## 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.

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**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 $CO_2$ 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, …."

# 2015 A-Level H2 Chemistry Paper 1 Suggested Solutions

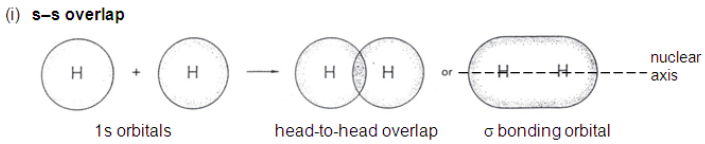
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B | B | C | C | B | D | B | C | A | B | D | C | D | B | D | D | A | C | B | A |
| **21** | **22** | **23** | **24** | **25**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

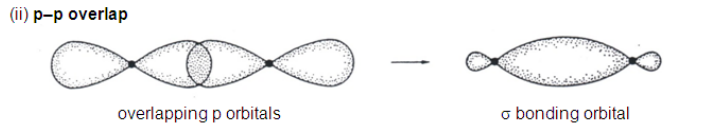
## Q1 (B)

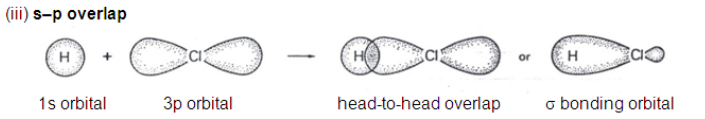
| | | |
|---|---|---|
| **A** | $1s^2\,2s^1\,2p^1$ | Excited state of Group 2 |
| **B** | $2s^2\,2p^2$ | Ground state of Group 14 |
| **C** | $2s^1\,2p^3$ | Excited state of Group 14 |
| **D** | $3p^4$ | Excited state |

## Q2 (B)

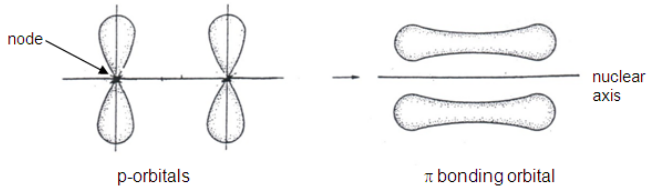
**σ bonds** formed by head-on overlap of either s or p orbitals.



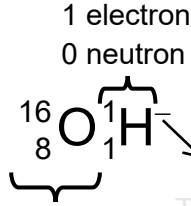




**π bonds** formed by side-to-side overlap of p-orbitals.




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

## Q3 (C)




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

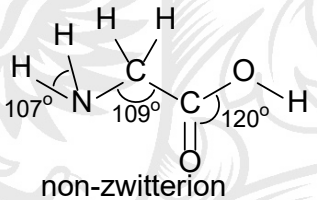
(*high charge & small size ⇒ high charge density ⇒ stronger attraction for delocalised electrons.*)

- no. of valence electrons which can be delocalised

(*more delocalised electrons ⇒ greater attraction between metal cations and delocalised electrons*)

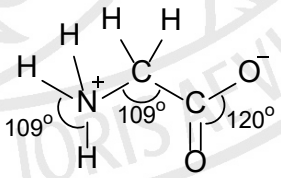
| | |
|---|---|
| **A** | true, but irrelevant |
| **B** | true, but irrelevant |
| **C** | $Ca^{2+}$ has a higher charge and hence higher charge density than $Na^+$. |
| **D** | true, but irrelevant. This option discusses the total no. of electrons *in each cation* and not the no. of delocalised electrons.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

## Q5 (B)




non-zwitterion

90° bond angle absent




zwitterion

90° bond angle absent

$-NH_2 \longrightarrow -NH_3^+$
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. $Na_2O(s)$]** is formed from **its constituent gaseous ions [i.e. $Na^+(g)$ and $O^{2-}(g)$]** under **standard conditions** of **298 K and 1 bar**.

| | |
|---|---|
| **D** | $2Na^+(g) + O^{2-}(g) \longrightarrow Na_2O(s)$<br>(from gaseous ions) (to 1 mol of solid ionic compound) |

**Q7 (B)**

Amt of NaOH used
= (12.5 / 1000)(0.0500)
= 0.000625 mol
= Amt of HC*l* reacted

Amt of HC*l* remaining
= (25/1000)(0.100) – 0.000625
= 0.001875 mol

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

**Q8 (C)**

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

$CH_4 + O_2 \longrightarrow \mathbf{9}CO_2 + \mathbf{1}CO + H_2O$

Balance the equation:
$10CH_4 + 19.5O_2 \longrightarrow \mathbf{9}CO_2 + \mathbf{1}CO + 20H_2O$

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**.

