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 $Mg(NO_3)_2$ is no longer in syllabus. The following equation will help you solve this question:

$Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + ½O_2$

18 Amend question – Options C & D not in syllabus

C is not true. $Mg(OH)_2$ 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

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Paper 3

No amendments

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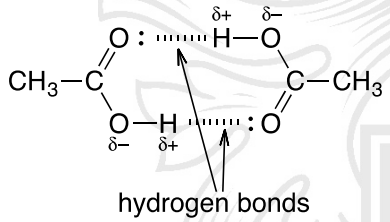
1 Answer: B
Amount of Q = 1.0 g ÷ x g mol^{-1} = 1/x mol
Number of molecules = L mol^{-1} x (1/x) mol = L/x
Number of atoms = 2(L/x) = 2L/x

2 Answer: D
$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$
$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$
Combining both equations: $2H_2S + CS_2 + 6O_2 \rightarrow 4SO_2 + CO_2 + 2H_2O$
Mole ratio of SO_2 : CO_2 = 4 : 1

3 Answer: C
A_r for Cu = [65(63) + 29(65)] ÷ (65 + 29) = 63.6

4 Answer: D
$^{36}S^{2-}$: 16 protons, 20 neutrons, 18 electrons
$^{37}Cl^-$: 17 protons, 20 neutrons, 18 electrons
Option A: The nucleon numbers for S and C*l* are <u>36 and 37</u> respectively.
Option B: Both ions have an outer electronic configuration of <u>$3s^23p^6$</u>.
Option C: Both ions have <u>fewer</u> 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 $C^1–C^2{\equiv}N$ (C-1 has 1 lone pair and 1 unpaired electron; N has a lone pair)
② $C^1{=}C^2{=}N$ (C-1 has 1 lone pair; N has 1 lone pair and 1 unpaired electron)
③ $C^1{\equiv}C^2–N$ (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 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
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ΔH_f of KC*l* = 90 + ½(242) + 418 + (–355) + (–710) = –436 kJ mol^{-1}

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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
$E^{\ominus}$cell = $E^{\ominus}(Ag^+/Ag) - E^{\ominus}(Fe^{3+}/Fe^{2+}) = (+0.80) - (+0.77) = +0.03$ V
To obtain a cell potential of 0.00 V, $E^{\ominus}(Ag^+/Ag)$ needs to become less positive or $E^{\ominus}(Fe^{3+}/Fe^{2+})$ needs to become more positive, or both electrode potentials have to be adjusted to the same value.
Option A: Increase in $[Ag^+]$ will make $E^{\ominus}(Ag^+/Ag) > +0.80$ V
Option B: Increase in $[Fe^{2+}]$ will make $E^{\ominus}(Fe^{3+}/Fe^{2+}) < +0.77$ V
Option C: Increase in $[Fe^{3+}]$ will make $E^{\ominus}(Fe^{3+}/Fe^{2+}) > +0.77$ 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: $2O^{2-} \rightarrow O_2 + 4e^-$
Amount of electricity passed = 8 C s^{-1} x (100 x 60) s = 48000 C
When 4 x 96500 C are passed, 1 mol of O_2 is liberated.
When 48000 C are passed, 48000 / (4 x 96500) = 0.1244 mol of O_2 is liberated.
Volume of O_2 liberated at s.t.p. = 0.1244 x 22.7 = 2.8 dm^3 (1 d.p.)

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

14 Answer: B
$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H_3O^+(aq)$
$[H^+] = \sqrt{(1.0 \times 10^{-5} \times 0.1)} = 1.0 \times 10^{-3}$ mol dm^{-3}
$pH = -\log (1.0 \times 10^{-3}) = 3.0$

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

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.

