H2 Chemistry TYS 2016 suggested answers

Questions that are no longer in syllabus

Paper 1	
Paper 2	5(b)(ii)
Paper 3	

Paper 1 Answer Key

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

2016 A level Paper 1 suggested answers

1) Amount of molecule = $\frac{1.0}{x}$ mol

Amount of atom = ($\frac{1.0}{x}$ × 2)mol

No of atoms = $\frac{2.0}{x}$ × L

Ans: **B**

2) $2H_2S + CS_2 + 6O_2 \rightarrow CO_2 + 4SO_2 + 2H_2O$

Ans: **D**

3) From the data, the isotopes of copper have mass number of 63 and 65.
Note: mass number 197 is Au

A_r of Cu = $\frac{63\times65+65\times29}{94}$ = 63.6

Ans: **C**

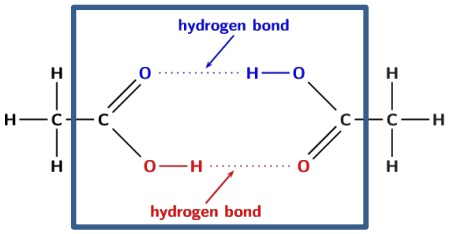
4)

	No. of protons	No. of neutrons	No. of electrons
$^{36}S^{2-}$	16	20	18
$^{37}Cl^{-}$	17	20	18

Nucleons = protons + neutrons (different nucleon no. for the 2 ions)
The ions have the same outer electronic configuration of $3s^2 3p^6$

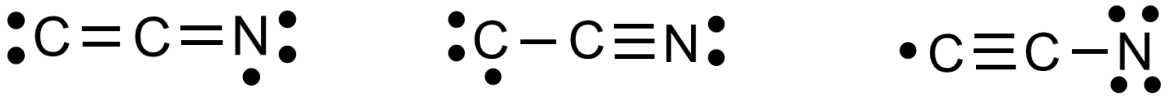
Ans: **D**

5)



Ans: **A**

6) Possible structures of C_2N



Ans: **C**

7) $pV = nRT = \frac{m}{M_r}RT$ (Note: Vol of gas collected = 78–2 = 76 cm^3)

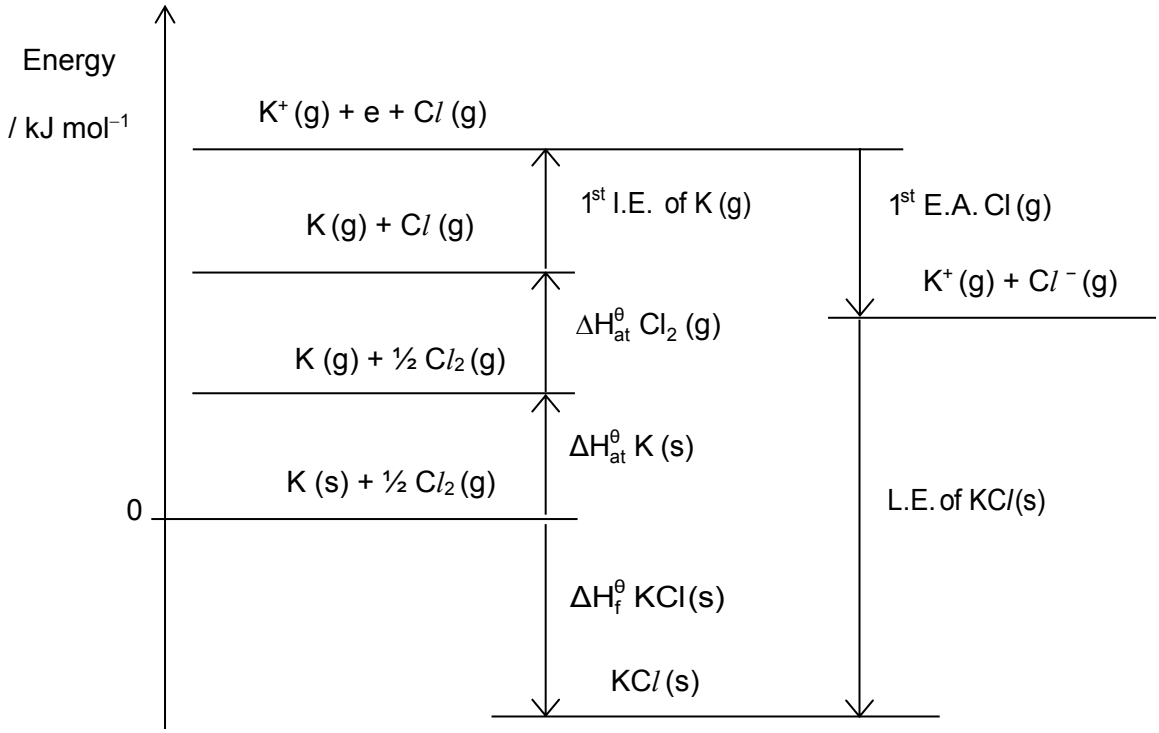
$M_r = \frac{mRT}{pV} = \frac{0.293\times8.31\times(97+273)}{(101000)\times(76\times10^{-6})} = 117$

Ans: **C**

8) Lattice Energy is the amount of energy released when 1 mole of ionic solid is formed from its gaseous ions.

Ans: **D**

9)



By Hess' Law,

ΔH_f^θ KCl(s) = ΔH_{at}^θ K(s) + ΔH_{at}^θ Cl_2(g) + 1st I.E.of K(g) + 1st E.A. of Cl(g) + L.E. of KCl(s)

ΔH_f^θ KCl(s) = +90 + ½ ×(+242) + (418) + (–355) + (–710) = –436 kJmol^{-1}

Ans: **B**

10) $\Delta S > 0$ as there is an increase in number of gaseous molecules after the reaction
$\Delta G = \Delta H - T\Delta S$
For ΔG to be > 0 at 378 K, ΔH must be a positive value.

Ans: **D**

11) $E^{\ominus}_{cell} = E^{\ominus}(Ag^+/Ag) - E^{\ominus}(Fe^{3+}/Fe^{2+}) = +0.03V$.

When $[Fe^{3+}]$ increases, position of eqm $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ shifts to the right, $E(Fe^{3+}/Fe^{2+})$ increases and thus $E^{\ominus}_{cell}$ could become 0.00V.

