + \bullet\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
4	Not possible. The five-carbon pentane requires the reaction between a $\text{CH}_3\text{CH}_2\bullet$ radical and a $\text{CH}_3\text{CH}_2\text{CH}_2\bullet$. However, it is not possible to form a $\text{CH}_3\text{CH}_2\bullet$ radical in this reaction.

Q19 (A)

In this electrophilic substitution reaction, the electrophile is generated for the reaction between $\text{CH}_3\text{COC}\ell$ and AlCl_3 .



Two of the six π electrons in the benzene ring are used to form a bond with CH_3CO^+ , disrupting the continuous π electron cloud of benzene. The remaining π electrons are delocalized over the 5 sp^2 C atoms and not the sp^3 C atom. This is due to the lack of a p-orbital for side-on overlap on the sp^3 carbon atom.

**Q20 (D)**

Since the major organic products form a racemic mixture (i.e. a 1:1 mixture of enantiomers), X contains at least 1 chiral centre.

A	$\text{CH}_3(\text{CH}_2)_6\text{Cl}$ does not contain any chiral centres.
B	$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2-\text{C}-\text{Cl} \\ \\ \text{CH}_2\text{CH}_3 \end{array}$ does not contain any chiral centres.
C	$\begin{array}{c} \text{CH}_3 & & \text{CH}_3 \\ & & \\ \text{H}-\text{C}-\text{CH}_2-\text{C}-\text{Cl} \\ & & \\ \text{CH}_3 & & \text{CH}_3 \end{array}$ does not contain any chiral centres.
D	$\begin{array}{c} \text{CH}_3 & \text{CH}_2\text{CH}_3 \\ & \\ \text{H}-\text{C}-\text{C}^*-\text{Cl} \\ & \\ \text{CH}_3 & \text{CH}_3 \end{array}$ contains one chiral centre.

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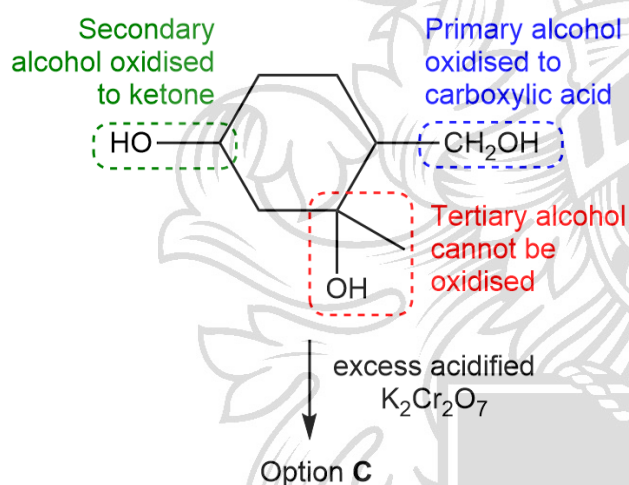
Q21 (D)

Both the -OH of the phenol group and -COOH group are acidic and react with NaOH .

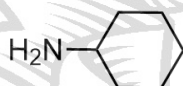
No substitution reaction occurs with the iodobenzene groups due to the partial double bond character of the C-I bond in the iodobenzene groups, which results from the overlap between the p -orbital of iodine and the π electron cloud of benzene.

Q22 (C)

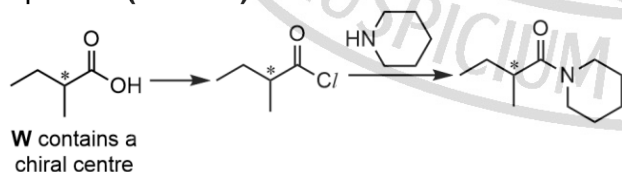
When heat with excess acidified $\text{K}_2\text{Cr}_2\text{O}_7$, Q undergoes strong oxidation of the following functional groups.

**Q23 (A)**

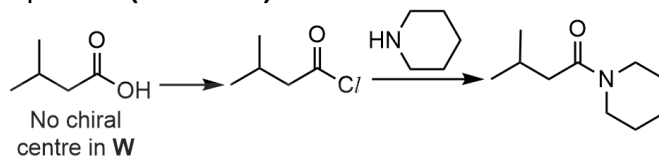
- **W** is chiral \Rightarrow **W** contains chiral centre(s)
- Since **X** reacted with an amine to form an amide **Y**, **X** is an acyl chloride.
- Options **C** and **D** are incorrect. The amide formed implies that the amine used has the following structure, which is different from the question.



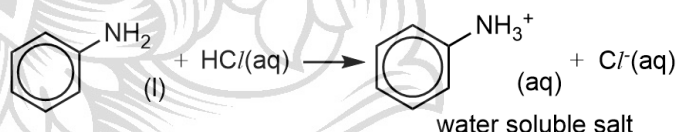
- **Option A (Correct)**



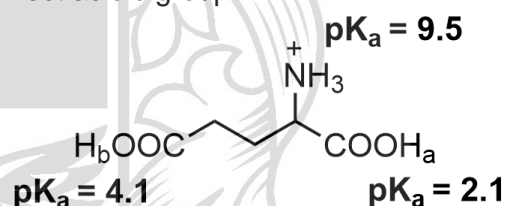
- **Option B (Incorrect)**

**Q24 (C)**

- **P** is sparingly soluble in water but dissolves readily in cold HCl(aq)
 - \Rightarrow Acid-base reaction between basic group in **P** and H^+ to form a soluble salt. Since cold acid was used, no acidic hydrolysis occurred.
 - \Rightarrow **A** is a ketone which is neutral.
 - B** is an amide which is neutral.
 - D** is a phenol which is weakly acidic.
 - \Rightarrow **C** is phenylamine which is basic and reacts with HCl(aq) .

**Q25 (B)**

Students first need to assign the 3 pK_a values to the correct acidic group.



The 2 -COOH groups are more acidic than the -NH_3^+ group. -COOH_a is more acidic than -COOH_b because -COOH_a is closer to the electron-withdrawing N atom which disperses the negative charge on and stabilizes the conjugate base of -COOH_a to a greater extent.

When $\text{pH} < \text{pK}_a$, the acidic group remains protonated. When $\text{pH} > \text{pK}_a$, the acidic group becomes deprotonated. Therefore at $\text{pH} 7$, the 2 -COOH groups are deprotonated (since $\text{pH} = 7 > \text{pK}_a = 2.1$ and 4.1) while the -NH_3^+ group remains protonated (since $\text{pH} = 7 < \text{pK}_a = 9.5$).

Q26 (B)

Electronic configuration of Mo = [Kr] 4d⁵ 5s¹

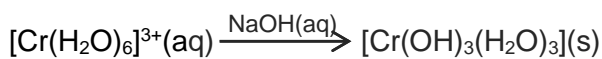
The considerations when writing the electronic configuration of Mo are similar to that of Cr ([Ar] 3d⁵ 4s¹).

Mo⁴⁺ is obtained by removing 4 e⁻ from Mo.

Electronic configuration of Mo⁴⁺ = [Kr] 4d² 5s⁰

Q27 (C)

Cr³⁺(aq) exists as [Cr(H₂O)₆]³⁺(aq).



Green solution

Option B

Grey-green ppt

Option D

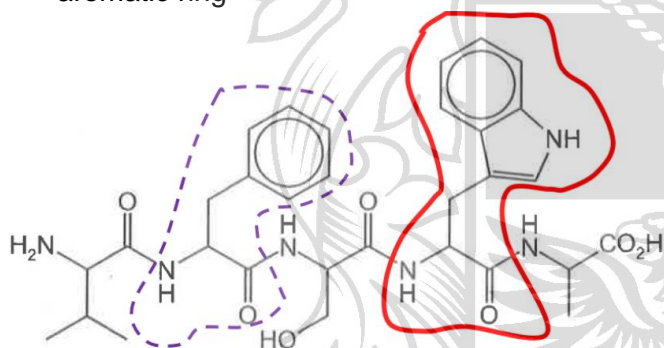


[Cr(OH)₆]³⁻(aq)
Deep-green solution
Option C

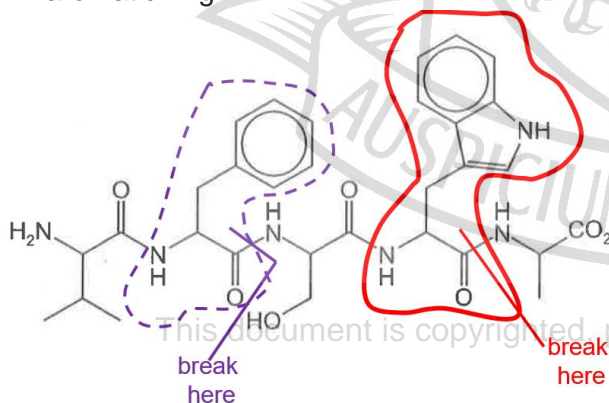
Q28 (C)

From the information provided in the question, students need to

1. look for amino acid residues which contain an aromatic ring



2. hydrolyse the peptide bond on the carboxyl (–CO–) end of the residue which contains an aromatic ring.

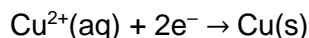


Applying the information to polypeptides in the options.

A	<p>After hydrolysis, this portion gives a tripeptide</p>
B	<p>The products contain one dipeptide and two monoamino acids.</p>
C	<p>After hydrolysis, this portion gives a dipeptide</p> <p>After hydrolysis, this portion gives a dipeptide</p>
D	<p>The products contain two monoamino acids and one dipeptide.</p>

Q29 (B)

$[\text{HOC}] = [\text{H}^+] = [\text{C}^-] = 1 \text{ mol dm}^{-3}$ so that the **standard** electrode potential can be measured. The concentrations used are not based on the stoichiometry of the half-equation representing the electrode potential.



$$\begin{aligned}\text{Amount of electrons transferred} &= 2(1.844) \\ &= 3.688 \text{ mol}\end{aligned}$$

Q30 (Intended answer: C; B was also accepted)

This working results in C as the answer.

$$\begin{aligned}\text{No. of Cu atoms in } 0.1\text{m length} &= \frac{0.1}{3.0 \times 10^{-12}} \\ &= 3.333 \times 10^{10}\end{aligned}$$

$$\begin{aligned}\text{No. of Cu atoms in } 0.1\text{m} \times 0.1\text{m electrode} \\ &= (3.33 \times 10^{10})^2 = 1.111 \times 10^{21}\end{aligned}$$

$$\begin{aligned}\text{No. of Cu atoms if electrode was coated with a total} \\ \text{of 2000 atoms (1000 atoms on each side)} &= 2000 \times \\ 1.111 \times 10^{21} &= 2.222 \times 10^{24}\end{aligned}$$

$$\begin{aligned}\text{Amount of Cu atoms if electrode was coated with a} \\ \text{total of 2000 atoms} &= \frac{2.222 \times 10^{24}}{6.02 \times 10^{23}} = 3.691 \text{ mol}\end{aligned}$$



$$\begin{aligned}\text{Amount of electrons transferred} &= 2(3.691) \\ &= 7.382 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Since } Q &= It = n_e F \\ (4.0)(t) &= 7.382(96500) \\ t &= 178110 \text{ s} = (178110 / 3600) \text{ h} \\ &= 49.4 \text{ h}\end{aligned}$$

This working results in B as the answer.

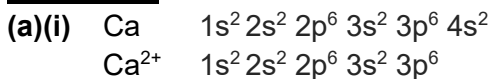
$$\begin{aligned}\text{No. of Cu atoms in } 0.1\text{m length} &= \frac{0.1}{3.0 \times 10^{-12}} \\ &= 3.333 \times 10^{10}\end{aligned}$$

$$\begin{aligned}\text{No. of Cu atoms in } 0.1\text{m} \times 0.1\text{m electrode} \\ &= (3.33 \times 10^{10})^2 = 1.111 \times 10^{21}\end{aligned}$$

$$\begin{aligned}\text{No. of Cu atoms if electrode was coated with a total} \\ \text{of 1000 atoms} &= 1000 \times 1.11 \times 10^{21} = 1.111 \times 10^{24}\end{aligned}$$

$$\begin{aligned}\text{Amount of Cu atoms if electrode was coated with a} \\ \text{total of 1000 atoms} &= \frac{1.111 \times 10^{24}}{6.02 \times 10^{23}} = 1.844 \text{ mol}\end{aligned}$$

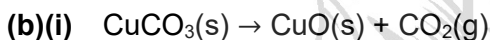
Question 1



(a)(ii) Ca²⁺ has the same number of protons but one less electronic shell than Ca. Hence the electrostatic attraction between the nucleus and the valence electrons in Ca²⁺ is greater, resulting in the smaller size of the Ca²⁺ ion.

(a)(iii) Down Group 2, the number of electronic shells increases, increasing the distance between the nucleus and the valence electrons, causing the shielding experienced by valence electrons to increase. Despite the increasing nuclear charge, the electrostatic attraction between the nucleus and the valence electrons decreases, resulting in an increase in the size of the electron cloud down the group.

(a)(iv) Although the Sr atom is larger than the Ca atom, meaning that there will be fewer Sr atoms per unit volume compared to Ca, Sr has a higher molar mass. Since density = (mass/volume), the significantly larger molar mass of Sr causes the density of Sr to be greater than that of Ca. *(Students should involve the sizes of the atoms in their answers)*



(b)(ii) Since the ionic radius of the cations decrease from Ca²⁺ (0.099 nm) to Cu²⁺ (0.073 nm) to Mg²⁺ (0.065 nm), the polarizing power of the cations increase from Ca²⁺ to Cu²⁺ to Mg²⁺. The extent to which the C–O bond in CO₃²⁻ is weakened increases from Ca²⁺ to Cu²⁺ to Mg²⁺, requiring decreasing amounts of energy to overcome.

Hence, the minimum temperature is likely to be between 350 °C and 832 °C.

Suggested minimum temperature

$$= 350 + \frac{(832 - 350)}{(0.099 - 0.065)}(0.073 - 0.065) = 463 \text{ °C}$$

(c)(i) Possible answers include:

1. Compounds of Cu²⁺ are coloured, while compounds of Mg²⁺ are not.
2. Compounds of Cu²⁺ are able to act as catalysts, while compounds of Mg²⁺ do not.
3. Mg²⁺ can only be reduced to one oxidation state i.e. Mg⁰, but Cu²⁺ can be reduced to more than one oxidation state (Cu⁺ and Cu).
4. Cu²⁺ forms a variety of complexes, but Mg²⁺ generally does not.

(c)(ii) Answers to this part tend to focus on their similarity as ionic compounds. Possible answers include:

1. Compounds of Cu²⁺ and Mg²⁺ conduct electricity in molten or aqueous phase but not in the solid phase.
2. Compounds of Cu²⁺ and Mg²⁺ are hard and brittle.
3. Compounds of Cu²⁺ and Mg²⁺ have high melting and boiling points.

Question 2

(a)(i) H₂O₂ is acting as a reducing agent as it reduced silver from +1 in Ag₂O to 0 in Ag metal.

(a)(ii) The two variables are the volume of oxygen produced and time i.e. monitor the volume of oxygen gas produced with time.

When Ag₂O and H₂O₂ are mixed in a conical flask, a stopwatch is started and the flask is stoppered with a delivery tube leading to a graduated syringe which collects the O₂ gas evolved. At suitable time intervals, the volume of O₂ gas evolved is recorded.

(b)(i) Amount of O₂ produced

$$= \frac{20}{24000} = 0.0008333 \text{ mol}$$

$$\text{Amount of H}_2\text{O}_2 = 2(0.0008333) = 0.001667 \text{ mol}$$

$$[\text{H}_2\text{O}_2] = \frac{0.001667}{\frac{1.0}{1000}} = 1.67 \text{ mol dm}^{-3}$$

- (b)(ii)** Amount of H_2O_2 in 10.0 cm^3
 $= \frac{10.0}{1000} (1.667) = 0.01667 \text{ mol}$
 Amount of Ag_2O
 $= 0.01667 \text{ mol}$
 Mass of Ag_2O
 $= 0.01667 (107.9 + 107.9 + 16.0)$
 $= 3.86 \text{ g}$

Using the point (2.0, 10.6) from the graph,

$$k' = \text{gradient} = \frac{10.6}{2.0} = 5.30 = k[\text{H}_2\text{O}_2]$$

$[\text{H}_2\text{O}_2]$ in the reaction mixture

$$= \frac{1.0}{10.0} (0.1) = 0.0100 \text{ mol dm}^{-3}$$

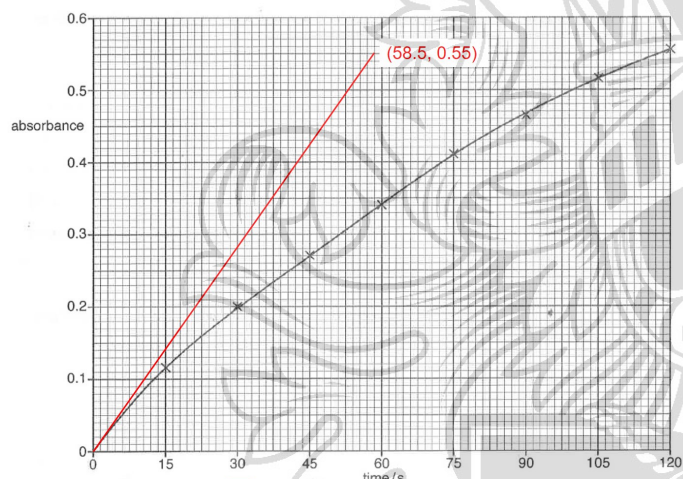
Therefore, $5.30 = k(0.0100)$

$$k = 530$$

Units of $k = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

(c)(v)

(c)(i)



Gradient of tangent at $t = 0$
 $= \text{initial rate}$
 $= \frac{0.55 - 0}{58.5 - 0} = 0.009402 \text{ s}^{-1}$

- (c)(ii)** Since the graph of rate again $[\text{I}^-]$ is a straight line with a positive gradient passing through the origin, $\text{rate} \propto [\text{I}^-]^1$ i.e. the order of reaction wrt I^- is 1.

- (c)(iii)** Since the slow step involves the reaction between 1 H_2O_2 and 1 I^- , $\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$.

- (c)(iv)** Since $[\text{H}_2\text{O}_2]$ was kept constant for all experiments to obtain Fig. 2.2., $\text{rate} = k'[\text{I}^-]$ where $k' = k[\text{H}_2\text{O}_2]$. The value of k' can be obtained from the gradient of the graph in Fig. 2.2.

rate

$k[\text{H}_2\text{O}_2][\text{I}^-]$

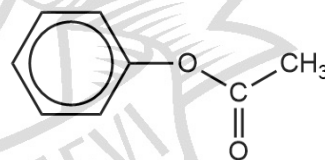
0

$[\text{I}^-]$

Question 3

- (a)(i)** Due to the overlap between the p-orbital of oxygen atom and the π electron cloud of the benzene ring, the lone pair of electrons on oxygen is delocalized in the benzene ring, reducing the availability of the lone pair of electrons to attack a carboxylic acid. Therefore, phenol does not react directly with carboxylic acids.

- (a)(ii)** Phenylethanoate is an ester with the following structure:



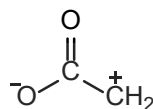
Step 1 : NaOH(aq)

Step 2 : $\text{CH}_3\text{COC/}$

- (b)(i)** Ethanolic KCN, heat

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- (b)(ii) The carbocation formed from **A** has the following structure.



With two highly electronegative oxygen atoms, the COO^- group is highly electron-withdrawing and intensifies the positive charge on CH_2^+ significantly. There are also no electron-donating alkyl groups to disperse the positive charge on CH_2^+ . Hence, the carbocation formed from **A** is unstable.

- (b)(iii) Possible answers include:

Resonance stabilized COO^-

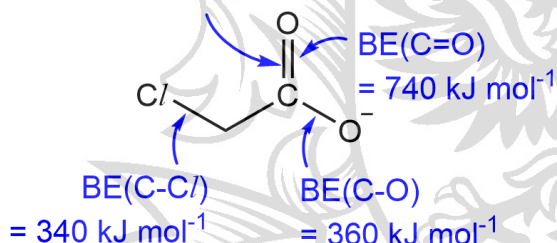
Due to the delocalisation of the negative charge on O across the O-C-O moiety, the carboxylate group is resonance stabilised. If the nucleophile attacks the C=O , the C=O carbon becomes sp^3 hybridised and the resonance stabilisation is destroyed. Therefore, it is more favorable for substitution to occur at the carbon of the C-Cl bond, which preserves the resonance stabilization at carboxylate group.

Consider alternative sites of reaction

BE(CO pi bond)

$$= 740 - 360$$

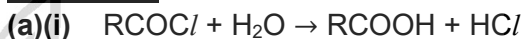
$$= 380 \text{ kJ mol}^{-1}$$



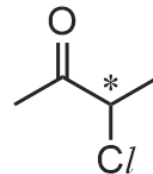
If substitution occurs at the C=O carbon atom, the bonds broken could be C=O or C-O , which require more energy to break than the C-Cl bond. Addition reaction at C=O which involves breaking the carbon-oxygen π bond, also requires more energy than breaking the C-Cl . Hence, it is more

favourable for substitution to occur at the C-Cl bond.

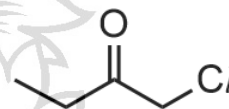
Question 4



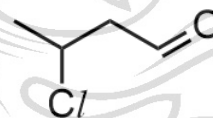
- (a)(ii) Structure of **D**



- (a)(iii) Skeletal formula for isomer **E**

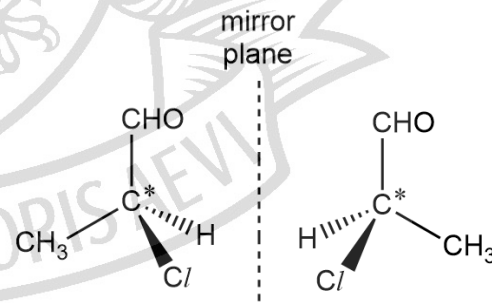


- (a)(iv) Structure of **F**

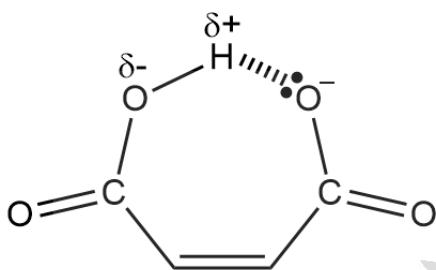


- (b)(i) **G** and **H** are non-superimposable mirror images of each other i.e. they are enantiomers. Hence, **G** is able to rotate plane-polarised light. **H** will rotate plane-polarised light to the same extent but in the opposite direction. The mixture contains a 1:1 mixture of **G** and **H** (i.e. a racemic mixture). The rotating power of **G** exactly cancels that of **H**. Therefore, the mixture does not rotate plane-polarised light.

- (b)(ii)



(c)(i) Monoanion of cis-isomer



(c)(ii) In the trans-isomer, the -COOH and -COO^- are too far away to be able to form an intramolecular hydrogen bond. Moreover, there is restricted rotation about the $\text{C}=\text{C}$ which prevents the trans-isomer from easily converting to the cis-isomer, preventing the formation of an intramolecular hydrogen bond.

(c)(iii) The intramolecular hydrogen bond helps to disperse the negative charge on -COO^- and stabilise the monoanion, the conjugate base of cis-butenedioic acid, to a greater extent. Hence, cis-butenedioic acid is a stronger acid and has a large K_a value than trans-butenedioic acid.

(c) 1 part per million of free chlorine

$$= \frac{1 \text{ free chlorine}}{10^6 \text{ water molecules}}$$

$$= \frac{1 \text{ mol of free chlorine}}{10^6 \text{ mol of water}}$$

Since M_r of water = 18.0,

$$= \frac{1 \text{ mol of free chlorine}}{(10^6 \times 18.0) \text{ g of water}}$$

Since density of water = 1.0 g cm^{-3} ,

$$= \frac{1 \text{ mol of free chlorine}}{(10^6 \times 18.0) \text{ cm}^3 \text{ of water}}$$

$$= \frac{1 \text{ mol of free chlorine}}{(10^6 \times 18.0) \text{ dm}^3 \text{ of water}}$$

$$= \frac{1 \text{ mol of free chlorine}}{1.0 \times 1000}$$

$$= 5.56 \times 10^{-5} \text{ mol dm}^{-3}$$

(d) amount of $\text{S}_2\text{O}_3^{2-} = \frac{37.50}{1000} (4.00 \times 10^{-4})$

$$= 1.50 \times 10^{-5} \text{ mol}$$

amount of $\text{I}_2 = 0.5(1.50 \times 10^{-5})$

$$= 7.5 \times 10^{-6} \text{ mol}$$

amount of $\text{HC/O} = 7.5 \times 10^{-6} \text{ mol}$

$$[\text{HC/O}] = \frac{7.50 \times 10^{-6}}{\frac{150}{1000}}$$

$$= 5.00 \times 10^{-5} \text{ mol dm}^{-3}$$

Since the concentration of free chlorine is less than the recommended amount of free chlorine ($5.56 \times 10^{-5} \text{ mol dm}^{-3}$ from (c)), the water is not of an acceptable quality.

Question 5

(a) From equation 4,

$$K_c = \frac{[\text{HC/O}][\text{H}^+][\text{Cl}^-]}{[\text{Cl}_2]}$$

$$4.5 \times 10^{-4} = \frac{[\text{HC/O}]}{[\text{Cl}_2]} (10^{-7})(10^{-3})$$

$$\frac{[\text{HC/O}]}{[\text{Cl}_2]} = 4.50 \times 10^6$$

Since $[\text{HC/O}]$ is 4.5×10^6 times of $[\text{Cl}_2]$, the amount of Cl_2 in the swimming pool is negligible

(b) **Similarity** : Both HCl and HC/O are monobasic acids.

Difference : HCl is a strong acid, while HC/O is a weak acid.

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(e)(i) From equation 5,

$$K_a = \frac{[H^+][ClO^-]}{[HClO]}$$

$$3.7 \times 10^{-8} = \frac{[10^{-8}][ClO^-]}{[HClO]}$$

$$\frac{[ClO^-]}{[HClO]} = 3.7$$

$$[ClO^-] = 3.7[HClO]$$

$$\text{Since } [ClO^-] + [HClO] = 6.0 \times 10^{-5},$$

$$3.7[HClO] + [HClO] = 6.0 \times 10^{-5}$$

$$[HClO] = 1.28 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[ClO^-] = 3.7(1.28 \times 10^{-5})$$

$$= 4.72 \times 10^{-5} \text{ mol dm}^{-3}$$

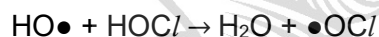
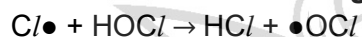
(e)(ii) The $[H^+]$ at pH 8.0 is lower than at pH 7.0. Therefore, at pH 8.0, the position of equilibrium of equation 5 lies more to the right, reducing $[HClO]$ in the sample of pool water. With less $HClO$ at pH 8.0, the pool water at pH 8.0 is less effective at disinfecting than the pool water at pH 7.0.

(f)(i) A free radical is a chemical species which contains an unpaired electron.

(f)(ii) Since the $O-Cl$ (203 kJ mol^{-1}) bond is weaker than the $H-O$ bond (460 kJ mol^{-1}), the $O-Cl$ bond undergoes homolytic fission more readily to form $HO\bullet$ and $Cl\bullet$ radicals.

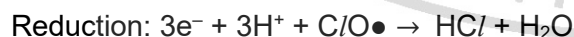


(f)(iii) Choose 1 of the following:



(f)(iv) Oxidation state of Cl in $ClO\bullet$ = +2
Oxidation state of Cl in $HOCl_2$ = +3
Oxidation state of Cl in HCl = -1

*Note that another approach using
Oxidation state of Cl in $ClO\bullet$ = +1
is also acceptable



(f)(v) When free chlorine decomposes due to the presence of UV light, $[ClO^-]$ decreases. The position of equilibrium of the equation in (f)(v) would shift right to increase $[ClO^-]$, maintaining the level of free chlorine in the swimming pools.

(g)(i) $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$

The addition of calcium chloride increases $[Ca^{2+}]$ in the pool water, causing the position of equilibrium of the above equilibrium to shift to the left, decreasing the solubility of calcium sulfate, preventing the plaster from dissolving.

(g)(ii) $pH 8.0 \Rightarrow [H^+] = 10^{-8} \text{ mol dm}^{-3}$
 $[OH^-] = (10^{-14} / 10^{-8}) = 10^{-6} \text{ mol dm}^{-3}$

If the cloudiness is due to precipitation of $Ca(OH)_2$, then the $[Ca^{2+}]$ is such that the ionic product exceeds the K_{sp} of $Ca(OH)_2$.

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

$$5.5 \times 10^{-6} = [Ca^{2+}](10^{-6})^2$$

$$[Ca^{2+}] = 5.5 \times 10^6 \text{ mol dm}^{-3}$$

In order for precipitation of $Ca(OH)_2$ in pool water, $[Ca^{2+}]$ needs to exceed $5.5 \times 10^6 \text{ mol dm}^{-3}$. Such high concentrations are not possible to reach. Hence, the cloudiness is not due to the presence of $Ca(OH)_2(s)$ in the water.

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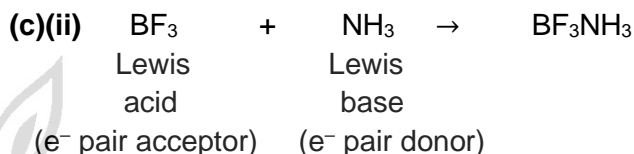
Question 1

- (a) The 3 bond pairs (and no lone pairs) of BF_3 would arrange themselves in such a way to minimise electronic repulsion and adopt a trigonal planar shape with a bond angle of 120° .

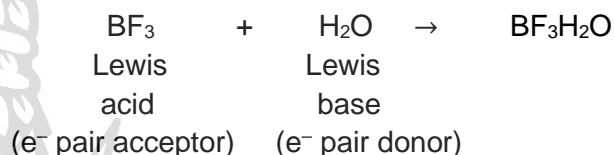
The 4 regions of electron densities of NH_3 and H_2O would arrange themselves in such a way to minimise electronic repulsion and adopt a tetrahedral electron pair geometry.

NH_3 , with 3 bond pairs and 1 lone pair, has a bond angle of 107° (smaller than 109.5°) due to the lone pair-bond pair repulsion being stronger than the bond pair-bond pair repulsion.

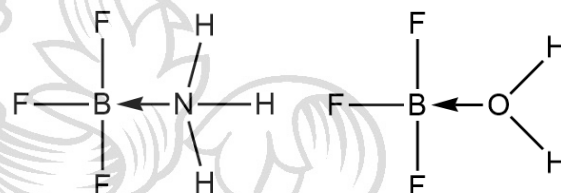
H_2O , with 2 bond pairs and 2 lone pairs, has additional lone pair-lone pair repulsion which is stronger than lone pair-bond pair repulsion which is stronger than bond pair-bond pair repulsion, leading to a smaller angle of 105° .



OR



FYI: Structures of products

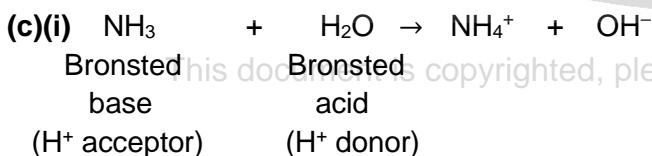
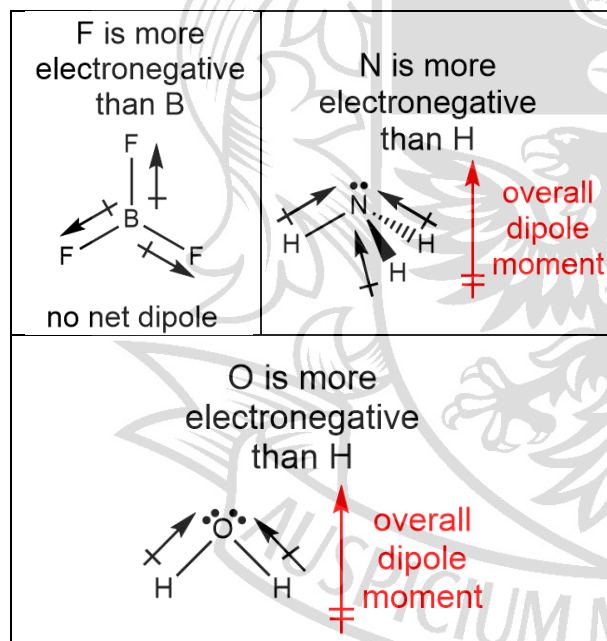


- (d)(i) For a gas to approach ideal behavior, the gaseous particles exert negligible intermolecular forces of attraction on one another. The size of gaseous particles are also small compared to the volume of the container.

- (d)(ii) Since the non-polar BF_3 possesses only instantaneous dipole-induced dipole interactions which are weaker than the hydrogen bonding between NH_3 molecules and between H_2O molecules, BF_3 deviates the least from ideality. Due to the more extensive hydrogen bonding between H_2O molecules than NH_3 molecules, H_2O deviates more from ideality than NH_3 .

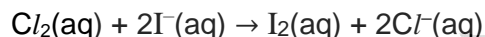
- (e)(i) Down group 17, the electron clouds of the halogens become larger and more polarisable. Hence, more energy is required to overcome the increasing strength of the instantaneous dipole-induced dipole (id-id) interactions between the halogen molecules down the group, leading to decreasing volatility.

(b)



- (e)(ii) The colours of the aqueous solutions of the halogens can be found at the bottom of the last page of the Data Booklet. Students are required to give the colour of the mixture even if no reaction takes place.

Cl₂(aq) + KI(aq)



- Brown colour due to production of I₂(aq) is observed.

Br₂(aq) + KCl(aq)

No reaction occurs.

- Orange colour due to unreacted Br₂(aq) is observed.

I₂(aq) + KBr(aq)

No reaction occurs.

- Brown colour due to unreacted I₂(aq) is observed.

Question 2

- (a)(i) Since concentration of dissolved gas is proportional to its partial pressure,

$$[\text{CO}_2] \propto p_{\text{CO}_2}$$

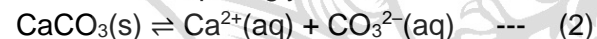
$$\frac{[\text{CO}_2]_{300 \text{ bar}}}{[\text{CO}_2]_{1.0 \text{ bar}}} = \frac{p_{\text{CO}_2}(300 \text{ bar})}{p_{\text{CO}_2}(1.0 \text{ bar})}$$

$$[\text{CO}_2]_{300 \text{ bar}} = \frac{300}{1.0} (0.040) = 12.0 \text{ mol dm}^{-3}$$

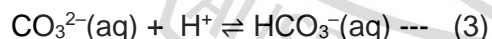
- (a)(ii) CO₂ establishes the following equilibrium in water:



Limestone is sparingly soluble in water:

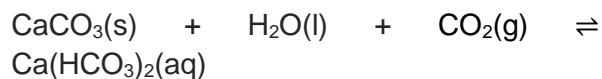


The H⁺ from (1) reacts with CO₃²⁻ from (2) to form HCO₃⁻.



As a result, the position of equilibrium of (2) shifts right to increase the [CO₃²⁻], causing more CaCO₃ to dissolve. The overall effect is that CaCO₃ dissolves, forming Ca(HCO₃)₂ where HCO₃⁻ are formed in equilibria (1) and (3).

Note: Students who are familiar with the following equilibrium can use it as part of their explanation.



$$\begin{aligned} \Delta H_r &= -1273.3 + 6(-285.8) + 12(0) \\ &\quad - 6(-393.5) - 12(-20.6) \\ &= -379.9 = -380 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\ominus &= \Delta H^\ominus - T\Delta S^\ominus \\ -83 &= -379.9 - 298\Delta S^\ominus \\ \Delta S^\ominus &= -0.996 \text{ kJ mol}^{-1} \text{ K}^{-1} \end{aligned}$$

- (c)(i) Due to the high partial pressure (greater than standard conditions of 1 bar) of CO₂ and H₂S at deep-sea hydrothermal vents, the position of equilibrium of the reaction between CO₂ and H₂S lies *further* to the right i.e. the reaction is more favoured than at standard conditions, causing ΔG to be more negative than -83 kJ mol⁻¹.

Note: Students who discuss their answers in terms of the higher temperatures (100 to 400 °C) of the hydrothermal vents will obtain a contradictory outcome. Since ΔS[⊖] is negative, -TΔS[⊖] is positive. At high T, the positive -TΔS[⊖] term outweighs the negative ΔH[⊖] term, causing ΔG to become (more) positive at higher temperatures.

$$\begin{aligned} \text{Ar of sulfur} &= \frac{93.5}{100}(32) + \frac{1.5}{100}(33) + \frac{4.5}{100}(34) + \frac{0.5}{100}(36) \\ &= 32.13 \end{aligned}$$

- (d)(ii) Half-life is the time taken for the concentration of the reactant to fall to half its original concentration.

- (d)(iii) Let c be the original concentration.

$$c \xrightarrow{t_{1/2}} \frac{1}{2}c \xrightarrow{t_{1/2}} \frac{1}{4}c \xrightarrow{t_{1/2}} \frac{1}{8}c$$

Time taken for radioactivity to drop to 1/8 its initial value = 3 half-lives = 3(87) = 261 days.

(d)(iv) $k = 0.693/87 = 0.007966 \text{ day}^{-1}$

$$\frac{(^{35}\text{S})_t}{(^{35}\text{S})_0} = 10^{\frac{(0.007966)(3)}{2.3}} = 0.9764$$

i.e. percentage of ^{35}S **remaining** 3 days later = 97.64%

$$\text{Percentage decrease} = 100 - 97.64 = 2.364 = 2.36\%$$

(e)(i) SH^- undergoes hydrolysis.

concentration / mol dm ⁻³	$\text{HS}^-(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{H}_2\text{S}(\text{aq})$	+	$\text{OH}^-(\text{aq})$	(f)(i)
initial	0.10	--			0		0	
change	-x	--			+x		+x	
equilibrium	0.10-x	--			x		x	

$$\text{p}K_b = 14 - 7.05 = 6.95$$

$$K_b = 10^{-6.95} = \frac{x^2}{0.10 - x}$$

$$x = [\text{OH}^-] = 0.0001059 \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg(0.0001059) = 3.975$$

$$\text{pH} = 14 - 3.975 = 10.0.$$

(e)(ii) H_2S is more acidic than $\text{CH}_3\text{CH}_2\text{SH}$ due to the greater stability of HS^- compared to $\text{CH}_3\text{CH}_2\text{S}^-$. The electron donating CH_3CH_2- group intensifies the negative charge on $\text{CH}_3\text{CH}_2\text{S}^-$, making it less stable than HS^- .

$\text{C}_6\text{H}_5\text{SH}$ is more acidic than $\text{CH}_3\text{CH}_2\text{SH}$ due to the greater stability of $\text{C}_6\text{H}_5\text{S}^-$ compared to $\text{CH}_3\text{CH}_2\text{S}^-$. Due to the overlap between the p-orbital of S and the π electron cloud of the benzene ring in $\text{C}_6\text{H}_5\text{S}^-$, the negative charge is delocalized into the benzene ring, stabilizing the $\text{C}_6\text{H}_5\text{S}^-$ ion by resonance.

(e)(ii) $\text{CH}_3\text{CH}_2\text{SH}$ is more acidic than $\text{CH}_3\text{CH}_2\text{OH}$ due to the greater stability of $\text{CH}_3\text{CH}_2\text{S}^-$ compared to $\text{CH}_3\text{CH}_2\text{O}^-$. Since S is larger than O, the negative charge on S^- is spread over a large volume compared to O^- , dispersing the charge of S^- to a larger extent.