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17 Answer: A
$Mg(NO_3)_2(s) \rightarrow MgO(s) + 2NO_2(g) + ½O_2(g)$
Amount of $Mg(NO_3)_2$ = 10.4 / 148.3 = 0.07013 mol
Amount of O_2 (neutral gas) = ½ (0.07013) = 0.03507 mol
Mass of O_2 (neutral gas) = 0.03507 x 32.0 = 1.12 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
$2VO_2^+ + SO_2 \rightarrow 2VO^{2+} + SO_4^{2-}$ $E^{\ominus}_{cell}$ = 1.00 – 0.17 = +0.83 V (feasible)
$2VO^{2+} + SO_2 \rightarrow 2V^{3+} + SO_4^{2-}$ $E^{\ominus}_{cell}$ = 0.34 – 0.17 = +0.17 V (feasible)
$2V^{3+} + SO_2 + 2H_2O \rightarrow 2V^{2+} + SO_4^{2-} + 4H^+$ $E^{\ominus}_{cell}$ = –0.26 – 0.17 = –0.43 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.
$PtCl_4 + 4NH_3 \rightarrow [Pt(NH_3)_4Cl_2]^{2+} + 2Cl^-$
Option A: The cation, $[Pt(NH_3)_3Cl_3]^+$, has a 1+ charge.
Option C: The oxidation state of platinum in $[Pt(NH_3)_6]^{2+}$ is +2.
Option D: The cation, $[Pt(NH_3)_6]^{4+}$, has a 4+ charge.

23 Answer: B
There are 2 π bonds found in the C≡C bond.
Both C atoms in the C≡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 H● free radical is not formed, so options C and D are incorrect.

25 Answer: D
The rate-determining step of this S_N1 mechanism involves the breaking of the C–Br or C–Cl bond.
Since the C–Br bond is weaker, reaction 1 is faster.

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26 Answer: C
Na reacts with the phenolic group (ROH) in compound C.
$ROH + Na \rightarrow RO^-Na^+ + ½H_2$

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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.

$ROH + D_2O \rightarrow ROD + HDO$ and $RCOOH + D_2O \rightarrow RCOOD + HDO$

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 a ketone which does not have the $–COCH_3$ functional group.

The reduction of X will give a secondary alcohol which does not have the $–CH(OH)CH_3$ functional group.

Option A shows a tertiary alcohol.

Option C shows a secondary alcohol with a $–CH(OH)CH_3$ 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	^{4}He	^{12}C	^{24}Mg
No. of protons	2	6	12
No. of neutrons	2	6	12

Option 2

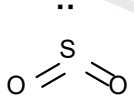
Isotope	^{14}N	^{20}Ne	^{30}P
No. of protons	7	10	15
No. of neutrons	7	10	15

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		O=C=O
Net dipole	Yes	No

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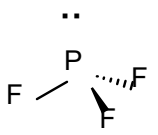
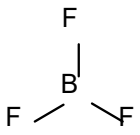
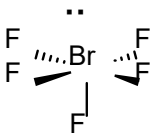
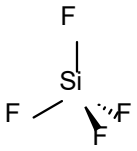
Option 2

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: NH_3 is a nucleophile, while CH_3Cl is an electrophile.
Option 2: CH_3OH accepted an H^+ ion, while $HClO_4$ donated an H^+ ion.
Option 3: HNO_3 accepted an H^+ ion, while H_2SO_4 donated an H^+ ion.

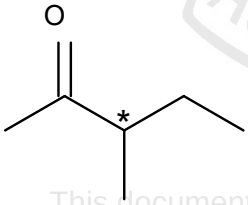
34 Answer: D (1 only)
The ethoxide ion, $C_2H_5O^-$, is a nucleophile and it attacks the primary iodoalkane, CH_3I, in a nucleophilic substitution reaction.
From experiments 1 and 3, when $[C_2H_5ONa]$ is doubled and $[CH_3I]$ is kept constant, the relative initial rate of reaction is doubled. Hence, the reaction is first order with respect to $[C_2H_5ONa]$. So, option 1 is correct.
From experiments 2 and 3, when $[C_2H_5ONa]$ is kept constant and $[CH_3I]$ is halved, the relative initial rate of reaction is halved. Hence, the reaction is first order with respect to $[CH_3I]$. So, option 3 is incorrect.
The overall order reaction is 1 + 1 = 2. So, option 2 is incorrect.

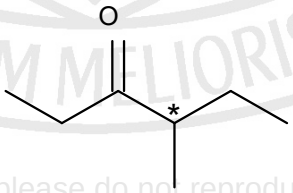
35 Answer: C (2 and 3 only)
Brønsted-Lowry acid: H^+ donor
Option 1: $BeCl_2$ did not donate any H^+ ions, so it is not a Brønsted-Lowry acid.
Option 2: $Be(H_2O)_4^{2+}$ donated 2 H^+ ions to 2 Cl^- ions, so $Be(H_2O)_4^{2+}$ is a Brønsted-Lowry acid.
Option 3: $Be(H_2O)_2(OH)_2$ donated 2 H^+ ions to 2 OH^- ions, so $Be(H_2O)_2(OH)_2$ is a Brønsted-Lowry acid.