Ans: **C**
(Note: Surface area of electrode would not affect $E^{\ominus}$ values)

12) [O] $2O^{2-} \rightarrow O_2 + 4e$
$Q = It = n_eF$
$n_e = \frac{8\times60\times100}{96500} = 0.4974$ mol
$n_{O2} = \frac{0.4974}{4} = 0.12435$ mol
$V_{O2} = 0.12435 \times 22.7 = 2.82\ dm^3$

Ans: **A**

13) Let solubility of $ZnF_2(s)$ be s mol dm^{-3}

	$ZnF_2(s)$	+ aq	$\rightleftharpoons$	$Zn^{2+}(aq)$	+ 2 F^- (*aq*)
Initial / mol dm^{-3}	–			0	0
Change / mol dm^{-3}	–s			+s	+2s
Eqm / mol dm^{-3}	–			s	2s

$K_{sp} = [Zn^{2+}][F^-]^2 = 4s^3$
s = 0.2 mol dm^{-3}
$[F^-] = 2s = 0.4$ mol dm^{-3}

For precipitation of BaF_2, $[Ba^{2+}][F^-]^2 = K_{sp}$ and $[F^-] = 0.4$ mol dm^{-3}
$[Ba^{2+}] = \frac{1.6\times10^{-7}}{(0.4)^2} = 1\times10^{-6}$ mol dm^{-3}

Ans: **C**

14) For weak acid, $[H^+] = \sqrt{K_a \times c} = 1\times10^{-3}$ mol dm^{-3}
$pH = -\lg [H^+] = 3$

Ans: **B**

15) Rate = $k[IO_3^-][I^-]^2[H^+]^2$
Expt 1: $y = k\,(a)(a)^2(a)^2$ – eqn (1)
Expt 2: rate 2 = $k\,(\frac{1}{2}a)(2a)^2(3a)^2$ – eqn (2)
$\frac{eqn\ 2}{eqn\ 1} : \frac{rate\ 2}{y} = \frac{k\times18a^5}{k\times a^5}$

Rate 2 = 18y

Ans: **D**

16) Both Al_2O_3 and MgO exist as giant ionic lattice. Since Al^{3+} has a higher charge density than Mg^{2+}, Al_2O_3 has the most covalent character.

Ans: **A**

17) $Mg(NO_3)_2(s) \rightarrow MgO(s) + 2NO_2(g) + ½\ O_2(g)$
Amount of $Mg(NO_3)_2 = \frac{10.4}{24.3+2\times14+6\times16} = 0.07013$ mol

Amount of $O_2 = ½ \times 0.07013 = 0.03506$ mol
Mass of $O_2 = 0.03506 \times 32.0 = 1.12$ g

Ans: **A**

18) $MgCl_2$ is soluble in water to give a solution of pH = 6.5

Mg has a metallic lattice structure with strong metallic bond between Mg^{2+} and sea of delocalised electrons. Sulfur exists as S_8 with simple molecular structure with weak intermolecular forces of attraction between S_8 molecules. Hence melting point of Mg is higher than sulfur.

$Mg(OH)_2$ is a white ppt that is only sparingly soluble in water.

Option **D** is not in syllabus. Mg solid reacts slowly with cold water.

Ans: **A**

19) $AgCl$ (white ppt), AgBr (cream ppt) and AgI (yellow ppt) are formed. Both $AgCl$ and AgBr are soluble in excess concentrated NH_3, only AgI remains insoluble due to the extremely small K_{sp} value. A small $[Ag^+]$ will easily lead to precipitation of AgI.

Note: can refer to *Data Booklet* for the reactions of AgX with NH_3.

Ans: **D**

20) As the element contains a partially filled 3d subshells, it is a transition element.

Ans: **D**

21) Redox reaction between SO_2 and VO_2^+, $E^{\ominus}_{cell} = 1.00 - 0.17 = +0.83$ V > 0, rxn is feasible
Redox reaction between SO_2 and VO^{2+}, $E^{\ominus}_{cell} = 0.34 - 0.17 = +0.17$ V > 0, rxn is feasible
Redox reaction between SO_2 and V^{3+}, $E^{\ominus}_{cell} = -0.26 - 0.17 = -0.43$V < 0, rxn is not feasible

VO_2^+ can be reduced to V^{3+} in the presence of excess SO_2.

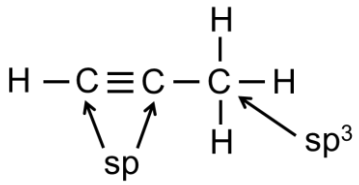
Ans: **B**

22) As Pt has a oxidation number of +4, there are total of 4 Cl^- in the compound.
Complex ion has a +2 charge and hence there are two free Cl^- anion. The other 2 Cl^- are acting as ligands.The coordination number is 6, there are 4 other NH_3 ligands.

The compound is $[Pt(NH_3)_4Cl_2]^{2+} + 2\ Cl^-$

Ans: **B**

23) C≡C bond consists of 1 σ + 2 π bonds. C−C and C−H bonds consist of 1 σ bond.



Ans: **B**

24) Termination step for free radical substitution mechanism involves the reaction of two radicals.

H• is not produced during the free radical substitution mechanism.

Ans: **A**

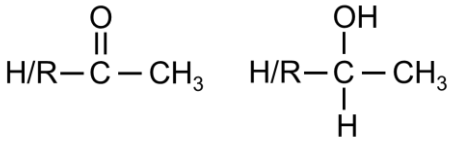
25) The slow step of S_N1 mechanism involves the breaking of C−X bond to give carbocation intermediate. Since C−C*l* bond (BE 340 kJ mol^{-1}) is stronger than C−Br bond (BE 280 kJ mol^{-1}), the activation energy for reaction 1 is lower than reaction 2. Reaction 1 is faster than reaction 2 under identical conditions.

Ans: **D**

26) Na(s) undergoes redox reaction with −OH groups in alcohol, phenol and carboxylic acids to give $H_2(g)$ and $-O^-Na^+$.

Ans: **C**

27) Compound **Z** has empirical formula of CH_2O and
- contains the following structure [gives yellow ppt CHI_3 with alkaline $I_2(aq)$]



- contains a −OH group from alcohol or carboxylic acid [gives white fume HC*l* with PCl_5]

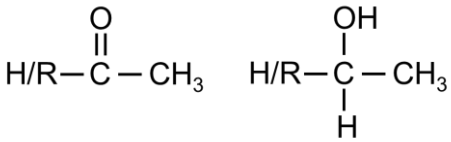
Ans: **A**

28) H atoms in the phenol −OH and carboxylic acid −COOH can easily be replaced by deuterium, D, due to the weak acid dissociation equilibrium of H^+ from phenol and carboxylic acid group in aqueous medium.

$RCOOH \rightleftharpoons RCOO^- + H^+$
$RCOO^- + D_2O \rightleftharpoons RCOOD + OD^-$

Ans: **B**

29) Compound X
- does not contain the following structure [no reaction with alkaline $I_2(aq)$]



- does not contain aldehyde functional group [no reaction with Tollens' reagent]
- contain a ketone functional group [reduced by $NaBH_4$]

Compound X, $CH_3CH_2COCH_2CH_3$, reacts with $NaBH_4$ to give $CH_3CH_2CH(OH)CH_2CH_3$
Ans: **B**

30) Reaction **A** and **D** is the hydrolysis of ester, which requires heating and acid/alkaline catalyst.
Reaction **B** is the hydrolysis of acyl chloride, which occurs readily at room temperature.
Reaction **C** is the hydrolysis of amide, which requires prolonged heating and acid/alkaline catalyst.