OR

The S-H bond in $\text{CH}_3\text{CH}_2\text{SH}$ is weaker and requires less energy to break than the O-H bond in $\text{CH}_3\text{CH}_2\text{OH}$. This is due to the less effective orbital overlap between the larger and more diffuse valence orbital of S and H, compared to the more effective overlap between the smaller and less diffuse valence orbitals of O and H.

CH_3OCH_3 vs $\text{CH}_3\text{CH}_2\text{OH}$

More energy is required to overcome the stronger hydrogen bonding between $\text{CH}_3\text{CH}_2\text{OH}$ than the permanent dipole-permanent dipole (pd-pd) interactions between CH_3OCH_3 . Hence, $\text{CH}_3\text{CH}_2\text{OH}$ has a higher boiling point.

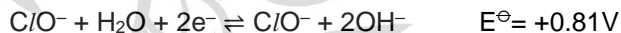
CH_3OCH_3 vs CH_3SCH_3

Due to the larger and more polarisable electron cloud of CH_3SCH_3 , the instantaneous dipole-induced dipole (id-id) interactions between CH_3SCH_3 molecules are stronger than the id-id and pd-pd interactions between CH_3OCH_3 molecules. Hence, CH_3SCH_3 has a higher boiling point.

(f)(ii) Both CH_3SCH_3 and $\text{CH}_3\text{CH}_2\text{SH}$ are polar and have similar electron cloud sizes, resulting in similar strengths of id-id interactions. Hence, they have similar boiling points.

Question 3

(a)(i) Relevant half-equation from Data Booklet.



Overall Equation



(a)(ii) $E^\ominus_{\text{cell}} = +0.81 - (+0.26) = +0.55 \text{ V}$

(a)(iii) $\Delta G^\ominus = -nFE^\ominus$

Since 6 mol of electrons were transferred in the redox reaction, $n = 6$.

$$\Delta G^\ominus = -(6)(96500)(0.55)$$

$$= -318450 \text{ J mol}^{-1}$$

$$= -318 \text{ kJ mol}^{-1}$$

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(b)(i) Formula of lanthanum(III) iodate(V) = $\text{La}(\text{IO}_3)_3$

Amount of $\text{La}(\text{IO}_3)_3$

$$= \frac{1.00}{138.9 + 3[(126.9 + 3(16.0))]}$$

$$= 0.001507 \text{ mol}$$

$$\begin{aligned} \text{Amount of } \text{IO}_3^- &= 3(0.001507) \\ &= 0.004521 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Amount of } \text{S}_2\text{O}_3^{2-} &= \frac{36.20}{1000} (0.100) \\ &= 0.00362 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Amount of } \text{I}_2 &= (0.5)(0.00362) \\ &= 0.00181 \text{ mol} \end{aligned}$$

Mole ratio of $\text{IO}_3^- : \text{I}_2$

$$= 0.004521 : 0.00181$$

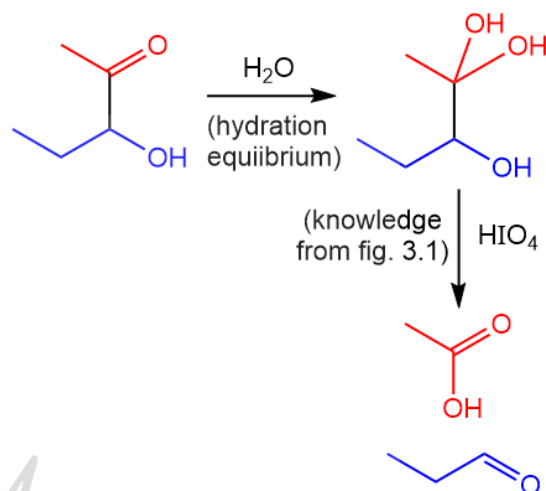
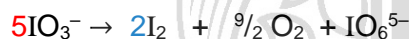
$$= 2.5 : 1$$

$$= 5 : 2 \text{ (shown)}$$

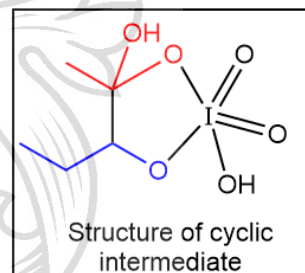
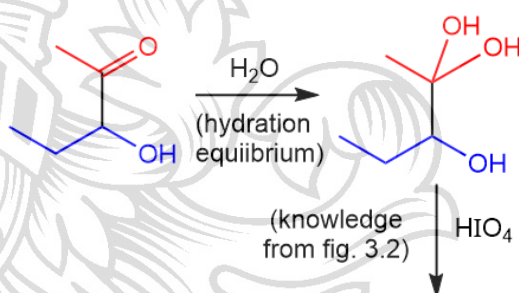
From mole ratio,



Total charge on left hand side = 5-. To achieve charge balance, total charge of right hand side should be 5- i.e. the formula of periodate(VII) is IO_6^{5-} .



(c)(i)

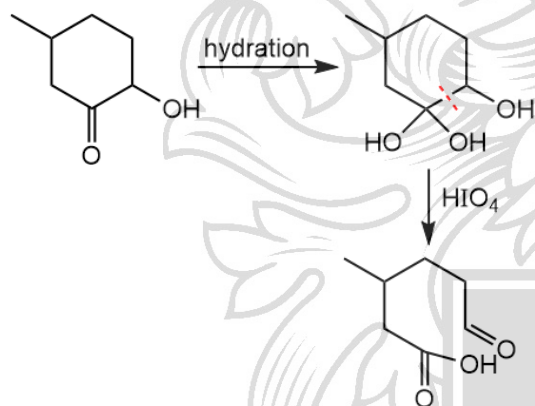
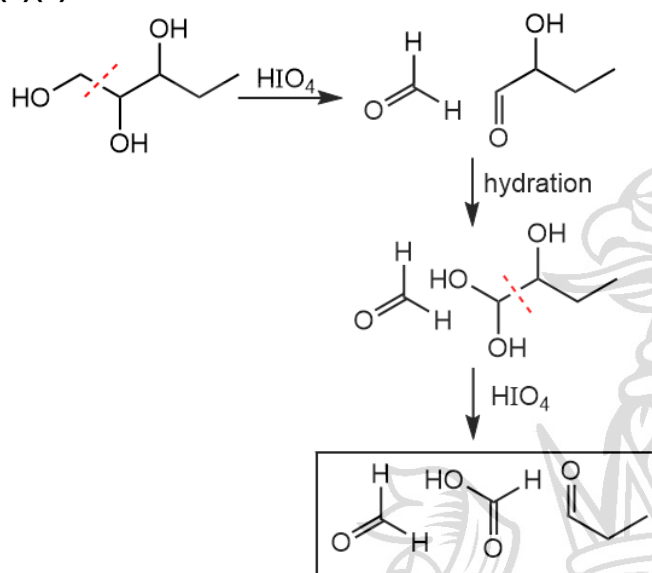


(b)(ii) Multiplying a factor of 3 to the previous equation:


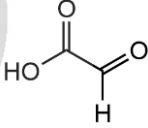
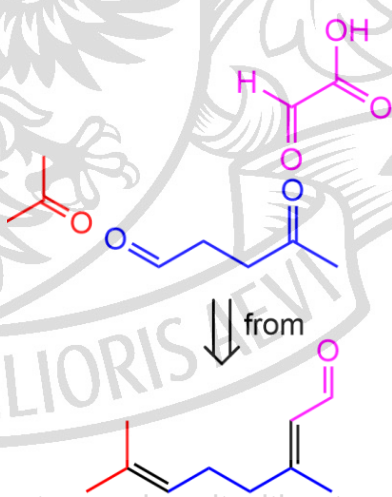


(c) **Note:** Students need to learn from all the information provided on page 8 to answer the question. The following diagram shows how the hydration equilibrium is relevant to the example in figure 3.3.

(c)(ii)



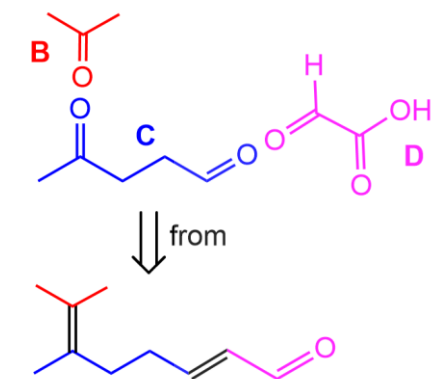
(d)(i)

Observation	Deductions
Citral gives Ag mirror with Tollens' reagent.	Oxidation occurred. - Aldehyde group present in Citral.
Citral decolourises bromine water.	Electrophilic addition occurred. - $\text{C}=\text{C}$ present in Citral
Citral reacts with cold KMnO_4 to give A ($\text{C}_{10}\text{H}_{20}\text{O}_6$).	Mild oxidation occurred. - $\text{C}=\text{C}$ oxidised to form 1,2-diols - Gain in 5 O atoms. o 4 O atoms due to gain in 4 $-\text{OH}$ groups \Rightarrow 2 $\text{C}=\text{C}$ present in citral
A does not react with Tollens' reagent but liberates CO_2 with Na_2CO_3 .	A does not reduce Tollen's reagent - Aldehyde absent in A Acid-base reaction with Na_2CO_3 - $-\text{COOH}$ present in A - Aldehyde in citral oxidised to $-\text{COOH}$.
A reacts with HIO_4 to give B , C and D .	Oxidation to split alcohol with two adjacent hydroxy groups
B ($\text{C}_3\text{H}_6\text{O}$) and C ($\text{C}_5\text{H}_8\text{O}_2$) gives yellow ppt with aqueous alkaline iodine.	Oxidation occurred - B and C contains the $-\text{COCH}_3$ group. - B is CH_3COCH_3
C and D ($\text{C}_2\text{H}_2\text{O}_3$) gives a red ppt with Fehling's solution.	Oxidation occurred - C and D contains an aliphatic aldehyde group.
<p>C is  and D is </p> <p>The structure of citral could be</p>  <p style="text-align: right;">Citral</p>	

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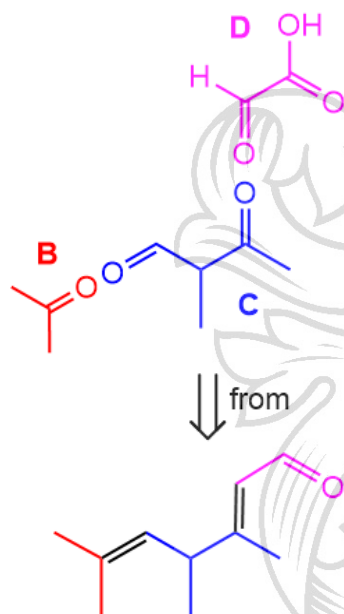
(d)(ii) Cis-trans isomerism present

Alternative combinations of structures



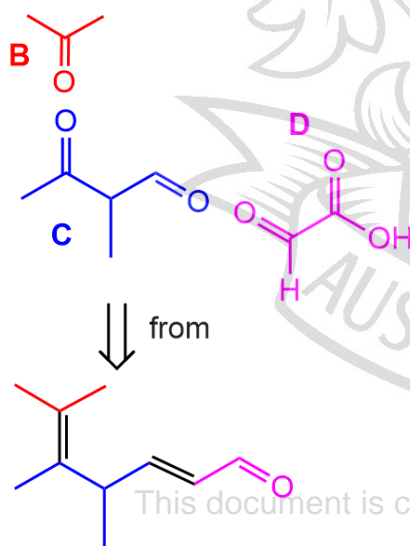
Citral

OR

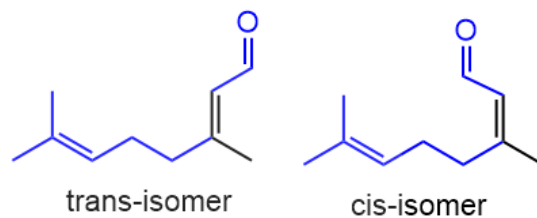


Citral

OR



Citral



trans-isomer

cis-isomer

Note: The structures of the isomers will be marked according to structure of Citral you have deduced in (d)(i).

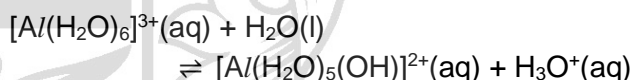
Question 4

(a) NaCl is an ionic compound. When dissolved in water, water molecules form ion-dipole interactions with Na^+ and Cl^- ions to form hydrated ions. No further reactions take place. Therefore the resultant solution is at pH 7.0

AlCl_3 exists as simple covalent molecules but dissolves in water to form $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ions.



In $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, the high charge density of Al^{3+} polarises and weakens the O–H bond of the water molecules, allowing the complex ion to undergo hydrolysis to form H_3O^+ . A weakly acidic solution of pH 3 results.



PCl_5 exists as simple covalent molecules, which hydrolyses in water as the low-lying d-orbitals of the central P atom accepts a lone pair of electrons from H_2O . The reaction produces HCl as a product which dissolves in water to form a strongly acidic solution of pH 2.0.



(b)(i) $K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$ units: $\text{mol}^3 \text{dm}^{-9}$

- (b)(ii)** Let x and y be the molar concentrations of PbCl_2 and PbI_2 dissolved in their respective saturated solutions.

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$1.7 \times 10^{-5} = (x)(2x)^2$$

$$x = 0.01620 \text{ mol dm}^{-3}$$

$$\text{Amount of } \text{PbCl}_2 \text{ in } 10 \text{ cm}^3$$

$$= 0.01620 \times 10/1000 = 0.0001620 \text{ mol}$$

$$\text{Mass of } \text{PbCl}_2 \text{ formed}$$

$$= 0.0001620 (207.2 + 35.5 + 35.5)$$

$$= \underline{0.0451 \text{ g}}$$

$$K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2$$

$$9.8 \times 10^{-9} = (y)(2y)^2$$

$$y = 0.001348 \text{ mol dm}^{-3}$$

$$\text{Amount of } \text{PbI}_2 \text{ in } 10 \text{ cm}^3$$

$$= 0.001348 \times 10/1000 = 1.348 \times 10^{-5} \text{ mol}$$

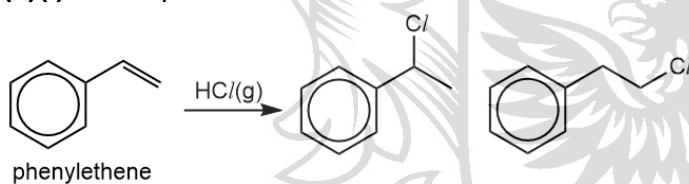
$$\text{Mass of } \text{PbI}_2 \text{ formed}$$

$$= 1.348 \times 10^{-5} (207.2 + 126.9 + 126.9)$$

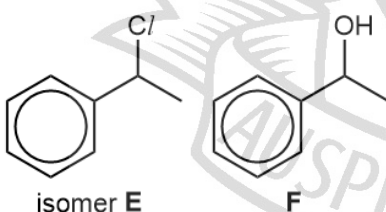
$$= \underline{0.00621 \text{ g}}$$

Therefore, the saturated solution of PbCl_2 produces the larger mass of solid.

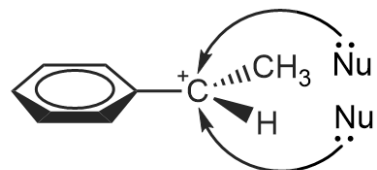
- (c)(i)** Two possible structural isomers



- (c)(ii)**



- (c)(iii)** In the slow step of the electrophilic addition of phenylethene, a planar carbocation (shown below) is formed. In the fast step, the chloride ions can attack the planar carbocation centre from above and below the plane with equal probability, forming a 50: 50 mixture of two enantiomers.



$\text{Nu} = \text{Cl}^- \text{ or } \text{OH}^-$

In the slow step of the $\text{S}_{\text{N}}1$ reaction of **E** with NaOH(aq) , the same planar carbocation (as shown above) is formed which allows the attack of OH^- in the fast step to occur from above and below the plane of the carbocation with equal probability, forming a 50:50 mixture of two enantiomers.

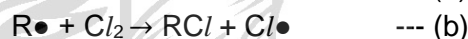
Note: The structure of the carbocation should be shown in your answer.

- (d)(i)** Free radical substitution mechanism

Initiation



Propagation

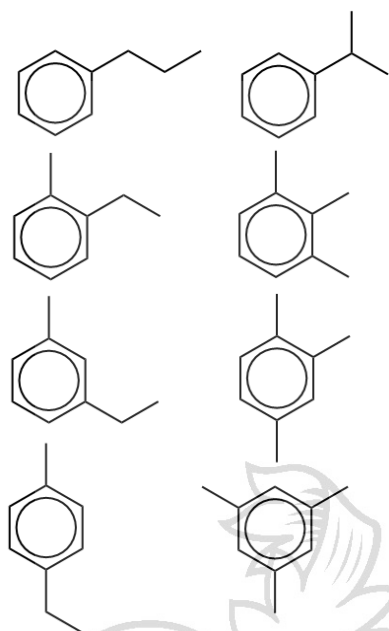


then (a), (b), (a), (b), ...

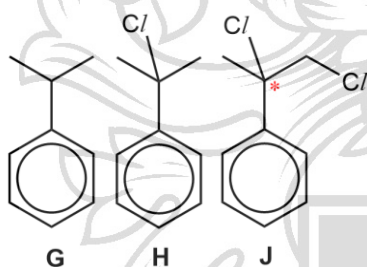
Termination



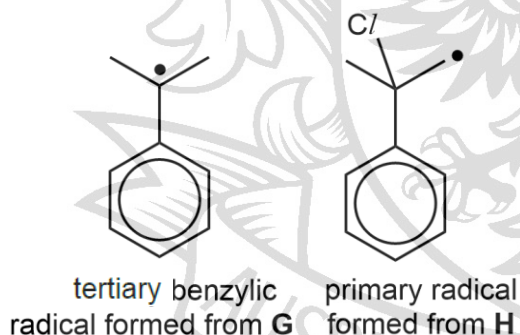
(d)(ii)



(d)(iii)



(d)(iv) The free radical substitution reaction to form **H** involves the formation of a tertiary (benzylic) radical, which is more stable and formed at a faster rate than the primary radical formed in the formation of **J**.



Question 5

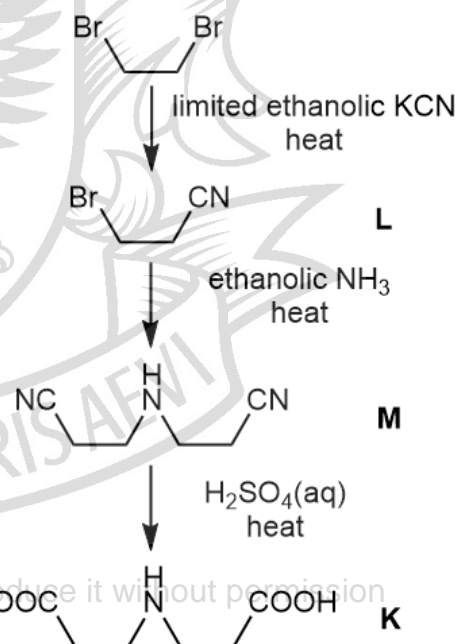
(a) $\text{Fe} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
 Removing 3 e^- from the above,
 $\text{Fe}^{3+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

(b)(i) Degenerate orbitals are orbitals having the same energy.

(b)(ii) In an octahedral complex, six ligands approach the metal ion along the x, y and z axes. This results in electrostatic repulsion between the electrons in the 3d orbitals and the lone pairs on the ligands, and there is an increase in energy i.e. the energy of the d subshell in an octahedral complex is higher than that in the gas-phase ion.

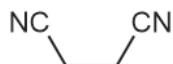
However, the extent of repulsion differs for different orbitals depending on the orientation of their orbitals on a 3D axis. The electron densities of $3d_{x^2-y^2}$ and $3d_{z^2}$ are concentrated along the x, y and z axes and hence experience repulsion to a greater extent and are promoted to a higher energy level. The electron densities of $3d_{xy}$, $3d_{yz}$, $3d_{zx}$ are concentrated between the x, y and z axes and hence experience repulsion to a smaller extent and are promoted to a lower energy.

(c)(i)

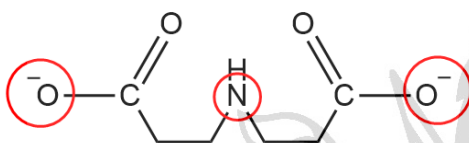


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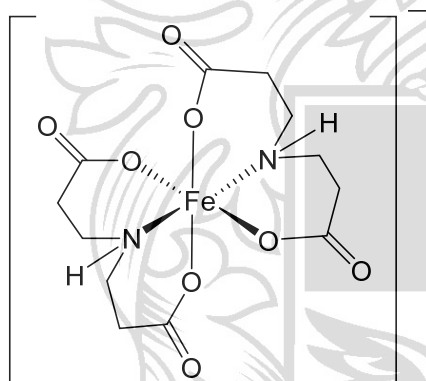
(c)(ii) A possible side product of step 1 has the following structure and its formation can be minimised by using limited amounts of ethanolic KCN.



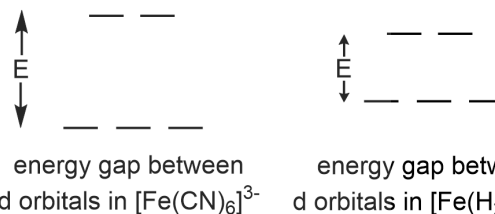
(c)(iii) In basic solution, the acidic -COOH groups are deprotonated.



(c)(iv) Each deprotonated **K** acts as a tridentate ligand, coordinating to the central Fe^{3+} using the atoms circled in (c)(iii). Since each deprotonated **K** has a $2-$ charge and the central iron ion has a $3+$ charge, the overall charge = $(3+) + 2(2-) = 1-$.



(c)(v) Since CN^- is a stronger ligand than H_2O , the energy gap between the two levels of d-orbitals in $[\text{Fe}(\text{CN})_6]^{3-}$ is larger than that in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.



The larger energy gap between the two levels of d-orbitals in $[\text{Fe}(\text{CN})_6]^{3-}$ means that more energy is required to place electrons in the higher energy level, hence the electrons remained paired in the lower energy level, leading to fewer unpaired d-electrons in $[\text{Fe}(\text{CN})_6]^{3-}$.

(d)(i)

$$K_p = \frac{(p_{\text{CO}_2})^3}{(p_{\text{CO}})^3}; \text{ no units}$$

Note: Students are required to explicitly mention that K_p , in this case, has no units.

(d)(ii)

partial pressure / bar	$\text{Fe}_2\text{O}_3(\text{s})$	$+ 3\text{CO}(\text{g})$	\rightleftharpoons	$2\text{Fe}(\text{l})$	$+ 3\text{CO}_2(\text{g})$
initial	--	1.00	--	--	0
change	--	-y	--	--	+y
equilibrium	--	1.00-y	--	--	y

$$19.9 = \frac{y^3}{(1-y)^3}$$

$$\frac{y}{(1-y)} = \sqrt[3]{19.9}$$

$$y = 0.730 \text{ bar}$$

Equilibrium partial pressure of CO_2 0.730 bar

(d)(iii) The entropy change is positive because the reaction involves the conversion of solid reactants, with low disorder, to liquid products, with slightly greater disorder, causing an increase in entropy.

The entropy change is small in magnitude because the liquid state is only slightly more disordered than the solid state and there is no change in the amount of the significantly more disordered gaseous state.

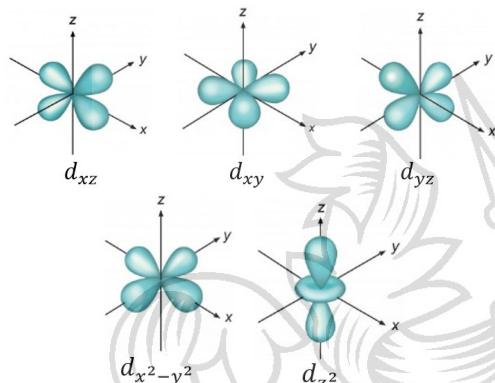


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1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
C	D	B	D	A	B	B	A	D	B	C	C	D	C	B
16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
B	C	D	D	B	C	B	A	D	C	D	A	C	A	D

Q1 (C)

There are a total of five 3d orbitals. However, only the $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals have four lobes.

**Q2 (D)**

Since there is a large jump from the 8th to 9th ionisation energy, the element has eight valence electrons and is a Group 18 element, i.e. Ar.

Q3 (B)

When nucleon number = 217,

	atomic number	no. of neutrons	no. of electrons
Po ²⁺	84	217 – 84 = 133	84 – 2 = 82
At ³⁺	85	217 – 85 = 132	85 – 3 = 82
Rn ⁴⁺	86	217 – 86 = 131	86 – 4 = 82
Fr ⁵⁺	87	217 – 87 = 130	87 – 5 = 82

From the above table, only At³⁺ has 50 more neutrons than electrons.

Q4 (D)

The three alkanes are constitutional isomers with the same M_r and number of electrons. All three are simple, non-polar molecules with only instantaneous dipole-induced dipole (id-id) interactions.

Since boiling involves overcoming the intermolecular forces of attraction (NOT covalent bonds), the differences in boiling points among the three alkanes are due to differences in the strength of their id-id interactions.

Pentane, a straight-chained hydrocarbon, has greater surface area for intermolecular interactions compared to its branched isomers, 2-methylbutane and 2,2-dimethylpropane. Thus, intermolecular id-id interaction is the strongest in pentane. As branching increases from 2-methylbutane to 2,2-dimethylpropane, the surface area for intermolecular interaction decreases.

Hence the boiling point decreases from pentane to 2-methylbutane to 2,2-dimethylpropane.

Q5 (A)

Both liquids are initially at 20 °C. Since stronger intermolecular forces between CHCl₃ and CH₃COCH₃ are formed (compared to their original intermolecular forces), energy is released upon mixing and initial temperature of the mixture will be above 20 °C.

Since the intermolecular forces between CHCl₃ and CH₃COCH₃ are stronger (than their original intermolecular forces) and require more energy to overcome, the boiling point of the mixture will be above 61 °C.

Q6 (B)

Since all four gases behave as ideal gases and temperature is kept constant,

$$pV = nRT = \text{constant}$$

Graph of pV against V is a horizontal straight line. Hence, the gas with a larger n will have a larger pV .

Since M_r of CH₄ < Ne < N₂ < C_l₂, for equal masses of the four gases, amount, n , of CH₄ > Ne > N₂ > C_l₂.

Hence, graph **B** corresponds to Ne.

Q7 (B)

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
initial amt / mol	0		0		0.040
change in amt / mol	+x		+x		-2x
eqm amt / mol	x		x		0.040 - 2x

At equilibrium,

$$n_{\text{total}} = x + x + (0.040 - 2x) = 0.040 \text{ mol}$$

$$P_{\text{total}} = 1.0 \text{ atm}$$

$$K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}} = \frac{\left(\frac{0.040 - 2x}{0.040} \times 1.0\right)^2}{\left(\frac{x}{0.040} \times 1.0\right)^2} = 54$$

$$x = 0.004279 \text{ mol}$$

$$P_{\text{HI}} = \frac{0.040 - 2(0.004279)}{0.040} \times 1.0 = 0.79 \text{ atm}$$

Q8 (A)

Cationic radius of $\text{Mg}^{2+} < \text{Ca}^{2+}$, resulting in Mg^{2+} having a higher charge density and stronger polarising power than Ca^{2+} .

Consequently, there is greater extent of distortion of the electron cloud of the CO_3^{2-} anion and hence greater extent of weakening of covalent bonds within the CO_3^{2-} anion for MgCO_3 . Less heat energy is required to break the covalent bonds within the CO_3^{2-} anion, causing the decomposition temperature of MgCO_3 to be lower.

Q9 (D)

$$n(\text{B}_2\text{O}_3) = \frac{2.50}{2(10.8) + 3(16.0)} = 0.03592 \text{ mol}$$

$$n(\text{CO}_2) = \frac{0.80}{12.0 + 2(16.0)} = 0.01818 \text{ mol}$$

$$\begin{aligned} \text{ratio of B : C in boron carbide} \\ &= 2(0.03592) : 0.01818 \\ &= 4 : 1 \end{aligned}$$

Hence, the empirical formula of boron carbide is B_4C .

Q10 (B)

Since the reaction is zero order with respect to I_2 , the rate of reaction is constant and independent of $[\text{I}_2]$.

Hence, the graph of $[\text{I}_2]$ against time is a downward sloping straight line with a constant gradient (since rate = - gradient).

Q11 (C)

$$\Delta G = \Delta H - T\Delta S$$

A reaction is spontaneous when $\Delta G < 0$.

statement	ΔH	ΔS	ΔG
1	> 0	< 0	> 0 at all temperatures
2	< 0	> 0	< 0 at all temperatures
3	< 0	< 0	< 0 at low temperatures (when the negative ΔH outweighs the positive $-T\Delta S$)

Q12 (C)

(This is an autocatalytic reaction where Mn^{2+} acts as the autocatalyst.)
For the graph of volume of CO_2 against time, the gradient of the graph at a particular time gives the instantaneous rate of the reaction.

Since the gradient of the graph at t_2 is greater than that at t_1 , the reaction is occurring at a faster rate at t_2 .

$$\begin{aligned} n(\text{MnO}_4^-) \text{ added} &= n(\text{C}_2\text{O}_4^{2-}) \text{ added} \\ &= 25.0 / 1000 \times 0.01 \\ &= 0.000250 \text{ mol} \end{aligned}$$

Since mole ratio of $\text{MnO}_4^- : \text{C}_2\text{O}_4^{2-} = 2 : 5$, $\text{C}_2\text{O}_4^{2-}$ is the limiting reagent.

$$\begin{aligned} \text{mole ratio of } \text{C}_2\text{O}_4^{2-} : \text{CO}_2 &= 5 : 10 \\ n(\text{CO}_2) &= 0.000250 / 5 \times 10 = 0.0005 \text{ mol} \end{aligned}$$

$$\text{At s.t.p., } z = 0.0005 \times 22.7 = 0.0114 \text{ dm}^3 = 11.4 \text{ cm}^3$$

Q13 (D)

$$\text{Since } t_{1/2} = 40 \text{ min, } 120 \text{ min} = 3 t_{1/2}$$

$$\begin{aligned} \text{At r.t.p.,} \\ n(\text{O}_2) \text{ formed at } 120 \text{ min} &= 6.00 / 24 = 0.250 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{mole ratio of } \text{H}_2\text{O}_2 : \text{O}_2 &= 2 : 1 \\ \text{Let the initial amount of } \text{H}_2\text{O}_2 &\text{ be } x \text{ mol.} \end{aligned}$$

	amt of H_2O_2 / mol	amt of O_2 / mol
$t = 0 \text{ min}$	x	0
$t = 40 \text{ min}$	$\frac{1}{2}x$	$\frac{1}{2}(x - \frac{1}{2}x)$
$t = 80 \text{ min}$	$\frac{1}{4}x$	$\frac{1}{2}(x - \frac{1}{4}x)$
$t = 120 \text{ min}$	$\frac{1}{8}x$	$\frac{1}{2}(x - \frac{1}{8}x)$ $= 0.250$

$$x = 0.5714 \text{ mol}$$

$$\begin{aligned} \text{Initial concentration of } \text{H}_2\text{O}_2 &= 0.5714 / 200 \times 1000 \\ &= 2.9 \text{ mol dm}^{-3} \end{aligned}$$

Q14 (C)

$$K_c = \frac{[R][S]^2}{[P][Q]} \text{ mol dm}^{-3}$$

$$K_c \text{ for experiment 1} = 0.0375 \text{ mol dm}^{-3}$$

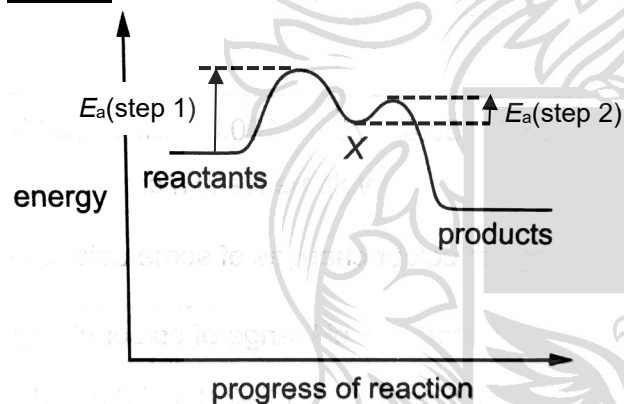
$$K_c \text{ for experiment 2} = 0.0510 \text{ mol dm}^{-3}$$

Comparing experiments 1 and 2, as temperature is increased from 300 K to 400 K, K_c increases. This shows that the equilibrium position shifted right with increasing temperature. Hence, the forward reaction must be endothermic.

Q15 (B)

A suitable indicator is one where its pH range coincides with the region of rapid pH change in the titration curve (i.e. the pH range of the indicator must fall on the vertical portion of the titration curve).

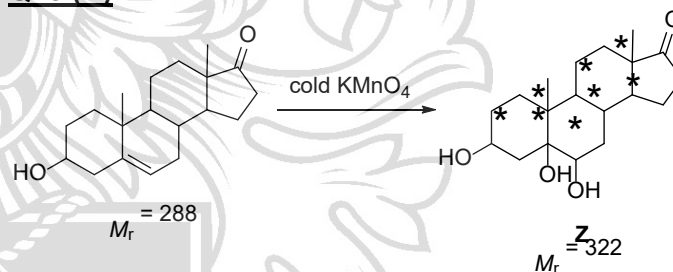
equivalence point	rapid change in pH occurs around	Suitable indicator
first	approx. 3 – 6	naphthyl red
second	approx. 8.5 – 10.5	thymol blue

Q16 (B)

A	Incorrect. Point X is an intermediate. A transition state cannot be isolated (unstable) and exists at a potential energy maximum.
B	Correct. See above diagram.
C	Incorrect. Although step 1 is an endothermic process, the reaction involves both the breaking of C=O π bond and formation of C-C bond. Besides, bond formation is always an exothermic process.
D	Incorrect. The reaction pathway diagram does not give any conclusion about the reversibility of the reaction.

Q17 (C)

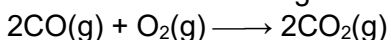
A	Incorrect. There are only two constitutional isomers of C_4H_{10} :
B	Incorrect. Constitutional (Structural) isomers have the same molecular formula but different structural formula, i.e. different arrangement of atoms. But-1-ene (C_4H_8) and pen-1-ene (C_5H_{10}) are not constitutional isomers as they have different molecular formula.
C	Correct. Constitutional isomers with different functional groups can differ in their chemical properties. E.g. cyclobutane (C_4H_8) does not undergo electrophilic addition but but-1-ene (C_4H_8) does.
D	Incorrect. Refer to definition of constitutional isomers in option B.

Q18 (D)**Q19 (D)**

statement 1	Incorrect. $\bullet C/$ and $\bullet CC/F_2$ should be the major free radical products formed in the initiation step as the C-C/ bond is weaker and can be broken more easily than the C-F bond.
statement 2	Correct. $X\bullet$ is consumed in the first step and regenerated in the second step of the chain reaction.
statement 3	Incorrect. The termination step should involve the reaction between radicals instead. E.g. $2X\bullet \rightarrow X_2$

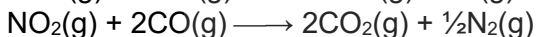
Q20 (B)

The reactions occurring in the catalytic converter are:

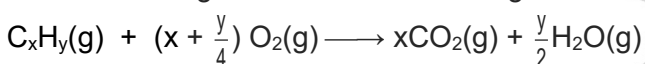


Carbon monoxide is oxidised to carbon dioxide.

Carbon dioxide is not further converted in the catalytic converter.



Oxides of nitrogen are reduced to nitrogen.



Unburnt hydrocarbons are oxidised to carbon dioxide.

Q21 (C)

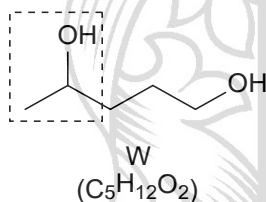
Order of reactivity towards nucleophilic substitution:
acyl halides > alkyl halides > aryl halides

Benzoyl chloride, an acyl chloride, is the most reactive with ethanolic AgNO_3 , followed by the chloroalkanes, 2-chloro-2-methylpropane and 1-chloropropane.

Chlorobenzene, an aryl halide, is the least reactive and does not undergo reaction with ethanolic AgNO_3 .

Q22 (B)

All three structures can be reduced to form the following compound, which can react with alkaline aqueous I_2 due to the presence of the $-\text{CH}(\text{OH})\text{CH}_3$ group.



	V ($\text{C}_5\text{H}_8\text{O}_2$)	reacts with Tollens' reagent
1		Yes
2		Yes
3		No

Only structures 1 and 2 contain the aldehyde group which will give a positive test with Tollens' reagent.

Q23 (A)

Information	Conclusion
$\text{T} \xrightarrow{\text{NaBH}_4} \text{C}_x\text{H}_{y+2}\text{O}_z$ (only product)	<ul style="list-style-type: none"> Addition of 2 H atoms T has only one carbonyl group
$\text{T} \xrightarrow{\text{single reaction}} \text{C}_x\text{H}_y\text{O}_{z+1}$ (single reaction)	<ul style="list-style-type: none"> Addition of 1 O atom in a single reaction, i.e. oxidation, without any changes in the number of H atoms. T has one aldehyde group
T gives orange ppt with 2,4-DNPH	T has carbonyl group
T does not react with Na	T has no $-\text{OH}$ or $-\text{COOH}$ group

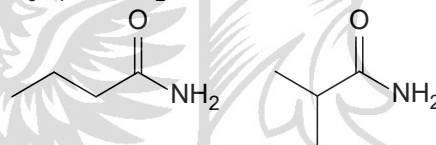
Q24 (D)

$\text{C}_2\text{H}_5\text{NH}_2$ is a primary amine with one electron-donating alkyl ($-\text{C}_2\text{H}_5$) group while $(\text{C}_2\text{H}_5)_2\text{NH}$ is a secondary amine with two electron-donating alkyl ($-\text{C}_2\text{H}_5$) groups. Hence, the electron density on the nitrogen atom of $(\text{C}_2\text{H}_5)_2\text{NH}$ is greater and its lone pair of electrons is more available for coordination with a proton.

As $(\text{C}_2\text{H}_5)_2\text{NH}$ is a stronger base, equilibrium position of (2) will lie further right than that of (1).

Q25 (C)

$\text{C}_3\text{H}_7\text{CONH}_2$ can be either of the following structures:

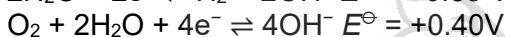
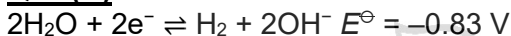


Considering the straight-chain isomer:

A	Incorrect. The name is butanamide.
B	Incorrect. Alkaline hydrolysis of the amide group will form sodium butanoate.
C	Correct. Acidic hydrolysis of the amide group will form butanoic acid.
D	Incorrect. Butanoic acid will undergo acid-base reaction with $\text{NH}_3(\text{aq})$ to form a salt instead of an amide.

Q26 (D)

statement 1	Alcoholic OH group is too weak an acid to react with cold NaOH(aq).
statement 2	Amide group will only undergo basic hydrolysis when heated with NaOH(aq). Hence, the amide group will not react with cold NaOH(aq).
statement 3	Phenolic OH group, which is a stronger acid than alcoholic OH group, will undergo acid-base reaction with cold NaOH(aq).

Q27 (A)

Hence, for the hydrogen-oxygen fuel cell,

cathode: oxygen electrode ($E^\ominus = +0.40 \text{ V}$)

anode: hydrogen electrode ($E^\ominus = -0.83 \text{ V}$)

Electrons will flow from X to Y.

