Suggested Answers for 9729 H2 CM 2019 JC 2 Prelim

Paper 3

1 (a) (i) When dissolved in a polar solvent such as water, they dissociate to form strong acids, releasing H^+ and X^- ions forming ion-dipole interactions with water. **[1]**

(ii) HF has an exceptionally high boiling point compared to the other hydrogen halides as hydrogen bonds exist between HF molecules but not between the rest of the HX molecules. More energy is needed to overcome the stronger hydrogen bonds.

Boiling point of the hydrogen halides increases from HC*l* to HBr to HI.

The strength of instantaneous dipole-induced dipole interactions between the hydrogen halide molecules increases as the number of electrons in the molecules increases. More energy is needed to overcome the stronger id-id interactions. **[2]**

(iii) When a red-hot steel needle is introduced, HBr produces red brown bromine vapour. HI gives violet fumes of iodine. HF and HC*l* do not/show little tendency to decompose.

Bond	Bond Energies/ kJ mol^{-1}
H–F	+562
H–C*l*	+431
H–Br	+366
H–I	+299

Less energy is required to break the weaker H–X bond.

The thermal stability of hydrogen halides decreases down the Group due to decreasing H–X bond energy. **[3]**

(b) (i) Solubility of AgBr = $0.140 \times 10^{-3} / (107.9 + 79.9)$

$= 7.45 \times 10^{-7}$ mol dm^{-3}

$[Br^-] = 4.00 \times 10^{-12} / 0.100 = 4.00 \times 10^{-11}$ mol dm^{-3}

$[Ag^+][Br^-] = K_{sp}$

$[Ag^+](4.00 \times 10^{-11}) = (7.45 \times 10^{-7})^2$

$[Ag^+] = 0.0139$ mol dm^{-3} **[2]**

(ii) In the saturated AgC*l*,

$[Ag^+][Cl^-] = K_{sp}$

$(0.0139)(0.0139 + 0.001) = K_{sp}$

$K_{sp} = 0.000206$ mol^2 dm^{-6}

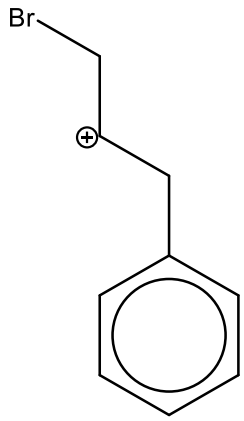
Solubility = $(0.00206)^{1/2} = 0.0144$ mol dm^{-3} **[2]**

(iii) Mass of AgC*l* dissolved in 1 dm^3 = (0.0139)(107.9 + 35.5)

= 1.99 g

Mass of residue = 5.00 – 1.99 = 3.01 g **[1]**

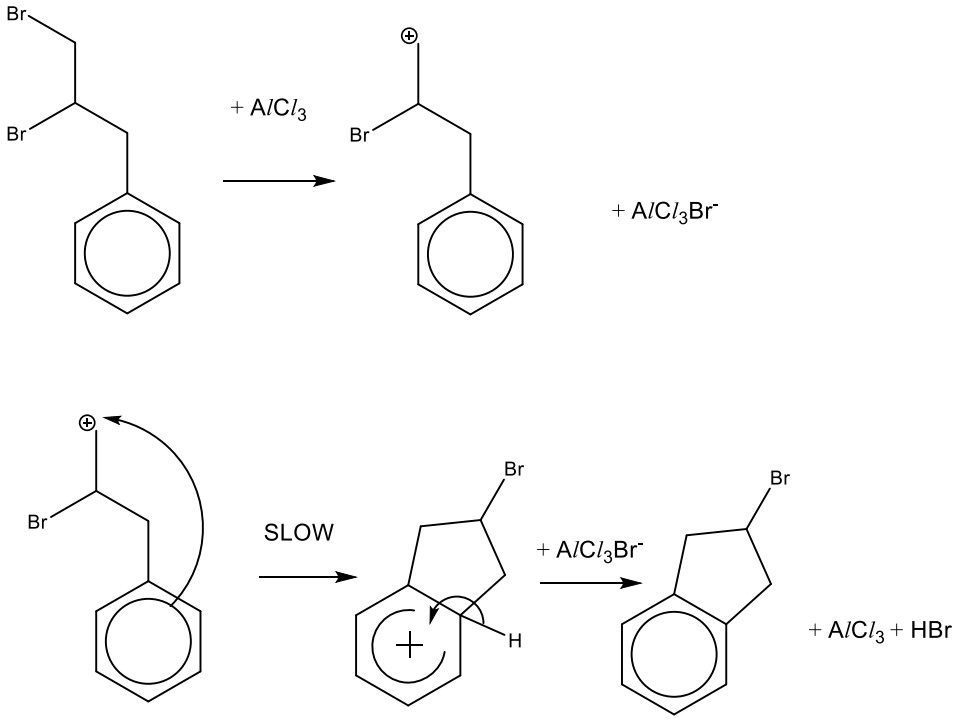
(c) (i)



The higher the number of electron donating groups attached to carbocation, the more stable the carbocation.