36 Answer: B (1 and 2 only)

oxidation no.	0	–1	+5
	Cl_2	$NaCl$	$NaClO_3$
	reactant	products	

37 Answer: C (2 and 3)
There is no such molecule with x = 5.
When x = 6 When x = 7





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E.g. 3-methyl-pentan-2-one E.g. 4-methyl-hexan-3-one

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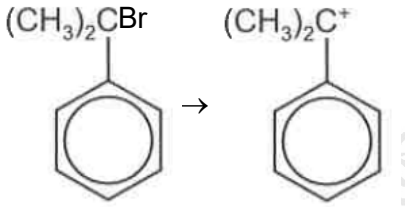
38 Answer: B (1 and 2 only)

Option 1: $OH^- + CH_3Cl \rightarrow [HO\text{----}CH_3\text{----}Cl]^-$ (S_N2 mechanism)

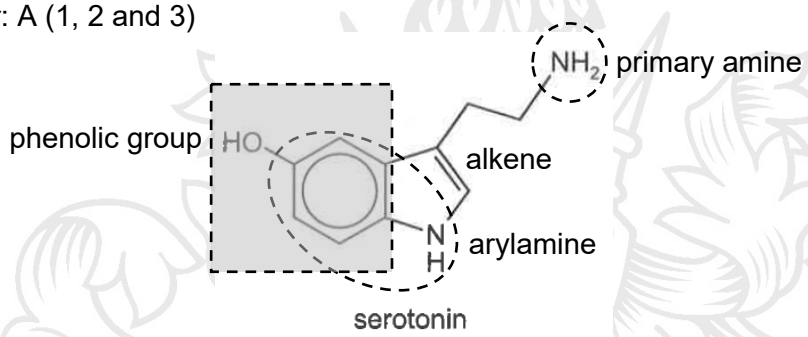
transition state

Option 2:  (S_N1 mechanism)

carbocation intermediate

Option 3: This cationic species is not formed in a nucleophilic substitution reaction.

39 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

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Q1 Planning

(a) Effervescence would be seen; colourless gas which forms a white ppt with $Ca(OH)_2(aq)$ would be evolved.
The deep blue azurite would dissolve completely to give a blue solution.

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

$Cu_3(CO_3)_2(OH)_2 \equiv 3H_2SO_4$

Amt of H_2SO_4 in 50.00 cm^3 = 1.00 x 50.00 x 10^{-3} = 0.0500 mol
Amt of azurite that reacts with 75% of H_2SO_4 = $\frac{1}{3}$ x 0.75 x 0.0500 = 0.0125 mol
Mass of azurite in 0.0125 mol = 0.0125 x 344.5 = 4.306 g
Mass of powered rock to be used = $\frac{4.306}{0.90}$ = 4.78 g

<u>Dilution and Volume of unreacted sulfuric acid required for titration</u>
Amt of excess H_2SO_4 in reaction mixture = 0.25 x 0.0500 = 0.0125 mol

Assume that **<u>average</u>** volume of NaOH required for titration is 25.00 cm^3
Amt of excess H_2SO_4 used for titration = ½ x 0.100 x 25 x 10^{-3} = 0.00125 mol (ie 10% of 0.0125 mol)
Hence, 10% of excess H_2SO_4 is needed for titration with NaOH(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.

<u>Procedure</u>

1. 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.

2. 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.

3. Reweigh the emptied weighing bottle and record its mass.

4. 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.

4. 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.

5. Stopper the graduated flask and shake the solution thoroughly to ensure that it is homogeneous. Label the solution **FA 3**.

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6. Pipette 25.0 cm^3 of **FA 3** into a 250 cm^3 conical flask. Add 2 drops of phenolphthalein indicator.

7. Fill the burette with the 0.100 mol dm^{-3} NaOH(aq) provided. Titrate the solution in the conical flask with the standard dilute NaOH(aq) placed in the burette.