Hence, [HOC*l*] = $[H^+]$ = $[Cl_2]$ = 1 mol dm$^{-3}$

**Q11 (D)**

| | $CH_3CO_2H$ | $\rightleftharpoons$ | $CH_3CO_2^-$ | + | $H^+$ |
|---|---|---|---|---|---|
| Initial | C | | 0 | | 0 |
| Change | $-\alpha C$ | | $+\alpha C$ | | $+\alpha C$ |
| Eqm | $(1-\alpha)C$ | | $\alpha C$ | | $\alpha C$ |

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

**Q12 (C)**

To ↑ amt of methanol ⇒ 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 $CO_2$.

| | $H_2O(g)$ | + | $CO(g)$ | $\rightleftharpoons$ | $H_2(g)$ | + | $CO_2(g)$ |
|---|---|---|---|---|---|---|---|
| Initial / mol | 1.0 | | 1.0 | | 0 | | 0 |
| Change / mol | –x | | –x | | +x | | +x |
| Eqm /mol | 1.0 – x | | 1.0 – x | | x | | x |

Total amt of gases at eqm = 2(1.0 – x) + 2(x) = 2 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 = $k[H_2][NO]^2$

From expt 1 to 2, $[H_2]$ remains the same when [NO] x ½, initial rate x $(½)^2$ = ¼
⇒ **x = ¼(6.0) = 1.5**

From expt 2 to 3, [NO] remains the same when $[H_2]$ x 2, initial rate x 2
⇒ **y = 2(1.5) = 3.0**

From expt 3 to 4, $[H_2]$ remains the same and initial rate x ¼ (from 3.0 to 0.75).
Since rate ∝ $[NO]^2$, [NO] must have halved from 1.0 to 0.5 mol $dm^{-3}$ ⇒ **z = 0.5**

**Q15 (D)**

| | |
|---|---|
| **A** | charge density $\propto \left\|\frac{\text{charge}}{\text{radius}}\right\|$<br>Down Group 2, charge of $M^{2+}$ remains the same, but ionic radius increases.<br>⇒ 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.<br>Down Group 2,<br>• ionic radii of Group 2 cations increase<br>• charge density, and hence polarising power of cations decrease,<br>• covalent bonds in carbonate anion are less polarised / weakened to smaller extent,<br>• more thermal energy required to break covalent bonds in carbonate anion,<br>• thermal stability increases. |

**Q16 (D)**

Period 3 elements: Na Mg A*l* Si P S C*l* 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. *(Reaction of $PCl_3$ with water in not in syllabus)* |
| **D** | True. **P**, S and C*l* exist as simple molecules with formula $\mathbf{P_4}$, $S_8$ and $Cl_2$ respectively. |

**Q17 (A)**

| | | |
|---|---|---|
| **A✓** | $[Cu(NH_3)_4(H_2O)_2]^{2+}SO_4^{2-}$ | dark blue solution |
| **B✗** | $[Cu(NH_3)_6]^{2+}SO_4^{2-}$ | dark blue ~~precipitate~~ solution |
| **C✗** | $Cu(OH)_2)(H_2O)_4$ | pale blue ~~solution~~ precipitate<br>• essentially $Cu(OH)_2$ which is a precipitate |
| **D✗** | $[Cu(H_2O)_6]^+Cl^-$ | ~~pale blue~~ colourless solution<br>• $Cu^+$ has a fully filled d-subshell and hence no d-d transition can occur ⇒ $Cu^+$ is colourless |

**Q18 (C)**

Atomic radii: Mg > A*l* > 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 < A*l* < 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** → $[Cr(H_2O)_6]^{3+}$ + organic pdt

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

⇒ 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

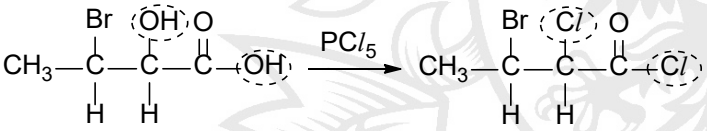
⇒ **X** is an acid i.e. $H_2SO_4$ (option B)

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)**

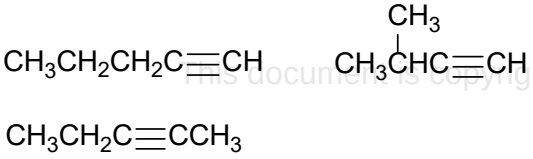
P*Cl*$_5$ reacts with functional groups containing –OH except phenols i.e. it reacts with alcohols (R–OH) and carboxylic acids (RCOOH). –OH group is substituted by C*l*.




**Q21 (B)**

Information from the question:

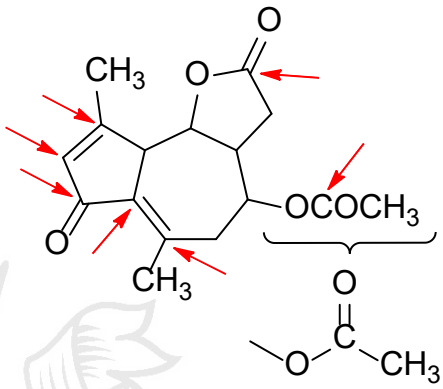
1. non-cyclic hydrocarbon
2. general formula: $C_nH_{2n-2}$
3. one carbon-cyclic triple bond per molecule






**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.

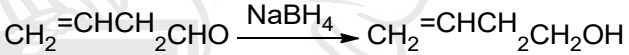



**Q23 (B)**

$NaBH_4$ only reduces ketones and aldehydes.

$CH_2$=$CHCH_2CHO$ contains

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




**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: Ph–Cl < R–Cl < RCOCl. Hence, ethanoyl chloride ($CH_3COCl$) hydrolyses most easily and gives a white precipitate of AgCl most rapidly.

| | |
|---|---|
| **A** | Large –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, $H_2O \rightarrow CCl_4$. 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<br>• the C atom in –COCl being more electron deficient due to the presence of 2 highly electronegative atoms, compared to 1 such atom in 2-chlorobutane<br>• trigonal planar geometry around C atom in –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. |
| **D** | |

**Q26 (D)**

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

$$-NH_3^+ \longrightarrow -NH_2$$
$$-COOH \longrightarrow -COO^-$$

In the case of aspartic acid, the two –COOH groups will be deprotonated to $-COO^-$.