As the 2 possible intermediate contains a primary carbocation and secondary carbocation respectively, intermediate with the secondary carbocation is more stable. **[2]**

(ii)



[2]

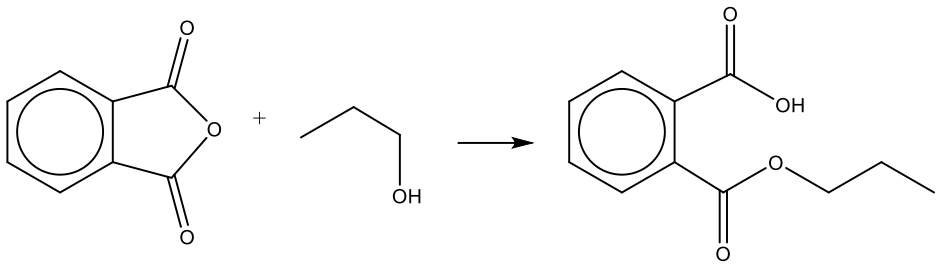
(iii) Compound **B** has a 4 membered ring form in place of the 5 membered ring presented in the reaction scheme.

The 4 membered ring consist of 2 carbon atoms with sp^2 hybridised orbitals 120° from each other and 2 carbon atoms with sp^3 hybridised orbitals at 109.5° from each other.

To fit into 4 membered ring, all 4 carbons are forced into 90° bond angle which exerts high angle strains making the 4 membered ring formation unfavourable. **[2]**

[Total: 17]

2 **(a)** **(i)**



[1]

(ii) H_2O/Water **[1]**

(b) **(i)** For pK_1, the H^+ is removed from a neutral molecule. For pK_2, the removal of a H^+ from the anion that already carries a negative charge is electrostatically unfavourable.

OR Favourable intramolecular hydrogen bonding in the anion will be disrupted when it dissociates in pK_2. **[1]**

(ii) Phthalic acid is the limiting reagent/NaOH is in excess

Amount of excess NaOH = $\frac{50}{1000} \times 0.1 - \left(\frac{10}{1000} \times 0.2 \times 2\right)$

= 1.0×10^{-3} mol

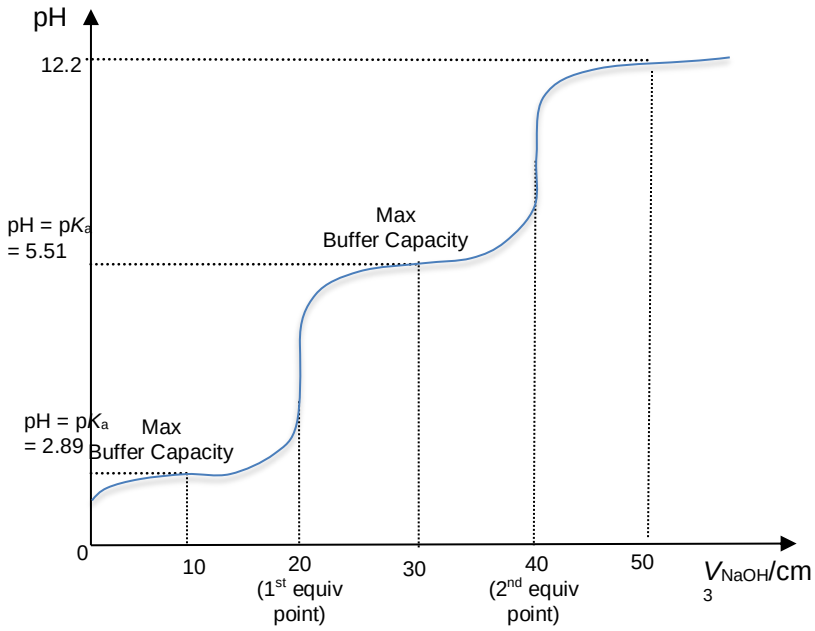
$[OH^-] = \frac{1.0 \times 10^{-3}}{\frac{60}{1000}} = 1.667 \times 10^{-2}$ mol dm^{-3}