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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 cm^3.

Calculations

Let that the **average** values of two consistent titres be 1000b cm^3 or b dm^3.
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 cm^3 of **FA3** = ½ x b x 0.100 = 0.0500b mol

Amt of excess sulfuric in reaction mixture = 0.0500b x $\frac{250}{25.0}$ = 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 = $\frac{1}{3}$ x (0.0500 – 0.500b) mol
Mass of pure azurite present in the powdered rock sample = $\frac{1}{3}$ x (0.0500 – 0.500b) x 344.5
= 114.8 x (0.0500 – 0.500b) g
Percentage by mass of pure azurite present in the powdered rock sample
= $\frac{114.8 \text{ x } (0.0500 - 0.500\text{b})}{c}$ x 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 C=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

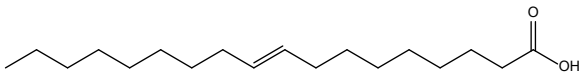
(b)(ii) Mass of iodine that would react with 100g of olive oil = (100/0.256) x 0.237 = **92.6 g**

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

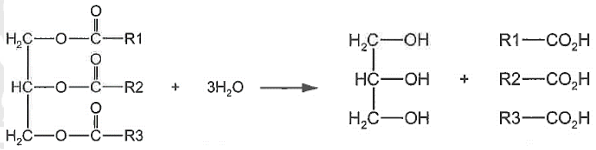
(b)(iv) Triesters containing 3 oleic acids contain 3 C=C bonds per molecule.
As the average number of C=C bond in each molecule of olive oil is 2.85 which is less than 3 and triesters of olive oil are mainly formed from oleic acid, olive oil should contain triesters of palmitic acid and/or stearic acid as the other significant component. Since the average Mr of olive oil is smaller than that of triester of oleic acid (Mr = 282 x 3 + 12 x 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

(c)(ii)



(d) ester undergoes hydrolysis



alkene(C=C) undergoes oxidative cleavage

$R_1CH{=}CHR_2CO_2H + 4[O] \longrightarrow R_1COOH + HO_2CR_2CO_2H$ or

$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H + 4[O] \longrightarrow CH_3(CH_2)_7COOH + HO_2C(CH_2)_7CO_2H$

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 carbride has very high melting point.

(b)(i) $C_xH_y + (x + \frac{y}{4})\, O_2 \longrightarrow x\, CO_2 + \frac{y}{2} H_2O$

(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

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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

(ii) $8NH_3 + 6NO_2 \longrightarrow 7N_2 + 12H_2O$

(d) **(i)** $NO_2 + SO_2 \longrightarrow SO_3 + NO$ (I)

$NO + ½\ O_2 \longrightarrow NO_2$ (II)

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

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

(iii) $K_p = \dfrac{p_{N_2O_4}}{p_{NO_2}^2} = \dfrac{p_{N_2O_4}}{(1.5x10^{-3})^2}$

$= 6.25 \times 10^{-5}\ Pa^{-1}$

$p_{N_2O_4} = 1.41 \times 10^{-10}\ Pa$

Question 4

(a) **(i)** K: $1s^22s^22p^63s^23p^64s^1$

Cu: $1s^22s^22p^63s^23p^63d^{10}4s^1$

(ii)

First ionisation energy of K is +418 $kJmol^{-1}$ while that for Cu is +745 $kJmol^{-1}$. Much more energy is required to remove an electron from Cu than K.

$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^\ominus = +0.34\ V$

$K^+ + e^- \rightleftharpoons K \qquad E^\ominus = -2.92\ V$

Furthermore, the more negative $E^\ominus(K/K^+)$ shows that K undergoes oxidation more readily than Cu. Hence, the reducing power and reactivity of K is greater than Cu.

(b) **(i)**

$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^\ominus = +0.34\ V$

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \quad E^\ominus = +1.23\ V$

$2H^+ + 2e^- \rightleftharpoons H_2 \qquad E^\ominus = 0.00\ V$

In acid without O_2,

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

In acid with O_2,

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

(ii) Even though the reaction is spontaneous, the activation energy is high as the metallic bonds in Cu need to be overcome / the reactants are in different phases and have small surface area of contact.