Note: Standard conditions should be 1 bar, instead of 1 atm.

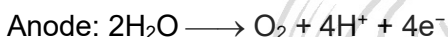
Q28 (C)

$$Q = It = n_e F$$

$$n_e = It / F$$

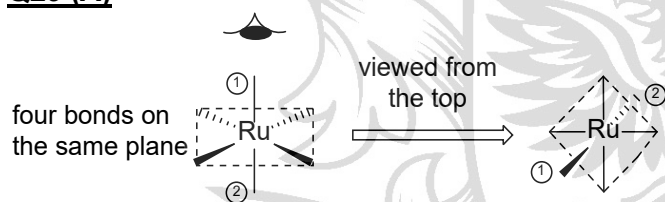
$$= 20.0 \times 3.00(60) / 96500$$

$$= 0.03731 \text{ mol}$$



mole ratio of $\text{O}_2 : \text{e}^- = 1 : 4$

$$n(\text{O}_2) = 0.03731 / 4 = 9.33 \times 10^{-3} \text{ mol}$$

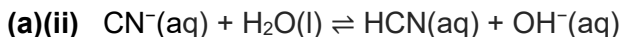
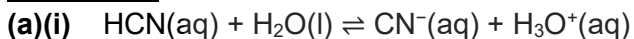
Q29 (A)**Q30 (D)**

Vanadium, a transition metal, has a higher density and melting point than strontium, a Group 2 metal.

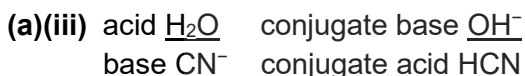
From the options, we can conclude that:

metal	density / g cm^{-3}	melting point / $^\circ\text{C}$
vanadium	6.0	1900
strontium	2.6	770

Hence, row D shows two properties of vanadium.

Question 1

Note: An equation for the reaction between NaCN and H₂O is required (not the dissociation of NaCN in water).



(a)(iv) $K_a = 10^{-4.79} = 1.62 \times 10^{-5} \text{ mol dm}^{-3}$

(a)(v) $\text{p}K_b \text{ of } \text{CN}^-(\text{aq}) = 14 - 4.79 = 9.21$

(b)(i) Nucleophilic addition

(b)(ii) Unlike HCN which undergoes partial dissociation in water, KCN is a soluble salt that undergoes complete dissolution in water to form the CN⁻ nucleophile needed in the rate-determining step of the nucleophilic addition reaction.

Also, the acidic condition provides the H⁺ ions required for the protonation of the intermediate to form the hydroxynitriles.

(b)(iii)

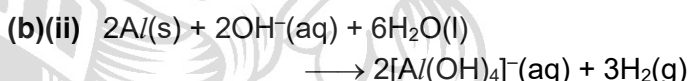
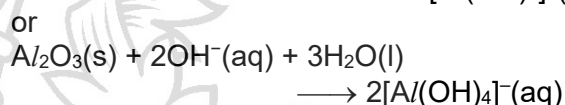
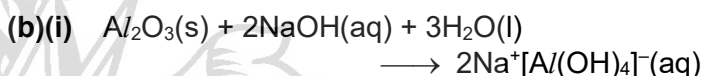


(b)(iv) In CN⁻, the negative charge is on the carbon atom. This makes the carbon atom more electron rich and more nucleophilic than the nitrogen atom. Hence, the carbon atom, and not the nitrogen atom, attacks the electron deficient carbonyl carbon in the nucleophilic addition reaction.

(c)(i) The CN⁻ ions act as ligands by donating a lone pair of electrons on the carbon atom into the low-lying vacant orbital of the Au⁺ central metal ion forming a dative covalent/co-ordinate bond.

**Question 2**

(a) Due to the high charge of Al³⁺ and O²⁻ ions and the small interionic distance/ionic radii of both ions, Al₂O₃ has strong ionic bonds/highly exothermic lattice energy. As a result, the energy required to overcome the strong ionic bonds cannot be compensated by the hydration energy released upon hydration of the ions. Hence, dissolution of Al₂O₃ is energetically unfavourable and Al₂O₃ is insoluble in water.



After the insoluble oxide layer is removed, the Al is exposed and undergoes redox reaction with hydroxide ions to form [Al(OH)₄]⁻ and bubbles of H₂ gas.

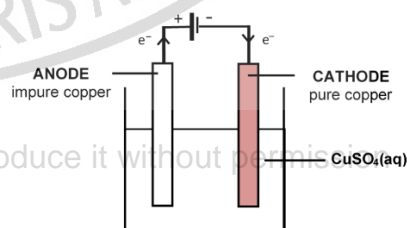
(c)(i) Aluminium objects are highly reactive and not resistant to corrosion. Anodising them will form the protective layer of aluminium oxide which protects the underlying aluminium metal from water and any further chemical attack. The oxide layer is also hard, resistant to wear and a good electrical insulator.

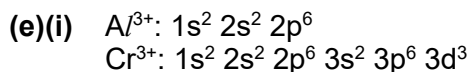
Note: Avoid the use of the term 'rust' as this is specific to the corrosion of iron.

(c)(ii)

	type of reaction occurring	half-equation(s)
anode	oxidation	$2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$
cathode	reduction	$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

(d)





(e)(ii) Compared to Al^{3+} , Cr^{3+} has one more electronic shell and its valence electrons are further away from the nucleus. There is also greater shielding effect in Cr^{3+} as it has more electrons. However, Cr^{3+} has a higher nuclear charge than Al^{3+} , and its 3d electrons provides poor shielding. Hence, the effective nuclear charge in both Cr^{3+} and Al^{3+} are similar, resulting in their similar ionic radii.

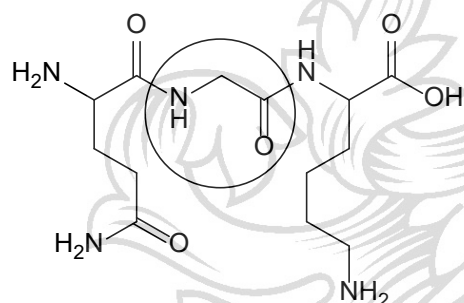
(e)(ii) The amide side-chain in **Z** is neutral. This is because the lone pair of electrons on the nitrogen atom interacts with the π electron cloud of the adjacent $C=O$ bond and is delocalised. Hence, this lone pair of electrons on the nitrogen atom is not available for coordination to a proton to form an acidic group. Hence the side-chain in **Z** does not have a K_a value.

The amine side-chain in **Y** is basic as the lone pair electrons on the nitrogen atom is available for protonation to form an acidic $-NH_3^+$ group which has a K_a value.

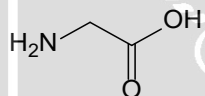
Question 3

(a) Condensation

(b)

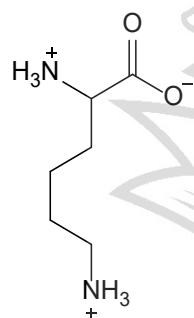


Since **X** does not rotate plane-polarised light, **X** has a plane of symmetry/does not contain a chiral carbon. Hence, **X** is



(c) A zwitterion is an electrically neutral molecule with oppositely charged ends.

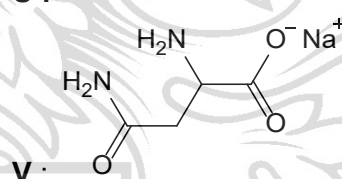
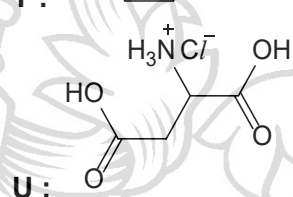
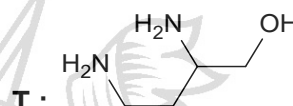
(d)(i)



(d)(ii) $pH = \frac{1}{2} (9.16 + 10.67)$
 $= 9.92$ (accept: $9.16 < pH < 10.67$)

(e)(i) side-chain of **Y**: primary amine
side-chain of **Z**: primary amide

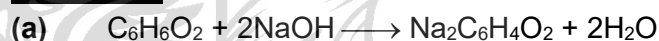
(f)



(g)

step a: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat with immediate distillation
step b: $H_2SO_4(aq)/HC/(aq)/HNO_3(aq)$, heat

Question 4



(b)

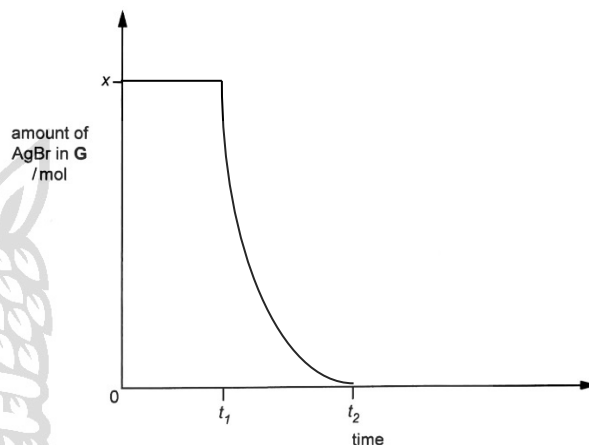
All three compounds contain the $-OH$ group and will react with Na to form effervescence of H_2 gas. However, the rate of formation of H_2 will be the slowest for ethanol as ethanol is a weaker acid than phenol and hydroquinone. Between phenol and hydroquinone, hydroquinone will produce more H_2 gas as it contains one more $-OH$ group than phenol. Once reaction has ceased, only the reactions with ethanol and phenol will contain excess unreacted Na metal.

Note: Na is only present in excess for ethanol and phenol.

(c)(i) Silver bromide has a giant ionic lattice structure with strong ionic bonds/electrostatic forces of attraction between the Ag^+ and Br^- ions. As large amount of energy is required to overcome the strong ionic bonds, silver bromide has a relatively high melting point.

(c)(ii) $\text{AgBr} \longrightarrow \text{Ag} + \text{Br}$

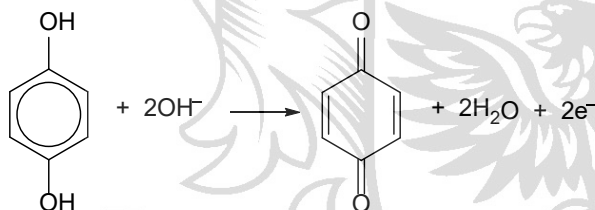
(c)(iii) $\text{Br}^- \longrightarrow \text{Br} + \text{e}^-$
 $\text{Cl}^- \longrightarrow \text{Cl} + \text{e}^-$



Although Br^- has a higher nuclear charge and shielding effect, Br^- also has one more electronic shell than Cl^- . Hence, the distance between the nucleus and valence electrons in Br^- is larger resulting in weaker electrostatic attraction between the nucleus and valence electrons. Hence, less energy is required to remove the valence electron from Br^- than Cl^- ions. Thus, Br^- ions are more affected by light of a lower energy/frequency.

(c)(iv) Photographic film is developed in the dark to prevent stage 1 from occurring which will turn more AgX to Ag , resulting in the loss of the original hidden image.

(d)



(e)(i) Ag acts as the autocatalyst in step 4.

(e)(ii)

Note:
The autocatalyst, Ag , is already formed in stage 1 (after brief exposure to light).

Upon addition of excess alkaline aqueous hydroquinone at t_1 , the reaction in stage 2 will immediately be catalysed by Ag (i.e. initial rate will not be slow).

Question 5

(a)(i) For every 100 g of reaction mixture,
 mass of $\text{C}_6\text{H}_6\text{O}_2 = 10 \text{ g}$
 mass of $\text{H}_2\text{O}_2 = 25 \text{ g}$

$$n(\text{C}_6\text{H}_6\text{O}_2) = \frac{10}{6(12.0) + 6(1.0) + 2(16.0)} = 0.09091 \text{ mol}$$

$$n(\text{H}_2\text{O}_2) = \frac{25}{2(1.0) + 2(16.0)} = 0.7353 \text{ mol}$$

From equation 1,

mole ratio of $\text{C}_6\text{H}_6\text{O}_2 : \text{H}_2\text{O}_2 = 1 : 1$

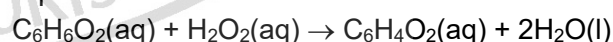
Since $n(\text{H}_2\text{O}_2) > n(\text{C}_6\text{H}_6\text{O}_2)$, H_2O_2 is present in excess in the reaction mixture.

(a)(ii) The excess unreacted H_2O_2 is decomposed by catalase to form O_2 gas, which increases the number of gas particles inside the reaction chamber, resulting in an increase in pressure.

(b)

reaction	$\Delta H / \text{kJ mol}^{-1}$
equation 3: $\text{C}_6\text{H}_6\text{O}_2(\text{aq}) \rightarrow \text{C}_6\text{H}_4\text{O}_2(\text{aq}) + \text{H}_2(\text{g})$	+177.2
equation 2 $\times \frac{1}{2}$: $\text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g})$	$\frac{1}{2}(-189.0)$
equation 4: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-285.5

Summing the above equations gives equation 1:



$$\therefore y = +177.2 + \frac{1}{2}(-189.0) + (-285.5) = -202.8 = \underline{-203}$$

(c) For $1.0 \times 10^{-3} \text{ g}$ of reaction mixture,

$$n(\text{C}_6\text{H}_6\text{O}_2) = (0.09091 / 100) \times 10^{-3} \\ = 9.091 \times 10^{-7} \text{ mol}$$

$$\text{Energy released from equation 1} \\ = 9.091 \times 10^{-7} \times 202.8 \\ = 1.844 \times 10^{-4} \text{ kJ}$$

$$\text{Remaining amount of H}_2\text{O}_2 \\ = [(0.7353 - 0.09091) / 100] \times 10^{-3} \\ = 6.444 \times 10^{-6} \text{ mol}$$

$$\text{Energy released from decomposition of} \\ \text{unreacted H}_2\text{O}_2 \\ = (6.444 \times 10^{-6}) \times \frac{1}{2}(189.0) \\ = 6.089 \times 10^{-4} \text{ kJ}$$

$$\text{total energy released} \\ = (1.844 \times 10^{-4}) + (6.089 \times 10^{-4}) \\ = \underline{7.93 \times 10^{-4} \text{ kJ}}$$

Note:

- The total energy released will need to include both the energy released from the reaction between H_2O_2 and hydroquinone AND the energy released from the decomposition of the unreacted H_2O_2 .
- ΔH_{eqn2} involves 2 moles of H_2O_2 undergoing decomposition.

(d)(i) Given that $\Delta G_{\text{eqn1}} = -206.5 \text{ kJ mol}^{-1} < 0$, the reaction between hydroquinone and hydrogen peroxide (shown in equation 1) is spontaneous.

(d)(ii) Though spontaneous, the reaction has a significantly high E_a and hence does not occur in the reservoir. However, once the reaction mixture enters the reaction chamber containing the enzymes catalase and peroxidase, the enzymes catalyse the reaction by providing an alternative reaction pathway with a lower E_a . Hence, the reaction occurs quickly in the reaction chamber.

sites of the enzyme catalase become saturated with the substrate H_2O_2 . Any increase in $[\text{H}_2\text{O}_2]$ will not have any effect on the reaction rate and the reaction is zero order with respect to H_2O_2 .

(f)

$$\Delta G_{\text{eqn1}} = \Delta G^{\ominus}_{\text{eqn1}} \\ = -n_e F E^{\ominus}_{\text{cell}} \\ = -2 \times 96500 \times E^{\ominus}_{\text{cell}} \\ = -206.5 \text{ kJ mol}^{-1} \\ = -206500 \text{ J mol}^{-1}$$

$$E^{\ominus}_{\text{cell}} = +1.070 \text{ V}$$

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{cathode}} - E^{\ominus}_{\text{anode}} \\ = E^{\ominus}(\text{H}_2\text{O}_2/\text{H}_2\text{O}) - E^{\ominus}(\text{C}_6\text{H}_4\text{O}_2/\text{C}_6\text{H}_6\text{O}_2) \\ = +1.77 - E^{\ominus}(\text{C}_6\text{H}_4\text{O}_2/\text{C}_6\text{H}_6\text{O}_2) \\ = +1.070$$

$$E^{\ominus}(\text{C}_6\text{H}_4\text{O}_2/\text{C}_6\text{H}_6\text{O}_2) = +1.77 - (+1.070) \\ = \underline{+0.70 \text{ V}}$$

(e) At high $[\text{H}_2\text{O}_2]$, all the active sites on the enzyme catalase are occupied / the active

Question 1

(a)(i) A transition element is a d-block element which can form one or more stable ions with a partially filled d subshell.

(a)(ii) Let x be the percentage abundance of ^{63}Cu and $(100 - x)$ be the percentage abundance of ^{65}Cu .

$$\left(\frac{x}{100} \times 62.930\right) + \left(\frac{100 - x}{100} \times 64.928\right) = 63.546$$

percentage abundance of $^{63}\text{Cu} = x = 69.2\%$

$^{65}\text{Cu} = 100 - x = 30.8\%$

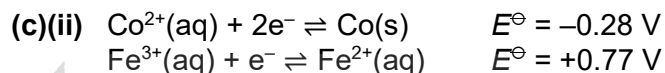
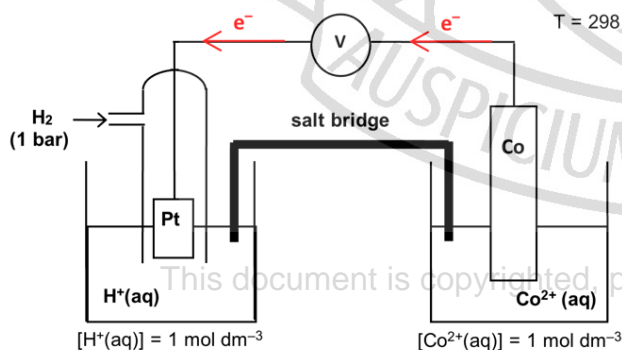
Note: Use the accurate isotopic masses in the calculation.

(b)(i) The presence of ligands in the transition element complexes causes the splitting of the five d orbitals into two sets of slightly different energy levels. Since the d subshell of these transition elements are usually partially filled, electrons from the lower-energy d orbital can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher-energy d orbitals (d-d transitions). This results in the complexes being coloured, and the colour observed is the complement of the colour absorbed.

(b)(ii) electronic configurations of
 Cu^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
 Cu^+ : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

Compounds containing Cu^{2+} are often coloured as Cu^{2+} has a partially filled 3d subshell and d-d transition is possible. However, compounds containing Cu^+ are colourless as Cu^+ has a fully filled 3d subshell and d-d transition cannot occur.

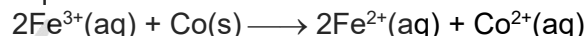
(c)(i)



$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}} \\ &= E^\ominus(\text{Fe}^{3+}/\text{Fe}^{2+}) - E^\ominus(\text{Co}^{2+}/\text{Co}) \\ &= +1.05 \text{ V} > 0 \text{ (spontaneous reaction)} \end{aligned}$$

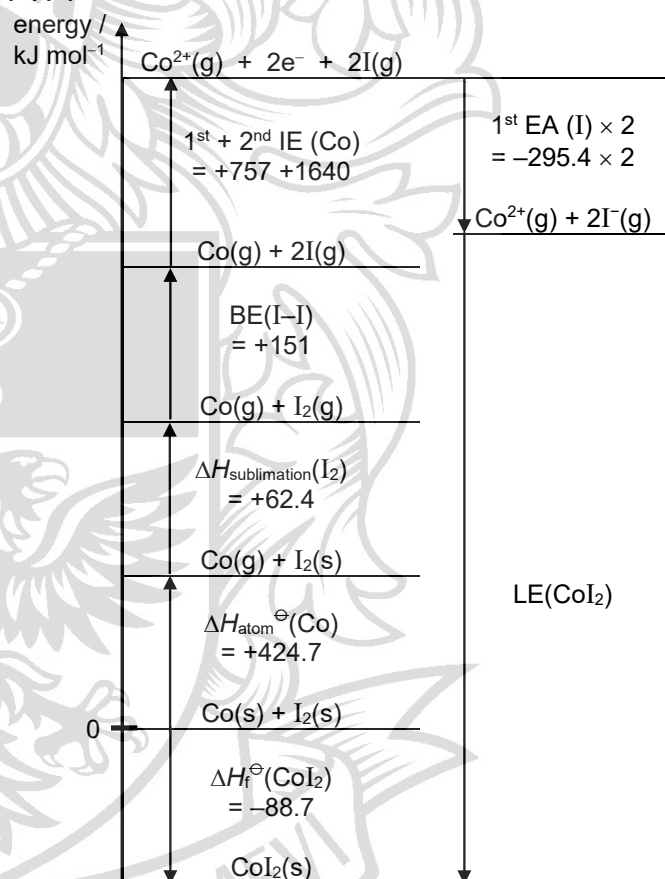
$\text{Fe}^{3+}(\text{aq})$ will be reduced to $\text{Fe}^{2+}(\text{aq})$ and $\text{Co}(\text{s})$ will be oxidised to $\text{Co}^{2+}(\text{aq})$.

Equation:



(d)(i) Lattice energy of an ionic compound is the energy released when one mole of the solid ionic compound is formed from its constituent gaseous ions at 298 K and 1 bar.

(d)(ii)



By Hess' law,

$$\begin{aligned} \text{LE}(\text{CoI}_2) &= -(-295.4 \times 2) - (+757 + 1640) - (+151) \\ &\quad - (+62.4) - (+424.7) + (-88.7) \\ &= -2533 \text{ kJ mol}^{-1} \\ &= -2530 \text{ kJ mol}^{-1} \end{aligned}$$

- (d)(iii) Order of lattice energy (in decreasing magnitude): $\text{CoO} > \text{CoF}_2 > \text{CoI}_2$

All three ionic compounds have the same cation, Co^{2+} .

$$|\text{LE}| \propto \frac{q_+ q_-}{r_+ + r_-}$$

Since O^{2-} has a higher charge than F^- and I^- , CoO has the greatest magnitude of lattice energy. As the ionic radius of F^- is smaller than that of I^- / interionic distance in CoF_2 is smaller than that in CoI_2 , the magnitude of lattice energy of CoF_2 is greater than that of CoI_2 .

(e)

compound	formula	M_r
A	$[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$	247.9
B	$[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{NO}_2)_6]^{3-}$	495.8

Since the oxidation number of the cobalt is the same in **A** and **B**, using formula of **A**:

overall oxidation number
= oxidation number of cobalt + $3(0) + 3(-1)$
= 0

\therefore oxidation number of cobalt = +3

(Since the M_r of $\text{CoH}_9\text{N}_6\text{O}_6$ is 247.9, **A** has molecular formula $\text{CoH}_9\text{N}_6\text{O}_6$. As there are only 9 H atoms and 6 O atoms, there must be 3 NH_3 and 3 NO_2^- in **A**. Since **A** is not an ionic salt, the 3 NH_3 and 3 NO_2^- must be ligands bound to the cobalt ion center.

Since **B** is an ionic salt with an M_r twice that of **A**, the molecular formula of **B** must be $\text{Co}_2\text{H}_{18}\text{N}_{12}\text{O}_{12}$. **B** is likely to contain one complex cation and one complex anion, both of which have charges of equal magnitude.)

(f)(i) Overall ionic equation:



(f)(ii) $n(\text{S}_2\text{O}_3^{2-}) = \frac{22.40}{1000} \times 0.0150 = 0.000336 \text{ mol}$

$$n(\text{I}_2) = \frac{1}{2} \times 0.000336 = 0.000168 \text{ mol}$$

mole ratio of $\text{I}_2 : \text{e}^- : \text{MnO}_4^-$

1 : 2

= 5 : 10 : 2

$$n(\text{MnO}_4^-) \text{ that reacted with } \text{I}^- = \frac{0.000168}{5} \times 2 = 0.0000672 \text{ mol}$$

$$n(\text{MnO}_4^-) \text{ that reacted with } \text{NO}_2^- = \left(\frac{50.00}{1000} \times 0.00500 \right) - 0.0000672 = 0.0001828 \text{ mol}$$

$$n(\text{NO}_2^-) \text{ in } 1.00 \text{ g sample of preserved meat} = \frac{0.0001828}{2} \times 5 = 0.0004570 \text{ mol}$$

$$\begin{aligned} \text{mass of } \text{NaNO}_2 \text{ in } 1.00 \text{ g sample of preserved meat} \\ = 0.0004570 \times (23.0 + 14.0 + 2(16.0)) \\ = 0.03153 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{percentage by mass of } \text{NaNO}_2 \\ = \frac{0.03153}{1.00} \times 100\% \\ = 3.15\% \end{aligned}$$

Question 2

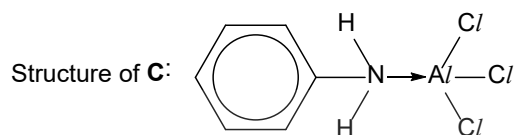
- (a) Relative basicity:
 $\text{CH}_3\text{CH}_2\text{NH}_2 > \text{C}_6\text{H}_5\text{NH}_2 > \text{CH}_3\text{CONH}_2$

In $\text{CH}_3\text{CH}_2\text{NH}_2$, the $-\text{CH}_2\text{CH}_3$ group is electron-donating and increases the electron density at the nitrogen atom, making the lone pair of electrons on the nitrogen atom more readily available for coordination to a proton.

In phenylamine, the orbital containing the lone pair of electrons on the nitrogen atom overlaps with the π electron cloud of the benzene ring. Thus the lone pair of electrons on the nitrogen atom is delocalised into the benzene ring and is less available for coordination to a proton.

CH_3CONH_2 is the least basic/neutral because the lone pair of electrons on the nitrogen atom interacts with the π electron cloud of the adjacent $\text{C}=\text{O}$ bond and is delocalised. Hence, this lone pair of electrons on the nitrogen atom is least/not available for coordination to a proton.

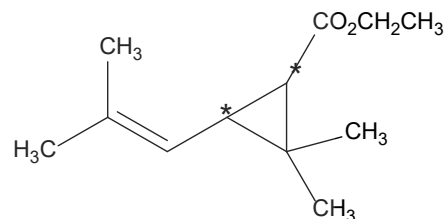
(b)



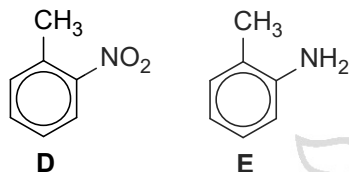
(Phenylamine acts as a Lewis base, donating its lone pair of electrons on the N atom to a low-lying vacant orbital of Al atom in AlCl_3 .)

(e)(ii)

There are a total of $2^2 = 4$ stereoisomers of **J** due to the presence of 2 chiral carbons. The C=C bond in **J** does not exhibit cis-trans isomerism as one of the doubly bonded C atom has two identical $-\text{CH}_3$ bonded to it.



(c)(i)



(f)(i)

The C–C bond energy in cyclopropane is lower than that in propane as the ring strain in the three-membered ring of cyclopropane weakens the C–C bond / smaller bond angle (60°) in cyclopropane results in greater repulsion between the bond pairs or less effective overlap of orbitals that weakens the C–C bond.

(c)(ii)

step 1:	concentrated HNO_3 , concentrated H_2SO_4 , 30°C
step 2:	Sn, concentrated HCl , heat, followed by NaOH(aq)
step 3:	limited $\text{CH}_3\text{CH}_2\text{Cl}$, heat (in sealed tube) (using limited $\text{CH}_3\text{CH}_2\text{Cl}$ will help to prevent polysubstitution)

(f)(ii)



(d)

Two possible non-cyclic structures:
 $\text{N}\equiv\text{C}-\text{NH}_2$ and $\text{HN}=\text{C}=\text{NH}$

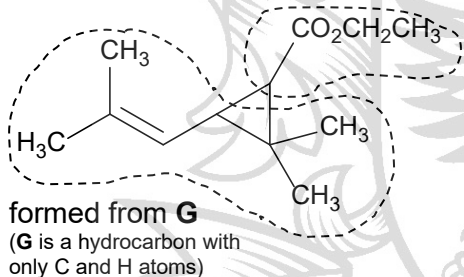
$$\Delta H = 6\text{BE}(\text{C}-\text{H}) + 3(289) - 6(410) - 350 - 610 = -31 \text{ kJ mol}^{-1}$$

(e)(i)

Using information from Fig. 2.2,
formed from **H**

$$6\text{BE}(\text{C}-\text{H}) = +2522 \text{ kJ mol}^{-1}$$

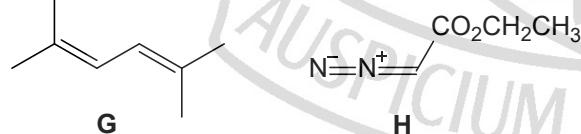
$$\text{average C-H bond energy} = \frac{2522}{6} = +420 \text{ kJ mol}^{-1}$$



(f)(iii)

Using the results, plot the graph of concentration of cyclopropane against time for each experiment. Draw a tangent to the graph at $t = 0$ min and calculate the gradient of the tangent \Rightarrow initial rate = -gradient

Structures of **G** and **H**:



Compare the initial rates and the initial concentrations of cyclopropane. If the initial rate is directly proportional to the initial concentration of cyclopropane, then the reaction is first order with respect to cyclopropane.

- (f)(iv) A catalyst increases the rate of a reaction by providing an alternative reaction pathway with lower activation energy, without itself undergoing any permanent chemical change.

Hence, the presence of a catalyst will increase the magnitude of the rate constant, k , and decrease the magnitude of the activation energy, E_a .

Question 3

(a)(i)

There are <u>6 bond pairs</u> and <u>0 lone pairs</u> .	There are <u>2 bond pairs</u> and <u>2 lone pairs</u> .
To minimise repulsion between the electron pairs, the shape is <u>octahedral</u> .	To minimise repulsion between the electron pairs, the shape is <u>bent</u> .
The bond angle is <u>90°</u> .	As <u>lone pairs exert greater repulsion than bond pairs</u> , the bond angle is <u>105°</u> . (90° < bond angle < 109.5°)

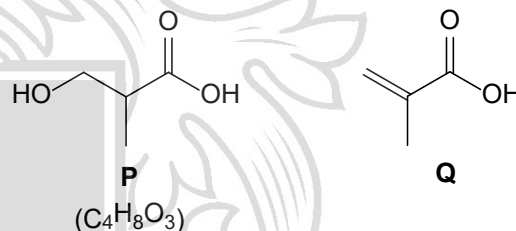
The more stable the conjugate base, the stronger the acid.

2-chlorobutanoic acid and 2-iodobutanoic acid have the electronegative Cl and I atoms which disperse the negative charge on the COO^- . This stabilises their corresponding conjugate bases and hence they are stronger acids than butanoic acid.

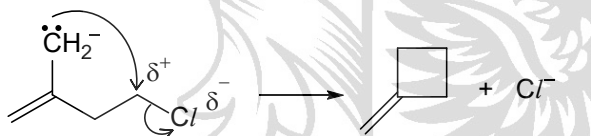
As Cl is more electronegative than I, it disperses the negative charge on the COO^- and stabilises the conjugate base to a greater extent. Hence 2-chlorobutanoic acid is more acidic than 2-iodobutanoic acid.

(c)

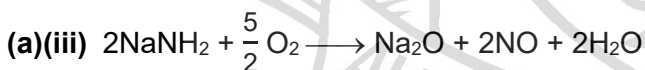
step 1	NaOH(aq), heat followed by $\text{HCl}/\text{HNO}_3/\text{H}_2\text{SO}_4(\text{aq})$ <i>Note: acidification is required as a carboxylate salt would be obtained after heating N with NaOH(aq).</i>
step 2	excess concentrated H_2SO_4 , heat
step 3	dry HBr



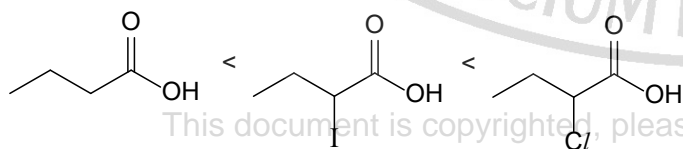
(a)(ii) $\text{S}_{\text{N}}2$



(Since step 2 involves an intramolecular nucleophilic substitution of a primary chloroalkane, the reaction is likely to proceed via the $\text{S}_{\text{N}}2$ mechanism.)



(b) Order of increasing Bronsted-Lowry acidity:



(d)

As HA is a weak acid with partial dissociation,
 $[\text{H}^+] = \sqrt{K_a \times [\text{HA}]}$
 $10^{-3.28} = \sqrt{(1.38 \times 10^{-5}) \times [\text{HA}]}$
 $[\text{HA}] = 0.01996 \text{ mol dm}^{-3}$

Since 1 dm^3 contains 1.76 g sample of HA,

$$M_r \text{ of HA} = \frac{1.76}{0.01996} = 88.2$$

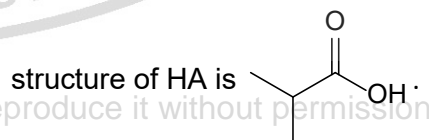
Let HA be $\text{C}_n\text{H}_{2n+1}\text{COOH}$.

$$(n+1)(12.0) + (2n+2)(1.0) + 2(16.0) = 88.2$$

$$n = 3$$

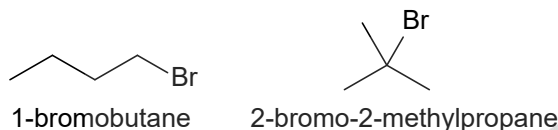
Hence, HA is $\text{C}_3\text{H}_7\text{COOH}$.

Since HA is a branched-chain carboxylic acid,



Question 4

(a)(i)



1) Reaction of 1-bromobutane with $\text{OH}^- (\text{aq})$

Predominant mechanism: $\text{S}_{\text{N}}2$

1-bromobutane is a primary bromoalkane with little steric hindrance around the C bonded to Br for nucleophilic attack, making $\text{S}_{\text{N}}2$ mechanism favourable. $\text{S}_{\text{N}}1$ mechanism will be less preferred as the primary carbocation formed will be unstable as there is only one electron-donating alkyl group to disperse the positive charge.

2) Reaction of 2-bromo-2-methylpropane with $\text{OH}^- (\text{aq})$:

Predominant mechanism: $\text{S}_{\text{N}}1$

2-bromo-2-methylpropane is a tertiary bromoalkane with greater steric hindrance around the C bonded to Br, making $\text{S}_{\text{N}}2$ mechanism less favourable. $\text{S}_{\text{N}}1$ mechanism is preferred as the tertiary carbocation formed is stabilised by three electron-donating alkyl groups.

(a)(ii) For the $\text{S}_{\text{N}}2$ mechanism, a single enantiomer (with inversion of configuration if the C bonded to halogen is a chiral carbon) is formed. This is due to the backside attack of the nucleophile on the C bonded to halogen.

For the $\text{S}_{\text{N}}1$ mechanism, a racemic mixture is formed. In the reaction, the carbocation intermediate formed has a trigonal planar shape around the positively charged C. The subsequent attack by the nucleophile on either side of the plane with equal probability results in the formation of a pair of enantiomers in a 1:1 ratio.

(b)
$$\begin{aligned}\Delta H_{\text{sol}}^{\ominus} &= \sum n\Delta H_f^{\ominus}(\text{pds}) - \sum m\Delta H_f^{\ominus}(\text{rxts}) \\ &= +64.8 + 2(-230.0) - (-449.8) \\ &= +54.6 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G_{\text{sol}}^{\ominus} &= \Delta H_{\text{sol}}^{\ominus} - T(\Delta S_{\text{sol}}^{\ominus}) \\ &= (+54.6) - (298)\left(\frac{-196.2}{1000}\right) \\ &= +113 \text{ kJ mol}^{-1}\end{aligned}$$

$\text{Cu}(\text{OH})_2(\text{s})$ is only sparingly soluble in water at 25 °C (298 K) as the $\Delta G_{\text{sol}}^{\ominus} > 0$, showing that the dissolution process is non-spontaneous.

(c)(i) A buffer solution is a solution which is able to resist pH changes when a small amount of an acid or a base is added.

(c)(ii) When a small amount of base is added:
 $\text{HSO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

When a small amount of acid is added:
 $\text{SO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \longrightarrow \text{HSO}_3^-(\text{aq})$

(c)(iii) $n(\text{NaHSO}_3) \text{ added} = \frac{50.0}{1000} \times 0.500 = 0.0250 \text{ mol}$

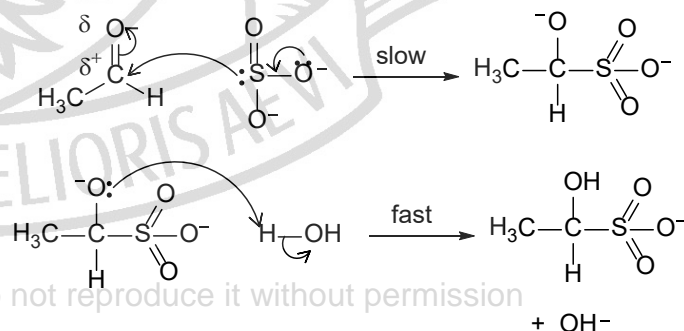
$$n(\text{NaOH}) \text{ added} = \frac{25.0}{1000} \times 0.600 = 0.0150 \text{ mol}$$

Upon mixing, NaHSO_3 reacts with NaOH :
 $\text{HSO}_3^-(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$$\begin{aligned}n(\text{SO}_3^{2-}) \text{ formed} &= n(\text{NaOH}) = 0.0150 \text{ mol} \\ n(\text{HSO}_3^-) \text{ left} &= 0.0250 - 0.0150 = 0.0100 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{pH} &= \text{p}K_{\text{a}} + \lg \frac{[\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} \\ &= -\lg (6.73 \times 10^{-8}) + \lg \frac{0.0150 / V_{\text{T}}}{0.0100 / V_{\text{T}}} \\ &= 7.35\end{aligned}$$

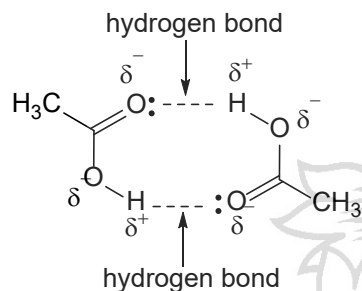
(c)(iv) Nucleophilic addition



Question 5

(d)(i) Dynamic equilibrium refers to a state in a reversible system in which the rates of the forward and backward reactions are continuing at the same rate, resulting in no net change in the macroscopic properties (e.g. concentrations, partial pressure) of the reactants and products.

(d)(ii)



(d)(iii)

	$2\text{CH}_3\text{CO}_2\text{H}$	\rightleftharpoons	$(\text{CH}_3\text{CO}_2\text{H})_2$
initial conc / mol dm ⁻³	0.100		0
change in conc / mol dm ⁻³	$-2(0.0417)$		$+0.0417$
eqm conc / mol dm ⁻³	0.0166		0.0417

$$\begin{aligned}\text{ratio of } [(\text{CH}_3\text{CO}_2\text{H})_2] / [\text{CH}_3\text{CO}_2\text{H}] \\ &= 0.0417 / 0.0166 \\ &= 2.51\end{aligned}$$

(d)(iv) $\Delta G^\ominus = -RT \ln K_c$

In an aqueous solution, the equilibrium position will lie further left as the system favours the formation of the monomer, which can form more extensive hydrogen bonding with surrounding water molecules. As a result, K_c will be smaller in an aqueous solution.

Hence, ΔG^\ominus in an aqueous solution will be less negative (or more positive) than that in a non-polar solvent.