Ans: **B**

31)

	^{4}He	^{12}C	^{24}Mg	^{14}N	^{20}Ne	^{30}P	^{28}Si	^{34}S	^{40}Ca
Protons	2	6	12	7	10	15	14	16	20
Neutrons	2	6	12	7	10	15	14	18	20

Ans: **B**

32)

1	SO_2 Bent (polar)	CO_2 Linear (non-polar)
2	PF_3 Trigonal pyramidal (polar)	BF_3 Trigonal planar (non-polar)
3	BrF_5 Square pyramidal (polar)	SiF_4 Tetrahedral (non-polar)

Ans: **A**

33) A Bronsted-Lowry base is a proton (H^+) acceptor.
In reaction 1, NH_3 acts as a nucleophile (electron pair donor/Lewis base)

Ans: **C**

34) Comparing experiments 1 and 3, when $[C_2H_5ONa]$ doubles while keeping $[CH_3I]$ constant, rate of reaction doubles. Hence it is first order with respect to C_2H_5ONa.

Comparing experiments 2 and 3, when $[CH_3I]$ doubles while keeping $[C_2H_5ONa]$ constant, rate of reaction doubles. Hence it is first order with respect to CH_3I.

Overall order of reaction is 2.

Ans: **D**

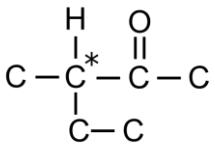
35) A Bronsted-Lowry acid is a proton (H^+) donor.
In reaction **1**, Be^{2+} acts as a Lewis acid (electron pair acceptor)
In reaction **2**, $[Be(H_2O)_4]^{2+}$ donates H^+ to give $Be(H_2O)_2(OH)_2$
In reaction **3**, $Be(H_2O)_2(OH)_2$ donates H^+ to give $[Be(OH)_4]^{2-}$

Ans: **C**

36) Oxidation number of C*l* changes from 0 in Cl_2 to −1 in NaC*l* and +5 in NaC*l*O_3

Ans: **B**

37) The structure of the compound could be



Minimum 6 C atoms in the molecule. Ans: **C**

38) Option **1** is the transition state for S_N2 reaction between OH^- and CH_3Cl.
Option **2** is the carbocation for S_N1 reaction between a nucleophile and $C_6H_5C(CH_3)_2X$.
Option **3** is not possible as the nucleophile is either no charge of negatively charged, it is not possible to give a transition state with positive charge in a nucleophilic substitution reaction.

Ans: **B**

39) Serotonin contains, phenol, alkene and phenylamine and primary amine functional groups.

CH_3COCl can undergo condensation reaction with phenol, phenylamine and primary amine.
HCl(g) can undergo electrophilic addition reaction with alkene
HCl(aq) can undergo acid-base reaction with phenylamine and primary amine.
NaOH(aq) can undergo acid-base reaction with phenol.

Ans: **A**

40) The polypeptide shown is gly − cys − lys − gly − lys.
Trypsin hydrolyses the peptide bonds at the carboxyl group of lysine and arginine. The fragments formed are gly − cys – lys and gly − lys

Ans: **C**

2016 A level Paper 2 suggested answers

1 Planning (P)

(a) The solid will dissolve to give a blue solution of $CuSO_4$. Effervescence of a colourless, odourless gas of CO_2 will also be observed.

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

Total amount of H_2SO_4 in conical flask = $(\frac{50.00}{1000} \times 1.00) = 0.0500$ mol

Amount of acid to be reacted (75%) = $\frac{75}{100} \times 0.0500 = 0.0375$ mol

Amount of $Cu_3(CO_3)_2(OH)_2$ required = $0.0375 \div 3 = 0.0125$ mol

Mass of $Cu_3(CO_3)_2(OH)_2$ required = $0.0125 \times 344.5 = 4.306$ g

Mass of powdered rock sample required = $\frac{100}{90} \times 4.306 =$ **4.785 g**

Practical details

Ensure a known mass of powdered rock is transferred to the acid and ensure the reaction is complete

1. Using a weighing balance (precision 2 d.p), record the mass of an empty weighing bottle.
2. Weigh out accurately about 4.79 g of powdered rock sample into the same weighing bottle. Record its mass.
3. Transfer the solid into a 250 cm^3 conical flask containing 50.00 cm^3 of 1.00 $moldm^{-3}$ sulfuric acid.
4. Reweigh the weighing bottle with residual solid and record the mass.

Recordings of mass of powdered rock used

Mass of weighing bottle	/ g	A
Mass of weighing bottle with given sample	/ g	B
Mass of weighing bottle and **residual** solid	/ g	C
Mass of solid transferred to conical flask	/ g	**B – C**

5. Swirl the conical flask gently to ensure even mixing. Continue swirling until all the solid has dissolved and there is no further effervescence of CO_2.

Dilute the final reaction mixture to provide sufficient solution for titration against 0.100 mol dm^{-3} sodium hydroxide

Amount of unreacted $H_2SO_4 = 0.0500 - 0.0375 = 0.0125$ mol in 50 cm^3

$[H_2SO_4]$ in the final reaction mixture = $\frac{0.0125}{50/1000} = 0.250$ mol dm^{-3}

When diluted to 250 cm^3, $[H_2SO_4]_{diluted} = 0.250 \times \frac{50}{250} = 0.0500$ mol dm^{-3}

If 25.0 cm^3 of the diluted H_2SO_4 is used for titration,

Amount of $H_2SO_4 = \frac{25}{1000} \times 0.0500 = 0.00125$ mol

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Amount of NaOH required = $0.00125 \times 2 = 0.00250$ mol

Volume of 0.100 mol dm^{-3} NaOH required = $\frac{0.0025}{0.100} = 0.0250$ dm^3 = 25.0 cm^3 (suitable vol for titrant)

1. Transfer the final reaction mixture into a 250 cm^3 volumetric flask. Rinse the beaker thoroughly with deionized water and transfer all washings into the volumetric flask and make up to the 250 cm^3 mark with deionised water.

2. Stopper the flask and shake thoroughly to obtain a homogeneous solution. Label this solution **FA1**.
3. Pipette 25.0 cm^3 of **FA1** into a conical flask add 2−3 drops of phenolphthalein indicator into the same conical flask.
4. Fill a burette with 0.100 mol dm^{-3} NaOH. Record the initial burette reading.
5. Titrate **FA1** against NaOH until the solution changes from colourless to first permanent pink.
6. Record the final burette reading.
7. Repeat titration until consistent titre results within ±0.10 cm^3 are obtained.