**Q27 (D)**

Information from question

- Q is oxidised to form R
- $M_r(R) = M_r(Q) + 14$

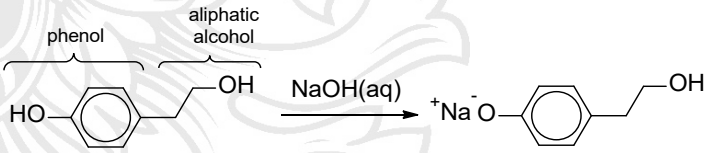
| | **Q → R** | |
|---|---|---|
| **A** | RCHO → RCOOH | $M_r(R) = M_r(Q) + 16$ |
| **B** | Reaction does not happen | |
| **C** | $RCH_2OH \rightarrow RCHO$ | $M_r(R) = M_r(Q) - 2$ |
| **D** | $RCH_2OH \rightarrow RCOOH$ | $M_r(R) = M_r(Q) + 14$ |

**Q28 (C)**

This question discusses thee 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)** | **$Na_2CO_3$(aq)** |
|---|---|---|---|
| Aliphatic alcohols (ROH) | ✓ to form $RO^-Na^+$ & $H_2(g)$ | × | × |
| Phenols (PhOH) | ✓ to form $PhO^-Na^+$ & $H_2(g)$ | ✓ to form $PhO^-Na^+$ & $H_2O$ | × |
| Carboxylic acids (RCOOH) | ✓ to form $RCOO^-Na^+$ & $H_2(g)$ | ✓ to form $RCOO^-Na^+$ & $H_2O$ | ✓ to form $RCOO^-Na^+$, $H_2O$, $CO_2$ |



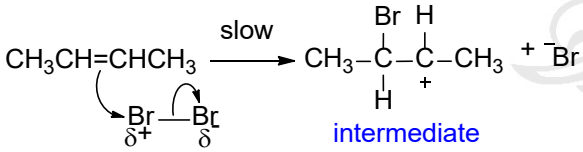

**Q29 (B)**

| | |
|---|---|
| **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 $Br_2(aq)$. |
| **C** | This combination does not produce the required electrophile ($Br^+$) for reaction with the phenols; $HBr + AlCl_3 \rightarrow H^+ + [BrAlCl_3]^-$. |
| **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 $Br_2(aq)$ 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, $H_2O$ acts as an nucleophile and attacks the carbocation intermediate to generate a bromohydrin as the major product.

**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 |

**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** | |
| **3** | Students should draw a parallel to $AlCl_3$.<br><br>$AlCl_3$ is covalent in nature due to significant polarisation of the electron cloud of $Cl^-$ by the small and highly charged $Al^{3+}$.<br><br>$Br^-$ 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. |

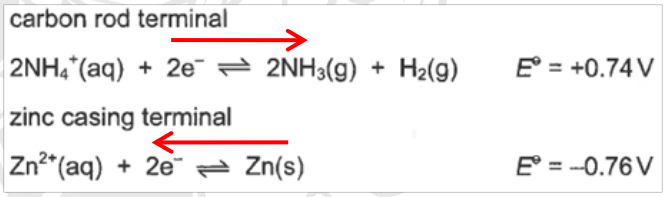
**Q33 (C)**

| | |
|---|---|
| **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.<br><br>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.

**Q34 (A)**




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

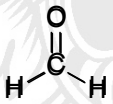
| | |
|---|---|
| **1** | $E^{\ominus}$ = +0.74 – (–0.76) = +1.50 V |
| **2** | reduction: $2NH_4^+(aq) + 2e^- \rightarrow 2NH_3(g) + H_2(g)$<br>oxidation : $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$<br><br>combining the above equations,<br>$2NH_4^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2NH_3(g) + H_2(g)$ |
| **3** | Since the zinc electrode is oxidised to $Zn^{2+}(aq)$, the zinc casing becomes thinner. |

**Q35 (B)**

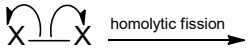
Rate constant, $k$, depends on temperature and the use of a catalyst. (Arrhenius equation: $k = Ae^{-E_a/RT}$)

| | |
|---|---|
| **1** | Introduction of a catalyst provides an alternative pathway of lower $E_a$.<br>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.<br>⇒ the 3 atoms around the C atom lie in the same plane as the C atom<br>⇒ all 4 atoms lie in the same plane  |
| **2** | Since electronegativity (EN) of C > H, H has an oxidation state of +1.<br>Since EN(O) > EN(C), O has an oxidation state of –2.<br>Let x be the oxidation state of C atom.<br>Since methanal has an overall charge of 0, then 2(+1) + (–2) + x = 0 ⇒ 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• is a radical which does not have any lone pair of electrons ⇒ this statement is not true. |
| **2** | A free radical is a species with unpaired electrons. |
| **3** |   X. + .X<br>In homolytic fission of a covalent bond, each atom takes 1 electron, resulting in the formation of free radicals. |