(a)

Across Period 3, the number of protons increases and hence nuclear charge increases. Although the number of electrons also increases, these electrons are added to the same outermost shell, and hence shielding effect remains approximately constant. Effective nuclear charge increases and electrostatic attraction between the nucleus and the valence electrons increases, resulting in an increase in the energy required to remove the valence electron from an atom. Hence the first ionisation energies of the elements generally increase across a period.

However, there are two irregularities in the trend.

The first ionisation energy of Al is lower than that of Mg. This is because the 3p electron to be removed from Al is at a higher energy level than the 3s electron to be removed from Mg. Hence less energy is required to remove the 3p electron in Al than the 3s electron in Mg.

Also, the first ionisation energy of S is lower than that of P. This is because the 3p electron to be removed from S is a paired electron while that to be removed from P is an unpaired electron. Due to inter-electronic repulsion between paired electrons in the same orbital, less energy is required to remove the paired 3p electron from S.

(b)(i)

Al_2O_3 does not react with water as it does not dissolve in water. pH of the resulting mixture is 7.

AlCl_3 dissolves in water to form the complex ion, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, which then undergoes appreciable hydrolysis in water to form an acidic solution with an approximate pH of 3.

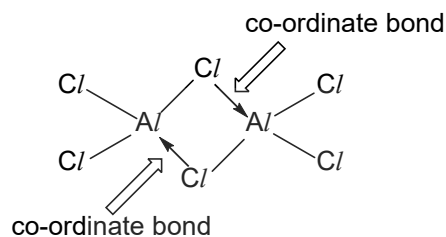
(equations are not required by question)



OR



(b)(ii)



(c)(i) K_{sp} of $Zn(OH)_2 = [Zn^{2+}][OH^-]^2 \text{ mol}^3 \text{ dm}^{-9}$

(c)(ii) Let s be the solubility of $Zn(OH)_2$ at 25°C .

$$\begin{aligned} K_{sp} &= [Zn^{2+}][OH^-]^2 \\ &= (s)(2s)^2 \\ &= 4s^3 \\ &= 2.0 \times 10^{-17} \text{ mol}^3 \text{ dm}^{-9} \end{aligned}$$

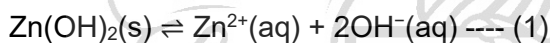
$$s = 1.710 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[OH^-] = 2s = 3.420 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg [OH^-] = 5.466$$

$$\text{pH} = 14 - \text{pOH} = 8.53$$

(c)(iii) In a saturated solution of $Zn(OH)_2$, the following equilibrium is established.



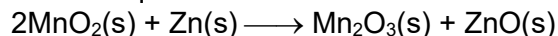
Addition of $HCl(aq)$:

H^+ from HCl will undergo acid-base reaction with OH^- . This decreases the concentration of $OH^-(aq)$. To counteract the decrease in concentration of $OH^-(aq)$, the equilibrium position of reaction (1) shifts right, resulting in the dissolution of $Zn(OH)_2(s)$ and hence solubility of $Zn(OH)_2$ increases.

Addition of $ZnCl_2(aq)$:

Zn^{2+} is the common ion and addition of $ZnCl_2(aq)$ increases the concentration of $Zn^{2+}(aq)$. To counteract the increase in concentration of $Zn^{2+}(aq)$, the equilibrium position of reaction (1) shifts left, resulting in precipitation of some $Zn(OH)_2(s)$. Hence, the solubility of $Zn(OH)_2$ decreases.

(d)(i) Overall equation:



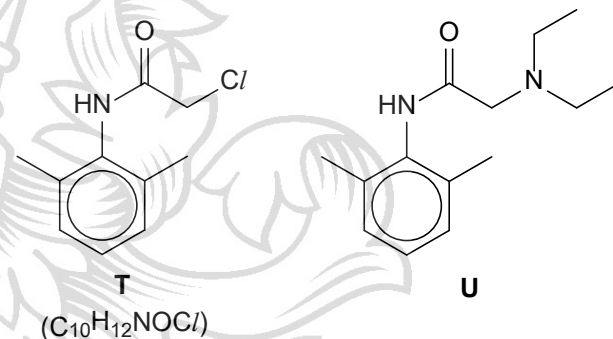
$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}} \\ &= E^\ominus(MnO_2/Mn_2O_3) - E^\ominus(ZnO/Zn) \\ &= +0.15 - (-1.28) \\ &= +1.43 \text{ V} \end{aligned}$$

(d)(ii) $\Delta G^\ominus = -n_e F E^\ominus_{\text{cell}}$

$$\begin{aligned} &= -(2)(96500)(+1.43) \\ &= -275990 \text{ J mol}^{-1} \\ &= -276 \text{ kJ mol}^{-1} \end{aligned}$$

(e)(i) 2,6-dimethylphenylamine

(e)(ii)



(e)(iii)

step 1	Cl/CH_2COCl (room temperature)
step 2	excess $(CH_3CH_2)_2NH$, heat (in sealed tube)

(e)(iv) acid-base reaction

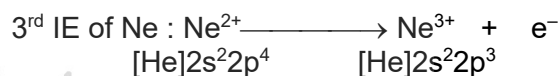
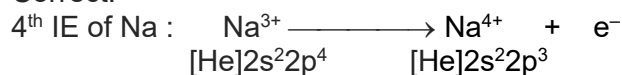
2021 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

Q1(B)

1	Correct. Angle of deflection is proportional to $\frac{q}{m}$. Since $m_{\text{electron}} < m_{\text{proton}}$, electrons have a greater angle of deflection and are deflected to a larger extent than protons.
2	Correct. Electrons are attracted to the positive plate while protons are attracted to the negative plate i.e. the electron beam are deflected in the opposite direction to the proton beam.
3	Incorrect. The proton beams will travel in a curve path towards the negative plate.

Correct.



C Na^{3+} and Ne^{2+} have the same electronic configuration and experience the same shielding effect. 4^{th} IE of Na is greater due to the greater nuclear charge of Na which causes the 2p electrons of Na^{3+} to experience a greater effective nuclear charge and greater attraction from the nucleus, requiring more energy to remove.

Incorrect. Successive IE's always increase even if the electrons are removed from different shells.

D Successive IE's always increase as an electron is removed from a species of increasing positive charge and does not depend on which

Q2(D)

Q in the ionic nitrate, QNO_3 , exists as Q^+ .

Since Q^+ has 80 electrons, **Q** has 81 electrons and 81 protons. From the Periodic table, **Q** is the element thallium which belongs to group 13.

The nucleon number of **Q** is $81 + 122 = 203$.

Q3(C)

A	Incorrect. $2^{\text{nd}} \text{ IE of F : } \text{F}^+ \longrightarrow \text{F}^{2+} + e^{-}$ $[\text{He}]2s^22p^4 \quad [\text{He}]2s^22p^3$ $3^{\text{rd}} \text{ IE of Al : } \text{Al}^{2+} \longrightarrow \text{Al}^{3+} + e^{-}$ $[\text{Ne}]3s^1 \quad [\text{Ne}]$ $2^{\text{nd}} \text{ IE of F is greater because the electrons are removed from an inner electronic shell.}$												
B	Incorrect <table border="1"> <thead> <tr> <th>3^{rd} IE of</th><th>electron removed from</th></tr> </thead> <tbody> <tr> <td>F</td><td>2p</td></tr> <tr> <td>Ne</td><td>2p</td></tr> <tr> <td>Na</td><td>2p</td></tr> <tr> <td>Mg</td><td>2p</td></tr> <tr> <td>Al</td><td>3s</td></tr> </tbody> </table>	3^{rd} IE of	electron removed from	F	2p	Ne	2p	Na	2p	Mg	2p	Al	3s
3^{rd} IE of	electron removed from												
F	2p												
Ne	2p												
Na	2p												
Mg	2p												
Al	3s												

Q4(B)

Since there is a large jump between the 7^{th} and 8^{th} IE for element W, the 8^{th} electron is removed from an inner shell i.e. W has 7 valence electrons and is from group 17.

Since W, X, Y and Z are consecutive elements, X is from group 18, while elements Y and Z are from groups 1 and 2 of the next period respectively.

X, the group 18 element, has a higher first IE than W, the group 17 element of the same period since IE increases across the period.

X also has the higher first IE than Y and Z since Y and Z are from the next period and their valence electrons are further away from the nucleus.

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Q5(C)

compound	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
carbon-carbon bond	C–C	C=C	C≡C
bond energy	Bond energy increases due to increased number of shared electrons and increased attraction between bonding electrons and nuclei.		
bond length	Bond length decreases. In general, the stronger the bond, the shorter the bond length.		

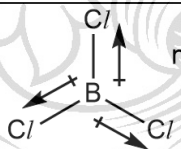
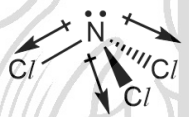
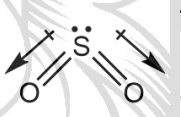
hydrogen bonding compared P and Q which have 1 –OH group each, forming an average of 1 hydrogen bond per molecule. Hence, M has a higher BP than P and Q.

Due to presence of an addition electron-withdrawing C=O group in Q, the –OH group in Q is more polar, forming stronger intermolecular hydrogen bonds compared to P. Hence Q has a higher BP than P.

Q8(D)

A	Incorrect. This is Avogadro's Law.
B	Incorrect. This is an application of Dalton's Law, not the definition of Dalton's Law.
C	Incorrect. The partial pressure of a gas is given by the product of its <i>mole fraction</i> and the total pressure. Even then, this is not Dalton's Law.
D	Correct.

Q6(D)

	molecule	molecular shape	polarity
A	BCl ₃	trigonal planar ✓	polar ✗ non-polar
			no overall dipole
B	NCl ₃	trigonal pyramidal ✓	non-polar ✗ polar
			overall dipole
C	SO ₂	linear ✗ bent	non-polar ✗ polar
			overall dipole
D	CHCl ₃	tetrahedral ✓	polar ✓

Q9(D)

Experiment 1 – SiO₂ solid does not dissolve in water i.e. SiO₂ solid remains.

Experiment 2 – SiO₂ solid does not react with, and hence does not dissolve in HCl(aq) i.e. SiO₂ solid remains.

Experiment 3 – SiO₂ solid does not react with, and hence does not dissolve in NaOH(aq) i.e. SiO₂ solid remains.

Note: SiO₂ only reacts with concentrated NaOH.

Q10(A)

No. of molecules = Amount in moles x Avogadro's constant

A	Ethyl methanoate, CH ₃ CH ₂ O–CHO (M _r = 74.0) No. of molecules = $\frac{2.00}{74.0} \times 6.02 \times 10^{23}$ = 1.63 × 10²²
B	Br ₂ (l) (M _r = 159.8) No. of molecules = $\frac{4.00}{159.8} \times 6.02 \times 10^{23}$ = 1.51 × 10²²
C	No. of molecules = $\frac{550}{24000} \times 6.02 \times 10^{23}$ = 1.38 × 10²²

Q7(B)

Since all 4 compounds have similar M_r, their strengths of id-id interactions are similar.

M, P and Q can form stronger intermolecular hydrogen-bonding (due to the presence of –OH groups) compared to the weaker pd-pd interactions in N. Hence, N has a lower bp than M, P and Q.

M has 3 –OH groups and an average of 3 hydrogen bonds per molecule, resulting in more extensive

D No. of molecules = 1.55×10^{22}

Q11(C)

$$\text{Amount of H}_2\text{SO}_4 = \frac{20.0}{1000} \times 5.00 = 0.100 \text{ mol}$$

$$\text{Amount of NaOH} = \frac{20.0}{1000} \times 5.00 = 0.100 \text{ mol}$$



Since H_2SO_4 reacts with NaOH in a 1:2 ratio, NaOH is limiting.

$$q = mc\Delta T = (20.0 + 20.0)(4.18)(50.0 - 25.0) = 4180 \text{ J}$$

$$\Delta H = -\frac{q}{n_{\text{NaOH}}} = -4180/0.100 = -41800 \text{ J mol}^{-1} = -41.8 \text{ kJ mol}^{-1}$$

Q12(A)

This is a graph of rate of forward reaction against time and the rate equation for the forward rate is $\text{rate} = k(p_{\text{CO}_2})$.

At time t , the pressure i.e. p_{CO_2} is lowered, causing a decrease in the forward rate just after time t as seen in options **A** and **B**.

The pressure was then allowed to return to atmospheric pressure, so p_{CO_2} increases back to the initial pressure and the forward rate increases back to the original rate as seen in option **A**.

Q13(B)

1	Correct. For the hydrogen and bromine reaction, HBr appears in the denominator of the rate equation. When $[\text{HBr}]$ increases, rate decreases i.e. the formation of HBr slows down the rate of reaction.
2	Correct. The rate equation for H_2 and Br_2 involves many species. It is unlikely that so many species will collide and be involved in a single step reaction. Also, the stoichiometry of the reactants reaction is not the same as the orders of reaction in the rate equation. This is not likely to be a single step reaction. Since the rate equation involves 1 mole of H_2 and 1 mole of I_2 which is the same as the stoichiometry of the reaction between H_2 and I_2 , it could be a single step reaction.
3	Incorrect. Using the rate equation for

reaction 1, when $[\text{Br}_2] \times 2$, $\text{rate} \times 2^{1.5} = 2.8$ i.e. the rate of reaction 1 is not doubled when $[\text{Br}_2]$ is doubled.

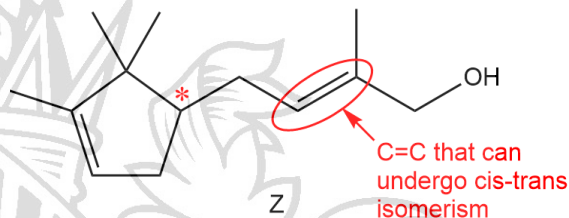
Q14(B)

Stereoisomers = cis-trans isomers and enantiomers

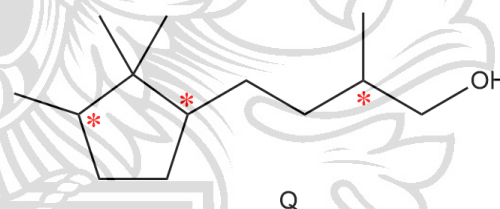
Max no. of stereoisomers = 2^{m+n}

m = no. of double bonds that can undergo cis-trans isomerism

n = no. of chiral centres



No. of stereoisomers = $2^{1+1} = 4$



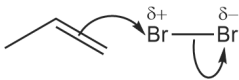
No. of stereoisomers = $2^3 = 8$

Q15(A)

A	Correct. In the propagation steps, methylpropane reacts with the $\text{X}\bullet$ radical generated in the initiation step. $(\text{CH}_3)_3\text{CH} + \text{X}\bullet \longrightarrow (\text{CH}_3)_3\text{C}\bullet + \text{HX} \quad \text{-- (a)}$ $(\text{CH}_3)_3\text{C}\bullet + \text{X}_2 \longrightarrow (\text{CH}_3)_3\text{CX} + \text{X}\bullet$ $(\text{CH}_3)_3\text{CX}$ i.e. $\text{C}_4\text{H}_9\text{X}$ is generated in one of the propagation steps.
B	Incorrect. In the termination steps, two radicals collide to form non-radical products. Radicals, like $(\text{CH}_3)_3\text{C}\bullet$, will not be produced. Incorrect. In the overall reaction, bonds broken = X-X and C-H bonds formed = H-X and C-X .
C	ΔH when $\text{X} = \text{Br}$ $= 193 + 410 - (366 + 280) = -43 \text{ kJ mol}^{-1}$ ΔH when $\text{X} = \text{Cl}$ $= 244 + 410 - (431 + 340) = -117 \text{ kJ mol}^{-1}$

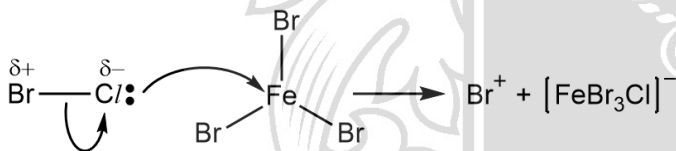
	The reaction with chlorine is more exothermic.
D	Incorrect. In the initiative step, a halogen <i>radical</i> , not ion, is produced.

Q16(A)

A	Correct. In the slow step, the carbon-carbon π bond is donated to the electrophile because the π bond is weaker than the σ bond (due to less effective orbital overlap in the π bond) and is more easily broken. 
B	Incorrect. See explanation in option A.
C	Incorrect. In the slow step, the electrons are <i>donated</i> from the C=C which makes the C=C a nucleophile.
D	Incorrect. See explanation in option A.

Q17(C)

In the absence of sunlight, homolytic breaking of the Br-Cl to form the respective radicals does not take place i.e. no reaction to the -CH₃ side chain of methylbenzene. Reject options **A** and **B**.



The iron-containing catalyst (e.g. FeBr₃) acts as a Lewis acid and accepts a pair of electrons from the δ^- chlorine in BrCl to generate the Br⁺ electrophile and [FeBr₃Cl]⁻. The Br⁺ electrophile then undergoes electrophilic substitution with the benzene ring in methylbenzene, substituting one Br atom into the benzene ring.

Q18(B)

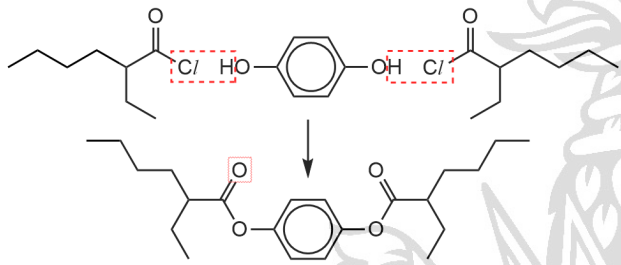
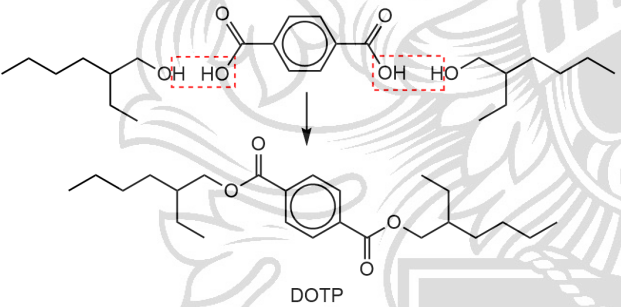
1	No. While the statement is true, it does not help to explain the difference in rate of the two halogenoalkanes.
2	Yes. Br has more electron shells than Cl. Hence, the valence electrons used in Br for bonding with carbon is further away, and more shielded, from its nucleus than in Cl. This results in weaker attraction by the Br nucleus for the shared electrons in the C-Br bond compared to the case with Cl, contributing to the C-Br bond being weaker than the C-Cl bond.
3	Yes. Br has more electron shells than Cl, resulting in a larger atomic radius of Br compared to Cl which contributes to the C-Br bond being weaker than the C-Cl bond.
4	No. While the statement is true, it does not help to explain the difference in rate of the two halogenoalkane. This is because the large number of electron shells causes a significant shielding of the valence electrons of Br from the attraction of the high nuclear charge, causing the resultant attraction experienced by the valence electrons to be lower.

Q19(D)

Student P is incorrect because organic compounds (e.g. alcohols) do not give a positive test with warm silver nitrate solution i.e. the organic compound does not have to be a halogenoarene either.

Student Q is incorrect because the organic compound can be a fluoroalkane, which is a halogenoalkane. Fluoroalkanes do not give a positive test with warm silver nitrate solution as the C-F bond very strong and is too strong to be broken to form F⁻ ions.


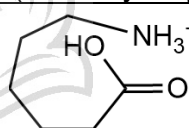

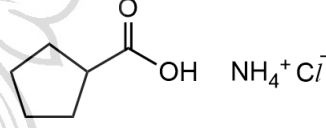
Q20(C)

A	Incorrect. In the H2 syllabus, acyl chlorides do not react with carboxylic acids. Therefore, mixing the two compounds does not give any product.
B	Incorrect. The reaction gives the following product which is not DOTP. 
C	Correct. In the presence of a suitable catalyst, a reaction takes place between the reactants to give DOTP as the product. 
D	Incorrect. The structure of the alcohol drawn has only 7 carbons whereas the alcohol part of the ester in DOTP has 8 carbons. The reaction with these reactants will not give DOTP as the product.

Q22(A)

1	Yes. The p-orbital on N overlaps with the π -electron cloud of the C=O which allows the lone pair of electrons on N to delocalize into the C=O, reducing the availability of the lone pair on N to form a dative bond with H^+ .
2	No. The delocalization gives the C–N bond a partial double bond character which strengthens the bond, but this does not affect the acid-base properties of an amide.
3	Yes. When the N atom of an amide is protonated, the lone pair of electrons on N is used to form a dative bond with H^+ and the delocalization of the lone pair on N to the C=O group is lost, causing the ion to be less stable.

Q23(A)

	Product of reaction with	
	LiAlH ₄ (reduction of amide)	warm HCl(aq) (acidic hydrolysis)
A	 C ₆ H ₁₃ N	 C ₆ H ₁₄ NO ₂ Cl
B	 C ₆ H ₁₃ N	 C ₆ H ₁₀ O ₂
C	CH ₃ (CH ₂) ₄ CH ₂ NH ₂ C ₆ H ₁₅ N	CH ₃ (CH ₂) ₄ COOH NH ₄ ⁺ Cl ⁻ C ₆ H ₁₂ O ₂
D	CH ₃ CH ₂ CH ₂ CH ₂ NHCH ₂ CH ₃ C ₆ H ₁₅ N	CH ₃ CH ₂ CH ₂ COOH Cl ⁻ H ₃ N ⁺ CH ₂ CH ₃

Q21(A)

The relative basicity of amines decrease in the order : tertiary > secondary > primary.

Tertiary, secondary and primary amines have 3, 2 and 1 alkyl groups bonded to the N atom respectively.

With more electron-donating alkyl groups (R–), there is increasing electron density at the N atom, increasing the availability of the lone pair of electrons to form a dative covalent bond with H^+ .

Q24(B)

The –COOH group is more acidic, and has a lower pK_a , than the –NH₃⁺ group. The reaction associated with pK_{a1} involves the dissociation of the more acidic –COOH, so it should have the lower pK_a value of 2.4. Therefore, pK_{a2} is 9.8. Reject options **C** and **D**.

Since the pH of 13 > pK_{a1} , the dominant form is where the –COOH group is deprotonated to form –COO⁻.

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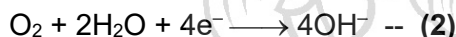
Since the pH of 13 > pK_{a2}, the dominant form is where the –NH₃⁺ group is deprotonated to form –NH₂.

The formula of glycine at pH 13 is therefore H₂N–CH₂–CO₂[–].

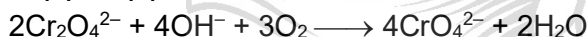
Note: when pH < pK_a of acidic group, the dominant form is the protonated form. When pH > pK_a of acidic group, the dominant form is the deprotonated form.

Q25(B)

The reaction of interest is O₂ + Cr₂O₄^{2–} → CrO₄^{2–} in alkaline medium (since the reaction is done in sodium hydroxide).



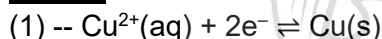
2x(1)+3x(2):



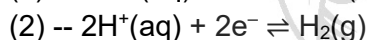
3 mol of O₂ react with 2 mol of Cr₂O₄^{2–}

i.e. 1.5 mol of O₂ react with 1 mol of Cr₂O₄^{2–}

Q26(D)



$$E^\ominus = +0.34 \text{ V}$$



$$E^\ominus = 0.00 \text{ V}$$

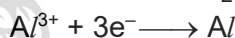
$$E^\ominus_{\text{cell}} = 0.34 - 0.00 = +0.34 \text{ V}$$

A	Incorrect. When pressure of H ₂ decreases, the position of equilibrium (2) shifts to the right, making the value of E(H ⁺ /H ₂) more positive, leading to a less positive cell potential.
B	Incorrect. Increasing [H ⁺] causes the position of equilibrium (2) to shift right, making the value of E(H ⁺ /H ₂) more positive, leading to a less positive cell potential.
C	Incorrect. Changing from CuSO ₄ (aq) to Cu(NO ₃) ₂ (aq) maintains the concentration Cu ²⁺ at 1 mol dm ^{–3} . There is no change in the position of equilibrium of (1) and the cell potential remains the same.
D	Correct. 1.0 mol dm ^{–3} ethanoic acid, a weak acid, provides less than 1.0 mol dm ^{–3} of H ⁺ in the hydrogen electrode. This causes the position of equilibrium (2) to lie more to the left,

making the value of E(H⁺/H₂) < 0, leading to a more positive cell potential.

Q27(B)

$$\text{Amount of Al} = \frac{0.27}{27.0} = 0.0100 \text{ mol}$$



$$\text{Amount of e}^- \text{ transferred} = 3(0.0100) = 0.0300 \text{ mol}$$

$$\text{Since } Q = n_e F,$$

$$F = \frac{Q}{n_e} = \frac{2904}{0.0300} = 96800 \text{ C mol}^{-1}$$

Since Faraday constant = Avogadro's number x charge of 1e[–]

$$\text{i.e. } 96800 = \text{Avogadro's number} \times 1.6 \times 10^{-19}$$

$$\text{Avogadro's number} = 6.05 \times 10^{23}$$

Q28(C)

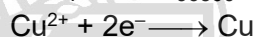
$$E^\ominus(\text{Ni}^{2+}/\text{Ni}) = -0.25 \text{ V}$$

$$E^\ominus(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$$

At the cathode, Cu²⁺ will be preferentially reduced since E[⊖](Cu²⁺/Cu) > E[⊖](Ni²⁺/Ni).

$$Q = It = n_e F$$

$$n_e = \frac{It}{F} = \frac{0.50(1.5 \times 60 \times 60)}{96500} = 0.02798 \text{ mol}$$



$$\text{Amount of Cu formed} = \frac{0.02798}{2} = 0.01399 \text{ mol}$$

$$\text{Mass of Cu formed} = 0.01399(63.5) = 0.888 = 0.89 \text{ g}$$

Q29(C)

Note:

- Students should be familiar with the data in the Data Booklet and be aware that a variety of E[⊖] values are provided for vanadium species.

$\text{V}^{2+} + 2\text{e}^- \rightleftharpoons \text{V}$	–1.20
$\text{V}^{3+} + \text{e}^- \rightleftharpoons \text{V}^{2+}$	–0.26
$\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{V}^{3+} + \text{H}_2\text{O}$	+0.34
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}^{2+} + \text{H}_2\text{O}$	+1.00
$\text{VO}_3^- + 4\text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}_2^+ + 2\text{H}_2\text{O}$	+1.00
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	–0.76

- Therefore, students should be aware of the possibility, and check by calculating relevant

$E^{\ominus}_{\text{cell}}$ value, that VO_2^+ may be reduced to VO^{2+} , which may be reduced to V^{3+} , which may be reduced to V^{2+} , which may be reduced to V .

3. This is especially since excess Zn was added, which would provide more than sufficient reducing agent to reduce the vanadium species.
4. To do this question, you do not need write the balanced equations in your working. You just need to check the final oxidation state of vanadium that VO_2^+ is reduced to.

Reaction (eqns are not balanced)	$E^{\ominus}_{\text{cell}} / \text{V}$
$\text{Zn} + \text{VO}_2^+ \rightarrow \text{Zn}^{2+} + \text{VO}^{2+}$	$1.00 - (-0.76) = +1.76 > 0$ i.e. VO_2^+ reduced to VO^{2+}
$\text{Zn} + \text{VO}^{2+} \rightarrow \text{Zn}^{2+} + \text{V}^{3+}$	$0.34 - (-0.76) = +1.10 > 0$ i.e. VO^{2+} reduced to V^{3+}
$\text{Zn} + \text{V}^{3+} \rightarrow \text{Zn}^{2+} + \text{V}^{2+}$	$-0.26 - (-0.76) = +0.50 > 0$ i.e. V^{3+} reduced to V^{2+}
$\text{Zn} + \text{V}^{2+} \rightarrow \text{Zn}^{2+} + \text{V}$	$-1.20 - (-0.76) = -0.44 > 0$ i.e. V^{2+} not reduced to V

Overall, Zn reduces VO_2^+ to V^{2+} i.e. option C.

Q30(D)

A transition element has high melting point (like in option 1) and high density (like in option 2).

Question 1

$$(a)(i) \quad A_r(\text{sulfur}) = \frac{[31.97(63.8) + 33.97(2.8)]}{63.8 + 2.8} = 32.05 \text{ (to 4 s.f.)}$$

(a)(ii)



(b)



(c)(i) It is the energy required to remove 1 mole of electrons from 1 mole of gaseous sulfur atoms to form 1 mole of gaseous S^+ ions.

Note: Energy *required*, **not** change or released

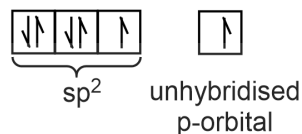
(c)(ii) The first ionization energy across Period 3 elements generally increases. Across Period 3, the nuclear charge increases while the shielding effect is approximately constant, leading increasing attraction of the nucleus for the valence electrons.

For sulfur, there is additional interelectronic repulsion between the paired electrons in the valence 3p subshell, requiring less energy to remove the valence electron.

Note: students need to mention that, for sulfur, the electron is removed from the 3p subshell.

(d)(i) In CS_2 , sp hybridisation results when one 2s and one 2p orbital of C mix to form two sp hybrid orbitals. There are two unhybridised p-orbitals in C.

(d)(ii) The sp^2 hybrid orbital of S with 1 electron overlaps **head-on** with the sp hybrid orbital of C to form a σ bond. The unhybridised p-orbital of S with 1 electron overlaps side-to-side with an unhybridised p-orbital of C to form a π -bond.



Note: Students can include diagrams to aid their explanation.

Question 2

(a)(i) Down group 1, the ionic radius increases due to the increase in the number electron shells, causing the valence electrons to be further away from the nucleus.

(a)(ii) Cs^+ has a larger ionic radius than Li^+ , Na^+ and K^+ which allows it to accommodate more anions around itself.

(b)

ionic solid	LE / kJ mol^{-1}	interionic distance / nm	cationic charge	anionic charge
NaCl	-771	0.276	+1	-1
NaF	-902	0.231	+1	-1
MgO	-3899	0.205	+2	-2

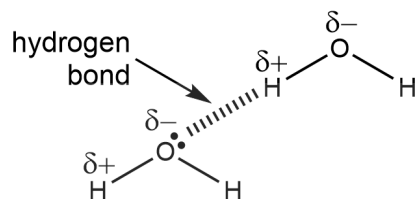
The two factors that affect the magnitude of lattice energy are ionic charge and interionic distance.

When the ionic distance increases from 0.231 nm (NaF) to 0.276 (NaCl), the magnitude of lattice energy decreases slightly from 902 to 771.

Comparing NaF and MgO, which have similar interionic distances, when the cationic and anionic charges are each doubled from NaF to MgO, the magnitude of lattice energy more than quadrupled.

Hence, the ionic charges have a greater effect on the magnitude of lattice energy.

(c)(i)



(Diagram should include lone pair of electrons on O, dipoles on O–H and labelling of the interaction)

(c)(ii) The energy released from the formation of the ion-dipole interactions between Na^+ and Cl^- ions with water compensate for the energy required to break the ionic bonds in NaCl , whereas the significantly weaker interactions formed between Na^+ and Cl^- ions and hexane is unable to do so.

(d)(i) When NH_4Cl dissolves, the NH_4^+ and Cl^- ions are no longer held in fixed positions in the ionic lattice as they become free-moving aqueous ions, increasing the disorder, resulting in a positive ΔS^\ominus .

(d)(ii) ΔG^\ominus is negative since NH_4Cl dissolves spontaneously in water at 298 K without any external assistance.

(d)(iii) For NH_4Cl to dissolve in water, $\Delta G^\ominus < 0$ i.e.

$$\Delta H^\ominus - T\Delta S^\ominus < 0$$

$$15.2 - T\left(\frac{73.5}{1000}\right) < 0$$

$$T > 207 \text{ K}$$

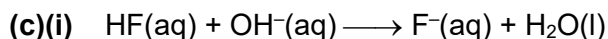
$$\text{Minimum } T = 207 \text{ K}$$

At 207 K i.e. -66°C , water exists as solid ice which NH_4Cl is unable to dissolve in.

Question 3

(a) More energy is required to break the stronger H–F bond (bond energy = 562 kJ mol^{-1}) than the H–C/ (bond energy = 431 kJ mol^{-1}) in the dissociation of the acids.

(b) $[\text{H}^+] = \sqrt{0.0500 \times 5.62 \times 10^{-4}}$
 $= 0.005301 \text{ mol dm}^{-3}$
 $\text{pH} = -\log(0.005301) = 2.28$



Note: students should make use of H_3O^+ (as specified in the question) instead of H^+ .

(c)(ii) In the mixture, there is no reservoir of undissociated HCl to react with and remove any OH^- added. Therefore, the mixture is unable to act as a buffer. **OR**

Cl^- is a very weak base as it is the conjugate base of a strong acid (HCl) and is unable to react with and remove any H_3O^+ added. Therefore, the mixture is unable to act as a buffer.

(c)(iii) Amount of NaF in 200 cm^3 of buffer **T** prepared = $\left(\frac{100}{1000}\right)(1.78) = 0.178 \text{ mol}$

Amount of NaF in 75.0 cm^3 of buffer **T**
 $= \left(\frac{75}{200}\right)(0.178)$
 $= 0.06675 \text{ mol}$

Amount of H^+ from $\text{H}_2\text{SO}_4(\text{aq})$
 $= 2\left(\frac{50.0}{1000}\right)(0.100) = 0.0100 \text{ mol}$

Since F^- from NaF reacts with H^+ added, amount of F^- remaining
 $= 0.06675 - 0.0100 = 0.05675 \text{ mol}$

$$[\text{F}^-]_{\text{remaining}} = \frac{0.05675}{\frac{50.0 + 75.0}{1000}} = 0.454 \text{ mol dm}^{-3}$$

(d)(i) The pK_a value of CCl_3COOH is smaller than CH_3COOH and tells us that the extent of dissociation of CCl_3COOH is greater than that of CH_3COOH .

(d)(ii) $x = 0.2$. F is more electronegative than Cl and exerts a stronger electron-withdrawing effect which disperses the negative charge on $-\text{COO}^-$ to a greater extent, making CF_3COO^- more stable than CCl_3COO^- . Hence, CF_3COOH is a stronger acid with a smaller value of pK_a .

- (e)(i) Let the solubility of CaF_2 be $s \text{ mol dm}^{-3}$. At equilibrium, $[\text{Ca}^{2+}] = s \text{ mol dm}^{-3}$ and $[\text{F}^-] = 2s \text{ mol dm}^{-3}$.

$$K_{sp} = (s)(2s)^2 = 3.90 \times 10^{-11}$$

$$s = 0.0002136 \text{ mol dm}^{-3}$$

$$[\text{F}^-] = 2s = 2(0.0002136)$$

$$= 0.000428 \text{ mol dm}^{-3}$$

- (e)(ii) In acidic solutions, H^+ reacts with F^- to form HF , causing the $[\text{F}^-]$ to be lower. This causes the position of equilibrium of $\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{F}^-(\text{aq})$ to shift right to counteract the decrease in $[\text{F}^-]$, causing more CaF_2 to dissolve.

Question 4

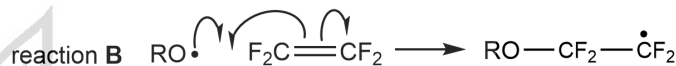
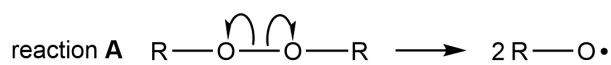
- (a) PTFE is a saturated organic compound containing a large number of C-F (485 kJ mol^{-1}) and C-C (350 kJ mol^{-1}) bonds which are very strong and require a lot of energy to break, making PTFE chemically unreactive.
- (b) In the atmosphere, UV light provides sufficient energy to break the C-Cl bond in CHCl_3 to form $\text{C}\cdot$ radicals which react with ozone, depleting the ozone in the atmosphere.
- (c) High temperature and low pressure.
- (d)(i) It is the breaking of a covalent bond such that one electron goes to each of the atoms, forming free radicals.

(d)(ii)

reaction	name
A	Initiation
B	Propagation
C	Propagation
D	Termination

- (d)(iii) Free radical addition

(d)(iv)



(d)(v) $\text{RO-OR} + 12 \text{ F}_2\text{C}=\text{CF}_2 \longrightarrow \text{product}$

		BE / kJ mol^{-1}
Bonds broken	1 O-O bond	1(150)
	12 carbon-carbon π bonds (Note: this can also be seen as *breaking 12 $\text{C}=\text{C}$ & **forming 12 $\text{C}-\text{C}$)	12(*610 - **350)
Bonds formed	2 C-O bonds	2(860)
	11 C-C bonds	11(350)

$$\Delta H_r^\ominus$$

$$= 150 + 12(610 - 350) - 2(860) - 11(350)$$

$$= -1300 \text{ kJ mol}^{-1}$$

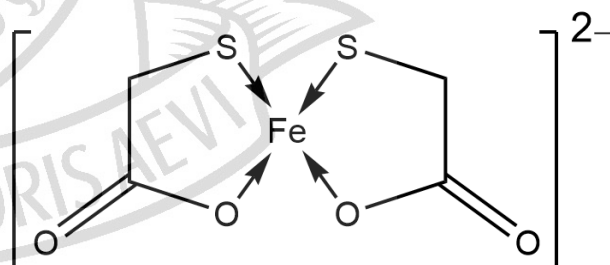
- (d)(vi) Free radical **P** would be the major species because it is a secondary radical and the p-orbital containing the lone-electron overlaps with the π -electron cloud of benzene, allowing radical **P** to be resonance stabilized.

(**Q** is a primary radical with only one electron-donating group and the absence of any resonance stabilisation of radical.)

Question 5

- (a) Thioglycolic acid acts as a reducing agent as it reduces Fe^{3+} to Fe^{2+} as shown in equation 5.1.

(b)



- (c) Ammonia was added to react with thioglycolic acid to form the corresponding anion, which can then complex with Fe^{2+} to form the pink-coloured complex, **M**.

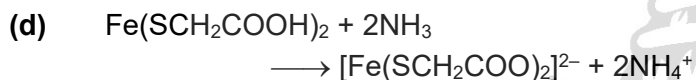
OR

Ammonia was added to provide the basic conditions necessary for thioglycolic acid to complex with Fe^{2+} to form the pink-coloured complex, **M**.

$$\text{Amount of Z} = \frac{1}{560.0} = 0.001786 \text{ mol}$$

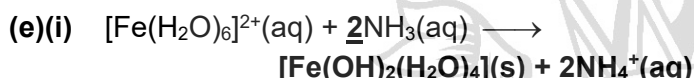
$$\begin{aligned} \text{Mole ratio of Z : Fe} \\ &= 0.001786 : 1.78 \times 10^{-3} \\ &= 1 : 1 \end{aligned}$$

Since the complex of **Z** and Fe is an octahedral complex, 1 mol of **Z** forms 6 dative bonds with the central Fe i.e. each **Z** forms six bonds.



Question 6

(a)(i)



- (e)(ii) Green ppt of $\text{Fe}(\text{OH})_2$ is oxidized by O_2 in the air to form a brown ppt of $\text{Fe}(\text{OH})_3$.