(iii)

$[Cu(NH_3)_4]^{2+} + 2e^- \rightleftharpoons Cu + 4NH_3 \quad E^\ominus = -0.05\ V$

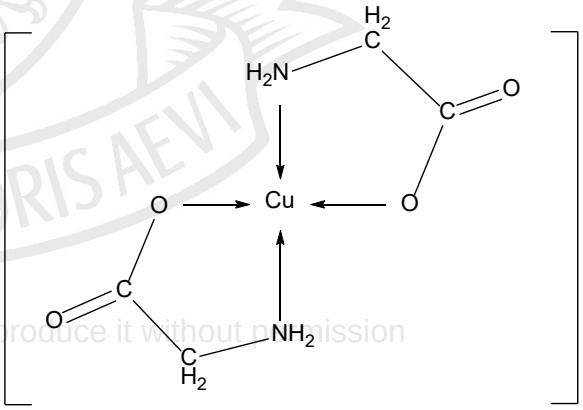
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \quad E^\ominus = +0.40\ V$

$2Cu + 8NH_3 + O_2 + 2H_2O \rightarrow 2[Cu(NH_3)_4]^{2+} + 4OH^-$

$E^\ominus_{cell} = +0.40 - (-0.05) = +0.45\ V$

(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.

(ii)



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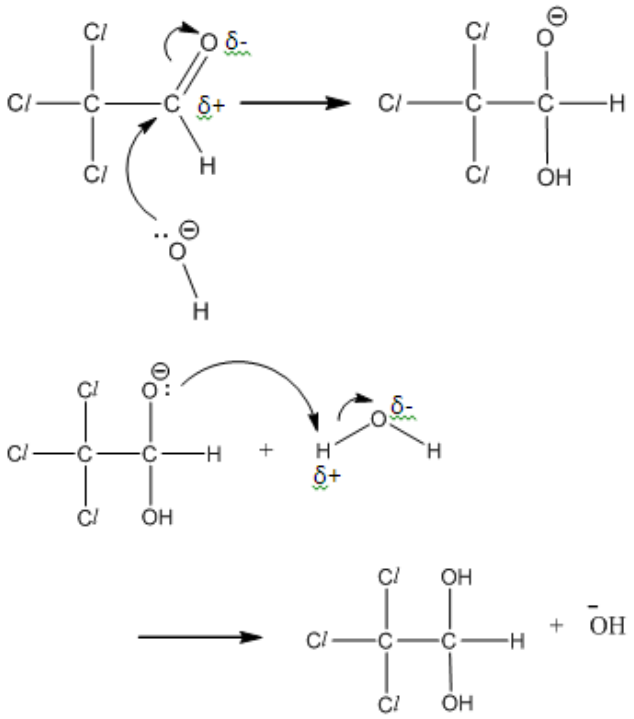
Question 5

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

(ii)



(iii) $CCl_3CHO + OH^- \rightarrow HCOO^- + CHCl_3$

(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.

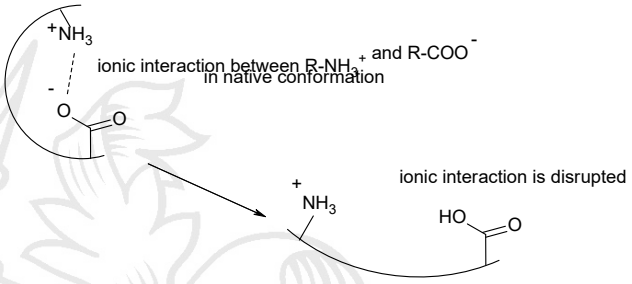
$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
$CCl_3COOH \rightleftharpoons CCl_3COO^- + H^+$

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

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

$$\sim COO^- + H^+ \longrightarrow \sim COOH$$

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



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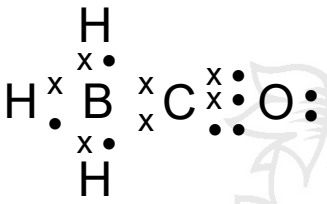
Question 1

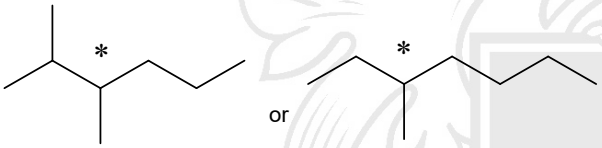
(a) Carbon monoxide bonds strongly (almost irreversibly), via a dative covalent bond, to the iron in haemoglobin. CO is a stronger ligand than O_2 and its presence destroys the O_2 carrying capacity of haemoglobin. Thus, CO is poisonous.