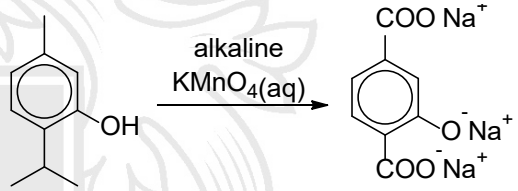
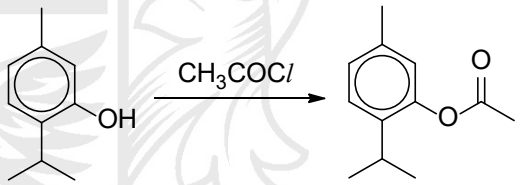
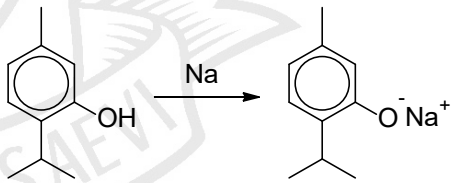
**Q38 (C)**

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 $–CH_3$.

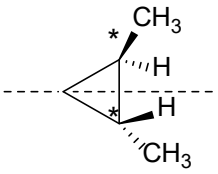
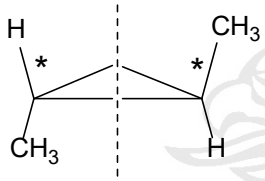
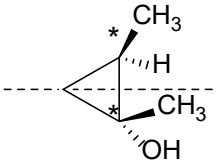
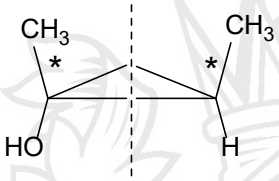
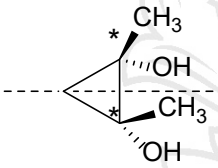
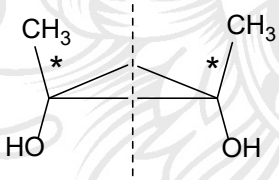
In order for the molecule to display cis-trans isomerism, **Y** cannot be H i.e. **reject option 1.** Options 2 and 3 allow the molecule to display cis-trans isomerism.

**Q39 (A)**

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

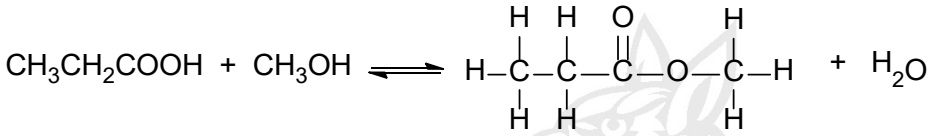
**Q40 (B)**

Molecules with no internal plane of symmetry are optically active.

| | |
|---|---|
| **1** |  top view  side view<br>No internal plane of symmetry ⇒ optically active |
| **2** |  top view  side view<br>No internal plane of symmetry ⇒ optically active |
| **3** |  top view  side view<br>Internal plane of symmetry exists (meso compound) ⇒ optically inactive |

**Q1 Planning**

**(a)**



**(b) Determine concentration of hydrochloric acid**

Pre-calculations (to determine volume of HC*l*(aq) to be used for titration)

Since [HC*l*(aq)] ~ 3 x [NaOH(aq)], 10 $cm^3$ of HC*l* would react completely with ~ 30 $cm^3$ of NaOH.
⇒ 10.0 $cm^3$ of HC*l*(aq) can be pipetted into a conical flask and be titrated against NaOH(aq) placed in a 50.00 $cm^3$ burette.

Procedure

1. Using a 10.0 $cm^3$ pipette, transfer 10.0 $cm^3$ of ~3 mol $dm^{-3}$ HC*l*(aq) into a 100 $cm^3$ conical flask.
2. Add 2–3 drops of thymolphthalein indicator.
3. Titrate HC*l*(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.
5. Repeat titrations until at least 2 consistent results (i.e. within $\pm$0.10 $cm^3$ of each other) are obtained.
6. Calculate the average titre value, $V_1$ $cm^3$, used.

Calculations

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

**Preparation of reaction mixtures**

Pre-calculations

The mixture at equilibrium will be titrated against 1.00 mol $dm^{-3}$ NaOH(aq) which reacts with **both** the HC*l* catalyst and $CH_3CH_2COOH$ present at equilibrium.

⇒ amt of NaOH used = amt of propanoic acid at eqm + amt of HC*l*

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 $cm^3$).

**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 = $\frac{50}{1000}(1.00)$
= 0.05 mol

Assuming 1 $cm^3$ of 3 mol $dm^{-3}$ HC*l* was used, then

0.05 = amt of propanoic acid at eqm + amt of HC*l*

0.05 = 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 $cm^3$ 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, $m_1$ 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, $m_2$ g.
4. Using a 50.00 $cm^3$ burette, transfer 1.00 $cm^3$ of HC*l*(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 $cm^3$ measuring cylinder, add 30 $cm^3$ 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 $cm^3$ 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, $V_2$ $cm^3$.
5. Repeat steps 1 to 4 for mixture **B** to obtain titre value, $V_3$ $cm^3$.