- (f) 10.0 ppm of Fe^{2+}
 $= 10.0 \times 10^{-3} \text{ g of Fe}^{2+} \text{ in } 1000 \text{ cm}^3 \text{ of solvent}$

$$\begin{aligned} \text{Mass of Fe}^{2+} \text{ in } 100 \text{ cm}^3 \text{ solution} \\ &= 1.0 \times 10^{-3} \text{ g of Fe}^{2+} \end{aligned}$$

$$\begin{aligned} \text{Amount of Fe}^{2+} \text{ in } 100 \text{ cm}^3 \text{ solution} \\ &= \frac{1.0 \times 10^{-3}}{55.8} = 1.792 \times 10^{-5} \text{ mol} \\ &= \text{Amount of Fe}^{2+} \text{ in } 10.00 \text{ cm}^3 \text{ solution} \\ &\text{drawn from } 250 \text{ cm}^3 \text{ volumetric flask.} \end{aligned}$$

$$\begin{aligned} \text{Amount of Fe}^{2+} \text{ in } 250 \text{ cm}^3 \text{ volumetric flask} \\ &= \left(\frac{250}{10}\right)(1.792 \times 10^{-5}) = 4.48 \times 10^{-4} \text{ mol} \\ &= \text{amount of Fe}^{2+} \text{ from } x \text{ g of solid} \end{aligned}$$

$$x = (4.48 \times 10^{-4})(392.0) = 0.176 \text{ g}$$

- (g) Amount of **Y** $= \frac{1}{139} = 0.007194 \text{ mol}$
Mole ratio of **Y** : Fe
 $= 0.007194 : 2.40 \times 10^{-3}$
 $= 3 : 1$

Since the complex of **Y** and Fe is an octahedral complex, 3 mol of **Y** forms 6 dative bonds with the central Fe i.e. each **Y** forms two bonds.

Element	Cr	H	N	S	Cl	O
No. of moles	$\frac{19.4}{52} = 0.3731$	$\frac{5.6}{1} = 5.6$	$\frac{26.1}{14} = 1.864$	$\frac{11.9}{32.1} = 0.3707$	$\frac{13.2}{35.5} = 0.3718$	$\frac{23.8}{16} = 1.488$
Mole ratio						
(divide by 0.3707 throughout)	1	15	5	1	1	4

Using the above mole ratio of the elements, the formula of complex **A** is $\text{CrH}_{15}\text{N}_5\text{SClO}_4$ since the M_r of the empirical formula is the same as that of complex **A**.

- (a)(ii) Since both complex cations contain 6 ligands, the shape of each complex cation is octahedral. The bond angle is 90° .



- (a)(iv) Reaction of **A** with $\text{HNO}_3(\text{aq})$ followed by AgNO_3 gave white ppt implies that **A** contains a chloride ion as the counter-anion i.e. the complex cation has the formula $[\text{CrH}_{15}\text{N}_5\text{SO}_4]^+$.

A has 2 different types of ligands, we can deduce from the formula that there is 1 SO_4^{2-} and 5 NH_3 ligands.

Complex ion in **A** is $[\text{Cr}(\text{NH}_3)_5(\text{SO}_4)]^+$.

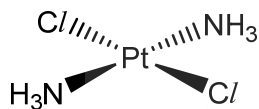
- (b)(i) Due to the higher proportion of H_2O in the cell, when cisplatin enters the cell, the position of equilibrium of equation 6.1 shifts

to the right, causing a significant amount of chloride to be substituted. **OR**

Due to the lower concentration of chloride in the cell, when cisplatin enters the cell, the position of equilibrium of equation 6.1 shifts to the right to increase the concentration of chloride in the cell, causing a significant amount of chloride to be substituted.

(b)(ii) The ligands contain electron pairs which can be donated to the central Pt ion to form dative covalent bonds.

(b)(iii)



(b)(iv) The 2 specific ligands on DNA are a specific distance from each other and the distance matches the distance of the 2 cis-H₂O groups in cis-[Pt(NH₃)₂(H₂O)₂]²⁺ which the specific ligands on DNA will substitute.

For the trans-[Pt(NH₃)₂(H₂O)₂]²⁺ from transplatin, the 2 trans-H₂O groups are much further away and do not match the specific distance of the ligands on DNA.

(c) Before heating, plane-polarised light passes through undisturbed because **D** has a plane of symmetry and is not optically active.

After heating, plane polarized light still passes through the sample undisturbed. The final mixture contains **D** (optically inactive) and a 1:1 ratio of **C** and **E**. Isomers **C** and **E** are enantiomers. Since **C** and **E** are in a 1:1 ratio, the optical activity of **C** is exactly cancels out the optical activity of **E**.

Question 2

- (a)(i) For an ideal gas, the size of the gas particles is negligible compared to the volume of the container.

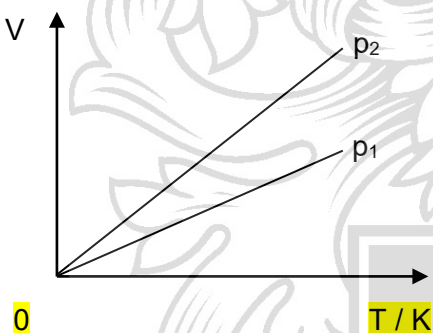
The gas particles **exert negligible attractive forces** on one another.

Collisions between the gas particles are perfectly **elastic**.

(a)(ii) $pV = nRT$
 $V = \left(\frac{nR}{p}\right)T$

Each graph is a straight line with a positive gradient of $\left(\frac{nR}{p}\right)$ passing through the origin.

Since $p_1 > p_2$, $\left(\frac{nR}{p_1}\right) < \left(\frac{nR}{p_2}\right)$ i.e. gradient at p_1 is less steep than gradient at p_2 .



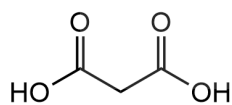
(b) $pV = nRT$
 $pV = \left(\frac{m}{M_r}\right)RT$
 $\frac{m}{V} = \frac{pM_r}{RT}$

density in $\text{g m}^{-3} = \frac{pM_r}{RT}$
 $= \frac{(700)(44)}{(8.31)(273 - 65)}$
 $= 17.82 \text{ g m}^{-3}$

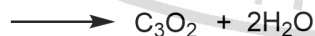
$1 \text{ m}^3 = 10^6 \text{ cm}^3 \rightarrow 17.82 \text{ g}$
 $1 \text{ cm}^3 \rightarrow 1.782 \times 10^{-5} \text{ g}$

Average surface density = $1.78 \times 10^{-5} \text{ g cm}^{-3}$

(c)



skeletal formula of propanedioic acid



(d) $M_r(\text{H}_2\text{O}) = 2(1.0) + 16.0 = 18.0$
 $M_r(\text{CO}_2) = 12.0 + 2(16.0) = 44.0$

Amount of $(\text{CO}_2)_8(\text{H}_2\text{O})_{46}$

$= \frac{650000}{8(44.0) + 46(18.0)}$
 $= 550.8 \text{ mol}$

1 mol of $(\text{CO}_2)_8(\text{H}_2\text{O})_{46}$ required 8 mol of CO_2 to form.

Amount of $\text{CO}_2 = 8(550.8) = 4406 \text{ mol}$

Volume of CO_2 at rtp
 $= 4406(24.0) = 106\,000 \text{ dm}^3$

- (e)(i) The shape is linear about each C atom in ethyne. On each of the C atom, one sp hybrid orbital overlaps head-on with the 1s orbital of H to form a σ -bond; another sp hybrid orbital overlaps head-on with the sp hybrid orbital of the other C atom to form another σ -bond.

The two unhybridised p-orbitals of one C atom overlaps side-on with the two unhybridised p-orbitals of the other C atom to form 2 π -bonds.

These result in a triple bond between the 2 C atoms.

(e)(ii)

	$2\text{CH}_4(\text{g})$	$\rightleftharpoons \text{C}_2\text{H}_2(\text{g})$	$+ 3\text{H}_2(\text{g})$
Initial amt / mol	0.800	0	0
Change in amt / mol	$-0.6(0.80)$ $= -0.48$	$0.5(+0.48)$ $= +0.24$	$1.5(+0.48)$ $= +0.72$
Eqm amt / mol	0.32	0.24	0.72

Total amount of gases at eqm
 $= 0.32 + 0.24 + 0.72 = 1.28 \text{ mol}$

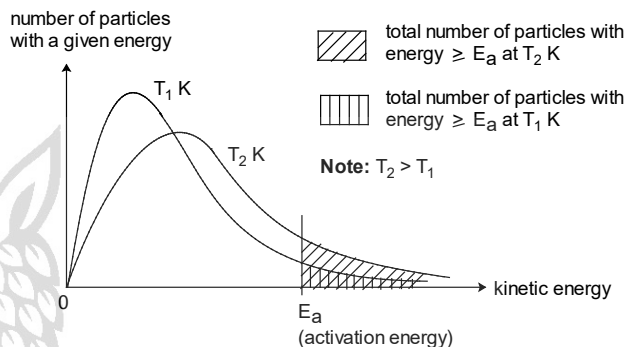
Eqm partial pressure of CH_4
 $= \frac{0.32}{1.28} \times 2.50 \times 10^6 = 625000 \text{ Pa}$

Eqm partial pressure of C_2H_2
 $= \frac{0.24}{1.28} \times 2.50 \times 10^6 = 468800 \text{ Pa}$

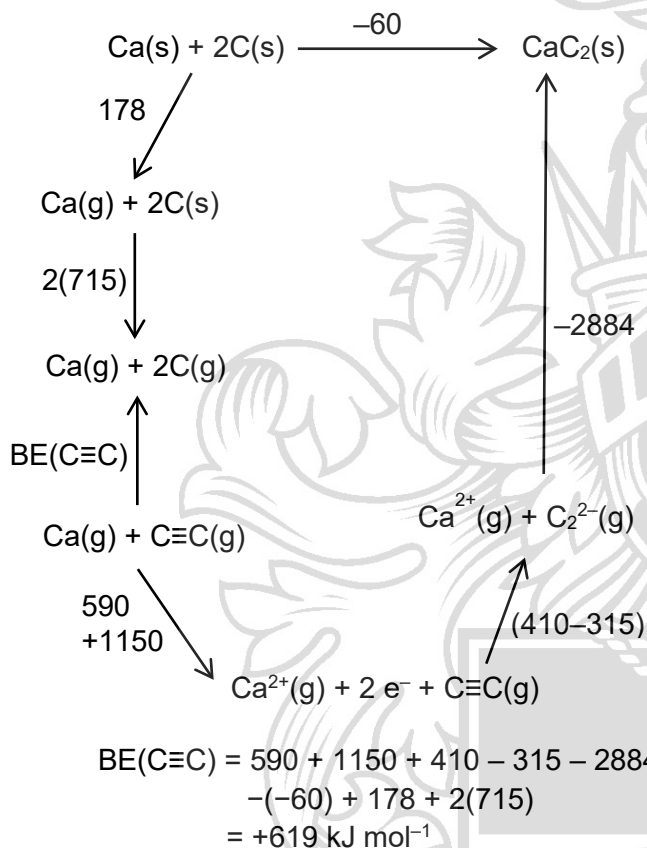
Eqm partial pressure of H_2
 $= \frac{0.72}{1.28} \times 2.50 \times 10^6 = 1406000 \text{ Pa}$

$$K_p = \frac{(468800)(1406000)^3}{(625000)^2}$$

$$= 3.34 \times 10^{12} \text{ Pa}^2$$



(f)



(b) The order of reaction is the power to which the concentration of a reactant is raised in the rate equation.

The rate constant of a reaction is the constant of proportionality in the rate equation of the reaction.

(c)(i) Step 1: rate = $k_f[\text{O}_3]$

Step 2: rate = $k_2[\text{O}_3][\text{O}]$

(c)(ii) At equilibrium, rate of forward reaction of step 1 = rate of reverse reaction of step 1

i.e. $k_f[\text{O}_3] = k_r[\text{O}][\text{O}_2]$

$$[\text{O}] = \frac{k_f[\text{O}_3]}{k_r[\text{O}_2]}$$

(c)(iii) Since step 2 is the slow step, rate = $k_2[\text{O}_3][\text{O}]$.

Using expression from (c)(ii),

$$\text{rate} = k_2[\text{O}_3][\text{O}] = k_2[\text{O}_3] \frac{k_f[\text{O}_3]}{k_r[\text{O}_2]} = \frac{k_2 k_f [\text{O}_3]^2}{k_r [\text{O}_2]}$$

order of reaction wrt $\text{O}_3 = 2$

order of reaction wrt $\text{O}_2 = -1$

overall order of reaction = $2 + (-1) = 1$

Question 3

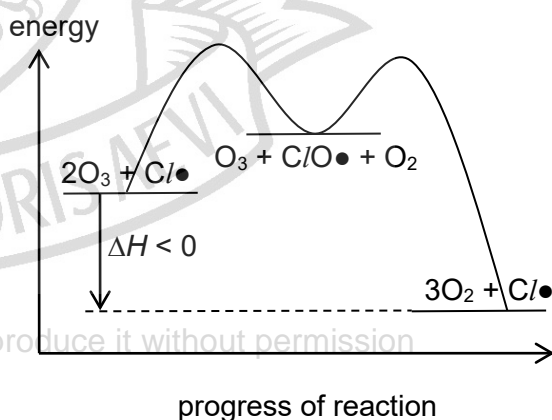
(a) As temperature increases from T_1 to $T_2 \text{ K}$, the average kinetic energy of the reactant particles increases. As such, significantly more reactant particles have energy greater than or equal to the activation energy of the reaction. This is shown by the significantly larger shaded area at a higher temperature in the diagram below.

Consequently, the frequency of effective collisions increases accordingly, and hence the reaction rate increases.

An increase in temperature also results in a larger rate constant, and hence an increase in the reaction rate.

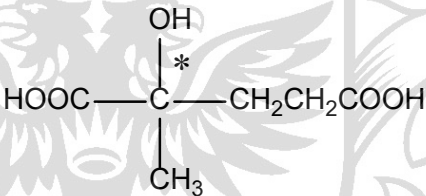
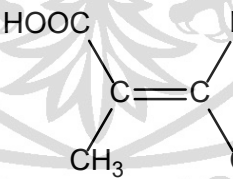
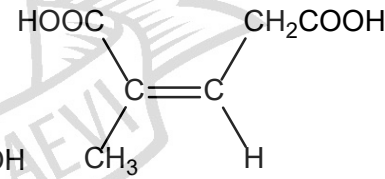
(d)(i) $\text{Cl}\cdot$ is a homogeneous catalyst as it is in the same phase as the reactant, O_3 , and is consumed in step 1 and regenerated in step 2.

(d)(ii)



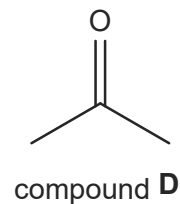
- (e)(i) Ni acts as a heterogeneous catalyst. Molecules of A and H₂ diffuse and are adsorb onto the surface of the Ni catalyst by forming weak interactions with Ni. This increases the concentration of A and H₂ at the catalytic surface, the reactant molecules are brought closer together with the correct orientation, and the covalent bonds within A and H₂ are weakened which reduces the activation energy for the reaction. A and H₂ then react on the Ni surface before they desorb and diffuse from the surface of the Ni catalyst, regenerating active sites for other A and H₂ molecules.

(e)(ii)

Observations	Deductions
$\text{A}(\text{C}_{10}\text{H}_{18}\text{O}) \xrightarrow{\text{excess H}_2} \text{B}(\text{C}_{10}\text{H}_{22}\text{O})$	Type of reaction : Reduction • Gain of 4 H \Rightarrow A contains 2 unsaturated bonds (C=C or C=O)
$\text{A}(\text{C}_{10}\text{H}_{18}\text{O}) \xrightarrow{\text{excess O}_3} \text{C}(\text{C}_6\text{H}_{10}\text{O}_5) + \text{D} + \text{E}(\text{CH}_2\text{O}_2)$	Type of reaction : Oxidation • A contains 2 C=C since oxidation of A gave 3 products. • D contains 3 carbon atoms.
C, E, F effervesce with Na ₂ CO ₃ (aq)	Type of reaction : Acid-base reaction • C, E and F contain the –COOH group.
$\text{C}(\text{C}_6\text{H}_{10}\text{O}_5) \xrightarrow[\text{H}_2\text{SO}_4]{\text{hot conc}} \text{F}(\text{C}_6\text{H}_8\text{O}_4)$ 1 chiral centre 0 chiral centre 2 stereoisomers C does not react with K ₂ Cr ₂ O ₇	Type of reaction : Elimination of water • Alcohol in C was eliminated to form C=C in F which exhibits cis-trans isomerism • –OH is on chiral carbon in C • Tertiary alcohol in present C We can deduce the following structures. <div style="text-align: center;">  <p>compound C</p> </div> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> </div> <p>compound F</p> <p>Note: Both stereoisomers should be shown.</p>
D gives yellow ppt with alkaline aq iodine, but does not react with Fehling's reagent.	Type of reaction with alkaline aq iodine : Oxidation (positive iodoform test) • No aldehyde present (negative Fehling's test)

- D contains 3 carbons (from previous deduction) and -COCH_3 .

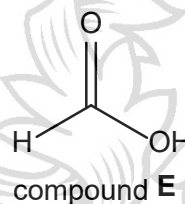
The structure of D is as follows.



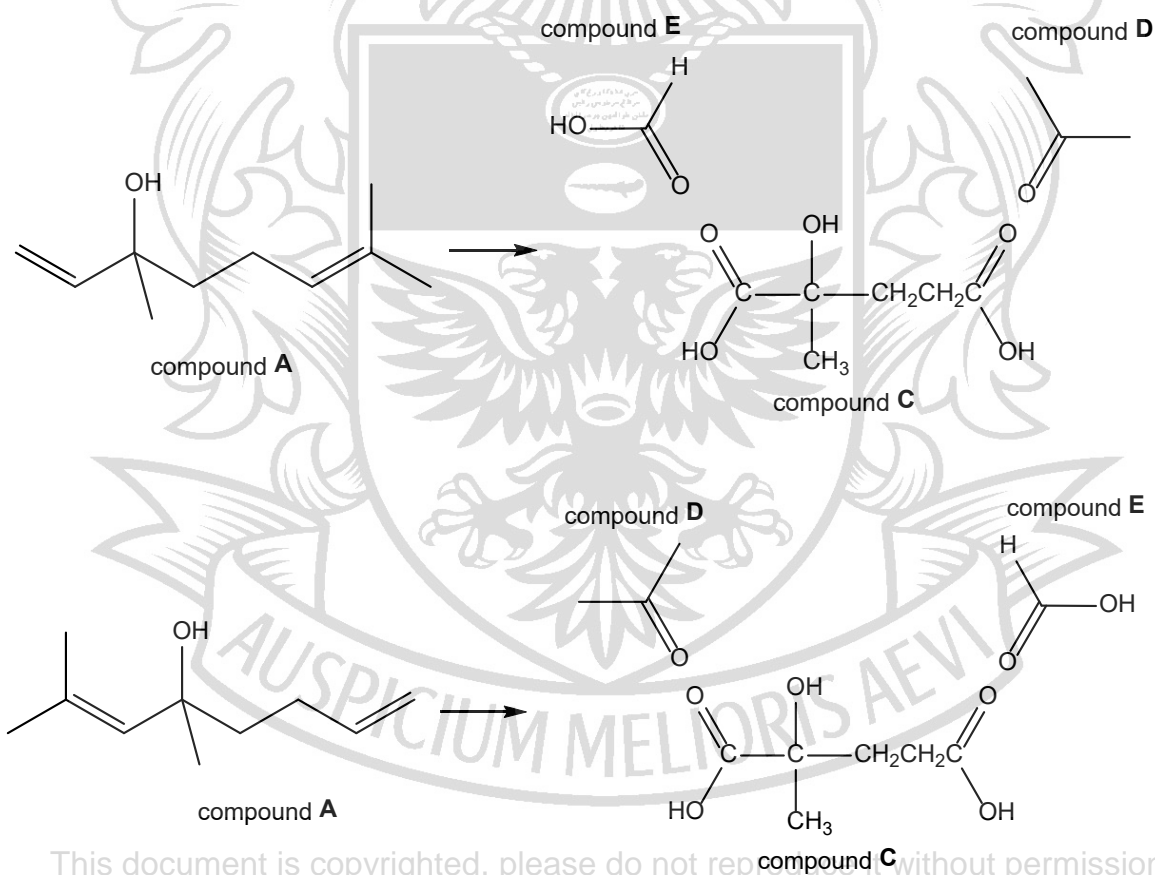
E (CH_2O_2)

- E contains -COOH (from previous deduction)

The structure of E is as follows.



Since A ($\text{C}_{10}\text{H}_{18}\text{O}$) $\xrightarrow{\text{excess O}_3}$ C ($\text{C}_6\text{H}_{10}\text{O}_5$) + D + E (CH_2O_2), possible structures of A are shown below.



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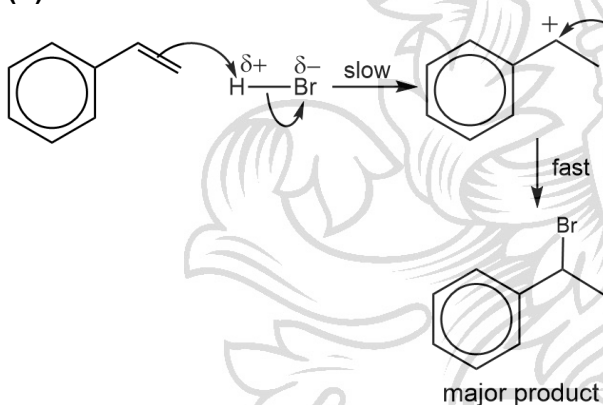
Question 4

- (a) Hydrogen chloride is thermally stable (does not decompose). Hydrogen bromide and hydrogen iodide thermally decompose to give hydrogen gas and their respective halogens as shown in the following equation.



Since the bond energy decreases from HCl to H-Br to HI, the bond strength decreases in the same order. [1] Thus, the thermal stability of the hydrogen halides decreases from H-Cl to H-Br to H-I.

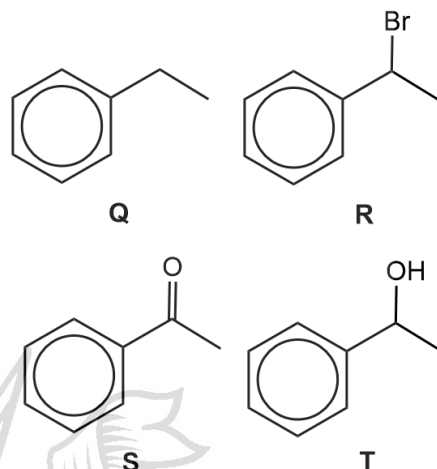
(b)



$\text{C}_6\text{H}_5\text{CH}^+\text{CH}_3$ is a more stable carbocation than $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2^+$ because it is resonance stabilised. In $\text{C}_6\text{H}_5\text{CH}^+\text{CH}_3$ the empty p-orbital of the positively charged carbon overlaps with the π electron cloud of benzene, allowing the π electrons of benzene to delocalize onto the empty p orbital of the positively charged carbon, dispersing the positive charge.

Hence, in the slow step, the more stable 2° carbocation ($\text{C}_6\text{H}_5\text{CH}^+\text{CH}_3$) is formed, instead of the less stable 1° carbocation ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2^+$), which dispersed the positive charge to a greater extent. The 2° carbocation then undergoes reaction with Br^- in the fast step to form the major product.

(c)(i)



(c)(ii)

step 1 : $\text{CH}_3\text{CH}_2\text{Cl}$, AlCl_3 (or FeCl_3)

step 2 : **limited** Br_2 , UV

step 3 : ethanolic KOH , heat

step II : NaBH_4 or LiAlH_4 in dry ether
or H_2 , Ni , heat

step III : excess concentrated H_2SO_4 , heat

(d)

Isomer 4-position will be formed the most.
Isomer 3-position will be formed the least.

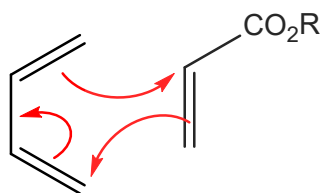
The carbocation intermediates leading to isomer 2-position and isomer 4-position are tertiary carbocations, which have 3 electron-donating alkyl groups attached to the C^+ , which stabilise these carbocations to a greater extent than the secondary carbocation leading to isomer 3-position. Thus, isomer 2-position and isomer 4-position are preferred over isomer 3-position.

The carbocation leading to isomer 2-position has the bulky $-\text{C}(\text{CH}_3)_3$ group in close proximity to the $-\text{NO}_2$ group, causing steric hindrance / additional repulsion between the two groups, which destabilises the carbocation more than in the case of the carbocation leading to isomer 4-position which have the bulky $-\text{C}(\text{CH}_3)_3$ group far away from the $-\text{NO}_2$ group. Thus, isomer

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4-position is preferred over isomer 2-position.

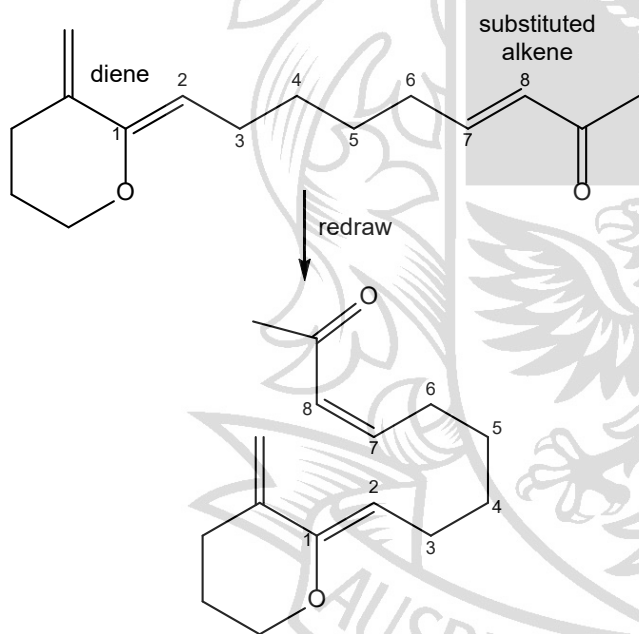
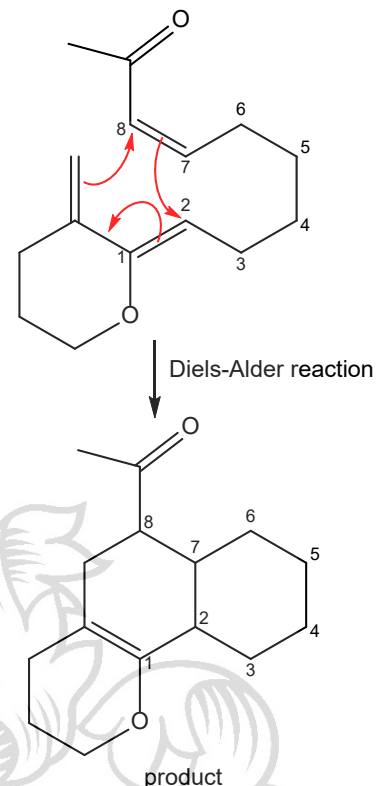
(e)(i)



(e)(ii) The diene can attack the substituted alkene from above or below the plane of the planar alkene of the substituted alkene with equal probability, forming a 1:1 mixture of enantiomers of **X**, causing **X** to have no effect on the plane of polarised light.

(e)(iii) **Note:**

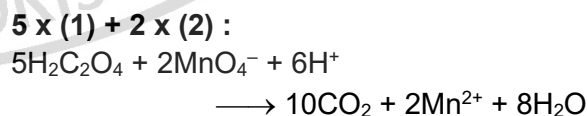
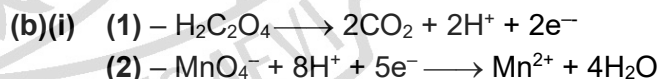
1. Start by redrawing **W** to position the diene and substituted alkene in closer proximity similar to what you see in Fig. 4.3.
2. Numbering the carbons on long chains is a strategy to make sure all carbons atoms are accounted for and not "lost" due to carelessness.



Question 5



Down group 2, the cationic radius increases, resulting in a lower charge density and weaker polarising power of the cations. Consequently, there is decreasing extent of distortion of the electron cloud of the CO_3^{2-} anion and hence decreasing extent of weakening of covalent bonds within the CO_3^{2-} anion. More heat energy is required to break the covalent bonds within the CO_3^{2-} anion, causing the decomposition temperature to increase. Hence, thermal stability of the Group 2 carbonates increases.



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(b)(ii) amount of $\text{MnO}_4^- = \left(\frac{22.4}{1000}\right)(0.001)$
 $= 2.24 \times 10^{-5} \text{ mol}$
 amount of $\text{H}_2\text{C}_2\text{O}_4 = \frac{5}{2}(2.24 \times 10^{-5})$
 $= 5.60 \times 10^{-5} \text{ mol}$



amount of $\text{CaC}_2\text{O}_4 = 5.60 \times 10^{-5} \text{ mol}$
 $= \text{amount of } \text{Ca}^{2+} \text{ in blood}$

mass of Ca^{2+} in blood $= (5.60 \times 10^{-5})(40.1)$
 $= 0.002246 \text{ g}$
 $= 2.25 \times 10^{-3} \text{ g}$
 $= 2.25 \text{ mg}$

(b)(iii) **Note:** since R is $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$, ΔG^\ominus needs to be convert to J mol^{-1} when using the given equation.

$$K_{sp} = 10^{-\frac{49200}{8.31(298)(2.3)}} \\ = 2.30 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$$

(c)(i) $\text{pH} = \text{pK}_a + \lg \frac{[\text{CH}_3\text{CH}(\text{OH})\text{CO}_2^-]}{[\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}]}$

$$6.50 = -\lg(1.38 \times 10^{-4}) + \lg \frac{0.028}{[\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}]}$$

$[\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}]$
 $= 6.42 \times 10^{-5} \text{ mol dm}^{-3}$

(c)(ii) $K_c = \frac{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-][\text{H}_2\text{NCONH}_3^+]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}][\text{H}_2\text{NCONH}_2]}$
 $= 1.74 \times 10^{-4} \text{ --- (1)}$

$$K_a = \frac{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}$$

$$= 1.38 \times 10^{-4} \text{ --- (2)}$$

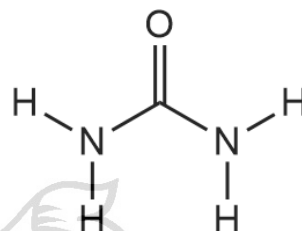
(1)
 (2)
 $= \frac{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-][\text{H}_2\text{NCONH}_3^+]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}][\text{H}_2\text{NCONH}_2]} \times \frac{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-][\text{H}^+]}$
 $= \frac{[\text{H}_2\text{NCONH}_3^+]}{[\text{H}_2\text{NCONH}_2][\text{H}^+]} = 1.26 \text{ --- (3)}$

$$K_b \text{ of urea} = \frac{[\text{H}_2\text{NCONH}_3^+][\text{OH}^-]}{[\text{H}_2\text{NCONH}_2]}$$

Comparing (3) and K_b of urea and since $K_w = [\text{H}^+][\text{OH}^-]$,

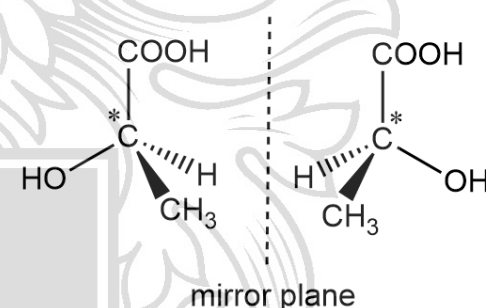
$$K_b \text{ of urea} = (3) \times K_w \\ = 1.26 \times 10^{-14} \text{ mol dm}^{-3}$$

(c)(iii) Urea (H_2NCONH_2) has the following structure.

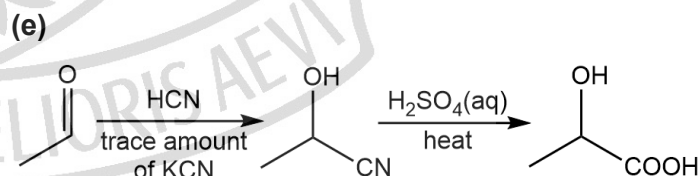
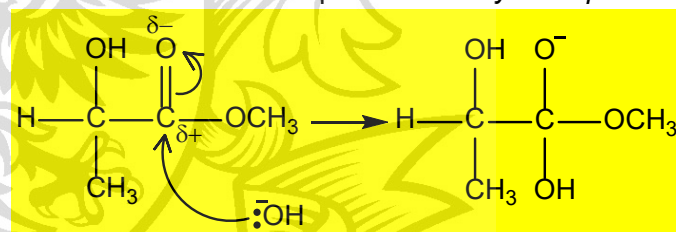


No. of σ -bonds = 7
 No. of π -bonds = 1

(d)(i) Lactic acid has a chiral centre and displays enantiomerism.

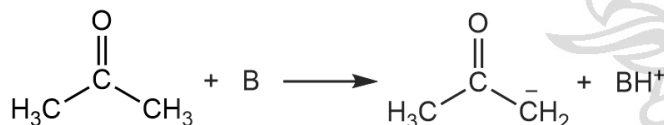


(d)(ii) **Note:** students need to draw from their knowledge of how a nucleophile attacks a $\text{C}=\text{O}$ from the topic of *Carbonyl Compounds*.

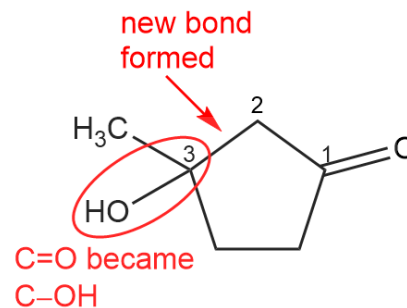
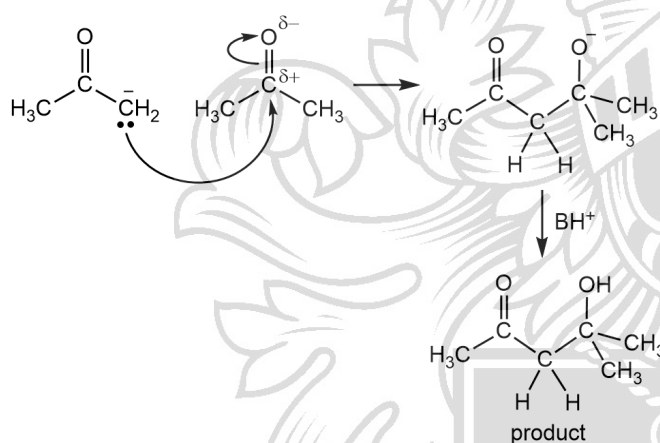


(f)(i) Note: it is important to learn from the information provided in the question stem and equations.

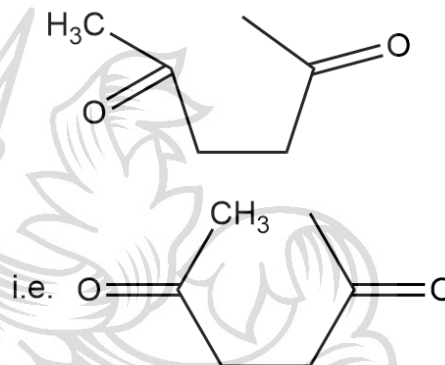
Since the H bonded to a C adjacent to carbonyl can be removed by a base,



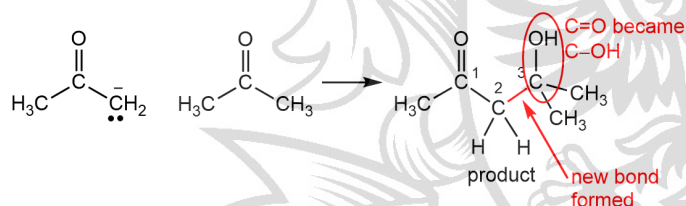
The anion acts as a nucleophile and reacts with the carbonyl group of another propanone.



Working backwards you will obtain **Y** as



(f)(ii) Note: using (f)(i) as an example, you can identify the changes that occur during the reaction.



1. The 2 original carbonyl carbons are three carbons apart in the final product.
2. Location of new bond formed.
3. C=O became C-OH

Applying this analysis to **Z**.

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2022 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

Q1(C)

The ionic bonds in NaF requires the most energy to overcome while the instantaneous dipole-induced dipole in $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ requires the least energy to overcome, thus NaF has the highest boiling point while $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ has the lowest boiling point.

Both $\text{CH}_3\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{CH}_2\text{OH}$ can form an average of one intermolecular hydrogen bond per molecule. The more polar O-H bond in $\text{CH}_3\text{CH}_2\text{OH}$ results in stronger hydrogen bonds between $\text{CH}_3\text{CH}_2\text{OH}$ molecules compared to the less polar N-H bond in $\text{CH}_3\text{CH}_2\text{NH}_2$, thus $\text{CH}_3\text{CH}_2\text{OH}$ has a higher boiling point than $\text{CH}_3\text{CH}_2\text{NH}_2$.

Q2(C)

A	Incorrect. Br is less electronegative than Cl.
B	Incorrect. Having the same outer shell electronic configuration does not explain why the Br-Cl bond is polar.
C	Correct. Since Br has one additional electronic shell than Cl, its outer shell electrons are more shielded from the nuclear charge and hence the shared pair of electrons in the Br-Cl bond is less attracted to Br, making Br less electronegative than Cl, resulting in a polar Br-Cl bond.
D	Incorrect. Since Br and Cl have the same outer shell electronic configuration, the repulsion between electrons in the outer shell will be similar in both atoms.

Q3(D)

1	Incorrect. Ethanoic acid has a higher pK_a and hence smaller K_a , thus is a weaker acid than thioacetic acid. So H^+ is not more easily removed from ethanoic acid.
2	Incorrect. Ethanoic acid has a higher pK_a and hence smaller K_a than thioacetic acid.
3	Correct. Thioacetic acid has a smaller pK_a and hence higher K_a , is a stronger weak acid than ethanoic acid. The weaker S-H bond in thioacetic acid allows for greater extent of ionisation, and at the same concentration, thioacetic acid will form a higher concentration

of H^+ , giving a solution of lower pH than ethanoic acid.

Q4(C)

At the same temperature and pressure, since there is same number of moles of O_2 and N_2O in entonox gas, $P_{\text{O}_2} = P_{\text{N}_2\text{O}}$.

Since $P_T = 3.55 \times 10^7 \text{ Pa}$,

$$P_{\text{N}_2\text{O}} = \frac{3.55 \times 10^7}{2} = 1.775 \times 10^7 \text{ Pa}$$

Assuming N_2O behaves as an ideal gas,

$$pV = nRT = \frac{m}{M_r} RT$$

$$\text{Mass of N}_2\text{O} = \frac{pVM_r}{RT} = \frac{1.775 \times 10^7 \times \frac{5}{1000} \times (14.0 \times 2 + 16.0)}{8.31 \times (273+20)} = 1604 \text{ g} \approx 1.60 \text{ kg}$$

Q5(A)

1	Correct. AlCl_3 hydrolyses in water to give a solution of pH 3, which will cause a vigorous effervescence when added to Na_2CO_3 . $\text{AlCl}_3(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \longrightarrow [\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3\text{Cl}^{-}(\text{aq})$ $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}(\text{aq}) + \text{H}^{+}(\text{aq})$
2	Incorrect. While MgCl_2 hydrolyses slightly in water to give a weakly acidic solution of pH 6.5, it will not give a vigorous effervescence when added to Na_2CO_3 due to the lower concentration of H^+ , resulting in a slower rate of reaction. $\text{MgCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \longrightarrow [\text{Mg}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$ $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) \rightleftharpoons [\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]^{+}(\text{aq}) + \text{H}^{+}(\text{aq})$
3	Incorrect. NaCl does not undergo hydrolysis in water to produce H^+ and hence would not react with Na_2CO_3 .