Titration of FA1 with NaOH

		1	2	3
Final burette reading	/ cm^3			
Initial burette reading	/ cm^3			
Volume of NaOH added	/ cm^3	V_1	V_2	V_3

Assuming V_2 and V_3 are within ±0.10 cm^3,
Average vol of NaOH used = $\frac{V_2 + V_3}{2}$ = $V_{average}$ cm^3

Processing of results

Amount of NaOH used for titration = $\frac{V_{average}}{1000}$ × 0.100 = ***v*** mol
Amount of excess H_2SO_4 in 25.0 cm^3 of the diluted sample = ½ × ***v*** = ***w*** mol
Amount of excess H_2SO_4 in 250 cm^3 of the diluted sample = ***w*** × $\frac{250}{25}$ = ***x*** mol
Amount of excess H_2SO_4 in the reaction mixture = ***x*** mol (no change in mol during dilution)

Amount of H_2SO_4 reacted with $Cu_3(CO_3)_2(OH)_2$ = 0.0500 – ***x*** = ***y*** mol
Amount of pure $Cu_3(CO_3)_2(OH)_2$ in the powdered rock sample = ***y*** ÷ 3 = ***z*** mol

Mass of pure $Cu_3(CO_3)_2(OH)_2$ in the powdered rock sample = ***z*** × 344.5 = ***m*** g
Mass of powdered rock sample transferred = m_{total} g
Percentage by mass of pure $Cu_3(CO_3)_2(OH)_2$ in the powdered rock sample = $\frac{m}{m_{total}}$ × 100%

2 (a) (i) The fatty acids and triester are covalent compounds with simple molecular structures, there are intermolecular forces between molecules. The hydrogen bonding and temporary dipole − induced dipole attraction (td−id) between fatty acids molecules are stronger than the permanent dipole – permanent dipole and td−id forces between triester molecules.

Hence less energy is required to overcome the weaker intermolecular forces of attraction between the triester molecules, resulting in its lower melting point as compared to the fatty acids.

(ii) Both stearic acid and palmitic acid are covalent compounds with simple molecular structures, there are intermolecular forces of hydrogen bonding and temporary dipole − induced dipole attractions (td−id) between molecules. However, stearic acid has a larger electron cloud size than palmitic acid, the electron cloud of stearic acid is more easily polarized and dipole is more easily induced. Thus, the td−id forces in stearic acid is stronger than in palmitic acid.

More energy is required to overcome the stronger intermolecular forces of attraction between the stearic acid molecules, resulting in higher melting point as compared to the palmitic acids.

(iii) Based on the data provided, increasing the number of C=C bonds will lower the melting point of the fatty acids

2 (b) (i) Electrophilic addition

2 (b) (ii) Mass of iodine required to react with 100 g of olive oil = $0.237 \times \frac{100}{0.256} = 92.58 \approx$ **<u>92.6 g</u>**

(iii) Amount of olive oil in 100 g = $\frac{100}{782}$ = 0.1279 mol

Amount of iodine required to react with 100 g of olive oil = $\frac{92.6}{126.9 \times 2}$ = 0.3649 mol

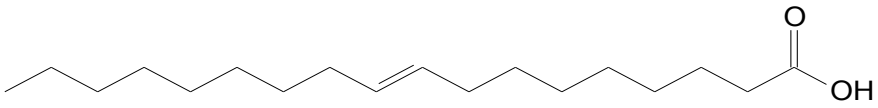
Since 1 mol of C=C reacts with 1 mol of I_2 during electrophilic addition,
average number of C=C bonds in each olive oil molecule = $\frac{0.3649}{0.1279}$ = 2.85

(iv) If the triester is formed purely from oleic acid, there will be 3 C=C bonds in each olive oil molecule. As the average number of C=C bonds is 2.85, the triester in olive oil is likely to be formed from oleic acid (majority), palmitic acid and stearic acid.

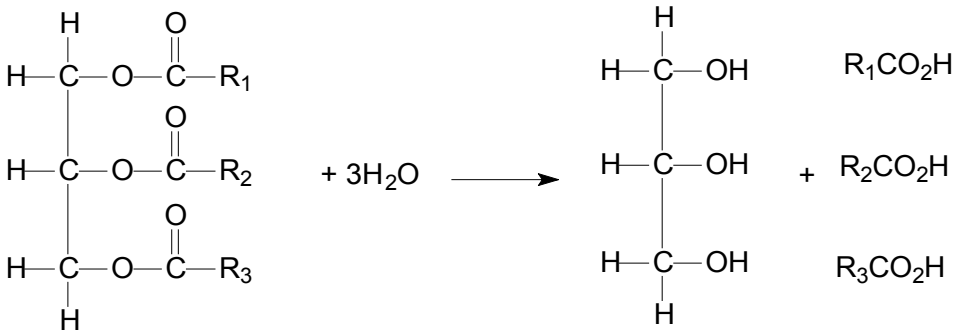
Note: Unlikely to contain linoleic acid and linolenic acid as these fatty acids will cause an increase in the average number of C=C bonds in each olive oil molecule.

2 (c) (i) $H_2(g)$, Pt(s) at room conditions OR $H_2(g)$, Ni(s), high temperature and pressure.

(ii) Note: must use skeletal formula.



2 (d) The ester functional groups in the original olive oil undergo hydrolysis to give glycerol and free fatty acids.



OR

The alkene functional groups in oleic acid undergo oxidation to give nonanoic acid and nonanedioic acid.

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

OR

$R{-}CH{=}CH(CH_2)_7CO_2H + 4[O] \rightarrow R{-}CO_2H + HO_2C(CH_2)_7CO_2H$

3 (a) Silicon carbide is a covalent compound with covalent lattice structure. Large amount of energy is required to overcome the strong C−Si covalent bond during melting. Hence silicon carbide has a very high melting point and makes it resistant to melting, even at higher temperatures.

3 (b) (i) $C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O$

Note: No reaction for NO_x

3 (b) (ii) Heterogeneous catalyst is involved in this reaction.

Stage 1: Adsorption of reactant molecules onto the surface of the catalyst. Weak interactions formed between the reactant and catalyst.

Stage 2: Reaction at the surface occurs at a faster rate as reactant molecules are brought closer together and existing interactions in the reactant molecules are weakened.

Stage 3: Desorption of products from the catalyst surface after the reaction.