**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

amt of propanoic acid $= \frac{m_1}{74.0}$ mol

amt of methanol $= \frac{m_2}{32.0}$ mol

amt of ester = 0 mol

amt of water from 1 $cm^3$ of HC*l* (aq) $= \frac{1.00}{18}$

= 0.0556 mol

**Note to student:**

$H_2O$ 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 HC*l*(aq). A hint was given in the question:

"… you may assume that 1.00 $cm^3$ of HC*l*(aq) contains 1.00 $cm^3$ 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 HC*l*

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

where [HC*l*] = 0.1 $V_1$ mol $dm^{-3}$

**amt of propanoic acid at eqm = (0.001 $V_2$ – 0.0001 $V_1$) mol**

Let amt of propanoic acid at eqm = (0.001 $V_2$ – 0.0001 $V_1$) mol = x mol and $V_T$ be the total volume of the mixture.

| | $CH_3CH_2COOH$ + | $CH_3OH$ ⇌ | $CH_3CH_3COOCH_3$ + | $H_2O$ |
|---|---|---|---|---|
| initial conc / mol $dm^{-3}$ | $\frac{\frac{m_1}{74.0}}{V_T}$ | $\frac{\frac{m_2}{32.0}}{V_T}$ | 0 | $\frac{0.0556}{V_T}$ |
| Δ conc / mol $dm^{-3}$ | $\frac{-\left(\frac{m_1}{74.0}-x\right)}{V_T}$ | $\frac{-\left(\frac{m_1}{74.0}-x\right)}{V_T}$ | $\frac{+\left(\frac{m_1}{74.0}-x\right)}{V_T}$ | $\frac{+\left(\frac{m_1}{74.0}-x\right)}{V_T}$ |
| eqm conc / mol $dm^{-3}$ | $\frac{x}{V_T}$ | $\frac{\frac{m_2}{32.0}-\frac{m_1}{74.0}+x}{V_T}$ | $\frac{\left(\frac{m_1}{74.0}-x\right)}{V_T}$ | $\frac{0.0556+\frac{m_1}{74.0}-x}{V_T}$ |

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, $\Delta H_c^{\ominus}$ cannot be accurately determined.

**(b)(i)** Since energy released per $dm^3$ at 25 °C & 101 kPa is 0.0358 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 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)** $\Delta H^{\ominus} = \Sigma n \Delta H_c^{\ominus}(\text{rxts}) - \Sigma m \Delta H_c^{\ominus}(\text{pdts})$
$= -726 - [2(-286) + (-283)]$
$= +129 \text{ kJ mol}^{-1}$



**(d)(ii)** For reaction to be spontaneous, $\Delta G^{\ominus} < 0$
$\Rightarrow \Delta H^{\ominus} - T\Delta S^{\ominus} < 0$

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

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.

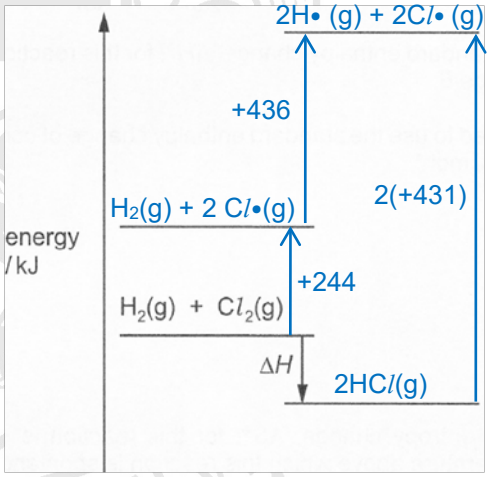
**C is less electronegative** than O, i.e. the **lone pair of electrons on C in CO are less tightly held** than the lone pair of electrons on O in $O_2$. **CO is more likely to form dative covalent bond** with the Fe(II) centre than $O_2$, preventing $O_2$ from being transported on the haemoglobin. The 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 C*l*–C*l* bond,** forming C*l*• radicals for reaction.

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

Initiation: $Cl_2 \xrightarrow{UV} Cl\bullet + Cl\bullet$

**(b)(iii)** Once initiated, the C*l*• radicals react with $H_2$. In the **propagation steps, the C*l*• 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:
1. why the reaction **continues** after brief exposure to light,
2. why it proceeds with **increasing rate**.

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

| | BE(H–H) + BE(X–X) | | 2BE(H–X) |
|---|---|---|---|
| X = C*l* | 436 + 244 | | 2(431) |
| X = Br | 436 + 193 | | 2(366) |

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

**(d)(i)** $NaCl + H_2SO_4 \longrightarrow HCl + NaHSO_4$ *(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 HC*l***. Therefore, HBr is reduces conc. $H_2SO_4$ while itself being **oxidised to $Br_2$**. This method will not generate significant amounts of HBr.

$2HBr(g) + H_2SO_4(l) \rightarrow Br_2(l) + SO_2(g) + 2H_2O(l)$

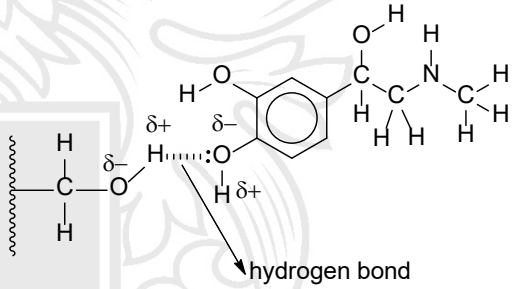
**(e)** **Test:**
To separate samples of HC*l*(aq) and HBr(aq), add $Cl_2$(aq) dropwise until in excess.

**Observations:**
An orange solution of $Br_2$(aq) will be observed for HBr(aq). The solution of HC*l*(aq) remains colourless.