Q6(B)

Since X is more electronegative than Arsenic, X is P (adjacent and above Arsenic in Group 15) as electronegativity decreases down a group. Since Y is more electronegative than X, Y is S (adjacent and in the same period as P) as electronegativity increases across a period. Thus proton number of Y is 16.

Q7(A)

In 1 g of solder glass, there is 0.16 g of B_2O_3 and 0.84 g of PbO .

$$n_B \text{ in } 0.16 \text{ g of } B_2O_3 = \frac{0.16}{(10.8 \times 2 + 16.0 \times 3)} \times 2 = 0.0045977 \text{ mol}$$

$$n_{Pb} \text{ in } 0.84 \text{ g of } PbO = \frac{0.84}{(207.2 + 16.0)} = 0.0037634 \text{ mol}$$

$$\frac{n_{Pb}}{n_B} = \frac{0.0037634}{0.0045977} = 0.8185 \approx 0.82$$

Q8(B)

Since more energy is required to remove an electron from an inner electronic shell and J and M have a higher sixth ionisation energy than G and H, J and M must be from Group 15 while G and H must be from the Group 16.

Since sixth ionisation energy decreases down the group and H has a higher sixth ionisation energy than J, so H must be above J in the Periodic Table and thus in Period 3.

Q9(B)

Outershell electronic configuration of I^- : $5s^2 5p^6$

Outershell electronic configuration of Xe : $5s^2 5p^6$

Outershell electronic configuration of Cs^+ : $5s^2 5p^6$

Since I^- , Xe and Cs^+ are isoelectronic, they have the same shielding effect. As nuclear charge increases from I^- to Xe to Cs^+ , more energy is required to remove the valence electron in Cs^+ than Xe than I^- due to stronger electrostatic attraction between valence electron and nucleus. Hence, $\Delta H_1 > \Delta H_3 > \Delta H_2$.

Q10(D)

Since $\left| \text{lattice energy} \right| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$ and all the cations have the same charge and all the anions have the same charge, the solid chloride with the smaller cationic radius will have the most exothermic lattice energy as chloride has a smaller anionic radius. From the *Data Booklet*, the cation radius of $Pb^{2+} = 0.120 \text{ nm}$ while that of $Zn^{2+} = 0.074 \text{ nm}$. Thus, $ZnCl_2$ will have the smallest interionic radii and most exothermic lattice energy.

Q11(D)

The increase in the number of moles of gaseous particles in the reaction causes $\Delta S^\ominus > 0$. Since, $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ and $\Delta S^\ominus > 0$, $\Delta H^\ominus < 0$, $\Delta G^\ominus < 0$ at all temperatures, thus the reaction is spontaneous at all temperatures.

Q12(C)

Since lead(IV) oxide remained chemically unchanged and increased the rate of reaction, it is acting as a catalyst. The activation energy of experiment 1 (uncatalysed) will be higher than experiment 2 (catalysed) and the rate constant in experiment 2 will be higher as the catalyst increases the rate constant by lowering the activation energy ($k = Ae^{\frac{-E_a}{RT}}$).

Q13(B)

	$2SO_2(g)$	+	$O_2(g)$	\rightleftharpoons	$2SO_3(g)$
initial amt. / mol	2.00		2.00		0
change / mol	-1.80		-0.90		+1.80
eqm. amt. / mol	0.20		1.10		1.80

Converting number of moles to concentration,

$$K_c = \frac{\left(\frac{1.80}{0.500}\right)^2}{\left(\frac{0.20}{0.500}\right)^2 \times \left(\frac{1.10}{0.500}\right)} \approx 36.8$$

Q14(B)

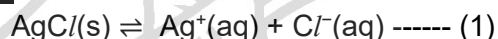
$$pH = pK_a + \lg \left(\frac{[HCO_3^-]}{[H_2CO_3]} \right)$$

$$7.4 = -\lg (2.5 \times 10^{-4}) + \lg \left(\frac{[HCO_3^-]}{[H_2CO_3]} \right)$$

$$7.4 + \lg (2.5 \times 10^{-4}) = \lg \left(\frac{[HCO_3^-]}{[H_2CO_3]} \right)$$

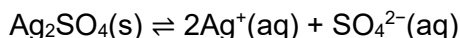
$$10^{7.4 + \lg (2.5 \times 10^{-4})} = \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\frac{[H_2CO_3]}{[HCO_3^-]} = 1.6 \times 10^{-4}$$

Q15(C)

Solubility of silver chloride will increase when $NH_3(aq)$ is added, due to the formation of soluble $Ag[(NH_3)_2]^+$ complex ion, which will shift the position of equilibrium of (1) to the right.

Solubility of silver chloride will decrease when $NaCl(aq)$ is added, due to the presence of the common ion Cl^- which increases the concentration of Cl^- , shifting the position of equilibrium of (1) to the left.

Q16(C)

Let the solubility of Ag_2SO_4 in water be $s \text{ mol dm}^{-3}$.

At equilibrium in the saturated solution,

$$[\text{Ag}^+] = 0.032 \text{ mol dm}^{-3}$$

$$[\text{SO}_4^{2-}] = 0.032/2 = 0.016 \text{ mol dm}^{-3}$$

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = 0.032^2 \times 0.016$$

$$K_{\text{sp}} = 1.6384 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$$

Let the solubility of Ag_2SO_4 in 0.50 mol dm^{-3} Na_2SO_4 solution be $y \text{ mol dm}^{-3}$.



At equilibrium in the saturated solution,

$$[\text{Ag}^+] = y \text{ mol dm}^{-3}$$

$$[\text{SO}_4^{2-}] = \frac{y}{2} + 0.50 \text{ mol dm}^{-3}$$

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = y^2 \times \left(\frac{y}{2} + 0.50\right) = 1.6384 \times 10^{-5}$$

Since Ag_2SO_4 is sparingly soluble in water and the presence of SO_4^{2-} ions from Na_2SO_4 further suppresses its solubility, $\frac{y}{2} \ll 0.50$. Thus, $\left(\frac{y}{2} + 0.50\right) \approx 0.50$.

$$y^2 \times (0.50) = 1.6384 \times 10^{-5}$$

$$y = 5.7 \times 10^{-3} \text{ mol dm}^{-3}$$

Hence, solubility of Ag_2SO_4 in 0.50 mol dm^{-3}

$$\text{Na}_2\text{SO}_4 = 5.7 \times 10^{-3} \text{ mol dm}^{-3}.$$

Q17(A)

1	Incorrect. $(\text{CH}_3)_3\text{C}^\bullet + \cdot\text{Cl} \longrightarrow (\text{CH}_3)_3\text{C}-\text{Cl}$
2	Correct. $(\text{CH}_3)_3\text{C}-\text{Cl} \longrightarrow (\text{CH}_3)_3\text{C}^+ + ^-\text{Cl}$ <p style="text-align: center;">carbocation</p>
3	Correct. $(\text{CH}_3)_3\text{C}-\text{OH}_2^+ \longrightarrow (\text{CH}_3)_3\text{C}^+ + \text{H}_2\text{O}$ <p style="text-align: center;">carbocation</p>
4	Incorrect. $(\text{CH}_3)_2\text{C}^\bullet-\text{Cl} \longrightarrow (\text{CH}_3)_2\text{C}=\text{O} + ^-\text{Cl}$

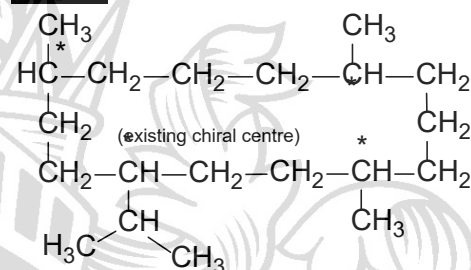
Q18(C)

1	Correct. Enantiomers interact differently with other chiral molecules.
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2	Incorrect. Enantiomers have the same chemical properties and are stereoisomers.
3	Incorrect. Enantiomers have identical physical properties except in the direction in which they rotate plane-polarised light.

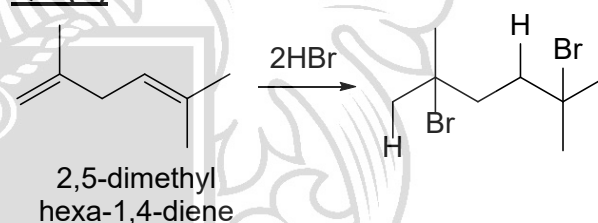
Q19(B)

Since the $\text{CH}_2=\text{CHCH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CHO}$ have the same molecular formula but different structural formula, they are isomers and the type of reaction is isomerisation.

Q20(C)

product of hydrogenation

3 new chiral centres are formed in this reaction.

Q21(A)

Major product of electrophilic addition of alkenes with HBr is formed via the more stable tertiary carbocation.

Q22(B)

1	Correct. Since a racemic mixture is obtained, there must be an equal likelihood of reaction arising from the intermediate which has a plane of symmetry.
2	Incorrect. There is only intermediate in the reaction and the presence of a plane symmetry means that their mirror images are superimposable and are the same.
3	Incorrect. Since the reaction resulted in a racemic mixture instead of inversion of configuration, the reaction proceeded via the $\text{S}_{\text{N}}1$ mechanism.

Q23(B)

NaOH(aq) favours in nucleophilic substitution while or ethanolic NaOH favours elimination reaction. The compounds were warmed with NaOH in aqueous ethanol so both types of reactions are possible.

compound	precipitate produced with AgNO ₃ (aq)	precipitate remains with NH ₃ (aq)
	compound undergo substitution with NaOH(aq), to form I ⁻ which gives AgI as a ppt.	AgI does not dissolve in excess NH ₃ (aq) so ppt remains
	compound undergo substitution with NaOH(aq) to form Cl ⁻ which gives AgCl as a ppt.	AgCl dissolves in excess NH ₃ (aq) to give a colourless solution so no ppt remains
	compound cannot undergo elimination nor substitution with NaOH (ethanol), no ppt formed.	-
	compound can undergo elimination with NaOH (ethanol) and also substitution with NaOH(aq) to form I ⁻ which gives AgI as a ppt.	AgI does not dissolve in excess NH ₃ (aq) so ppt remains

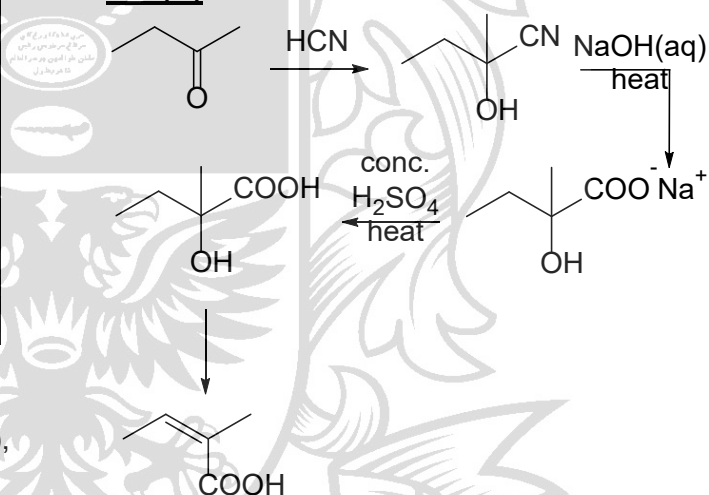
Q24(B)

To rotate plane polarised light (i.e. optically active), the molecule cannot have a plane of symmetry.

⇒ A molecule with only one chiral carbon will not have a plane of symmetry and is optically active.

1	Correct. <ul style="list-style-type: none"> Has only one chiral carbon. Absence of plane of symmetry.
2	Correct.

	<ul style="list-style-type: none"> Has two chiral carbons. Absence of plane of symmetry.
3	Incorrect. <ul style="list-style-type: none"> Has two chiral carbons. Presence of plane of symmetry.
4	Incorrect. [same molecule as option 3] <ul style="list-style-type: none"> Has two chiral carbons. Presence of plane of symmetry.

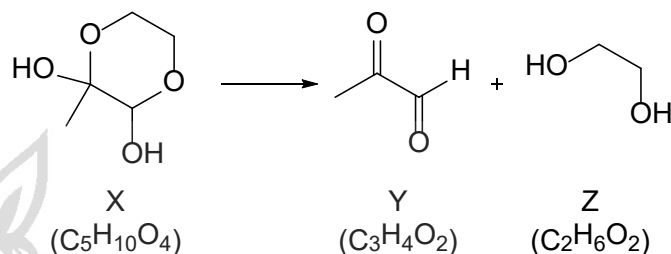
Q25(D)

Butanone undergoes nucleophilic addition with HCN to form cyanohydrin before the -CN group is hydrolysed with NaOH before being acidified while the alcohol is eliminated to form an alkene.

Note: The alkaline hydrolysis of cyanohydrin is not preferred because it can cause the backwards reaction of step 1 to occur. This was discussed in the Carbonyl Compounds lecture notes. However, for this question, this route is the only one which can produce the product.

Q26(D)

A	Incorrect. The conjugate base of HCO_2H , HCOO^- , is more stable than that of $\text{CH}_3\text{CO}_2\text{H}$, CH_3COO^- , due to the absence of the electron-donating $-\text{CH}_3$ group which intensifies the negative charge of the carboxylate group. Thus, HCO_2H will be a stronger weak acid with a larger K_a .
B	Incorrect. The conjugate base of $\text{CH}_2\text{C}/\text{CO}_2\text{H}$, $\text{CH}_2\text{C}/\text{COO}^-$, is more stable than that of $\text{CH}_3\text{CO}_2\text{H}$, CH_3COO^- , due to the presence of the electron-withdrawing $-\text{Cl}$ group which disperses the negative charge of the carboxylate group. Thus, $\text{CH}_2\text{C}/\text{CO}_2\text{H}$ will be a stronger weak acid with a larger K_a .
C	Incorrect. Both acids have different K_a and hence different extents of ionization, resulting in different concentrations of their conjugate bases.
D	Correct. The conjugate base of 4-chlorobenzoic acid, is more stable than that of benzoic acid, due to the presence of the electron-withdrawing $-\text{Cl}$ group which disperses the negative charge of the carboxylate group. Thus, 4-chlorobenzoic acid will be a stronger weak acid, with a larger K_a , ionising to a larger extent, resulting in a small concentration of the acid at equilibrium compared to benzoic acid.



Y can undergo reactions with Fehling's solution (presence of aliphatic aldehyde) and 2,4-DNPH (presence of carbonyl group).

Q29(D)

reaction	$E^\ominus_{\text{cell}} / \text{V}$
$\text{Zn(s)} + 2\text{VO}_2^+(\text{aq}) + 4\text{H}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{VO}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)}$	+1.76
$\text{Zn(s)} + 2\text{VO}^{2+}(\text{aq}) + 4\text{H}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{V}^{3+}(\text{aq}) + 2\text{H}_2\text{O(l)}$	+1.10
$\text{Zn(s)} + 2\text{V}^{3+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{V}^{2+}(\text{aq})$	+0.50
$\text{Zn(s)} + \text{V}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{V(s)}$	-0.44

Zinc is able to reduce VO_2^+ to V^{2+} (violet) as $E^\ominus_{\text{cell}} > 0$ for first three reactions given in the table. However, zinc is unable to further reduce V^{2+} to V since $E^\ominus_{\text{cell}} < 0$ (non-spontaneous).

Since $E^\ominus(\text{Sn}^{2+}/\text{Sn}) = -0.14\text{V}$ and $E^\ominus(\text{V}^{3+}/\text{V}^{2+}) = -0.26\text{V}$, for this reaction, $E^\ominus_{\text{cell}} < 0$ (non-spontaneous) and Sn is only able to reduce VO_2^+ to V^{3+} (green).

Q30(D)

The electron being removed comes from the 4s orbital. Across a period, proton number increases and thus nuclear charge increases. As electrons are added to the 3d subshell, the increase in the number of inner 3d electrons provide more shielding between the nucleus and the outer 4s electrons. This increase in shielding effect offsets the increase in nuclear charge considerably. Thus, energy required to remove the first electron is similar.

Q27(A)

Only the nitrogen atom in the secondary amine is protonated and not the nitrogen atom in the amide. In the amide, the p-orbital on N overlaps with the π -electron cloud of the $\text{C}=\text{O}$ which allows the lone pair of electrons on N to delocalize into the $\text{C}=\text{O}$, reducing the availability of the lone pair on N to form a dative bond with H^+ .

Q28(A)

Y does not react with sodium metal means that there is no $-\text{O}$ group. Y can be oxidized by hot $\text{K}_2\text{Cr}_2\text{O}_7$ means that it contains aldehyde (cannot be alcohol due to above). Y can react with alkaline aqueous iodine means that it contains a methyl ketone (cannot be alcohol due to above).

Solving the identities of Y and Z gives the following

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Question 1

- (a) - F and G
- D
- A and C

(b)(i) Both **C** (parent atom) and **D** (cation of **C**) have the same number of protons and hence the same nuclear charge. However, **C** has one more electronic shell than **D** and the shielding effect experienced by valence electrons in **C** is greater than **D**. Thus, electrostatic attraction between the nucleus and the valence electrons is lower in **C** than **D**, resulting in a larger electron cloud size in **C** than **D**.

(b)(ii) **D** is a cation with 20 protons while **E** is an anion with 18 protons and hence **D** has a greater nuclear charge than **E**. Both **D** and **E** have the same number of electrons and hence have the same shielding effect. Thus, electrostatic attraction between the nucleus and the valence electrons is lower in **E** than **D**, resulting in a larger electron cloud size in **E** than **D**.

Question 2

(a) For any atom, once the first electron is removed from the neutral atom, each successive electron is removed from an ion of increasing positive charge which attracts the electrons more strongly, resulting in an increase in energy required to remove each subsequent electron.

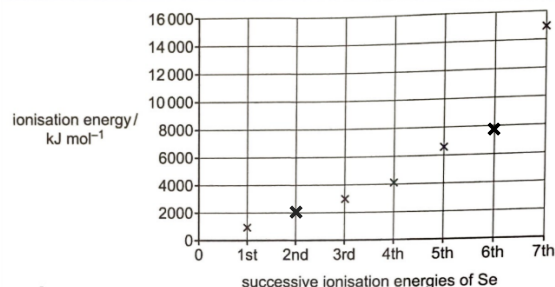
OR

For any atom, the successive ionization energy increases as the number of protons remains the same and hence nuclear charge remains the same. The number of electrons decreases, causing a decrease in shielding effect and hence electrostatic attraction between the nucleus and the remaining electrons increases, resulting in an increase in energy required to remove each subsequent electron.

(b) An atom of Se has 16 electron pairs.

Note: only 1 electron pair in 4p subshell

(c)



(d) Electronegativity value for Se: 2.4

Se is below O in Group 16 and has a greater number of electronic shells, greater distance between its nucleus and the bonding electrons, resulting in greater shielding experienced by bonding electrons than that in O. Despite the greater nuclear charge in Se than O, Se has a lower electrostatic attraction between its nucleus and the bonding electrons, thus Se has a lower electronegativity than O.

(e) Average mass of Se in each nut = $\frac{0.57 \times 10^{-3}}{6}$
= 9.5×10^{-5} g

Average number of atoms of Se in each nut
= $\frac{9.5 \times 10^{-5}}{79.0} \times 6.02 \times 10^{23} = 7.24 \times 10^{17}$



(f)(ii) NaOH(aq)

Question 3

(a) Acidic hydrolysis

(b)(i) Ethanoic acid



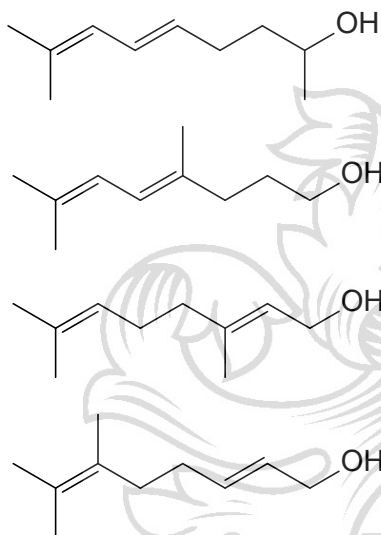
(b)(iii) Reduction

(c)

Evidence	Deduction
$\text{M} + \text{H}_2\text{O} \longrightarrow \text{L} + \text{K}$	Acidic Hydrolysis
Molecular formula of M : $\text{C}_{12}\text{H}_{20}\text{O}_2$	Molecular formula of K : $\text{C}_{10}\text{H}_{18}\text{O}$

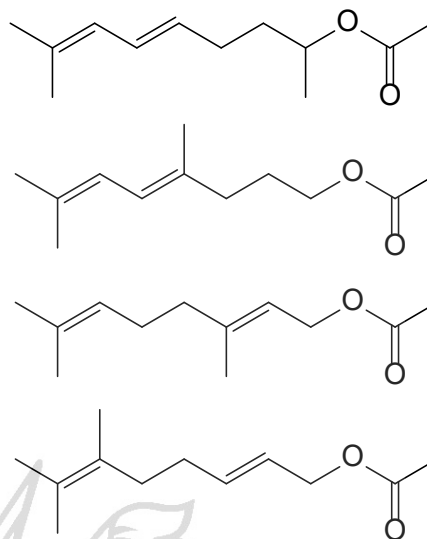
Molecular formula of L : C ₂ H ₄ O ₂	K is an alcohol
K does not react with Na ₂ CO ₃	No acid-base reaction K is not a carboxylic acid
K produced misty acid fumes with PCl ₅	Nucleophilic substitution K is an alcohol
K reacts with hot concentrated KMnO ₄ to form (CO ₂ H) ₂ , (CH ₃) ₂ CO and HO ₂ C(CH ₂) ₂ COCH ₃	Oxidative cleavage of C=C and oxidation of alcohol K contains C=C bonds HO ₂ C(CH ₂) ₂ COCH ₃ can be further oxidised to form CO ₂

Possible structures of **K**:



(d) The C=O in **L** is polarised by the highly electronegative oxygen atom causing the carboxyl carbon to be electron deficient and thus **L** can react with LiAlH₄. The C=C in alkene is not polarised and hence does not have electron deficient sites to react with LiAlH₄.

(e) Possible skeletal structures of **M** (depending on answer in (c)):



(f)
$$C_xH_yO + (x + \frac{y}{4} - \frac{1}{2})O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

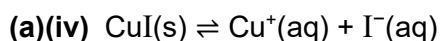
 Vol. of CO₂ + unreacted O₂ = 92.5 cm³
 Vol. of CO₂ = 92.5 – 77.5 = 15.0 cm³
 Amt. of CO₂ = $\frac{15.0}{24000} = 6.25 \times 10^{-4}$ mol
 Vol. of reacted O₂ = 100 – 77.5 = 22.5 cm³
 Amt. of reacted O₂ = $\frac{22.5}{24000} = 9.375 \times 10^{-4}$ mol
 mole ratio of C_xH_yO : reacted O₂ : CO₂
 = 6.25 × 10⁻⁴ : x + $\frac{y}{4} - \frac{1}{2}$: x
 = 6.25 × 10⁻⁴ : 9.375 × 10⁻⁴ : 6.25 × 10⁻⁴
 Thus, x = 1, y = 4,
 molecular formula of **N** = CH₄O

Question 4

(a)(i) oxidation: $Cu \longrightarrow Cu^{2+} + 2e^{-}$
 reduction: $HNO_3 + H^{+} + e^{-} \longrightarrow NO_2 + H_2O$
 Overall:
 $2HNO_3 + 2H^{+} + Cu \longrightarrow 2NO_2 + 2H_2O + Cu^{2+}$

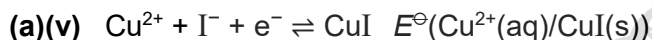
(a)(ii) The formation of NO₂(g), which escapes from the reaction mixture, and the use of high concentration of HNO₃ will cause the position of equilibrium of the reaction in (a)(i) to shift to the right, causing the reaction to proceed to completion and an equilibrium mixture is not produced.

(a)(iii) The standard electrode (redox) potential for the half-equation $Cu^{2+} + e^{-} \rightleftharpoons Cu^{+}$ involves Cu⁺ in the aqueous state which is the not case for equation 1 since Cu⁺ is in solid CuI.



$$K_{\text{sp}}(\text{CuI}) = [\text{Cu}^+][\text{I}^-]$$

$$\text{Units for } K_{\text{sp}}(\text{CuI}) = \text{mol}^2 \text{ dm}^{-6}$$



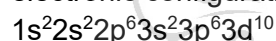
$$E^\ominus_{\text{cell}} = +0.32 = E^\ominus(\text{Cu}^{2+}(\text{aq})/\text{CuI(s)}) - 0.54$$

$$E^\ominus(\text{Cu}^{2+}(\text{aq})/\text{CuI(s)}) = +0.86 \text{ V}$$

(a)(vi) K_c (equation 1) is very large which means that the position of equilibrium for equation 1 lies very much to the right, favouring the formation of the products to a large extent and the reaction can be considered to go to completion. This allows the observation of the end-point colour to be more accurate since no more iodine will be produced from equation 1 during the titration.

(a)(vii) Oxidation state of CuI = +1

electronic configuration of $\text{Cu}^+ =$



(a)(viii) Cu(I) has a fully filled 3d subshell, hence there is an absence of partially filled d subshell and d-d transitions are not possible, thus CuI will be white.

(b)(i) Formula of **H** = $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

Number of ligands in **H** = 6

Shape of complex ion in **H** = octahedral

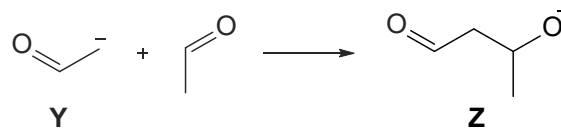
Number of ligands in **J** = 4

(b)(ii) The chloride ligand is bulkier than water ligand and hence a small number of chloride ligands can coordinate to the Cu^+ due to steric hindrance as compared to water ligands.

(b) total no. of e^- in σ bonds in **X** = 26

total no. of e^- in π bonds in **X** = 2

(c)(i) stage 2

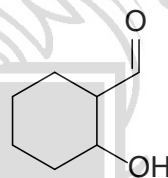


(c)(ii) stage 1: Ethanal behaves as a Brønsted-Lowry acid as it donates a proton to OH^- to form **Y**.

stage 2: Ethanal behaves as a Lewis acid as it accepts an electron pair from **Y** to form **Z**.

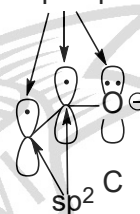
(c)(iii) NaOH acts as a catalyst as it is consumed in stage 1 and regenerated in stage 3.

(c)(iv) **Q**:



(d)(i) The p orbital of the adjacent O atom can overlap continuously side-on with the p orbitals of the sp^2 carbon atoms, resulting in delocalisation of the lone pair of electrons on the O atom.

continuous side-on overlap of p orbitals



(d)(ii) number of delocalised e^- = 4

Question 5

(a) aldehyde and secondary alcohol

(d)(iii) $\text{BE}(\text{C}-\text{C})$ in enolate ion = 480 kJ mol^{-1}

$\text{BE}(\text{C}-\text{O})$ in enolate ion = 550 kJ mol^{-1}

(d)(iv) O is more electronegative than C and hence will attract the delocalised electrons closer to itself the actual structure of the enolate ion will have a greater amount of the delocalised negative charge on O than C, similar to the negative charge on O in V.

Oxidation state of C in C = 0
Oxidation state of C decreased by 4.

Oxidation state of O in $\text{CO}_3^{2-} = -2$
Oxidation state of C in $\text{O}_2 = 0$
Oxidation state of O increased by 2.

4 mol of e^- are exchanged per mole of CO_3^{2-} .

Question 6

(a) The enhanced greenhouse effect is the impact on the climate from the additional heat retained due to the increased amounts of carbon dioxide and other greenhouse gases that humans have released into the earth's atmosphere.

(b) Acid rain OR photochemical smog

(c) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

$$\Delta H_f^\ominus = \sum n\Delta H_f^\ominus(\text{products}) - \sum m\Delta H_f^\ominus(\text{reactants})$$

$$\Delta H_c^\ominus(\text{CH}_4(\text{g})) = -393.5 - 285.8 \times 2 - (-74.8) \\ = -890 \text{ kJ mol}^{-1}$$

(d) The electrolysis of $\text{Li}_2\text{CO}_3(\text{l})$ produces $\text{O}_2(\text{g})$ which is fed back into the combustion chamber, increasing the percentage of $\text{O}_2(\text{g})$ in air mixture and hence increasing the percentage combustion efficiency for the same amount of methane combusted in the power plant.

(e) Total electricity produced per mole of $\text{CH}_4(\text{g})$
 $= 525 + 134 = 659 \text{ kJ}$

$$\text{Combustion efficiency} = 659 / 890.3 \times 100 \\ = 74.0\%$$

$$\text{Percentage of } \text{O}_2(\text{g}) \text{ in air mixture} \\ = \frac{74.02-60}{78-60} \times (38-21) + 21 = 34.2\%$$

(f) Melting of solid Li_2CO_3 to obtain the molten electrolyte.

(g) Oxidation state of C in $\text{CO}_3^{2-} = +4$

$$n_e = \frac{It}{F} = \frac{(1.00)(60 \times 60)}{96500} = 0.037305 \text{ mol}$$

$$n_C = 0.037305 / 4 = 9.3264 \times 10^{-3} \text{ mol}$$

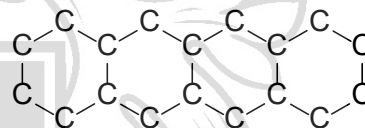
$$\text{Mass of C} = 9.3264 \times 10^{-3} \times 12 = 0.112 \text{ mol}$$

$$\text{Efficiency} = 0.110 / 0.11192 \times 100 = 98.3\%$$

The efficiency of this electrolysis process is very high.

(h)(i) Giant molecular lattice structure

(h)(ii) C-C-C bond angle = 120°

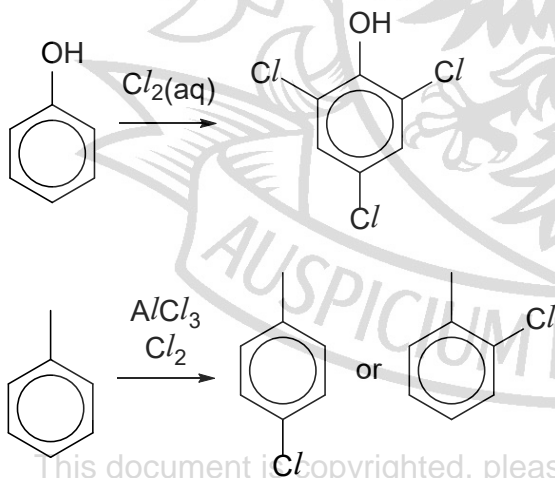


Question 1**(a)** Decreasing ease of hydrolysis: **C** > **A** > **B**

The carbon of the acyl group in **C** has a higher δ^+ charge (or is more electron deficient) as it is bonded to two electronegative atoms (O and Cl). The carbon bonded to the Cl atom in **A** has lower δ^+ charge (or is less electron deficient) as it is bonded to only one electronegative atom (Cl). Hence, **C** can attract nucleophiles more easily and is more susceptible to nucleophilic attack as compared to **A**.

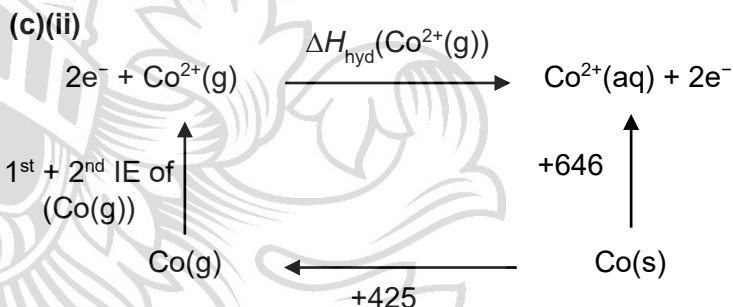
In addition, the carbon of the acyl group in **C**, being sp^2 hybridised and trigonal planar, provides less steric hindrance during nucleophilic attack compared to the carbon bonded to the chlorine atom in **A**, which is sp^3 hybridised and tetrahedral.

B is the least susceptible to hydrolysis. This is because the p orbital of Cl atom overlaps with the π electron cloud of the benzene ring, resulting in a lone pair of electrons in the p orbital of Cl delocalising into the benzene ring. As a result, the C-Cl bond has partial double bond character. Since the bond is strengthened, the cleavage of this bond (which is necessary during hydrolysis) is made very difficult.

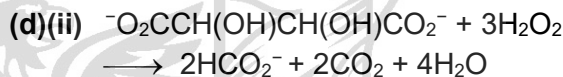
(b)(i)

(b)(ii) The $-OH$ group directly bonded to the benzene is a strongly activating group as lone pair of electrons on the O atom can interact with the delocalised π -electron cloud of the benzene ring and delocalises into the ring. This increases the electron density in the benzene ring and makes it more susceptible to electrophiles.

(c)(i) The standard enthalpy change of hydration of an ion is the energy released when 1 mole of the gaseous ion is hydrated under standard conditions (i.e. 1 bar and 298 K).



$$\Delta H_{hyd}(Co^{2+}(g)) = -757 - 1640 - 425 + 646 = -2180 \text{ kJ mol}^{-1}$$

(d)(i) 2,3-dihydroxybutanedioic acid

(e)(i) Some transition elements can act as homogenous catalyst as can exist in different oxidation states and can be easily converted from one oxidation state to another, facilitating the formation and decomposition of the intermediate formed from the transition metal ion catalyst and the reactants.

(e)(ii) Homogenous catalysis as **D** and H_2O_2 are both in the same state (aq).

(e)(iii) Increase the concentration of H_2O_2/Co^{2+} so that by Le Chatelier's Principle, the position of equilibrium of step 1 will lie more to the

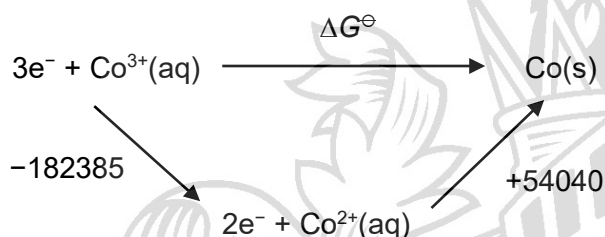
right and E_{cell} will be positive and step 1 becomes a spontaneous reaction.

as $\text{NH}_3(\text{g})$ has significantly higher entropy than $\text{NH}_3(\text{l})$.

(e)(iv) D is the conjugate base of a weak acid and will be protonated if the pH is too low and will be less attracted to Co^{3+} in step 2.

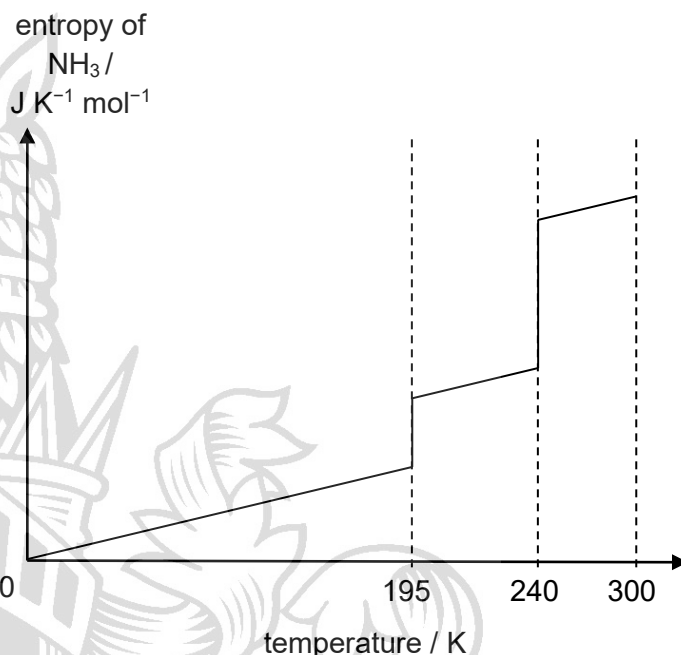
(e)(v) $\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$

	E^\ominus / V	$\Delta G^\ominus / \text{J mol}^{-1}$
$\text{Co}^{2+}(\text{aq}) / \text{Co}(\text{s})$	-0.28	+54040
$\text{Co}^{3+}(\text{aq}) / \text{Co}^{2+}(\text{aq})$	+1.89	-182385



By Hess's law, $\Delta G^\ominus = -182385 + 54040$
 $= -128345 \text{ J mol}^{-1}$

$$\begin{aligned}
 -128345 &= -(3)(96500)(E^\ominus(\text{Co}^{3+}(\text{aq}) / \text{Co}(\text{s})) \\
 E^\ominus(\text{Co}^{3+}(\text{aq}) / \text{Co}(\text{s})) &= +0.443 \text{ V}
 \end{aligned}$$



(c)(i) $K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}}$

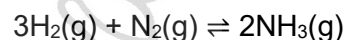
Question 2

(a)(i) $2\text{NO}_2(\text{g}) \longrightarrow \text{N}_2\text{O}_4(\text{g})$

The entropy of the chemical system decreases as there is a decrease in the number of moles of gaseous particles when $\text{NO}_2(\text{g})$ is converted to $\text{N}_2\text{O}_4(\text{g})$.

(a)(ii) The entropy of the chemical system increases as the dissolution of $\text{C}_6\text{H}_5\text{OH}(\text{s})$ disrupts the crystal structure of $\text{C}_6\text{H}_5\text{OH}(\text{s})$.

(b) Entropy generally increases from 0 K to 300 K as NH_3 molecules there is a broadening of the energy distribution of the particles. Thus, there are more possible energy states in which the particles can adopt at a higher temperature. There are sharp increase in entropy of NH_3 at 195 K and 240 K due to state changes from solid to liquid and liquid to gas respectively. The increase at 240 K is larger than that at 195 K



Initial / mol	3x	x	0
Change / mol	-1.2x	-0.4x	+0.8x
Eqm / mol	1.8x	0.6x	0.8x

$$n_T = 1.8x + 0.6x + 0.8x = 3.2x$$

$$\begin{aligned}
 K_p &= \frac{\left(\frac{0.8x}{3.2x} \times 2.80 \times 10^4\right)^2}{\left(\frac{1.8x}{3.2x} \times 2.80 \times 10^4\right)^3 \left(\frac{0.6x}{3.2x} \times 2.80 \times 10^4\right)} \\
 &= 2.39 \times 10^{-9} \text{ kPa}^{-2}
 \end{aligned}$$

(c)(ii) Since the forward reaction is exothermic, a lower temperature would result in a higher yield of ammonia. However, the rate of production is too slow at low temperature, hence a moderately high temperature of 450 °C is used to ensure a reasonable rate of production and yield.

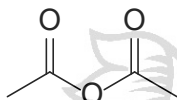
The forward reaction takes place with a reduction in the number of gaseous particles and a high pressure will favour the desired

reaction (increase yield). However, too high a pressure increases cost of production and increases safety concerns. Thus, a moderate pressure of 2.80×10^4 kPa is used.

Iron catalyst is added to increase the rate of reaction and reduce the time taken to reach equilibrium.

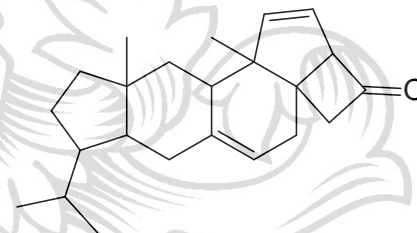


(d)(ii)

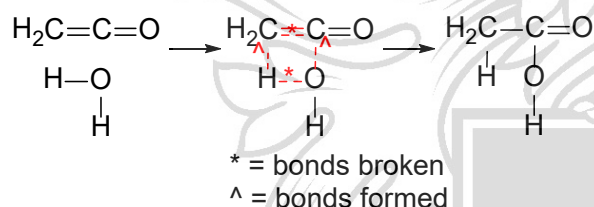


Note: This is a pattern recognition question that requires students to learn from the information provided and extend it to another unfamiliar situation.