(b)



(c)(i) $C_8H_{18} + \frac{23}{2}O_2 \rightarrow 6CO_2 + 2CO + 9H_2O$

(c)(ii)



(d) The presence of ligands causes the splitting of d-orbitals of transition metals into different energy levels. Since the d-subshell is partially filled, electrons from the lower energy level d-orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d-orbitals. The colour observed is the complement of the colour absorbed.

(e)(i) Homogeneous catalysis.
The catalyst is in the same phase as the reactants.

(e)(ii) $CH_3OH + CO \rightarrow CH_3CO_2H$

(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.
B is a catalyst as it is consumed in step 2 but regenerated in step 5 showing that it is not chemically changed in the reaction.
C is a reactant as it is consumed in step 4 but not regenerated at any steps.

(f)(i) $K_p = \dfrac{P_{CH_4}P_{H_2O}}{P_{CO}(P_{H_2})^3}$
Units: atm^{-2}

(f)(ii) P_{CO} = 0.19 x 32 = 6.08 atm
P_{CH_4} = 0.12 x 32 = 3.84 atm
$P_{H_2O} = P_{CH_4}$ = 3.84 atm
P_{H_2} = 32 – 6.08 – 3.84 – 3.84 = 18.24 atm
(or P_{H_2}= 3 P_{CO} = 3 x 6.08 = 18.24 atm)

(f)(iii) $K_p = \dfrac{P_{CH_4}P_{H_2O}}{P_{CO}(P_{H_2})^3}$ = 3.9965 x 10^{-4} atm^{-2}
= 4.00 x 10^{-4} atm^{-2}

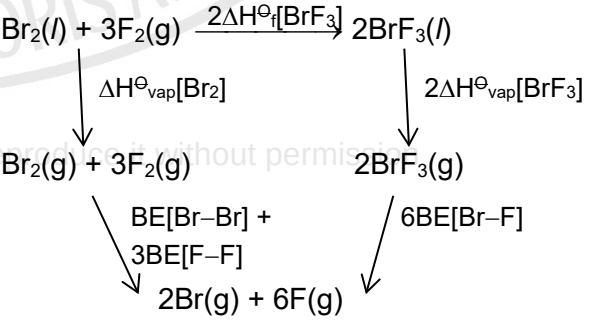
Question 2

(a) When aq KI is added to aq Cl_2, the colour of the solution changes from colourless to brown due a redox reaction between KI and Cl_2:
$2KI + Cl_2 \rightarrow 2KCl + I_2$
$E^{\ominus}_{cell} = E^{\ominus}_{Cl2/Cl^-} - E^{\ominus}_{I2/I^-}$= 1.36–0.54 = +0.82V > 0 so that the reaction is spontaneous under standard conditions.

When aq KCl is added to aq Br_2, no reaction occurs as Cl^- is not able to reduce Br_2 to Br^- as predicted by the negative $E^{\ominus}_{cell}$:
$E^{\ominus}_{cell}= E^{\ominus}_{Br2/Br^-} - E^{\ominus}_{Cl2/Cl^-}$=1.07–1.36 = –0.29 V < 0

When aq KBr is added to aq I_2, no reaction occurs as Br^- is not able to reduce I_2 to I^- as predicted by the negative $E^{\ominus}_{cell}$:
$E^{\ominus}_{cell} = E^{\ominus}_{I2/I^-} - E^{\ominus}_{Br2/Br^-}$=0.54–1.07 = –0.53 V < 0

(b)(i)



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$2\Delta H^{\ominus}_f[BrF_3] = \Delta H^{\ominus}_{vap}[Br_2] + BE[Br{-}Br] + 3BE[F{-}F]$

$- 6BE[Br{-}F] - 2\Delta H^{\ominus}_{vap}[BrF_3]$

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

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

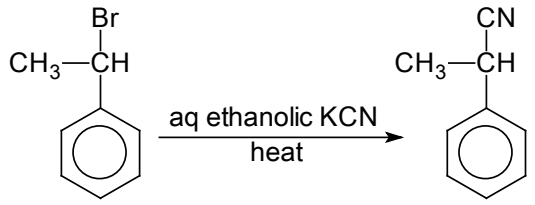
$BE[Br{-}F] = 1212/6 = +202$ kJ mol^{-1}