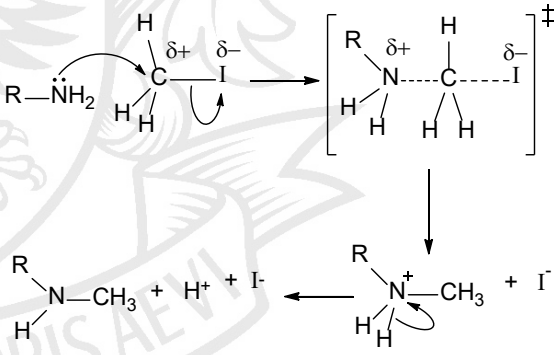
**Notes to student**:
1. It was the "**aqueous solutions** of these two gases" that needed distinguishing.
2. *(Not in syllabus)* Many students incorrectly suggested the use of concentrated $H_2SO_4$ to distinguish between the compounds. The addition of concentrated $H_2SO_4$ to an aqueous solution dilutes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

**Question 4**

**(a)**




**(b)(i)** **Nucleophilic substitution ($S_N2$)**

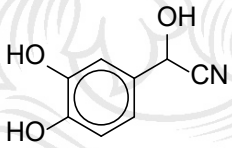


**Notes to student:**
1. all partial charges must be clearly shown
2. all curly arrows must be shown, **including the curly arrow which shows the breaking of the N–H bond in $RNH_3^+$.**

**(b)(ii)** If the reaction proceeded via an **$S_N1$ mechanism, the $CH_3^+$ 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**: LiA*l*$H_4$ 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)(i)** $2H^+ + 2e^- + Ag_2O \longrightarrow 2Ag + H_2O$

**(d)(ii)** amt of adrenaline $= \left(\frac{50}{1000}\right)(3.0\times10^{-3})$

$= 0.0015$ mol

Mole ratio of $Ag_2O$ : adrenaline = 2 : 1

Amt of $Ag_2O$ = 0.00015 x 2 = 0.00030 mol

Mass of $Ag_2O$ = 0.0030[2(108) + 16]

= 0.0696 g

**Question 5**

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

The **p-orbital containing the lone pair of electrons on C*l*** overlaps with the **$\pi$ electron cloud of benzene**, thereby allowing the lone pair of electrons to delocalise into the ring. As a result, the **C–C*l* bond is strengthened. The partial double bond character in the C–C*l* 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 | C*l* |
|---|---|---|---|
| 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 = $\underline{C_3H_2Cl}$

**(b)(ii)** pV = nRT

$$M_r = \frac{mass(RT)}{pV}$$
$$= \frac{(0.344)(8.31)(181+273)}{(101000)(87.4\times10^{-6})}$$
$$= 147.0$$

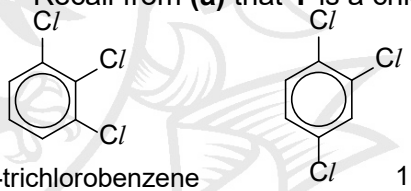
Let molecular formula of **X** be $C_{3n}H_{2n}Cl_n$

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

n = 2

Molecular formula of **X** = $C_6H_4Cl$

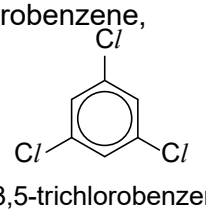
**(c)** Recall from **(a)** that **Y** is a chlorobenzene,




1,2,3-trichlorobenzene

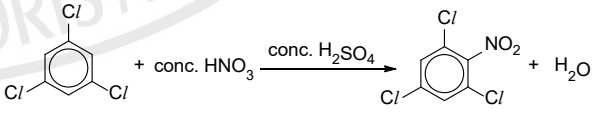



1,2,4-trichlorobenzene




1,3,5-trichlorobenzene

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




Compound **Y**

## Question 1

**(a)(i)** $ROH + Na \longrightarrow RO^-Na^+ + \frac{1}{2}H_2$

Mole ratio of ROH : $H_2$ = 2 : 1

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

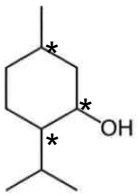
$M_r$ of menthol = 10(12) + 20(1) + 16 = 156

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

Percentage by mass of menthol

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

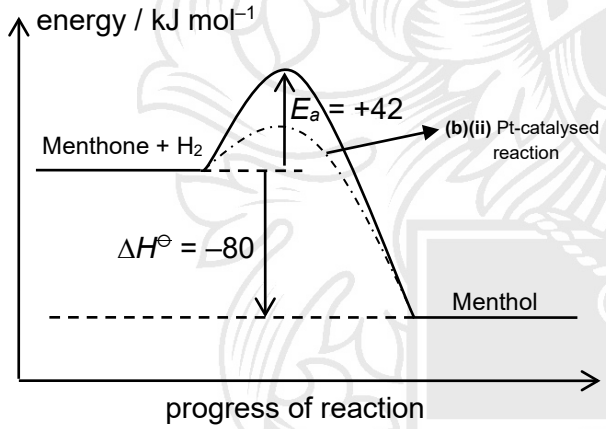
= 41.2%




**(a)(ii)** No. of chiral centres = 3

No. of enantiomers = $2^3 = 8$

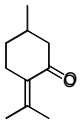
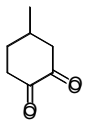
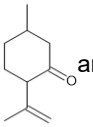
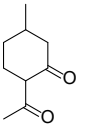
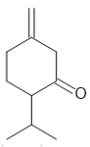
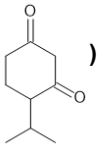
**(b)(i) & (ii)**