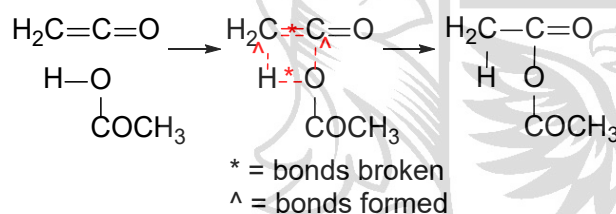
(f)



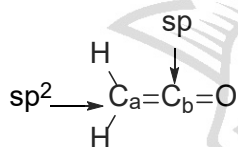
(i) Learn from reaction of ketene with water.



(ii) Apply above knowledge to reaction with ethanoic acid



(e)



C_a is sp^2 hybridised and each $\text{C}_a\text{-H}$ σ bond is formed from the head-on overlap of the sp^2 hybrid orbital of C_a atom with the $1s$ orbital of the H atom.

C_b is sp hybridised and the $\text{C}_a\text{-C}_b$ σ bond is formed from the head-on overlap of the sp^2 hybrid orbital of C_a atom with the sp hybrid orbital of the C_b atom while the $\text{C}_a\text{-C}_b$ π bond is formed from the sideways overlap of the unhybridised p orbitals in both C_a and C_b atoms.

The $\text{C}_b\text{-O}$ σ bond is formed from the head-on overlap of the sp hybrid orbital of C_b atom with the orbital of the O atom while the $\text{C}_b\text{-O}$ π bond is formed from the sideways overlap of the unhybridised p orbitals in both C_b and O atoms.

Question 3

(a) Both $^1\text{H}^+$ and $^2\text{H}^+$ will be deflected towards the negatively charged plate while the electron, e^- , will be deflected towards the positively charged plate. Since all 3 particles have the same magnitude of charge, their masses increase in this order $e^- < ^1\text{H}^+ < ^2\text{H}^+$, their angle of deflection will decrease in this order $e^- > ^1\text{H}^+ > ^2\text{H}^+$ as angle of deflection $\propto \frac{|q|}{|m|}$.

(b)(i)
$$A_r = \frac{83.91 \times 0.56 + 85.91 \times 9.86 + 86.91 \times 7.00 + 87.91 \times 82.58}{100}$$

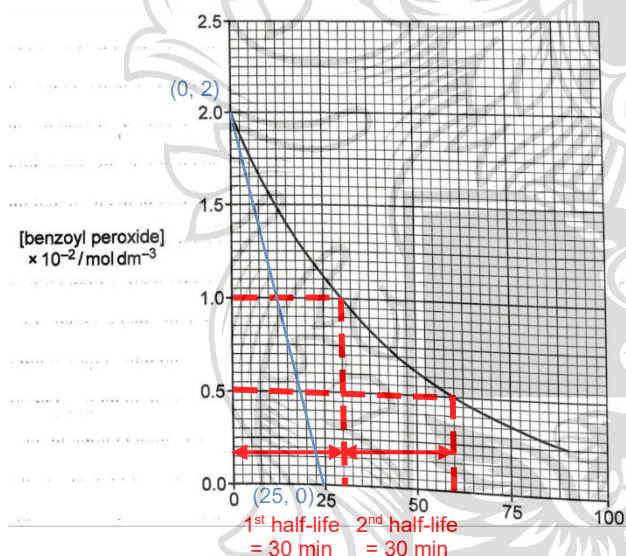
$$= 87.62 \text{ (2 d.p.)}$$

(b)(ii) The reactivity of the Group 2 elements increases down the group. Down the group, E^\ominus value becomes more negative (from $E^\ominus(\text{Be}^{2+}/\text{Be}) = -1.85 \text{ V}$ to $E^\ominus(\text{Ba}^{2+}/\text{Ba}) = -2.90 \text{ V}$), thus the tendency of metal losing electrons increases, the reducing power of metal increases and the reactivity of the metal increases.

(c) Down the group, cationic radius increases, resulting in a lower charge density and weaker polarising power of the cations. Consequently, there is decreasing extent of distortion of the electron cloud of the O_2^{2-} anion and hence decreasing extent of weakening of covalent bond within the O_2^{2-} anion. More heat energy is required to break the covalent bonds within the O_2^{2-} anion, causing the decomposition temperature to increase. Hence, thermal stability of the Group 2 peroxides increases down the group.

(d)(i) The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised in the rate equation.

(d)(ii)



Since half-life is constant, the overall reaction is first order.

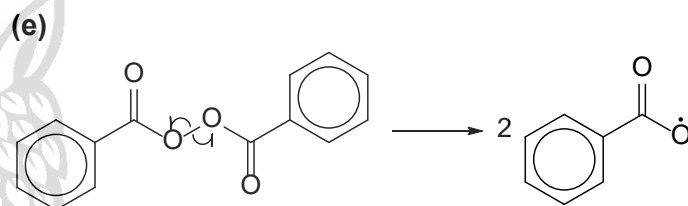
$$150\ minutes = 5 \times 30\ min = 5\ half-lives$$

$$[benzoyl\ peroxide]\ at\ 150\ min = 0.02 \times (0.5)^5 = 0.000625\ mol\ dm^{-3}$$

(d)(iii) gradient of tangent at $t = 0\ min = \frac{0.02 - 0}{0 - 25} = -0.000800\ mol\ dm^{-3}\ min^{-1}$

initial rate or reaction = $-(-0.0008) = 0.000800\ mol\ dm^{-3}\ min^{-1}$

(d)(iv) rate = $k[benzoyl\ peroxide]$
 $0.000800 = k \times 0.02$
 $k = 0.0400\ min^{-1}$



(f)(i)

first propagation step:

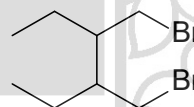


second propagation step:



The secondary radical intermediate is more stable than the primary radical intermediate due to one additional electron-donating alkyl group which stabilises the electron-deficient radical, causing it to form faster.

(f)(ii)



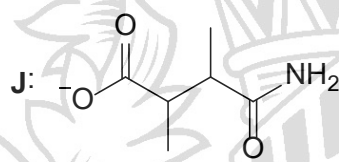
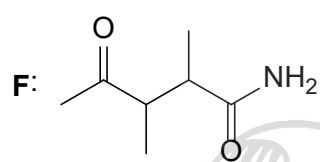
(g)

Note: State type of reactions clearly, deductions for reference only, not required by question.

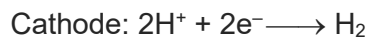
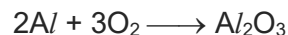
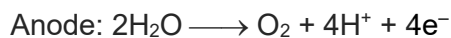
observations	deductions
F reacts with 2,4-DNPH to give orange ppt G , $C_{13}H_{17}N_5O_5$	<ul style="list-style-type: none"> Condensation F is a carbonyl compound
F reacts with alkaline $I_2(aq)$ to form yellow ppt H and J	<ul style="list-style-type: none"> Oxidation F contains either OH <div style="display: flex; align-items: center;"> <div style="text-align: center;"> $\begin{array}{c} \text{---}C-CH_3 \\ \\ H \end{array}$ </div> <div style="margin: 0 10px;">or</div> <div style="text-align: center;"> $\begin{array}{c} O \\ \\ \text{---}C-CH_3 \end{array}$ </div> </div> <ul style="list-style-type: none"> H is CHI_3 J contains COO^-
F does not react with Fehling's	<ul style="list-style-type: none"> No oxidation F is not an aldehyde

reagent	<ul style="list-style-type: none"> F is a ketone
F reacts with hot HCl(aq) to form K , $\text{C}_7\text{H}_{12}\text{O}_3$	<ul style="list-style-type: none"> Acidic hydrolysis Decrease in 1 N and no change in C, F is a 1° amide
F reacts with excess LiAlH_4 to form L , $\text{C}_7\text{H}_{17}\text{NO}$	<ul style="list-style-type: none"> Reduction Increase in 4 H and decrease in 1 O Both ketone and 1° amide are reduced to 2° alcohol and 1° amine respectively

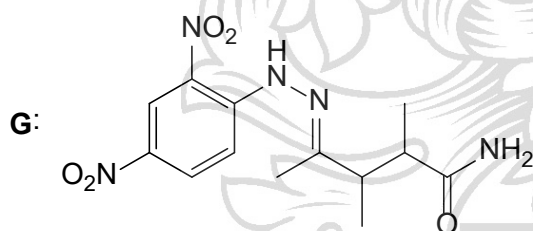
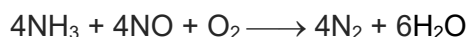
Since **F** must have 2 chiral carbon atoms,



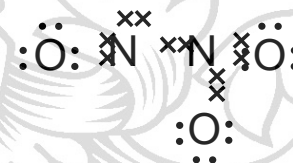
(b)



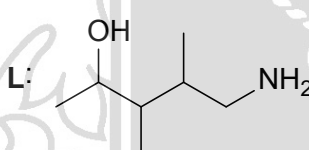
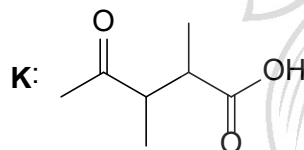
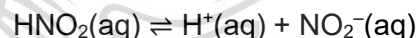
(c)



(d)(i)



(d)(ii)



$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

$$K_a = 10^{-\text{p}K_a} = 10^{-3.25} = 5.6234 \times 10^{-4} \text{ mol dm}^{-3}$$

Since HNO_2 is a weak acid with a small K_a ,
 $[\text{HNO}_2]_{\text{eqm}} \approx [\text{HNO}_2]_{\text{initial}} = 0.25 \text{ mol dm}^{-3}$

$$[\text{H}^+] = \sqrt{K_a[\text{HNO}_2]} = \sqrt{5.6234 \times 10^{-4} \times 0.25} \\ = 0.011856 \text{ mol dm}^{-3} = [\text{NO}_2^-]$$

$$\% \text{ ionisation} = \frac{0.011856}{0.25} \times 100\% = 4.74\%$$

(e)



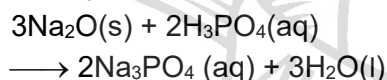
(f)(i)

Nucleophilic substitution ($\text{S}_{\text{N}}2$)

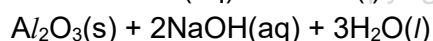
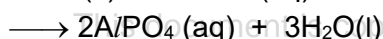
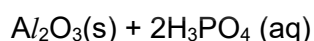
Question 4

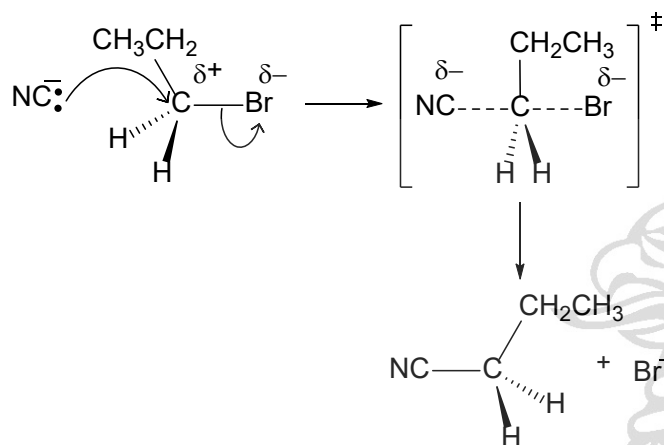
- (a) Across the period, Period 3 oxides exhibit varying acid-basic behaviours from basic (Na_2O) to amphoteric (Al_2O_3) to acidic (SiO_2).

As a basic oxide, Na_2O reacts with an acid like H_3PO_4 but not with a base.



As an amphoteric oxide, Al_2O_3 reacts with both an acid like H_3PO_4 and a base like NaOH .





(c)(i)

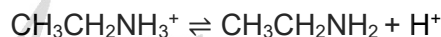
electrons on the N atom in $(\text{CH}_3)_3\text{N}$ are readily available for coordination to a proton compared to CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$.



$\text{CH}_3\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{CH}_2\text{NH}_3^+$ are acid-base conjugate pairs and the presence of both species at pH 8-10 forms a buffer solution which resists pH changes when HCl is added, causing pH to change gradually.

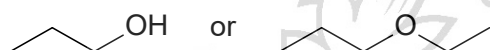
Note: Students reminded that when drawing the $\text{S}_{\text{N}}2$ mechanism, the transition state must be included.

(c)(ii)



$\text{CH}_3\text{CH}_2\text{NH}_3^+$ undergoes salt hydrolysis to produce H^+ , causing $[\text{H}^+] > [\text{OH}^-]$ and hence $\text{pH} < 7$.

(f)(ii)



(f)(iii) Relative rate of reaction with $\text{NaOH}(\text{aq})$:
N > M > O

All 3 compounds are primary bromoalkanes and hence the reaction proceeds via $\text{S}_{\text{N}}2$.

N reacts faster than **M** with $\text{NaOH}(\text{aq})$ as the C-I bond is weaker than the C-Br bond and requires less energy to break.

O reacts slower than **M** as **O** has a bulky $-\text{C}(\text{CH}_3)_3$ group adjacent to the carbon bonded to the Br atom which hinders the approach of the hydroxide nucleophile more than in **M**.

(d)

$$n(\text{S}_2\text{O}_3^{2-}) = 15.75/1000 \times 0.150 = 2.3625 \times 10^{-3} \text{ mol}$$

$$n(\text{I}_2) = 0.5(2.3625 \times 10^{-3})$$

$$= 1.1812 \times 10^{-3} \text{ mol}$$

$$= n(\text{C/O}^-) \text{ in } 25.0 \text{ cm}^3$$

$$n(\text{C/O}^-) \text{ in } 100 \text{ cm}^3 = 1.1812 \times 10^{-3} \times 4 = 4.725 \times 10^{-3} \text{ mol}$$

$$[\text{C/O}^-] \text{ in } 5.00 \text{ cm}^3 \text{ bleach}$$

$$= 4.725 \times 10^{-3} \times \frac{1000}{5.00} = 0.945 \text{ mol dm}^{-3}$$

(e)



(f)(i)

$$\Delta H_r^\ominus = \sum n\Delta H_f^\ominus(\text{products}) - \sum m\Delta H_f^\ominus(\text{reactants})$$

$$\Delta H^\ominus = 4(-241.8) + 2(-393.5) - (48.9) - 2(-19.6) = -1763.9 \text{ kJ mol}^{-1}$$

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$= -1763.9 - (298)(1141.2/1000)$$

$$= -2100 \text{ J mol}^{-1} \text{ (3 s.f.)}$$

(f)(ii)

$$n((\text{CH}_3)_2\text{N}_2\text{H}_2) = \frac{1.50 \times 1000}{2(12.0 + 1.0 \times 3) + 2(14.0) + 2(1.0)} = 25 \text{ mol}$$

Question 5

(a) More energy is required to overcome the stronger intermolecular hydrogen bonds in ethylamine than the weaker instantaneous dipole-induced dipole interactions in propane.

(b) Basicity: $\text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < (\text{CH}_3)_3\text{N}$

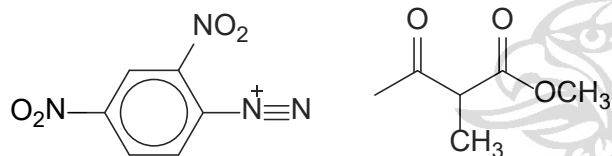
Since the number of electron-donating methyl groups bonded to the N atom increases from CH_3NH_2 to $(\text{CH}_3)_2\text{NH}$ to $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_3\text{N}$ has the highest electron density at the N atom and the lone pair of

Gas **Q** is N_2 since CO_2 reacted with KOH and H_2O is liquid at room temperature.

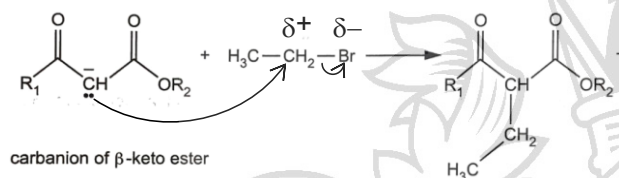
$$n(\text{N}_2) = 3 \times 25 = 75 \text{ mol}$$

$$V(\text{N}_2) = 75 \times 24 = 1800 \text{ dm}^3$$

(g)



(h)



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2023 A-Level H2 Chemistry Paper 1 Suggested Solutions

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

Q1(B)

species	proton no.	no. of protons + neutrons	no. of e ⁻	no. of neutrons
Nd	60	145	60	145 - 60 = 85
Nd ²⁺	60	145	58	85
Pm	61	145	61	145 - 61 = 84
Pm ³⁺	61	145	58	84

Q2(C)

The greater the difference in electronegativity between X/Y and C//O, the greater the ionic character.

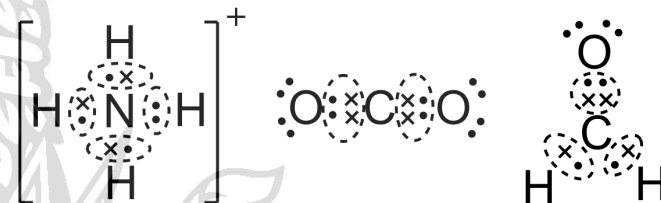
compound	difference in electronegativity
XC _l ₂	3.0 - 1.2 = 1.8
Y ₂ O	3.5 - 0.9 = 2.6
XO	3.5 - 1.2 = 2.3
YC _l	3.0 - 0.9 = 2.1
ZO ₂	3.5 - 1.8 = 1.7
ZC _l ₄	3.0 - 1.8 = 1.2

Q3(C)

A	While C _l is more electronegative than Br, causing CH ₃ C _l to be more polar and have stronger pd-pd interactions than CH ₃ Br, the significantly larger electron cloud side of Br causes the id-id interactions and hence the total IMF of CH ₃ Br to be stronger than that of CH ₃ C _l .
B	There are no H-bonds between molecules of each compound.
C	Correct. Explanation in option A.
D	The relative boiling points is dependent on the IMF between the molecules and not the strength of the covalent bonds within the molecules.

Q4(D)

Shared electrons are circled.



Q5(B)

molecule	structure	polar?
1,1-difluoroethene		Yes
cis-1,2-difluoroethene		Yes
trans-1,2-difluoroethene		No
tetrafluoroethene		No

Q6(D)

Period 3 element	Outermost shell
Na	<div> <div>↑</div> <div>3s</div> </div> <div> <div></div> <div>3p</div> </div>
Mg	<div> <div>↑↓</div> <div>3s</div> </div> <div> <div></div> <div>3p</div> </div>
Al	<div> <div>↑↓</div> <div>3s</div> </div> <div> <div>↑</div> <div>3p</div> </div>
Si	<div> <div>↑↓</div> <div>3s</div> </div> <div> <div>↑</div> <div>3p</div> </div>
P	<div> <div>↑↓</div> <div>3s</div> </div> <div> <div>↑</div> <div>3p</div> </div>
S	<div> <div>↑↓</div> <div>3s</div> </div> <div> <div>↑↓</div> <div>3p</div> </div>
Cl	<div> <div>↑↓</div> <div>3s</div> </div> <div> <div>↑↓</div> <div>3p</div> </div>
Ar	<div> <div>↑↓</div> <div>3s</div> </div> <div> <div>↑↓</div> <div>3p</div> </div>

Elements with only 1 orbital in outermost shell which contains just one electron = Na, Al & Cl

Elements with only 1 orbital in outermost shell which contains a pair of electrons = Mg, Al, Si & P

Q7(A)

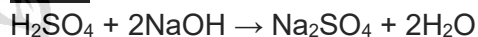
1	Correct. Down group 2, the E^\ominus values become more negative i.e. the position of equilibrium lies more to the left, indicating that the group 2 elements are more readily oxidised and become stronger reducing agents.
2	Correct. Down group 2, the size of the $2+$ cations increase, causing a decreasing in the charge density and polarizing power of the cations. The C–O bond of the carbonates are polarized to a lesser extent, requiring more energy to break, increasing the thermal stability of the metal carbonate.
3	Incorrect. See option 2.

Q8(C)

Let x be the percentage of ^{29}Si in the sample.

$$(92.23/100)(28) + (x/100)(29) + (0.0777-x)(30) = 28.10$$

$$x = 5.54.$$

Q9(A)

$$\text{Amt of H}_2\text{SO}_4 = (50.0/1000)(2.00) = 0.100 \text{ mol}$$

$$\text{Amt of NaOH} = (100/1000)(1.00) = 0.100 \text{ mol}$$

NaOH is the limiting reagent.

$$\Rightarrow \text{No. of moles of water formed} = 0.100 \text{ mol}$$

$$q = (100 + 50)(4.18)(29.0 - 20.0) = 5643 \text{ J}$$

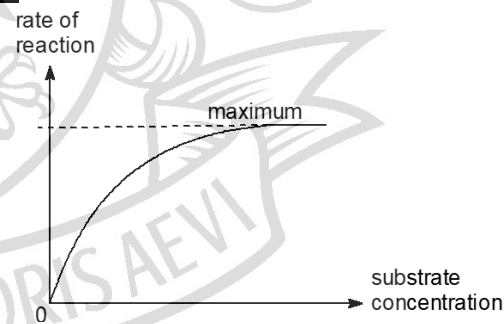
$$\Delta H = -\frac{5643}{0.100} = -56.4 \text{ kJ mol}^{-1}$$

Q10(A)

CaCl and CaCl_2 : Since Ca^{2+} has a higher charge and smaller cationic radius than Ca^+ , the magnitude of the lattice energy of CaCl_2 is greater than that of CaCl .

MgCl_2 and CaCl_2 : Since Mg^{2+} has a smaller cationic radius than Ca^{2+} , the magnitude of the lattice energy of MgCl_2 is greater than that of CaCl_2 .

$$\text{Hence, } |\text{LE}(\text{CaCl})| < |\text{LE}(\text{CaCl}_2)| < |\text{LE}(\text{MgCl}_2)|$$

Q11(D)

At low [substrate], not all of the active sites are occupied. In this case, $\text{rate} \propto [\text{substrate}]$ and the reaction is first order with respect to the substrate.

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At high [substrate], all the active sites are occupied i.e. the active sites of the enzyme become saturated with substrate. In this case, any increase in [substrate] will not have any effect on the reaction rate. The reaction is zero order with respect to the substrate.

Q12(D)

A	Incorrect. Adding a catalyst increases both the rate of the forward and backward reactant by the same extent, causing no change to the value of K_p .
B	Incorrect. K_p is only affected by changes in temperature. Hence, changing the pressure will not affect the value of K_p for all gas phase reactions.
C	Incorrect. K_p is only affected by changes in temperature. Hence, changing the pressure will not affect the value of K_p for all gas phase reactions.
D	Correct.

Q13(C)

Since equilibrium partial pressure of $\text{NH}_3 = 92 \text{ atm}$ and total pressure is 100 atm , the sum of partial pressure of N_2 and $\text{H}_2 = 100 - 92 = 8 \text{ atm}$.

The mole ratio and hence the partial pressure ratio of $\text{N}_2 : \text{H}_2$ remains as $1 : 3$ as the initial ratio and stoichiometric ratio are the same. Hence, equilibrium partial pressure of $\text{N}_2 = \frac{1}{4} \times 8 = 2 \text{ atm}$ while equilibrium partial pressure of $\text{H}_2 = \frac{3}{4} \times 8 = 6 \text{ atm}$.

$$K_p = \frac{92^2}{(2)(6^3)} = 19.6$$

Q14(C)

Total amt of $\text{Br}_2 = (30.0/1000)(0.500) = 0.0150 \text{ mol}$

Amt of $\text{Br}^- = [2.98 / (39.1 + 79.9)] = 0.0250 \text{ mol}$

Reduction: $\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$ (from Data Booklet)

Amt of e^- gained = amt of $\text{Br}^- = 0.0250 \text{ mol}$

Amt of Br_2 reduced = $0.0250/2 = 0.0125 \text{ mol}$

Let k be the stoichiometric coefficient of e^-

Oxidation: $\text{Br}_2 \rightarrow 2\text{BrO}_x^- + k\text{e}^-$ (unbalanced)

Amt of Br_2 oxidised = $0.015 - 0.0125$

= 0.00250 mol

Amt of BrO_x^- = amt of Br_2 oxidised $\times 2$

= $0.00250 \times 2 = 0.00500 \text{ mol}$

Since in a redox reaction, the amount of e^- gained = amount of e^- lost,

$$\text{mole ratio of } \text{BrO}_x^- : \text{e}^- = \frac{0.00500}{0.0250} = \frac{2}{k}, k = 10$$

Since 1 mol of Br_2 lost 10 mol of e^- , 1 mol of Br atom lost 5 mol of e^- and the oxidation state of Br increases from 0 in Br_2 to +5 in BrO_x^- .

Thus, $x = 3$ as the oxidation state of Br in $\text{BrO}_3^- = +5$.

Q15(B)

Mixing CH_3COONa and AgNO_3 gave a white ppt of CH_3COOAg .

$\Rightarrow \text{CH}_3\text{COOAg}$ is insoluble in water (1 is correct)

Mixing white ppt of CH_3COOAg and KBr causes CH_3COOAg to dissolve to form a cream ppt of AgBr .
 \Rightarrow Initially, $\text{CH}_3\text{COOAg} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{Ag}^+$. When Br^- was added, the IP of AgBr exceeded its K_{sp} despite the low $[\text{Ag}^+]$, implying that the K_{sp} of AgBr is very low and easily exceeded i.e. AgBr is less soluble than CH_3COOAg . (2 is correct)

No further change upon addition of CH_3COONa to $\text{AgBr} \Rightarrow$ no reaction took place i.e. 3 is incorrect.

Q16(C)

hybridisation	no. of p orbitals used for hybridisation	no. of s orbitals used for hybridisation
sp	1	1
sp^2	2	1
sp^3	3	1

The 3 carbons in propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, are sp^3 hybridised. Hence, $3 \times 3 = 9$ p orbitals were used for hybridization.

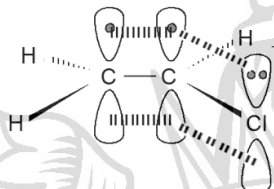
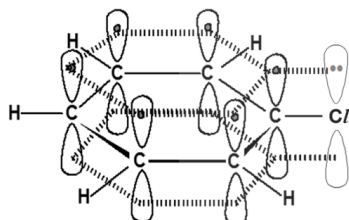
The 6 carbons in benzene, C_6H_6 , are sp^2 hybridised. Hence, $6 \times 2 = 12$ p orbitals were used for hybridization.

The 2 carbons in ethene, $\text{H}-\text{C}=\text{C}-\text{H}$, are sp^2 hybridised. Hence $2 \times 2 = 4$ p orbitals were used for hybridization.

In total, $9 + 12 + 4 = 25$ p orbitals were used for hybridization.

Q17(C)

The lack of reactivity of chloroethene to nucleophiles is similar to the case of chlorobenzene where the overlap of the p-orbital on C/ with the π electron cloud of C=C or benzene allows the lone pair on C/ to be delocalized into the C=C or benzene, giving rise to partial double bond character in the respective C–C/ bonds.



D	Incorrect. In benzene, single and double carbon-carbon bonds do not exist. Instead, the delocalisation of the 6 π electrons give rise to bond lengths that are equal and intermediate between single and double bonds.
----------	--

Q21(A)

Since 3-bromo-3-methylhexane is a tertiary halogenoalkane, its hydrolysis proceeds via an S_N1 mechanism where an intermediate carbocation is formed, which is subsequently attacked by a nucleophile.

**Q18(C)**

Non-cyclic constitutional isomers of C_5H_{10}

**Q22(B)**

A	Incorrect. Propanoyl chloride, an acyl chloride, reacts <i>more</i> readily with water than 1-chloropropane, a chloroalkane.
B	Correct. See reasoning in Q17.
C	Incorrect. The leaving group for each of the three compounds is the same i.e. Cl^- .
D	Incorrect. The carbon bonded to chlorine is most susceptible to <i>nucleophilic</i> attack in propanoyl chloride.

Q19(A)

Since X proceeds to give a 1,2-disubstituted product, X should contain a 2-directing group i.e. X should be chlorobenzene (the nitro group is 3-directing).

Since Y proceeds to give a 1,3-disubstituted product, Y should contain a 3-directing group. The methyl group that is present is 2,4-directing and can be oxidised to give $-COOH$ which is 3-directing. Hence Y is benzoic acid.

Q23(A)

	C_xH_y	$+(x + \frac{y}{4})O_2$	\rightarrow	xCO_2	$+ \frac{y}{2}H_2O$
Volume ratio	10	75		5	–
Mole ratio	1	7.5		5	–

Therefore, $x = 5$ and $5 + \frac{y}{4} = 7.5 \Rightarrow y = 10$

X is C_5H_{10} .

1	Correct. Given the formula of C_5H_{10} , X may be a cycloalkane e.g. cyclopentane.
2	Correct. Given the number of carbons, X may have a branched chain e.g. $CH_2=CHCH(CH_3)_2$.
3	Correct. Given the formula of C_5H_{10} , X may contain 1 C=C which will decolourise $Br_2(aq)$ in the dark e.g. $CH_3CH=CH(CH_2CH_3)$.

Q20(C)

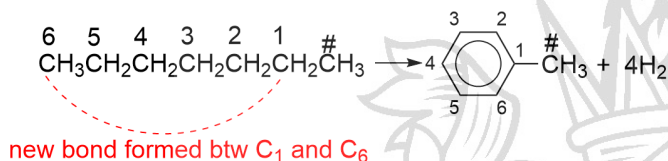
A	Incorrect. Benzene undergoes <i>electrophilic</i> substitution with the given reagents and conditions.
B	Incorrect. Hydrogenation of benzene requires high pressure, high temperature and the presence of a catalyst.
C	Correct. A carbocation acts as an electrophile in Friedel-Craft alkylation.

Q24(B)

This is a pattern recognition question. Students should learn the pattern from the example given and apply it to the new situation given. The common steps to identify and articulate the pattern involves

1. considering the bonds broken and formed.
2. numbering the atoms involved, particularly useful for ring structures.

From the example given:



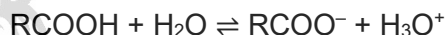
1	Correct. new bond formed btw C ₁ and C ₆
2	Correct.
3	Incorrect. No possible combinations to give 1,4-dimethylbenzene as the product.

Q25(D)

A	Incorrect. Such a reaction where --COCH_3 substitutes a --H on a methyl group does not occur.
B	Incorrect. Such a reaction resembles Friedel-Craft acylation which requires the presence of a Lewis acid catalyst such as AlCl_3 .
C	Incorrect. The original --OH group on 4-methylphenol is missing after the reaction.
D	Correct. Ethanoyl chloride reacts with the --OH on 4-methylphenol to form an ester.

Q26(B)

This question requires students to recognise the presence of acidic groups (phenol and RCOOH) in the molecule. Using RCOOH to illustrate the equilibrium processes which can take place.



In the forward reaction, RCOOH donates a H^+ to water to form H_3O^+ . In the reverse reaction, RCOO^- takes in one of 3 H in H_3O^+ to form RCOOH .

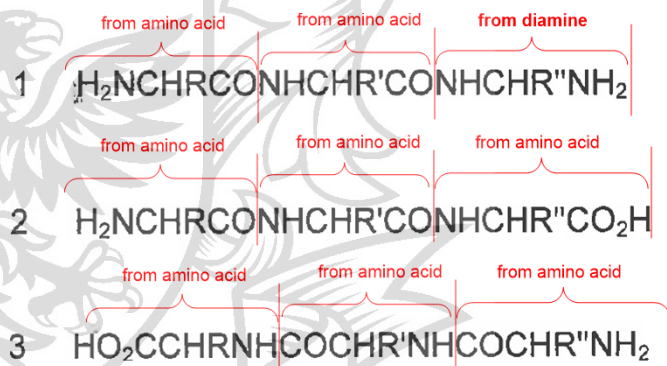


In the reverse reaction, RCOO^- can take in one of the 2 H or 1 D from H_2DO^+ . If RCOO^- takes in the D, then RCOOD is formed and deuterium atoms would be incorporated.

Since both the phenol and RCOOH are acidic groups, their H can be replaced by D i.e. a maximum of 2 H atoms can be replaced by D.

Q27(D)

Amino acids have the following formula $\text{H}_2\text{NCHRCOOH}$, where R is the side chain. When in a polypeptide, the amino acid residue becomes --HNCHRCO-- . We attempt to identify the residue in each option.

**Q28(A)**

1	Correct. The product of the reactions in the cell is water.
2	Correct. There is little loss of energy when converting to electrical energy.
3	Correct. At the anode, $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$.

Q29(B)

1	Correct. When the standard hydrogen electrode (SHE, with $E^\ominus = 0.00 \text{ V}$) is connected to a half-cell with a negative E^\ominus , the SHE is the cathode and H^+ undergoes reduction to form H_2 gas.
2	Incorrect. $E^\ominus(\text{H}^+/\text{H}_2) = 0.00 \text{ V}$.
3	Incorrect. $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ gives $2 \text{ mol dm}^{-3} \text{ H}^+$ and hence is not under standard conditions.

Q30(C)

Amt of Cu^{2+} converted to Cu

$$= (0.200)(250/1000) - (0.100)(250/1000)$$

$$= (0.100)(250/1000) \text{ mol}$$



$$\text{Amt of e}^- \text{ required} = 2(0.100)(250/1000) \text{ mol}$$

$$Q = It = n_e F$$

$$(0.65)(t) = 2(0.100)(250/1000) (96500)$$

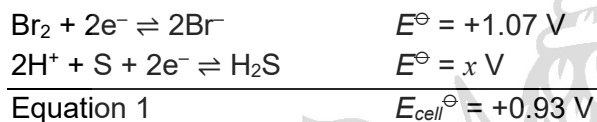
$$t = \frac{2 \times 0.100 \times 250 \times 96500}{1000 \times 0.65} \text{ s}$$

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Question 1

(a)(i) Br_2 has greater reactivity. In this reaction, Br_2 acts as an oxidising agent and has stronger oxidising power than I_2 .

(a)(ii) Half-equation for reaction of H_2S is $\text{H}_2\text{S} \rightarrow 2\text{H}^+ + \text{S} + 2\text{e}^-$.



$$1.07 - x = +0.93$$

$$x = +0.14$$

$$E^\ominus(\text{S}/\text{H}_2\text{S}) = +0.14 \text{ V}$$

(b)(i) **Similarity** – Both Br_2 and ICl have instantaneous dipole-induced dipole (id-id) interactions which are similar in strength due to their similar electron cloud sizes.

Difference – Since Cl is more electronegative than I , ICl is polar and has permanent dipole-permanent dipole (pd-pd) interactions which are absent in Br_2 which is non-polar. Overall, ICl has stronger intermolecular forces (id-id and pd-pd) than Br_2 (id-id only).

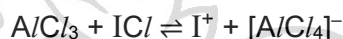
(b)(ii) While ICl is more polar and has stronger pd-pd interactions than IBr , IBr has a significantly larger and more polarisable electron cloud compared to ICl , causing the id-id interactions in IBr to be stronger than that in ICl . Hence, the sum of the id-id and pd-pd interactions in IBr is stronger than that in ICl , resulting in a higher melting point of IBr .

(c)(i) The delocalisation of the six π electrons in the ring structure of benzene causes resonance stabilisation. Addition reactions disrupt the delocalisation of the six π electrons in benzene while substitution

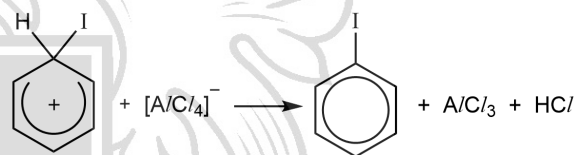
reactions restores the resonance stabilisation after temporarily disrupting it.

(c)(ii) Since Cl is more electronegative than I , Cl attracts the bonding electrons in ICl towards itself, causing I to acquire a δ^+ charge and become more electron deficient. Hence, the reaction of ICl and AlCl_3 forms an I^+ electrophile, which reacts with benzene to form iodobenzene.

(c)(iii) AlCl_3 acts as a Lewis acid when it reacts with ICl to form the I^+ electrophile.

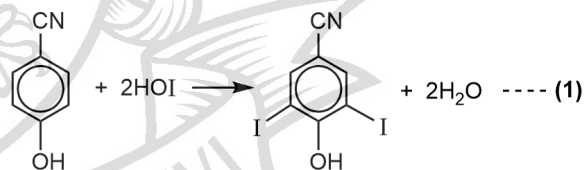


AlCl_3 acts as a catalyst as it is consumed in the generation of the I^+ electrophile (see above) and regenerated in the last step of the electrophilic substitution reaction.

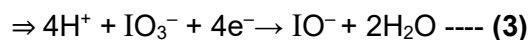
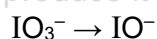
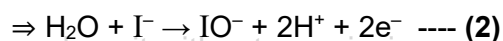


(d)(i) I^- is a reducing agent as iodine is oxidised and lost electrons to form IO_3^- . IO_3^- is an oxidising agent as iodine in IO_3^- is reduced and gained electrons to form IO^- .

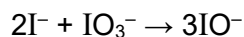
(d)(ii) First, consider the reaction between 4-hydroxybenzonitrile and HOI .



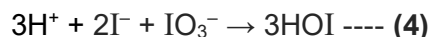
Since HOI is formed from the reaction of I^- and IO_3^- , we can write the following.



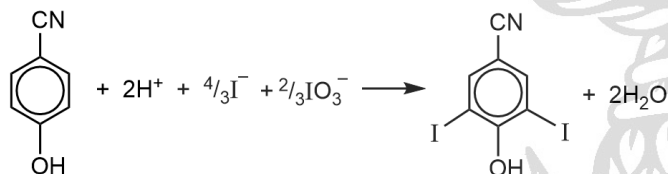
2 x (2) + (3):



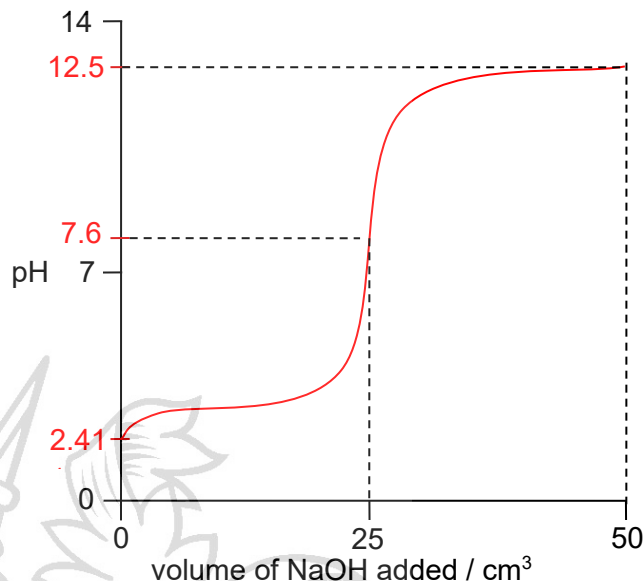
Add 3H^+ on both sides to form HOI:



(1) + $\frac{2}{3}$ (4):



(a)(iv)



Question 2

(a)(i) Since glycolic acid is a weak acid with a

small K_a , at equilibrium,

$$[\text{H}^+] = [\text{HOCH}_2\text{COO}^-]$$

$$[\text{glycolic acid}]_{\text{eqm}} = [\text{glycolic acid}]_{\text{initial}} = 0.10 \text{ mol dm}^{-3},$$

$$[\text{H}^+] \approx \sqrt{(1.48 \times 10^{-4})(0.100)}$$

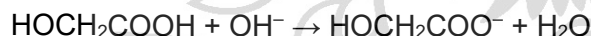
$$= 0.003847 \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg(0.003847) = 2.41$$

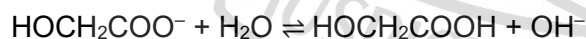
(a)(ii) $\text{pOH} = -\lg(0.100) = 1.00$

$$\text{pH} = 14 - 1.00 = 13.0$$

(a)(iii) When 25.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ of NaOH is added to 25.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ of glycolic acid, all the glycolic acid is converted to glycolate according to the following equation.