3 (c) (i) Oxidation number of N decreases from +4 (in NO_2) to 0 (in N_2)
Oxidation number of N increases from −3 (in NH_3) to 0 (in N_2)

(ii) [R] $2NO_2 + 8H^+ + 8e^- \rightarrow N_2 + 4H_2O$ ×3
[O] $2NH_3 \rightarrow N_2 + 6H^+ + 6e^-$ ×4

Overall equation: $8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$

3 (d) (i) NO_2 acts as a homogeneous catalyst in the oxidation of SO_2 to SO_3.
The oxidation process of $SO_2 + ½ O_2 \rightarrow SO_3$ has a high activation energy.
NO_2 is a radical and is able to provide an alternative reaction pathway of lower activation energy for the oxidation of SO_2.

Step 1: $NO_2 + SO_2 \rightarrow SO_3 + NO$
Step 2: $NO + ½ O_2 \rightarrow NO_2$

Note: NO_2 is regenerated in step 2.

(ii) NO_2 causes formation of smog through reaction with other air pollutants.
NO_2 also causes formation of ozone at lower atmosphere. High concentration of ozone at lower atmosphere causes respiratory problems.

(iii) Assuming $P_{NO2} = 1.5\times10^{-3}$ Pa at equilibrium

$$K_p = \frac{P_{N2O4}}{(P_{NO2})^2}$$

$$6.25\times10^{-5} = \frac{P_{N2O4}}{(1.5\times10^{-3})^2}$$

$P_{N2O4} = 1.41 \times 10^{-10}$ Pa

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

(ii) When K(s) and Cu(s) undergoes reaction, they are oxidized to $K^+(aq)$ and $Cu^{2+}(aq)$ respectively.
Since $E^\ominus (K^+/K) = -2.92$ V is more negative than $E^\ominus (Cu^{2+}/Cu) = +0.34$ V, K(s) undergoes oxidation much more readily as compared to Cu(s).
For example, for the reaction between metal and water:
$K(s) + H_2O(l) \rightarrow KOH + ½ H_2$ $E^\ominus_{cell} = -0.83 - (-2.92) = +2.09$ V, rxn is feasible
$Cu(s) + 2H_2O(l) \rightarrow Cu(OH)_2 + H_2$ $E^\ominus_{cell} = -0.83 - (+0.34) = -1.17$ V, rxn is not feasible

Note: We should not be comparing ionization energies of K and Cu, as it only account for the changes from $K(g) \rightarrow K^+(g)$ and $Cu(g) \rightarrow Cu^{2+}(g)$. $E^\ominus$ values provide a more comprehensive comparison of the reactivities of the two metals.

4 (b) (i) In the presence of O_2:
[R] $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
[O] $Cu \rightarrow Cu^{2+} + 2e^-$
$E^{\ominus}_{cell} = +1.23 - (+0.34) = +0.89\ V > 0$, the reaction is feasible.

Without O_2:
[R] $2H^+ + 2e^- \rightarrow H_2$
[O] $Cu \rightarrow Cu^{2+} + 2e^-$
$E^{\ominus}_{cell} = 0.00 - (+0.34) = -0.34\ V < 0$, the reaction is not feasible.

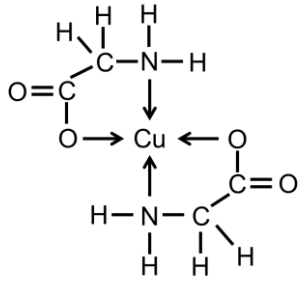
(ii) The concentration of dissolved O_2 could be very small, this decreases the frequency of effective collisions between the reacting particles. Hence the rate of corrosion of copper by O_2 and acid is very slow.
OR
The corrosion of copper **<u>may not be kinetically feasible due to high activation energy,</u>** even though it is thermodynamically feasible indicated by a positive $E^{\ominus}_{cell}$ value.

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

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

4 (c) (i) The term 'ligand' refers a molecule or anion that can donate a lone pair of electron to a metal cation to form a complex ion.

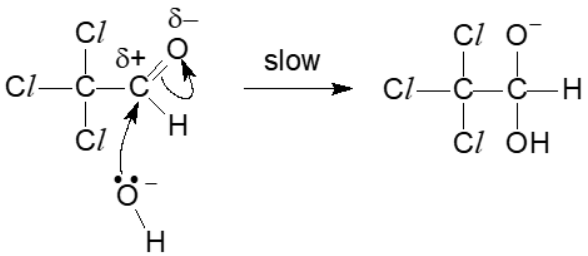
(ii)

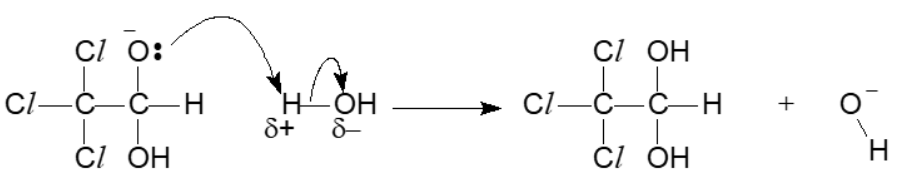


5 (a) (i) Add Tollens' reagent containing $[Ag(NH_3)_2]^+$ to the reaction mixture and warm.
If trichloroethanal is present, a silver mirror or grey solid of Ag will be formed.
If trichloroethanal is not present, no silver mirror or grey solid of Ag will be formed.

Other possible chemical tests:
1) Fehlings' solution containing alkaline Cu^{2+} complex and warm. Trichloroethanal will react to give a brick red ppt of Cu_2O.
2) 2,4−dinitrophenylhydrazine. Trichloroethanal will react to give an orange ppt.

(ii)





(iii) $CCl_3CHO + OH^- \rightarrow HCO_2^- + CHCl_3$
The product $CHCl_3$ can be obtained by balancing the atoms and charges on both sides.

5 (b) (i) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
$CCl_3COOH \rightleftharpoons CCl_3COO^- + H^+$

In CCl_3COO^-, the presence of electronegative Cl atoms helps to disperse the negative charge on the O^- through electron withdrawing effect. CCl_3COO^- is more stable than CH_3COO^-.

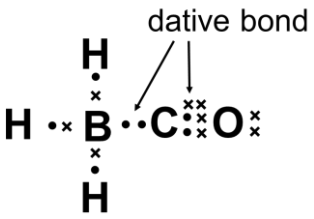
The dissociation of CCl_3COOH into H^+ is more favourable as compared to CH_3COOH. Hence CCl_3COOH is a stronger acid.

(ii) Not in syllabus.

2016 A level Paper 3 suggested answers

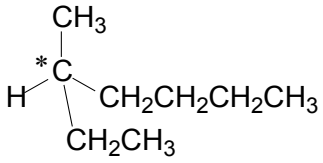
1 (a) CO acts as a ligand and it can form strong dative bond with the Fe^{2+} in haemoglobin in blood. This reduces the oxygen-carrying ability of the blood and can lead to oxygen starvation and eventually death.