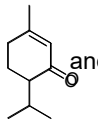
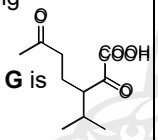
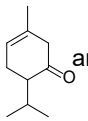
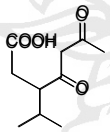



**(b)(iii)**

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

| (c) Evidence | Deductions |
|---|---|
| **A**, **B** and **C** are isomers<br>• with molecular formula $C_{10}H_{16}O$, and<br>• are reduced to menthol ($C_{10}H_{20}O$) | Reduction caused a gain in 2 $H_2$ ⇒ presence of 2 double bonds (C=C or C=O)<br><br>**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.<br>⇒ **A**, **B** and **C** contain C=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.<br>⇒ does not contains aliphatic aldehyde<br>⇒ contains 1 ketone<br>⇒ contains 1 C=C (since there are only 2 double bonds present) |
| **A**, **B** and **C** react with hot concentrated $KMnO_4$. | Strong oxidation occurred.<br>⇒ C=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 $CHI_3$.<br>⇒ $-COCH_3$ group present<br>(no $-CH(OH)CH_3$ group present because these are products of strong oxidation and the alcohol would have been oxidised) |
| **A** $\xrightarrow{\text{hot conc. } KMnO_4}$ **D** ($C_3H_6O$) + **E** ($C_7H_{10}O_2$) | **D** is  <br>⇒ **A** contains  group<br>⇒ **A** is  and **E** is  |
| **B** $\xrightarrow{\text{hot conc. } KMnO_4}$ $CO_2$ + **F** ($C_9H_{14}O_2$) | Strong oxidation of **B** gave $CO_2$<br><br>⇒ **B** contains $=CH_2$ group<br>⇒ **B** is  and **F** is  <br>**(NOT**  **and**  **)**<br>(–ve iodoform test) |

| | |
|---|---|
| hot conc. $KMnO_4$<br>**C** ⟶ **G**<br>($C_{10}H_{16}O_4$) | strong oxidation of **C** gave a single product (no C atom lost)<br>⇒ **C** contains a C=C in the cyclohexane ring<br>⇒ **C** is  and **G** is  <br>(Alternative answer:<br>**C** is  and **G** is  |

## 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)*

$6OH^- + 3Cl_2 \longrightarrow 5Cl^- + ClO_3^- + 3H_2O$

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 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,

$[H^+] = [HCl] = 0.50$ mol dm$^{-3}$

⇒ pH = –lg(0.50) = 0.3

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

$[H^+] = \sqrt{(0.5)(5.6\times10^{-4})} = 0.01679$ mol dm$^{-3}$

pH = –lg(0.01679) = 1.77

**(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 $[Ag(NH_3)_2]Cl(aq)$.

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)**

$$V = \frac{(0.40)(8.31)(300)}{12.0\times10^5} = 0.000831\ \text{m}^3 = 0.831\ \text{dm}^3$$

**(e)(iii)**

| $p$ / Pa | $V$ / dm$^3$ | pV / Pa dm$^3$ |
|---|---|---|
| 5.0 x 10$^5$ | 1.924 | 9.62 x 10$^5$ |
| 10.0 x 10$^5$ | 0.926 | 9.26 x 10$^5$ |
| 15.0 x 10$^5$ | 0.592 | 8.88 x 10$^5$ |

Estimated value of $pV$ when $p$ = 12.0 x 10$^5$ Pa

$$= \left[9.26 - \frac{2}{5}(9.26 - 8.88)\right]\times10^5$$

= 9.11 x 10$^5$ Pa dm$^3$

Value of $V$ when $p$ = 12.0 x 10$^5$ Pa

$$= \frac{9.11\times10^5}{12.0\times10^5} = 0.759\ \text{dm}^3$$

**(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 x 10$^5$ 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.

**(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 HC*l*(l) changes into to HC*l*(g), the number of gaseous particles increases, and hence, the disorder in the system increases. That is why $\Delta S_{vapourisation}$ is positive.

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

Since $\Delta G$ is negative, the vapourisation of HC*l* 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 $Mg(OH)_2$.

$MgO(s) + H_2O(l) \rightleftharpoons Mg(OH)_2(aq)$

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

$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

**(b)(i)** Suggested solubility of $Sr(OH)_2$

= 0.20 mol $dm^{-3}$ (a suitable value between 0.025 and 0.41 mol $dm^{-3}$)

**(b)(ii)** $Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$

$[OH^-] = 2(2.5 \times 10^{-2}) = 5.0 \times 10^{-2}$ mol $dm^{-3}$

$pOH = -lg(5.0 \times 10^{-2}) = 1.301$

$pH = 14 - 1.301 = 12.7$

**(b)(iii)** $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

$K_{sp} = [Mg^{2+}][OH^-]^2$

$K_{sp} = (1.6 \times 10^{-4})[2(1.6 \times 10^{-4})]^2$

$= 1.64 \times 10^{-11}$ $mol^3$ $dm^{-9}$

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

$[Mg^{2+}] = ½(1.6 \times 10^{-4}) = 8.0 \times 10^{-5}$ mol $dm^{-3}$

$[Ba^{2+}] = ½(4.1 \times 10^{-1}) = 2.05 \times 10^{-1}$ mol $dm^{-3}$

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

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

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

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

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

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

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

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

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

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)$^{th}$ amino acid residue**.