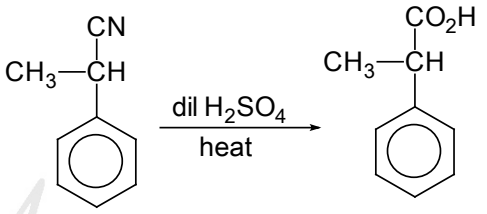
(b)(ii) $\Delta G^{\ominus}_f = \Delta H^{\ominus}_f - T\Delta S^{\ominus}_f$

$-241 = -301 - 298(\Delta S^{\ominus}_f)$

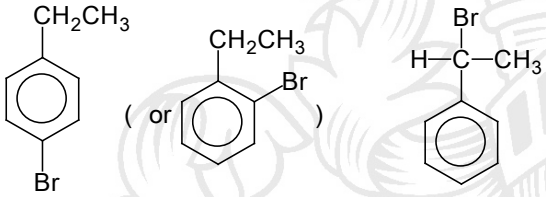
$\Delta S^{\ominus}_f = \frac{-301+241}{298} = -0.201$ kJ mol^{-1} K^{-1}

$\Delta S^{\ominus}_f$ is negative which is expected as the reaction results in a decrease in the number of moles of gas, which reduces entropy.



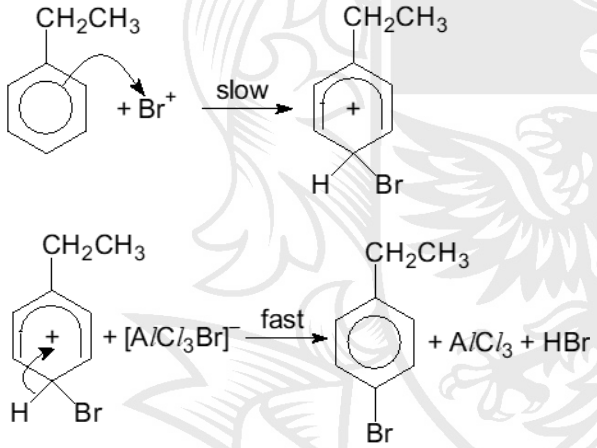


(c)(i) D E



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

(c)(iii) $Br_2 + AlCl_3 \rightarrow Br^+ + [AlCl_3Br]^-$



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

Step 1:
Reagent: Aqueous ethanolic KCN
Conditions: Heat with reflux

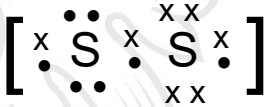
Step 2:
Reagent: Dil H_2SO_4 (or dil HC*l*)
Conditions: Heat with reflux

Question 3

(a)(i) $1s^22s^22p^63s^23p^63d^3$

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

(b)(i)



(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).

(c)(i) $5Sn^{2+} + 2MnO_4^- + 16H^+ \rightarrow 5Sn^{4+} + 2Mn^{2+} + 8H_2O$

(c)(ii) $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ $E^{\ominus}=+1.52$V
$Pb^{4+} + 2e \rightarrow Pb^{2+}$ $E^{\ominus}=+1.69$V
$E^{\circ}_{cell} = 1.52 - 1.69 = -0.17$ V < 0 V
Hence the reaction is not spontaneous/ thermodynamically feasible.

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

(c)(iv) Amt of $KMnO_4 = 0.0225 \times 0.0200$
$= 4.50 \times 10^{-4}$ mol

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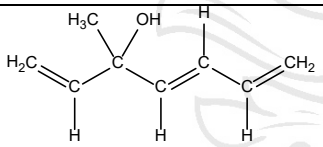
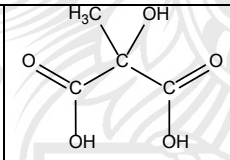
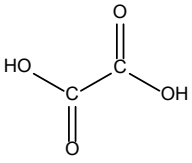
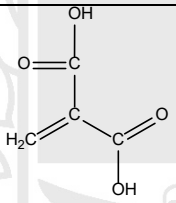
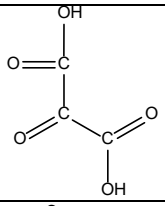
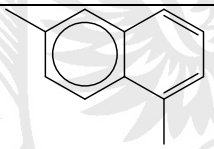
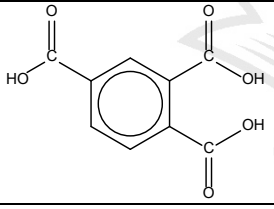
Amt of Sn^{2+} oxidised = 5/2 x 4.5 x 10^{-4}
= 1.125 x 10^{-3} mol