$pOH = -\lg(1.667 \times 10^{-2}) = 1.78$

$pH = 14 - 1.78 = 12.2$

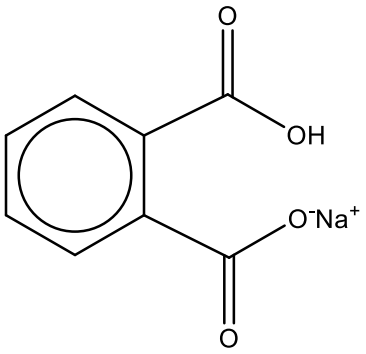
[2]

(iii)



[3]

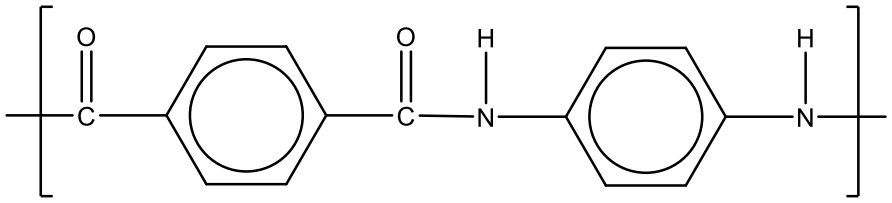
(iv)



[1]

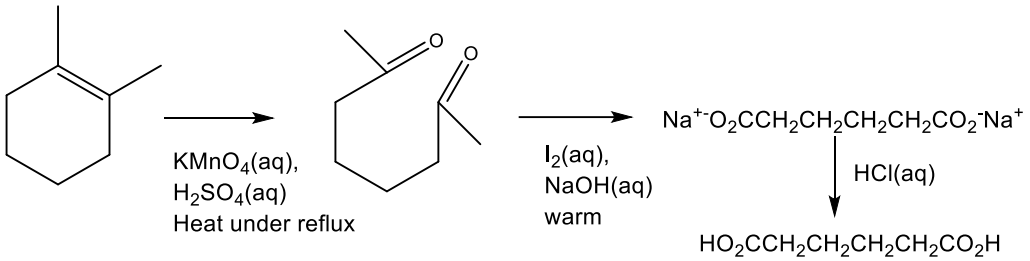
(c) **(i)** Condensation **[1]**

(ii)



[1]

(d)

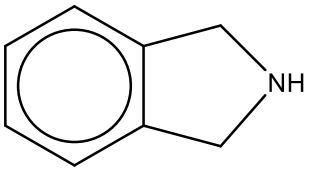


[2]

(e) Reaction **A**: PCl_5, room temperature

Reaction **B**: limited ethanolic NH_3, heat in a sealed tube

Structure of **C**:



[3]

(f) **(i)** I: acid-base reaction (alkaline hydrolysis is not accepted)

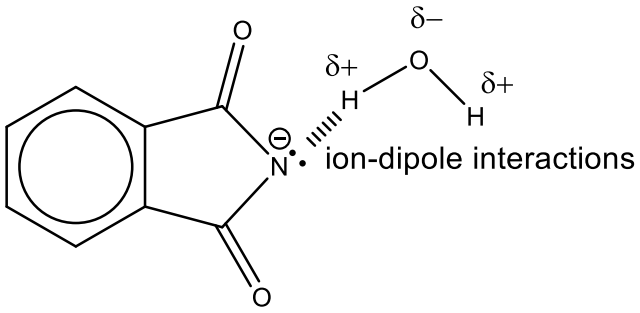
II: nucleophilic substitution

III: hydrolysis **[3]**

(ii) H_2SO_4(aq) and heat under reflux, followed by controlled amount of strong base.

Or NaOH(aq) and heat under reflux, followed by controlled amount of strong acid **[1]**

(iii)



[1]

(iv) Amt of **D** = $\frac{0.5}{147}$ = 3.401 × 10`3 mol

Amt of gaseous product = $\frac{pV}{RT} = \frac{(101325)(42.26\times10^{-6})}{8.31\times303}$ = 1.701× 10`3 mol

Since mole ratio of **D**: Gaseous Product = 2:1, gaseous product is N_2 gas.