1 (b)



1 (c) (i) $C_8H_{18} + 11½\ O_2 \rightarrow 6CO_2 + 2CO + 9H_2O$

(ii)



or any other branched isomer with a chiral centre.

1 (d) In the presence of ligands, all 3d orbitals of transition metal cation split into two different energy levels with a small energy gap, ΔE.
A specific wavelength in the visible light spectrum with energy corresponding to ΔE is absorbed to promote electrons from lower energy 3d orbitals to higher energy 3d orbitals.
The colour observed is the complementary colour of wavelength absorbed.

1 (e) (i) HI and $[Rh(CO)_2I_2]^-$ are the homogeneous catalyst in this reaction. HI and $[Rh(CO)_2I_2]^-$ has the same state as the reactants and they are regenerated at the end of the reaction.

(ii) $CH_3OH + CO \rightarrow CH_3COOH$

(iii) Step 3 involve a decrease of 6 ligands to 5 ligands bonded to the rhodium ion.
Step 5 involve a decrease of 6 ligands to 4 ligands bonded to the rhodium ion.

(iv) HI and $[Rh(CO)_2I_2]^-$ act as a catalyst as they are regenerated at the end of reaction.
CO is the reactant as it is used up during the reaction, and not regenerated at the end.

1 (f) (i) $K_p = \dfrac{P_{CH4} \times P_{H2O}}{P_{CO} \times (P_{H2})^3}$
Units = atm^{-2}

Note: Do not use [P_{CH4}] as square brackets is a notation for concentration.

1 (f) (ii)

	CO	+ 3H₂	⇌	CH₄	+ H₂O
Initial / mol	x	3x		0	0
Change / mol	−y	−3y		+y	+y
Eqm / mol	x−y	3x−3y		y	y

Mole fraction of CH_4 = H_2O = 0.12
Mole fraction of H_2 = 3×0.19 = 0.57

P_{CO} = 0.19 × 32 = 6.08 atm
P_{H2} = 0.57 × 32 = 18.24 atm
P_{CH4} = P_{H2O} = 0.12 × 32 = 3.84 atm

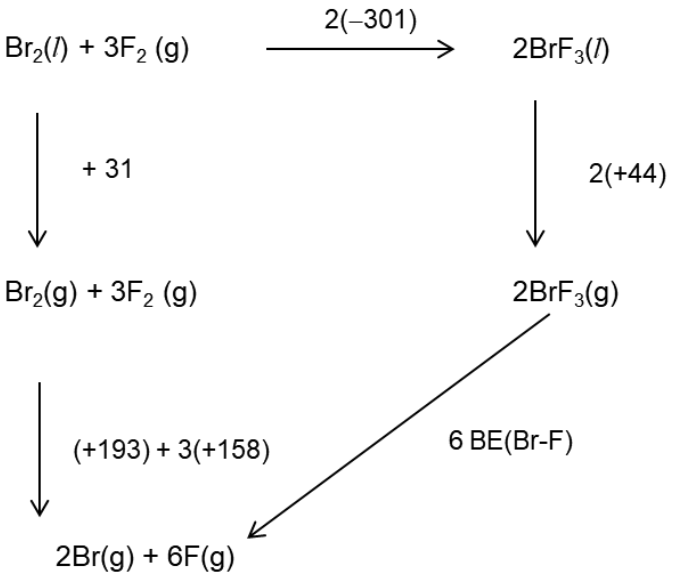
(ii) $K_p = \dfrac{3.84\times3.84}{6.08\times(18.24)^3}$ = 4.00 × 10^{-4} atm^{-2}

2 (a) $2KI + Cl_2 \rightarrow I_2 + 2KCl$
$E^{\ominus}_{cell}$ = +1.36 − (+0.54) = +0.82 V > 0
The reaction is feasible, the final solution is brown due to I_2(aq).

$KCl + Br_2 \rightarrow$ no reaction
$E^{\ominus}_{cell}$ = +1.07 − (+1.36) = −0.29 V < 0
The reaction is not feasible, the final solution is orange due to Br_2(aq).

$KBr + I_2 \rightarrow$ no reaction
$E^{\ominus}_{cell}$ = +0.54 − (+1.07) = −0.53 V < 0
The reaction is not feasible, the final solution is brown due to I_2(aq).

2 (b) (i)

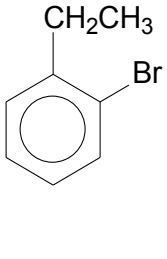


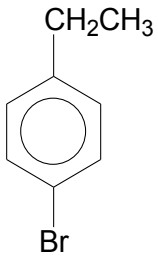
By Hess's Law
6×BE(Br−F) = −2(44) + 2(301) + 31 + 193 + 3(+158) = 1212
BE(Br−F) = 202 kJ mol^{-1}

(ii) $\Delta G^{\ominus}_f = \Delta H^{\ominus}_f - T\Delta S^{\ominus}_f$
$-241 = -301 - 298\Delta S^{\ominus}_f$
$\Delta S^{\ominus}_f$ = −0.201 kJ mol^{-1} K^{-1}

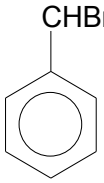
ΔS^{e}_{f} has a negative value as there is a decrease in number of gas particles after the reaction. Hence there are less ways to arrange the particles and the system is less disorderly.

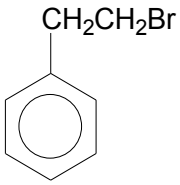
2 (c) (i) Compound **D**





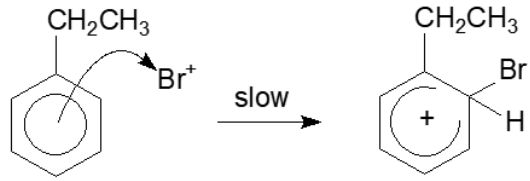
Compound **E**

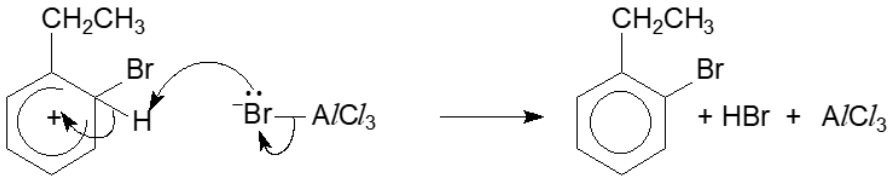




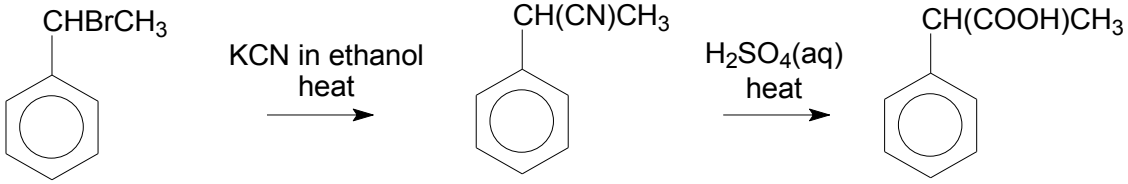
(ii) Reaction **1**: Electrophilic substitution
Reaction **2**: Free radical substitution

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





(iv) Compound **E** would be a suitable starting material.