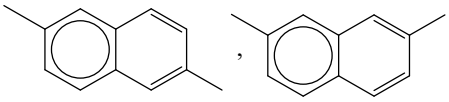
Amt of Sn^{2+} in 250 cm^3 = 1.125 x 10^{-3} x 10
= 0.01125 mol
Mass of Sn^{2+} in sample = 0.01125 x 118.7
= 1.335 g
% by mass in sample = 1.335 / 3.00 x 100%
= 44.5%

(d)(i) Compound **F** contains a tertiary alcohol group which cannot be oxidised by acidified $K_2Cr_2O_7$ 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

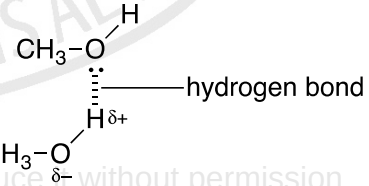
(d)(iv) 

(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:



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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**:

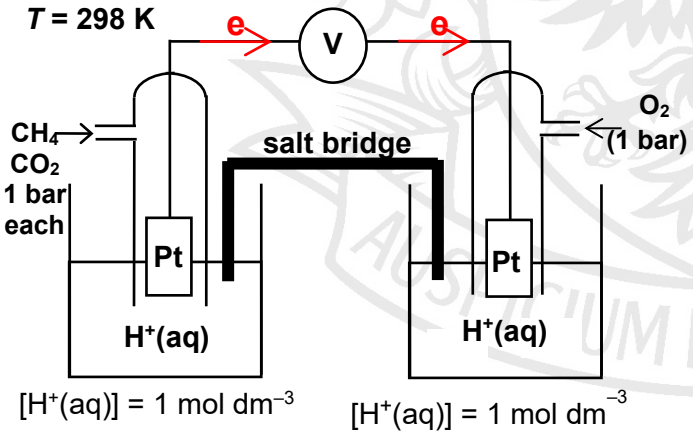
$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

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

$C_3H_8 + Cl_2 \longrightarrow C_3H_7Cl + HCl$

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

(c)(ii)



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

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$, $E^{\ominus} = -0.76$ V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$, $E^{\ominus} = +0.34$ V

Overall redox reaction:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

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

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

(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:
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$,

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:

$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

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

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.

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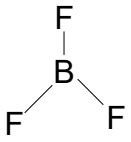
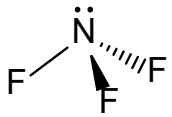
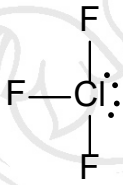


NF_3 has 3 bond pairs and 1 lone pair around N. Hence its electron pair geometry is tetrahedral and its molecular shape is trigonal pyramidal.



ClF_3 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 PCl_5 or $SOCl_2$ 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 sp^2 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 sp^3 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 CCl_4 at room temperature.

(c)(ii) The acidity of phenols depends on the stability of the phenoxide ion **Ph**O^- as shown in the equation:

$$\mathbf{Ph}OH \rightleftharpoons \mathbf{Ph}O^- + H^+$$

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 $KMnO_4$ and dil H_2SO_4

Condition: heat with reflux

Step 2

Reagent: PCl_3, PCl_5 or $SOCl_2$

Condition: anhydrous

Step 3

Reagent: HCl

Condition: anhydrous

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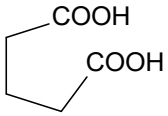
Step 4

Reagent: Conc NH_3

Condition: in ethanol, heat in a sealed tube

M:



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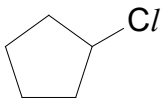

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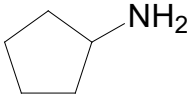

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