$4C_8H_5O_2N + 33O_2 \rightarrow 32CO_2 + 10H_2O + 2N_2$ **[3]**

[Total: 24]

3 (a) Amt of Fe^{3+} = $\frac{5}{1000}\times0.2 = 0.00100$ mol

Amt of CN^- = $\frac{6}{1000}\times0.6 = 0.00600$ mol

Since ratio of Fe^{3+} : CN^- = 1:6,

H_2O ligand is displaced.

Complex in red solution : $[Fe(CN)_6]^{3-}$

Formation of red solution : $[Fe(H_2O)_6]^{3+} + 6CN^- \rightarrow [Fe(CN)_6]^{3-} + 6H_2O$

Complex in yellow solution : $[Fe(CN)_6]^{4-}$ **[2]**

(b) (i) 3d and 4s electrons have similar energies. More valence electrons from Fe is contributed to the sea of delocalised (mobile) electrons then Ca, thus Fe has a higher electrical conductivity. **[1]**

(ii) Both aqueous Fe^{2+} and Fe^{3+} exist as aqua complexes with formulae $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ respectively.

Ionic radius of Fe^{2+} = 0.061 nm

ionic radius of Fe^{3+} is 0.055 nm

With a smaller radius and a higher charge, Fe^{3+} has a higher charge density**,** water molecules in $[Fe(H_2O)_6]^{3+}$ is polarised and the O–H bonds are weakened to a greater extent, $[H^+]/[H_3O^+]$ increases. Hence, the pH is lower.

$[Fe(H_2O)_6]^{3+}$ (aq) + H_2O (l) ⇌ $[Fe(H_2O)_5(OH)]^{2+}$ (aq) + H_3O^+(aq) **[2]**

(c) (i) Role of Fe^{3+} : Homogeneous catalyst

The reaction between peroxodisulfate ions $S_2O_8^{2-}$ and iodide ions I^- can be catalysed by either Fe^{2+} or Fe^{3+}.

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\ominus = +2.01$ V

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77$ V

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

Reaction catalysed by $Fe^{3+}(aq)$:

Step 1: Formation of an intermediate

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

$E^\ominus_{cell} = +0.77 - (+0.54) = +0.23$ V

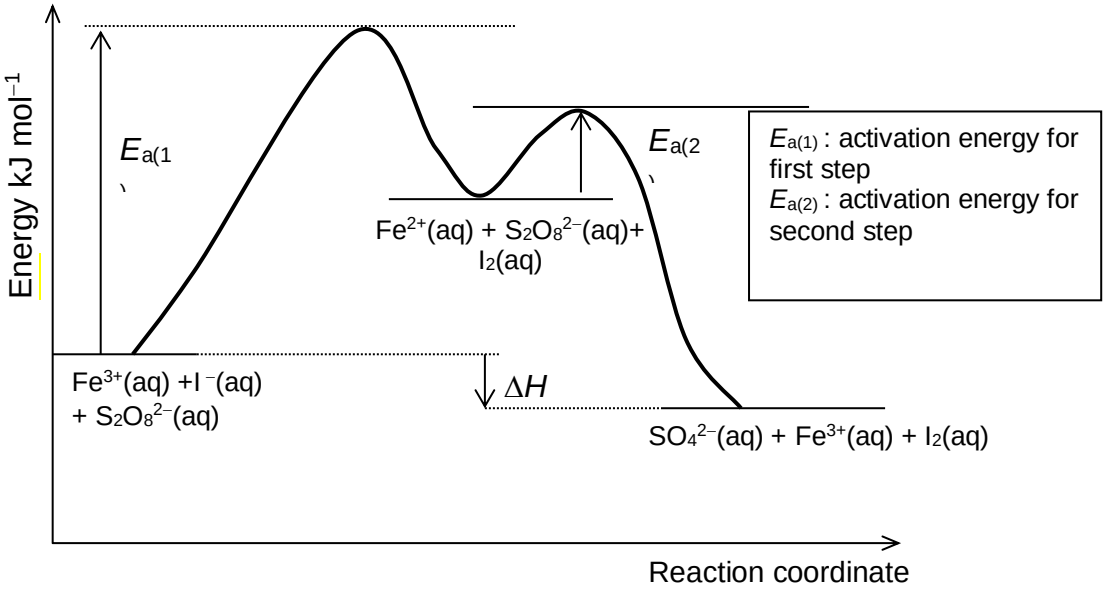
Step 2: Regeneration of catalyst

$S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

$E^\ominus_{cell} = +2.01 - (+0.77) = +1.24$ V

[2]

(ii) **[3]**



(c) **V** has a molecular formula of $C_8H_9NO_2$.