Glycolate undergoes hydrolysis in water and produces OH^- , causing the pH of the mixture to be alkaline i.e. more than 7.



(b)

Phenol red is the most suitable indicator as the equivalence pH of the titration (7.6) falls within the range of pH for the colour change of phenol red (6.8 – 8.4).

Note: Students should explicitly make reference to the equivalence pH of 7.6.

(c)

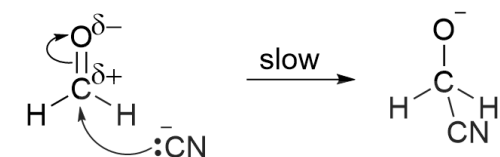
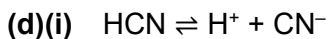
Glycolic acid is a weak acid which dissociates partially in water.



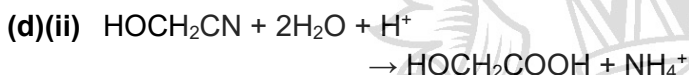
When ammonium glycolate is added, it undergoes complete dissociation.



This increases the concentration of glycolate ions and causes the position of equilibrium (1) to shift left, decreasing $[\text{H}^+]$, causing the pH of the mixture to increase.



Note: Partial charges on HCN should be clearly shown.

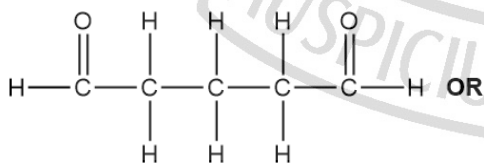
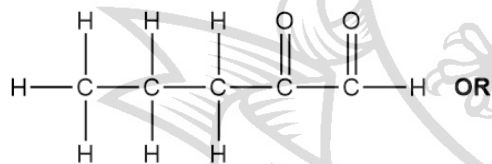
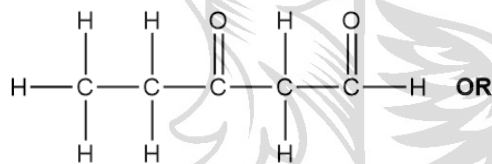


Question 3

(a)(i) Considerations

1. No reaction with Na(s)
⇒ no alcohol or $-\text{COOH}$ present.
2. Ag mirror with Tollens' reagent
⇒ presence of $-\text{CHO}$ group
3. No reaction with alkaline $\text{I}_2(\text{aq})$
⇒ no $-\text{CH}(\text{OH})\text{CH}_3$ or $-\text{COCH}_3$ present
4. No reaction with $\text{Br}_2(\text{l})$ in the dark
⇒ no alkene present

Since **A** is a straight-chain molecule, **A** could be



(a)(ii)

Note: This question required the answer to be in displayed formula.

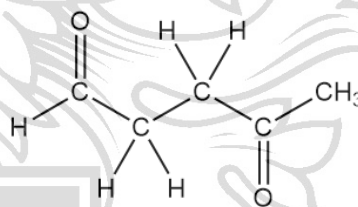
Since **A** contains $-\text{CHO}$, it gets oxidised to $-\text{COOH}$ by acidified $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ and gains 1 O in the molecular formula.



(a)(iii) Considerations

1. No reaction with Na(s)
⇒ no alcohol or $-\text{COOH}$ present.
2. Ag mirror with Tollens' reagent
⇒ presence of $-\text{CHO}$ group
3. Yellow ppt with alkaline $\text{I}_2(\text{aq})$
⇒ $-\text{COCH}_3$ present
4. No reaction with $\text{Br}_2(\text{l})$ in the dark
⇒ no alkene present

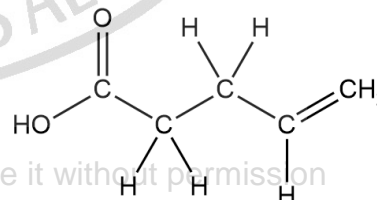
Since **B** is a straight-chain molecule, **B** is



(a)(iv) CHI_3

(a)(v) Considerations

1. Effervescence with Na(s)
⇒ alcohol or $-\text{COOH}$ present.
2. No reaction with Tollens' reagent
⇒ No $-\text{CHO}$ group present
3. No reaction with alkaline $\text{I}_2(\text{aq})$
⇒ no $-\text{CH}(\text{OH})\text{CH}_3$ or $-\text{COCH}_3$ present
4. Decolourises brown $\text{Br}_2(\text{l})$ in the dark
⇒ alkene present
5. Does not show stereoisomerism
⇒ No chiral centre and each doubly bonded C is not bonded to two different groups.

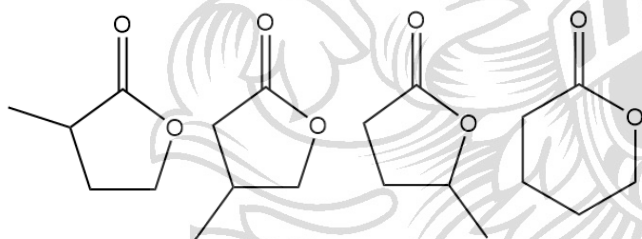


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(b)(i) Constitutional isomers have the same molecular formula but different structural formula, i.e. different arrangement of atoms.

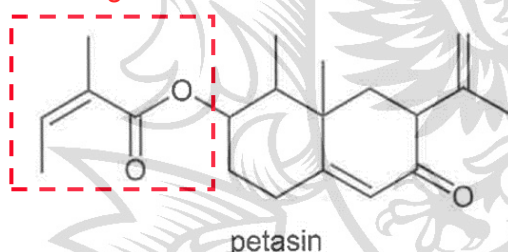
- (b)(ii)**
1. No reaction with Na(s)
⇒ no alcohol or -COOH present.
 2. No reaction with Tollens' reagent
⇒ No -CHO group present
 3. No reaction with alkaline $\text{I}_2(\text{aq})$
⇒ no -CH(OH)CH_3 or -COCH_3 present
 4. No reaction with $\text{Br}_2(\text{l})$ in the dark
⇒ no alkene present
 5. Undergoes acidic hydrolysis to form one organic molecule.
⇒ Cyclic ester present

Some possible structures include:

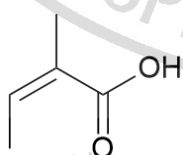


(c)(i) Since angelic acid has formula of $\text{C}_5\text{H}_8\text{O}_2$ and reacts to form petasin, we can identify the part of petasin which originated from angelic acid.

From angelic acid



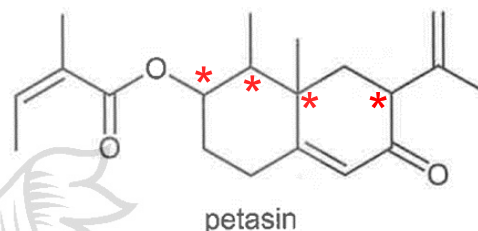
We can deduce angelic acid to have the following structure.



Functional groups present in angelic acid: carboxylic acid and alkene.

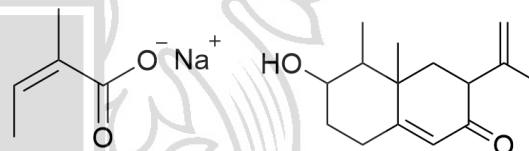
(c)(ii) Stereoisomerism refers to the existence of two or more compounds with the same molecular formula and structural formula but different spatial arrangement of atoms.

(c)(iii)



(c)(iv) No. of chiral centres = 4
No. of $\text{C}=\text{C}$ that can undergo cis-trans isomerism = 1 (only the $\text{C}=\text{C}$ from angelic acid)
Total number of stereoisomers = $2^{(4+1)} = 32$.

(c)(v) Products of alkaline hydrolysis



Question 4

(a) The two conditions are the partial pressure of any gas is at 1 bar and the concentration of any species in aqueous solution is 1 mol dm^{-3} .

(b)(i) $\Delta G = \Delta H - T\Delta S$

(b)(ii) Referring to Fig. 4.2, since the reaction goes to completion, the mole fraction of trans-but-2-ene in the cis/trans mixture will go from 0.0 to 1.0.

$$\begin{aligned}\Delta H_r &= \Delta H_f(\text{products}) - \Delta H_f(\text{reactants}) \\ &= -12.2 - (-7.8) = -4.4 \text{ kJ mol}^{-1}\end{aligned}$$

Referring to Fig. 4.1, since the reaction goes to completion, the mole fraction of trans-but-

2-ene in the cis/trans mixture will go from 0.0 to 1.0.

$$\begin{aligned}\Delta G_r &= \Delta G_f(\text{products}) - \Delta G_f(\text{reactants}) \\ &= 62.9 - 65.9 = -3.0 \text{ kJ mol}^{-1}\end{aligned}$$

$$\text{Since } \Delta G_r = \Delta H_r - T\Delta S_r,$$

$$-3.0 = -4.4 - 298(\Delta S)$$

$$\Delta S = -0.00470 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

(c)(i) Dynamic equilibrium refers to a state in a reversible closed system in which the rates of the forward and backward reactions are continuing at the same rate, resulting in no net change in the macroscopic properties (e.g. concentrations, partial pressure) of the reactants and products.

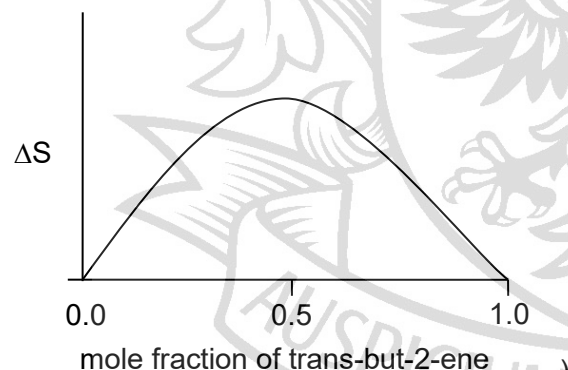
(c)(ii)

(b)(iii) **Approach** – The question asked us to consider $\Delta G = \Delta H - T\Delta S$. We know that ΔH changes linearly with a negative gradient when mole fraction of trans-but-2-ene increases from 0 to 1. We need to consider how ΔS changes with mole fraction of trans-but-2-ene, before applying $\Delta H - T\Delta S$ to the ΔH and ΔS graphs.

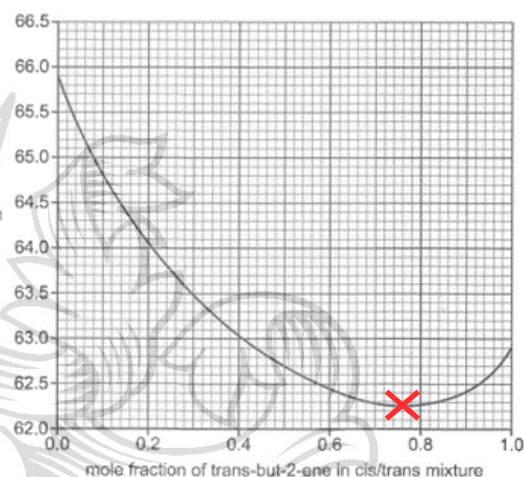
Graph of ΔS against mole fraction

At mole fraction = 0, there is purely cis-but-2-ene. From mole fraction 0 to 0.5, there is an increase in ΔS due to mixing as a result of the increase in proportion of trans-but-2-ene. At mole fraction = 0.5, ΔS is maximum. From mole fraction 0.5 to 1, there is a decrease in ΔS due to decreasing proportion of cis-but-2-ene until mole fraction = 1 where there is only trans-but-2-ene.

(Note: the graph of ΔS against mole fraction would look like the following.



Since ΔH decreases linearly, the combination of the graphs of ΔH and ΔS against mole fraction according to $\Delta G = \Delta H - T\Delta S$ would result in a curve.



The marked X is at mole fraction = 0.76.

From the graph, the ΔG_f values becomes more negative (less positive) from mole fraction = 0.0 to 0.76, indicating that the forward reaction which forms trans-but-2-ene becomes more favoured.

From mole fraction = 0.76 to 1.0, the ΔG_f values also becomes less negative (more positive), indicating that the formation of trans-but-2-ene becomes less favoured i.e. the formation of cis-but-2-ene is more favoured.

At X i.e. mole fraction = 0.76, the ΔG_f value is at its minimum and the formation of both trans-but-2-ene and cis-but-2-ene are equally favoured, indicating that dynamic equilibrium has been reached.

(c)(iii) $K_p = \frac{p_{\text{trans}}}{p_{\text{cis}}} = \frac{n_{\text{trans}}}{n_{\text{cis}}} = 3.36$

(V & T are constant)

$$\Rightarrow n_{\text{trans}} = 3.36 n_{\text{cis}}$$

Mole fraction of trans isomer

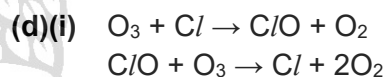
$$= \frac{n_{\text{trans}}}{n_{\text{cis}} + n_{\text{trans}}} = \frac{3.36n_{\text{cis}}}{n_{\text{cis}} + 3.36n_{\text{cis}}} = 0.77 \text{ (to 2 s.f.)}$$

Mole fraction of cis isomer

$$= 1 - 0.77 = 0.23$$

- (d) The trans-isomer is more stable. The two methyl groups in the cis-isomer are in close proximity and their electron clouds experience strong repulsion. Such repulsion is significantly less in the trans-isomer as the two-methyl groups are far away from each other.

- (c)(ii) From table 5.1, reaction 1 i.e. photolysis of O_2 occurs *above* the ozone layer and this consumes much of the ultra-violet light at 220 nm. Hence, significantly less ultra-violet light at 220 nm reaches the ozone layer, causing the rate of photolysis of O_2 in the ozone layer to be slower.



- (d)(ii) Chlorofluorocarbons (CFCs)

- (d)(iii) Since the ozone layer within the stratosphere contains 90% of all atmospheric ozone, there is a greater frequency of effective collisions between NO produced by an aircraft flying in the stratosphere and the ozone in the stratosphere, than on Earth's surface where the ozone concentrations are low.

Question 5

Note: This question is heavy on data-response and students need to read and understand the information provided on page 17 well in order to answer the questions.

- (a) Oxygen atom is a free radical as it contains unpaired electrons.



- (b)(i) **M** is likely to be N_2 as it is most abundant (78%) and will have the high chance of collisions with the other reacting gases.

- (b)(ii) Reaction 3 is likely to occur at a slower rate in the ozone layer. This is because the O_3 required for reaction 3 is significantly less abundant (<0.06%) compared to O_2 required for reaction 2 (21%). There is a lower frequency of effective collisions given the significantly lower abundance of O_3 , resulting in a slower rate for reaction 3.

- (c)(i) energy of 1 photon, $E = \frac{(6.63 \times 10^{-34})(3.00 \times 10^8)}{254 \times 10^{-9}}$
 $= 7.831 \times 10^{-19} \text{ J}$

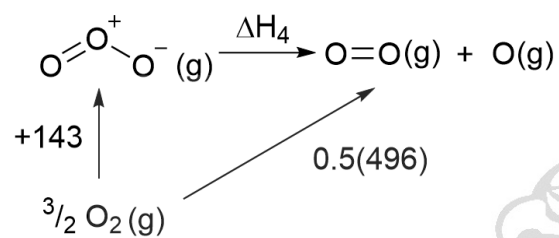
$$\begin{aligned} \text{energy of 1 mole of photons} &= 7.831 \times 10^{-19} \times 6.02 \times 10^{23} \\ &= 471400 \text{ J} \\ &= 471 \text{ kJ} \end{aligned}$$

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 Answer = 471 kJ mol⁻¹

- (e)(i) Based on Fig. 5.1, ozone should have two unequal bond lengths of 0.121 nm for the double bond and 0.148 nm for the single bond. However, the measured bond length of ozone is a single value at 0.128 nm. Hence, Fig. 5.1 does not accurately represent the bonding in ozone.

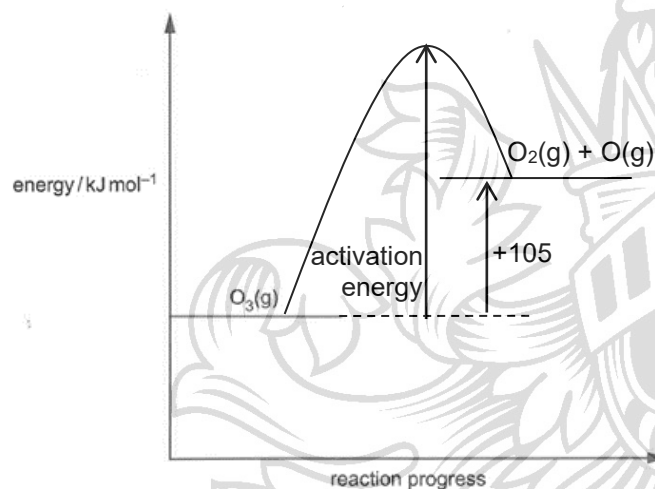
- (e)(ii) The central O atoms in O_3 is sp^2 -hybridised. Two sp^2 hybrid orbitals from the central O atom each undergoes head-on overlap with one of atomic orbital of each peripheral oxygen atom to form 2 O–O σ bonds. Each unhybridized p-orbital of the three O atoms overlaps side-on to form a continuously π electron cloud, delocalizing the π electrons over the entire bent structure. Hence, each O–O bond has partial double bond character, having equal bond lengths which are intermediate between the single and double bonds.

(e)(iii)

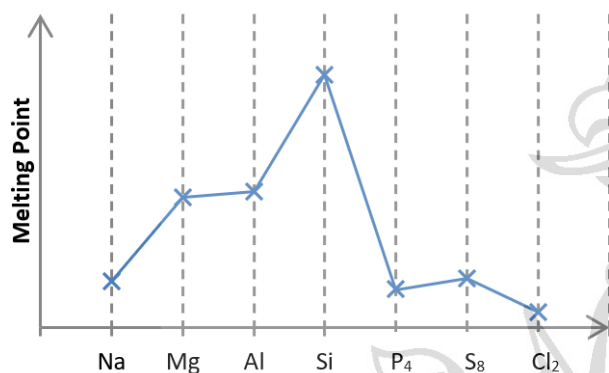


$$\Delta H_4 = -143 + 0.5(496) = +105 \text{ kJ mol}^{-1}$$

(e)(v)



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Question 1**(a)(i)**

Na, Mg and Al have metallic structures where strong electrostatic forces of attraction exist between positive metal ions and a sea of delocalised electrons.

From Na to Al, the number of delocalized valence electrons increase, leading to increasing cationic charge and decreasing cationic size i.e. increasing cationic charge density. More energy is required to break the increasingly stronger metallic bond strength from Na to Al.

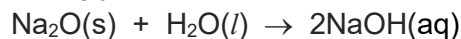
Si has a giant molecular structure where strong covalent bonds exist between Si atoms. Large amount of energy is required to break numerous Si-Si bonds. Hence its melting point is the highest among the Period 3 elements.

P₄, S₈ and Cl₂ have simple molecular structures where weak instantaneous dipole-induced dipole (id-id) interactions exist between their respective molecules.

From Cl₂ to P₄ to S₈, the size and polarizability of their electron cloud increases, leading to stronger id-id interactions. More energy is required to overcome the stronger id-id interactions, leading to an increase in melting point from Cl₂ to P₄ to S₈.

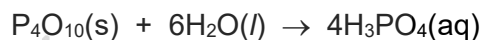
(b)

Na₂O reacts vigorously with water to form a strongly alkaline solution with a pH of 13.

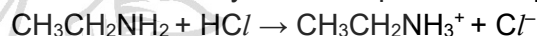


Al₂O₃ does not react with water and the mixture has a pH of 7.

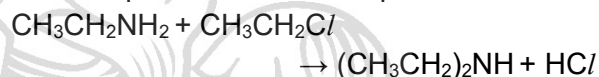
P₄O₁₀ reacts readily with water to form an acidic solution with a pH of 2.

**(c)**

A Bronsted-Lowry base is a proton-acceptor.



A nucleophile is an electron-pair donor.

**(d)**

A: Due to the overlap between the π electron cloud of the C=O and the orbital containing the lone pair of electrons on N, the lone pair of electrons can delocalize into the π electron cloud of the C=O, making it unavailable for coordination to a H⁺. Hence, **A** is the least basic.

Phenylamines (**B** and **C**) are less basic than aliphatic amines (**D**) because the orbital containing the lone pair of electrons on N overlaps with the π electron cloud of the benzene ring, allowing the lone pair on N to delocalize into the π electron cloud of the benzene ring, making it less available for coordination to a H⁺. In addition, the electron-donating PhCH₂- group increases the electron density on N in **D**, making the lone pair on N more readily available for coordination to H⁺.

In **B**, the orbital containing the lone pair of electrons on N overlaps with the π electron cloud of two neighbouring benzene rings instead of one benzene ring in **C**. Hence the lone pair of electrons on N in **B** is delocalized to a larger extent than in **C**, making it less available for coordination to a H⁺.

(e)(i) Route 1

Type of reaction: reduction

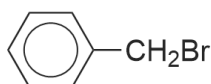
Reagents and condition : LiAlH_4 in dry ether

Route 2

Type of reaction: reduction

Reagents and condition: LiAlH_4 in dry ether
or H_2 , Ni, heat

(e)(ii) Starting organic compound:



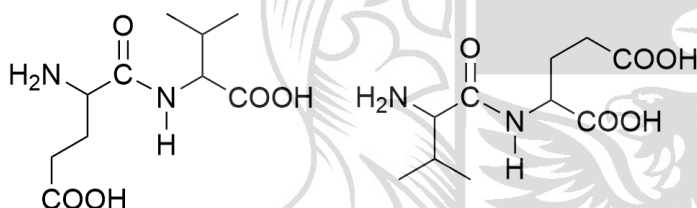
Reagent: NH_3 (given in question)

Conditions: excess concentrated NH_3 in ethanol, heat in sealed tube.

(f)(i) 2 different constitutional isomers (Glu-Val, Val-Glu)

Note: dipeptides are formed from the reaction between the $\alpha\text{-NH}_2$ group and the $\alpha\text{-COOH}$ group, not the $-\text{NH}_2$ and $-\text{COOH}$ groups in the side chains.

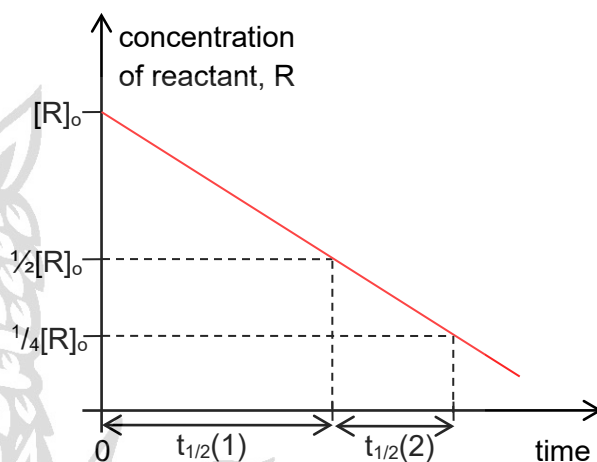
(f)(ii)



Question 2

(a)(i) The half-life of a reaction is the time taken for the concentration of a reactant to decrease to half its initial value.

(a)(ii)



For a zero-order reaction, consecutive half-lives decrease.

(b)

Number of half-lives = $660/220 = 3$

Partial pressure of SO_2Cl_2 after 3 half-lives
= $75 \times (\frac{1}{2})^3 = 9.38 \text{ kPa}$

(c)

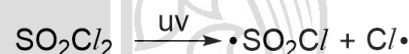
E = H_2SO_4

F = H_2SO_3

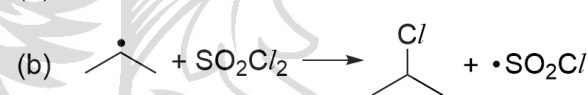
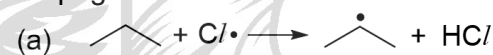
(d)

Free radical substitution

Initiation

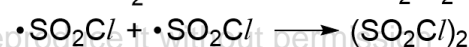
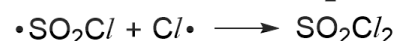
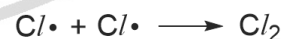


Propagation



then (a), (b), (a), (b),

Termination

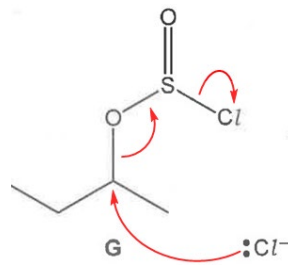


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- (e)(i) 1-bromobutane : 2-bromobutane
= 6 : 4 = 3 : 2

Based on probability, substitution of any 1 of the 4 hydrogens in $-\text{CH}_2\text{CH}_2-$ gives 1-bromobutane, while substitution of any 1 of the 6 hydrogens in the two $-\text{CH}_3$ groups gives 2-bromobutane.

- (g)(ii)



- (e)(ii) The formation of 2-bromobutane occurs via the secondary $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CH}\bullet$ radical which is more stable than the primary $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\bullet$ radical required for the formation of 1-bromobutane. This is due to the presence of two electron-donating alkyl groups in the secondary radical compared to one electron-donating alkyl group in the primary radical. Since the secondary radical is more stable, 2-bromobutane is formed in larger proportion than predicted in (e)(i).

- (g)(iii) A single enantiomer will be obtained. The reactions in steps 1 to 3 do not involve the chiral carbon on butan-2-ol. In step 4, the chloride ion attacks the chiral carbon via a $\text{S}_{\text{N}}2$ mechanism, resulting in an inversion of configuration, leading to a single enantiomer, now with inverted configuration.

- (f) Ease of bromination:
nitrobenzene < benzene < phenylamine

The $-\text{NO}_2$ group is deactivating and electron-withdrawing which decreases the electron density of the π electron cloud in benzene, making nitrobenzene less susceptible than benzene to electrophilic attack by Br^+ .

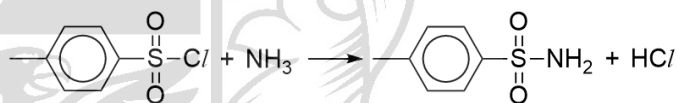
The $-\text{NH}_2$ group is activating and electron-donating which increases the electron density of the π electron cloud in benzene, making phenylamine more susceptible than benzene to electrophilic attack by Br^+ .

- (h)(i) $\text{CH}_3\text{SO}_2\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{SO}_2\text{O}^- + \text{H}_3\text{O}^+$
acid base conjugate base conjugate acid

- (h)(ii) H: $\text{CF}_3\text{SO}_2\text{OH}$
J: CH_3OH

Note: As suggested by the question stem at the beginning of (h), it is useful to draw a parallel to the carboxylic acids and esters.

- (h)(iii)



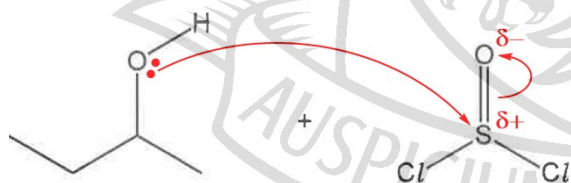
Question 3

- (a)(i) $\text{Cu} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
 $\text{Cu}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

- (a)(ii) Copper is a transition element because it is a d-block element which forms an ion, Cu^{2+} , with a partially filled d-subshell ($3d^9$) as shown in (a)(i).

- (b) In transition element complexes, the presence of ligands causes the splitting of the five originally degenerate 3d orbitals of the transition metal ion into two sets of slightly different energy levels. Since the 3d subshell is likely to be partially filled, the

- (g)(i)

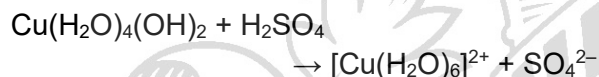


electrons from the lower energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d orbitals.

Such d-d transitions are responsible for the colour observed and the colour observed is the complement of the colour absorbed.

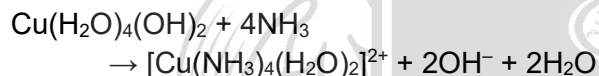
(c)(i) Reaction with $\text{H}_2\text{SO}_4(\text{aq})$

The pale blue solid, $\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2$, undergoes an acid-base reaction with $\text{H}_2\text{SO}_4(\text{aq})$, causing the pale blue solid to dissolve and form a pale blue solution of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.



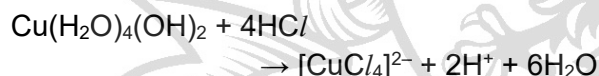
Reaction with excess $\text{NH}_3(\text{aq})$

The pale blue solid, $\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2$, undergoes a ligand exchange reaction with $\text{NH}_3(\text{aq})$, causing the pale blue solid to dissolve and form a dark blue solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.



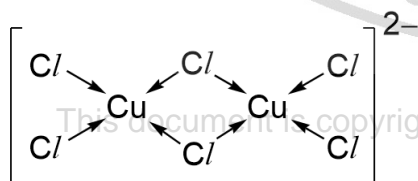
Reaction with concentrated HCl

The pale blue solid, $\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2$, undergoes a ligand exchange reaction and acid-base reaction with concentrated HCl , causing the pale blue solid to dissolve and to form a yellow solution of $[\text{CuCl}_4]^{2-}(\text{aq})$.



(c)(ii) The black solid is CuO . Decomposition reaction occurred.

(d)



(e)(i) $K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^-]^2$

Let the solubility of $\text{Cu}(\text{OH})_2$ be $x \text{ mol dm}^{-3}$.

$$K_{\text{sp}} = (x)(2x)^2 = 2.00 \times 10^{-19}$$

$$x = 3.684 \times 10^{-7}$$

$$[\text{OH}^-] = 2x = 7.368 \times 10^{-7}$$

$$\text{pOH} = -\lg(7.368 \times 10^{-7}) = 6.133$$

$$\text{pH} = 14 - 6.133 = 7.87$$

Question 4

(a)(i) High temperature and low pressure

(a)(i) For an ideal gas, $pV = nRT \Rightarrow pV/RT = n$. Hence the graph of pV/RT against p for an ideal gas is a horizontal line with y-intercept $= n$, which describes the graph of gas **M**, which is an ideal gas with negligible intermolecular forces.

For gas **L**, as the pressure increases, the volume of the system becomes smaller. The gas particles come closer together and intermolecular attractive forces between the gas particles become significant. This causes the gas to occupy a volume smaller than what it would occupy were it ideal, causing the decrease in the pV/RT observed in the initial part of the graph.

(b) $pV = nRT$

$$pV = \frac{m}{M_r} RT$$

$$M_r = \frac{mRT}{pV} = \frac{(0.160)(8.31)(250+273)}{(150 \times 10^3)(50.4 \times 10^{-6})} = 92.0$$

(c)(i) Electrolysis of $\text{AgNO}_3(\text{aq})$

At the cathode, Ag^+ or H_2O can be reduced. Since $E^\ominus(\text{Ag}^+/\text{Ag}) = +0.80 \text{ V}$ is more positive than $E^\ominus(\text{H}_2\text{O}/\text{H}_2) = -0.83 \text{ V}$, Ag^+ will be reduced to form $\text{Ag}(\text{s})$.

At the anode, H_2O will be oxidised to form $\text{O}_2(\text{g})$.

Electrolysis of concentrated $\text{CaBr}_2(\text{aq})$

At the cathode, Ca^{2+} or H_2O can be reduced.
Since $E^\ominus(\text{Ca}^{2+}/\text{Ca}) = -2.87 \text{ V}$ is less positive than $E^\ominus(\text{H}_2\text{O}/\text{H}_2) = -0.83 \text{ V}$, H_2O will be reduced to form $\text{H}_2(\text{g})$.

At the anode, Br^- or H_2O can be oxidised.

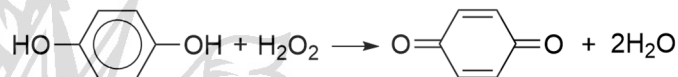
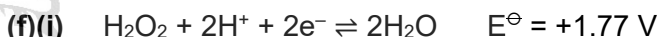
$$E^\ominus(\text{Br}_2/\text{Br}^-) = +1.07 \text{ V}$$

$$E^\ominus(\text{O}_2/\text{H}_2\text{O}) = +1.23 \text{ V}$$

Br^- will be preferentially oxidised to form Br_2 as due its less positive $E^\ominus(\text{Br}_2/\text{Br}^-)$.

(e) Since $E^\ominus(\text{MnO}_4^-/\text{Mn}^{2+}) = +1.52 \text{ V}$ and $E^\ominus(\text{Sn}^{4+}/\text{Sn}^{2+}) = +0.15 \text{ V}$, MnO_4^- oxidises Sn^{2+} to Sn^{4+} since the E^\ominus_{cell} of the reaction = $1.52 - 0.15 = +1.37 \text{ V} > 0$.

Since $E^\ominus(\text{MnO}_4^-/\text{Mn}^{2+}) = +1.52 \text{ V}$ and $E^\ominus(\text{PbO}_2/\text{Pb}^{2+}) = +1.47 \text{ V}$, MnO_4^- oxidises Pb^{2+} to PbO_2 since the E^\ominus_{cell} of the reaction = $1.52 - 1.47 = +0.05 \text{ V} > 0$.



$$E^\ominus_{\text{cell}} = 1.77 - 0.70 = +1.07 \text{ V}$$

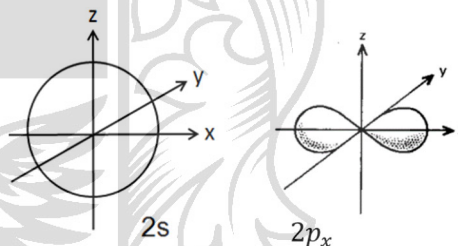
(f)(ii) $\text{pH} = (0.70 - 0.51) \left(\frac{2 \times 96500}{2.303 \times 8.31 \times 298} \right) = 6.43$

(g) 4-chloro-3,5-dimethylphenol

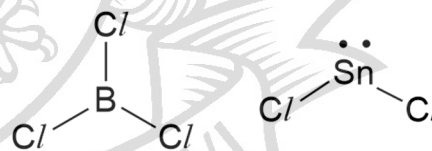
Question 5

(a) B: $1s^2 2s^2 2p^1$

The occupied atomic orbitals in the outer shell of boron are 2s and 2p.



(b)(i)



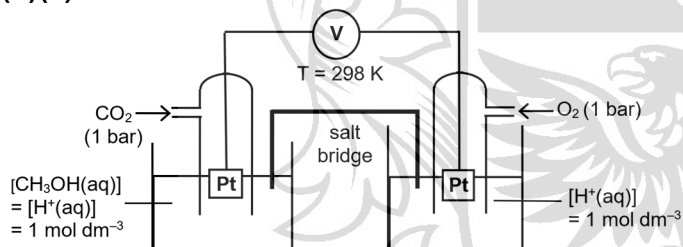
There are three bond pairs and no lone pairs around B in BCl_3 . By VSEPR theory, in order to minimize repulsion between the bond pairs, BCl_3 adopts a trigonal planar shape with a bond angle of 120° .

(c)(ii) Cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$
 $n_{\text{Cu}} = 0.350 / 63.5 = 0.005512 \text{ mol}$
 $n_{\text{e}} = 2(0.005512) = 0.01102 \text{ mol}$
 $Q = It = n_{\text{e}}F$
 $(0.500)(45.0 \times 60) = 0.01102F$
 $F = 122504 \text{ C mol}^{-1}$

$$\begin{aligned} \text{Since } F &= Le, \\ 122504 &= L(1.60 \times 10^{-19}) \\ L &= 7.66 \times 10^{23} \end{aligned}$$

(d)(i) The standard cell potential, E^\ominus_{cell} , is the potential difference between two half-cells under standard conditions.

(d)(ii)



(d)(iii) $\Delta G^\ominus = -nFE^\ominus$

$n = 6$ since there is one mol of CH_3OH in the overall equation and the half-equation in (d)(ii) shows 6 mol of e^- for one mol of CH_3OH .

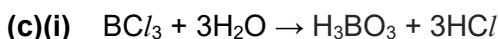
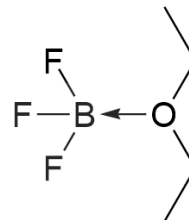
$$\begin{aligned} \Delta G^\ominus &= -(6)(96500)(1.61) \\ &= -932200 \text{ J mol}^{-1} \\ &= -932 \text{ kJ mol}^{-1} \end{aligned}$$

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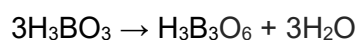
(b)(ii) Since SnCl_2 has two bond pairs and one lone pair around Sn, it has a bent shape. Since lone pair-bond pair repulsion is stronger than bond pair-bond pair repulsion, the presence of the lone pair on Sn causes the Cl-Sn-Cl bond angle to be smaller than in BCl_3 .

(e)(i) B in BF_3 is sp^2 hybridised and has an empty p-orbital which can accept a pair of electrons from ethoxyethane.

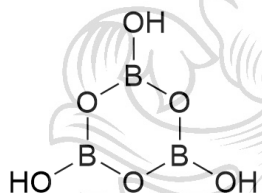
(e)(ii)



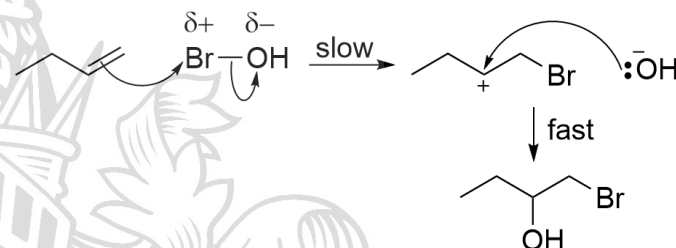
(c)(ii) When H_3BO_3 was heated to form $\text{H}_3\text{B}_3\text{O}_6$, 3 units of H_2BO_3 were required, evident from the number of boron atoms. The “extra” H and O will form H_2O .



A condensation reaction took place.



(f)(i)



(f)(ii)

(d)(i) A buffer solution is a solution which is able to resist pH changes when a small amount of an acid or a base is added.

(d)(ii) Initial amt of H_3BO_3
 $= (75/1000)(0.0200) = 0.00150 \text{ mol}$

Initial amt of NaOH
 $= (x/1000)(0.0300) = 3.00 \times 10^{-5}x$

	H_3BO_3	+	OH^-	\rightarrow	H_2BO_3^-	+	H_2O
Initial amt / mol	0.00150		$3.00 \times 10^{-5}x$		0.00		—
Final amt / mol	$0.00150 - 3.00 \times 10^{-5}x$		0		$3.00 \times 10^{-5}x$		—

(f)(iii) Intramolecular nucleophilic substitution, $\text{S}_{\text{N}}2$

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{H}_3\text{BO}_3]}{[\text{H}_2\text{BO}_3^-]}$$

$$8.8 = -\lg(5.37 \times 10^{-10}) + \lg \frac{(3.00 \times 10^{-5}x)}{(0.0015 - 3 \times 10^{-5}x)}$$

$$x = 12.7 \text{ cm}^3$$