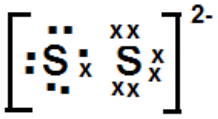


3 (a) (i) Mn^{4+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

(ii) $|\text{L.E.}| \propto \dfrac{q_+ \times q_-}{r_+ + r_-}$

Magnitude of L.E. of MnO_2 is larger than MnS_2 as the charge of the ions are the same, the ionic radius of O^{2-} is smaller than S^{2-}. Hence L.E. for MnO_2 is more exothermic.

3 (b) (i)



(ii) Mn^{4+} undergoes reduction. The oxidation number of Mn decreases from +4 in Mn^{4+} to +2 in Mn^{2+}.
S^{2-} undergoes oxidation. The oxidation number of S increases from −2 in S^{2-} to −1 in S_2^{2-}.

3 (c) (i) [R] $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
[O] $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

Overall equation: $5Sn^{2+} + 2MnO_4^- + 16H^+ \rightarrow 5Sn^{4+} + 2Mn^{2+} + 8H_2O$

3 (c) (ii) [R] $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
[O] $Pb^{2+} \rightarrow Pb^{4+} + 2e^-$

$E^e_{cell} = +1.52 - (+1.69) = -0.17\ V < 0$. The reaction is not energetically feasible.

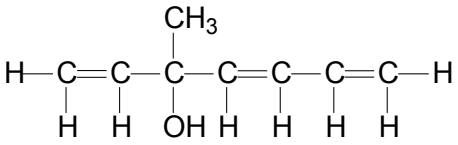
(iii) Conical flask contains Sn^{2+} initially.
The endpoint of the titration is when the colourless solution first turn permanent pink. (Due to 1 drop of excess $KMnO_4$)

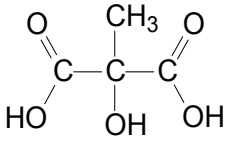
(iv) Amount of MnO_4^- used = $\frac{22.50}{1000} \times 0.02 = 0.00045$ mol
Amount of Sn^{2+} in 25.0 cm^3 sample = $\frac{5}{2} \times 0.00045 = 0.001125$ mol
Total amount of Sn^{2+} in 250 cm^3 = $\frac{250}{25} \times 0.001125 = 0.01125$ mol

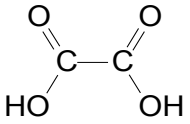
Mass of Sn in the 3.00 g sample = 0.01125 × 118.7 = 1.335 g
Percentage by mass of tin in the solder = $\frac{1.335}{3.0} \times 100\% = 44.5\%$

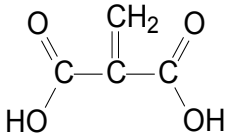
3 (d) (i) Compound **F** contains a tertiary alcohol which can react with Na(s) to produce $H_2(g)$ but cannot undergo oxidation reaction with hot acidified $K_2Cr_2O_7$.

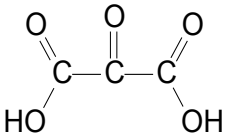
(ii)

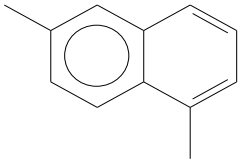

Compound **F**

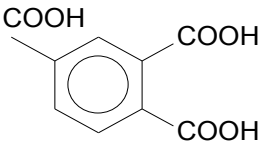

Compound **G**


Compound **H**


Compound **I**


Compound **J**

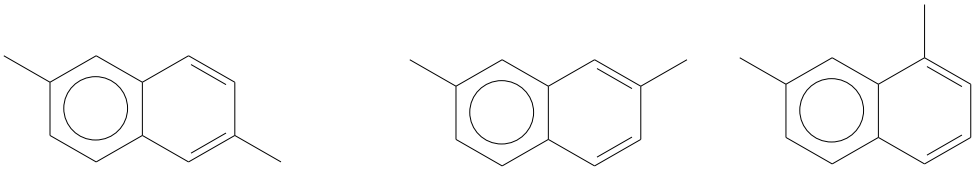

Compound **K**


Compound **L**

(iii) Compound **F** exhibits cis-trans isomerism and enantiomerism (optical isomerism).

Total number of isomers shown by **F** = 2^2 = 4 (1 chiral centre and 1 C=C for cis-trans)

(iv)


Positional isomerism.

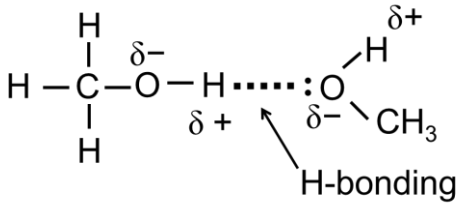
4 (a) Both ethane and methane have intermolecular forces of temporary dipole-induced dipole(td-id).

Td-id arises due to random movement of electrons giving rise to uneven distribution of electron cloud of a molecule, creating a temporary dipole. The temporary dipole induces a similar dipole moment on adjacent molecules.

Ethane is a larger molecule than methane, the larger electron cloud is more easily distorted and temporary dipoles are more easily induced. More energy is required to overcome the stronger td-id interactions between ethane molecules. Ethane has a higher boiling point than methane.

Methanol has intermolecular forces of hydrogen bonding which arises due to attraction between the lone pair electron of a highly electronegative element (O atom in methanol) and a highly electron deficient H atom bonded directly to highly electronegative element O.

More energy is required to overcome the stronger hydrogen bonding between methanol molecules. Methanol has a higher boiling point than ethane.



4 (b) (i) The C−C (BE = 350 kJ mol^{-1}) and C−H bonds (BE = 410 kJ mol^{-1}) are strong. Larger amount of energy is required for reaction to occur.

The C−C and C−H bonds are non polar, thus they do not attract electrophiles and nucleophiles.