**(c)(iii)** HC*l*(aq), heat under reflux

**OR** 6 mol $dm^{-3}$ HC*l*(aq), heat for several hours

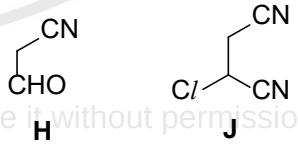
**Note to student**: Since this is a hydrolysis reaction, water must be present. Thus, terms such as "dilute" or "aqueous" are essential.

**(c)(iv)**

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

gly-asp-gly-tyr-ile-ser

**(d)(i)**




**H** **J**

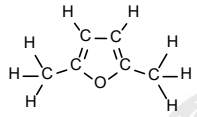
**(d)(ii)** **Step 4**: excess concentrated $NH_3$ in ethanol, heat in sealed tube
**Step 5**: $HCl$(aq) or $H_2SO_4$(aq), heat

## 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)

**(b)**

$$C_6H_8O + 7.5O_2 \xrightarrow{\Delta H_c} 6CO_2 + 4H_2O$$



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

**(c)** total amt of heat evolved

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

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

$$\text{experimental } \Delta H_c = \frac{-33440}{0.01042}$$

$$= -3.209 \times 10^6 \text{ J mol}^{-1}$$

$$= -3210 \text{ kJ mol}^{-1}$$

The experimental $\Delta H_c$ 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.

**(d)(i)** rate = $k[RCH_2OH][H^+]$

Step 1: $RCH_2OH + H^+ \longrightarrow RCH_2OH_2^+$ (fast)
Step 2: $RCH_2OH_2^+ \longrightarrow RCH_2^+ + H_2O$ (slow)
Step 3: $RCH_2^+ + Cl^- \longrightarrow RCH_2Cl$ (fast)

Step 2 is the rate-determining step.

**Note to student**:
A common mistake is to write the slow step as $RCH_2OH_2^+ + Cl^- \longrightarrow RCH_2Cl + H_2O$. This equation implies that $Cl^-$ participates in the rate-determining step. However, it was given that the rate was independent of [$Cl^-$].

**(d)(ii)** $K_2Cr_2O_7$, $H_2SO_4$(aq), heat
**Note to student**: Avoid the use of $KMnO_4$ as the C=C bond in HMF may be ruptured by vigorous oxidation.

**(e)(i)** ester

**(e)(ii)**

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

**Note to student**: Do not write "concentrated $H_2SO_4$(aq)". The "(aq)" implies that $H_2SO_4$ is dilute.

**(f)** Free radical substitution

Initiation

$$Cl\text{—}Cl \xrightarrow{UV} 2Cl\bullet$$

Propagation

$$R\text{—}CH_3 + Cl\bullet \longrightarrow R\text{—}CH_2\bullet + HCl \quad \textbf{(a)}$$

$$R\text{—}CH_2\bullet + Cl_2 \longrightarrow R\text{—}CH_2Cl + Cl\bullet \quad \textbf{(b)}$$

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

Termination

$$R\text{—}CH_2\bullet + R\text{—}CH_2\bullet \longrightarrow R\text{—}CH_2CH_2\text{—}R$$

$$R\text{—}CH_2\bullet + Cl\bullet \longrightarrow R\text{—}CH_2Cl$$

$$Cl\bullet + Cl\bullet \longrightarrow Cl_2$$

## 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.

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

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

$x = 7.39\%$

% of $^{6}Li$ = 7.39% (to 2 dp)
% of $^{7}Li$ = (100–7.39) = 92.61% (2 dp)

**(a)(iii)** **X:** $^{3}_{2}He$ **Y:** $^{7}_{3}Li$

**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 $\pi$ 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 $KMnO_4$(aq), NaOH(aq)

**(b)(v)** condensation reaction

**(c)(i)** $Li_2O_2 + CO_2 \longrightarrow Li_2CO_3 + ½O_2$

**(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 |
|---|---|
| $CH_3CH_2Br$ | $CH_3CH_2CH_2CHO$ |
| OR | |
| $CH_3CH_2CH_2Br$ | $CH_3CH_2CHO$ |

**(d)(ii)**

| R–Br | Carbonyl compound |
|---|---|
| $CH_3Br$ | $(CH_3CH_2)_2C=O$ |
| OR | |
| $CH_3CH_2Br$ | $CH_3CH_2COCH_3$ |

**(e)**

| Test | Observations |
|---|---|
| **1.** To separate test-tubes of each compound, add an equal volume of acidified $K_2Cr_2O_7$ and heat. | Orange $K_2Cr_2O_7$ turns green in test-tubes containing **P** and **Q**.<br><br>Orange $K_2Cr_2O_7$ 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**.<br><br>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 $Cr_2O_7^{2-}$ to $Cr^{3+}$; **R**, a tertiary alcohol, will not be oxidised by $Cr_2O_7^{2-}$.

  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 $PCl_5$(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 $K_2Cr_2O_7$ would react with $Na_2CO_3$ and the water in the aqueous reagents used will react with $PCl_5$(s). Hence, both tubes will produce false positive results.