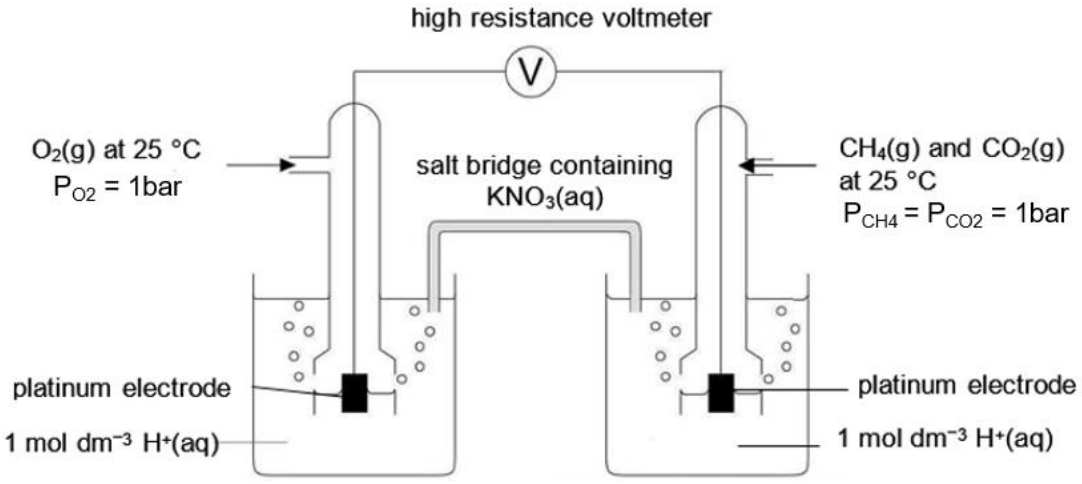
(ii) $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
Conditions: Burn propane in excess O_2
Type of reaction: Combustion

$C_3H_8 + Cl_2 \rightarrow CH_3CH_2CH_2Cl$ (or $CH_3CHClCH_3$) + HCl
Conditions: Cl_2(g), UV light
Type of reaction: Free radical substitution

Note: Mechanism for free radical substitution is not required.

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

(ii)



(d) (i) For each pair of Cu and Zn discs with the electrolyte containing Cu^{2+} and Zn^{2+},
$E^{\ominus}_{cell}$ = +0.34 − (−0.76) = +1.10 V

Since there are five pairs of the Cu and Zn discs connected in series,
the total $E^{\ominus}_{cell}$ = 5 × (+1.10) = +5.50 V

(ii) As the reaction proceeds, Cu^{2+}(aq) is reduced to Cu(s) and Zn(s) is oxidised to Zn^{2+}(aq).
The mass of copper discs increases and the mass of zinc discs decreases.

$Cu^{2+} + 2e^- \rightleftharpoons Cu$
$Zn^{2+} + 2e^- \rightleftharpoons Zn$

As $[Cu^{2+}(aq)]$ decreases, position of equilibrium for Cu^{2+}/Cu shift to the left, $E(Cu^{2+}/Cu)$ decreases.
As $[Zn^{2+}(aq)]$ increases, position of equilibrium for Zn^{2+}/Zn shift to the right, $E(Zn^{2+}/Zn)$ increases.

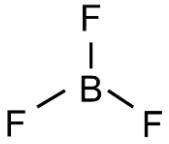
Since $E_{cell} = E(Cu^{2+}/Cu) - E(Zn^{2+}/Zn)$, the E_{cell} will decrease as the reaction proceeds.

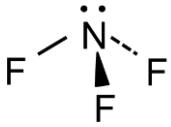
5 (a) (i) Valence Shell Electron Pair Repulsion (VSEPR) theory states that:

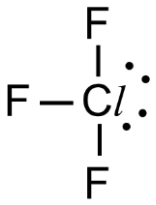
1) Electron pairs (bond pairs and lone pairs) in the valence shell around the central atom arrange themselves to be as far apart as possible to minimise mutual repulsion.
2) Lone pair−lone pair repulsion > Lone pair−bond pair repulsion > bond pair−bond pair repulsion

(ii)

BF_3	NF_3	ClF_3
3 b.p. 0 l.p.	3 b.p. 1 l.p.	3 b.p. 2 l.p.
Trigonal planar	Trigonal pyramidal	T-shaped







5 (b) (i) Add anhydrous PCl_3 / PCl_5 / $SOCl_2$ to the alcohol at room temperature.

(ii)

	Reaction with water
CH_3CH_2Cl	Reacts with water slowly upon heating to give $CH_3CH_2OH + HCl$
C_6H_5Cl	No reaction with water even with heating
CH_3COCl	Reacts with water vigorously to give $CH_3COOH + HCl$

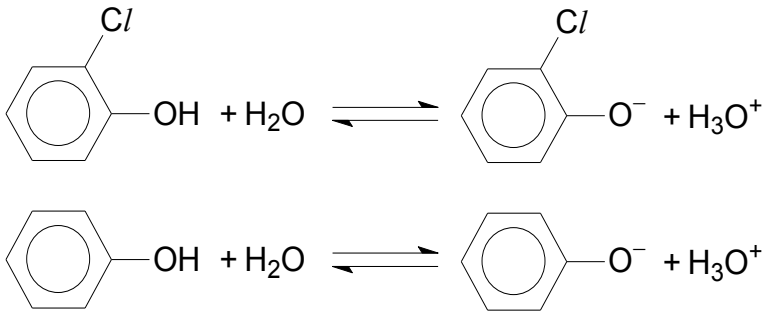
	Reaction with NaOH(aq)
CH_3CH_2Cl	Reacts with NaOH(aq) upon heating to give $CH_3CH_2OH + NaCl$
C_6H_5Cl	No reaction with NaOH(aq) even with heating
CH_3COCl	Reacts with NaOH(aq) vigorously to give $CH_3COO^-Na^+ + NaCl$

Ethanoyl chloride is the most reactive towards nucleophiles. The presence of highly electronegative O atom and C*l* atom attached to the carboxyl C atom makes it highly electron-deficient, hence most susceptible to nucleophilic attack.

Chlorobenzene is resistant towards nucleophilic substitution. C atom of C–C*l* is electron rich due to delocalized π electrons of benzene. This repels nucleophile.
OR
Partial double bond character of C–C*l* bond due to the overlapping of the p orbital of C*l* with the π electron cloud of the benzene ring. This increases the bond strength and lead to higher activation energy for reaction with nucleophile.

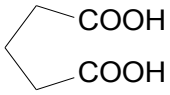
5 (c) (i) Phenol can react with $Cl_2(aq)$ or Cl_2 in CCl_4.

5 (c) (ii)

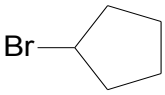


−C*l* is an electron-withdrawing group that decrease the intensity of the negative charge on the conjugate base, thus the dissociation into H^+ and conjugate base is more favourable for chlorinated phenol. Hence the acidity of chlorinated phenol is greater than phenol.

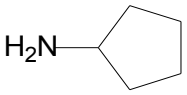
5 (d) Step 1: $KMnO_4$, H_2SO_4(aq), heat
Step 2: Anhydrous PCl_3 / PCl_5 / $SOCl_2$
Step 3: HBr(g)
Step 4: excess ethanolic NH_3, heat in sealed tube



M



N



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