The C:H ratio is ≈ 1:1.

⇒**V** contains a benzene ring

V is insoluble in water and acids

⇒**V** contains an amide

V undergoes acid-base reaction in NaOH

⇒**V** contains <u>a phenol or carboxylic acid group</u>

V undergoes <u>electrophilic substitution</u> with aq Br_2 to form **W**

⇒ **W** has a <u>side chain in either position 2, 4 w.r.t. OH</u>

V undergoes <u>acidic hydrolysis</u> to form compound **X** and **Y**

⇒ <u>salt and carboxylic acid</u> is formed.

X is soluble in water

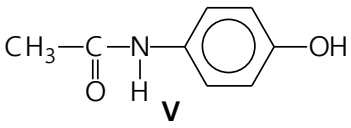
⇒ **X** is an <u>ammonium salt</u>

Y on reduction with $LiAlH_4$ forms **Z**

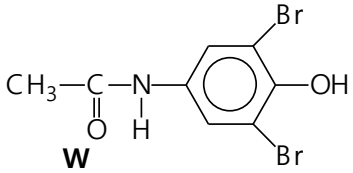
⇒ **Z** is an <u>alcohol</u>

Z undergoes <u>positive iodoform test/oxidation</u> to form a yellow precipitate.

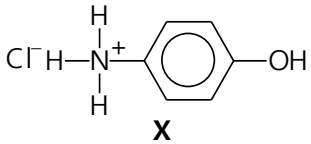
⇒ **Z** is $–CH(CH_3)(OH)$ group



V



W



X

CH_3COOH

Y

CH_3CH_2OH

Z

[9]

[Total: 19]

4 (a) (i) <u>ΔH_{vap} positive</u> due to the energy required to overcome the intermolecular forces between molecules.

<u>ΔS_{vap} positive</u> due to the changing from liquid to gaseous state, hence <u>$-T\Delta S_{vap}$ negative</u>

For vaporisation to be spontaneous, <u>$|-T\Delta S_{vap}| > |\Delta H_{vap}|$, hence it is an entropy-driven reaction</u>. **[2]**

(ii) <u>Benzene</u> is the most volatile VOC.

$\Delta G_{vap} = 33.9 - 330(\frac{113.6}{1000}) =$ <u>-3.59 kJ mol^{-1}</u>

(For the others: ethanol +2.40 , methylbenzene +9.29 , propanone −0.05) **[1]**

(b) (i) Excess chlorine, uv light, (limited methane) **[1]**

(ii) <u>Initiation</u>

U

$Cl_2 \rightarrow 2Cl\bullet$ **[3]**

Propagation

$CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$

$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

$CH_3Cl + Cl\bullet \rightarrow \bullet CH_2Cl + HCl$

$\bullet CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl\bullet$ (must show)

Termination

$\bullet CH_2Cl + Cl\bullet \rightarrow CH_2Cl_2$ (must show)

$2Cl\bullet \rightarrow Cl_2$

$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$

$\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$

$\bullet CH_2Cl + \bullet CH_2Cl \rightarrow ClCH_2CH_2Cl$ (Any 1 of these other 4)

(c) (i) 2-methyl-buta-1,3-diene or 2-methyl-1,3-butadiene **[1]**

(ii) Mass produced = $(0.15 \times 10^{-6} \times 68.0 \times 1000) \times 65 \times 24$

= 15.9 mg **[1]**

(iii) $C_5H_8 + 7O_2 \rightarrow 5CO_2 + 4H_2O$

$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$ **[2]**

(iv)

Let x be the volume of C_5H_8 and nx be the volume of CS_2 initially.

Combining the eqns: $C_5H_8 + 7O_2 \rightarrow 5CO_2 + 4H_2O$ & $nCS_2 + 3nO_2 \rightarrow nCO_2 + 2nSO_2$

Combustion Process:

	C_5H_8	+ nCS_2	+ $(3n+7)O_2$	→ $(n+5)CO_2$	+ $2nSO_2$	+ $4H_2O$
Initial vol	x	nx	excess V_{O2}	-	-	-
Change	*–x*	*–nx*	*–(3n+7)x*	*+(n+5)x*	*+2nx*	-
After rxn	0	0	(excess V_{O2} – 3nx – 7x)	(n+5)x	2nx	-

Volume of gas before combustion = excess V_{O2} + x + nx

Volume of gas after combustion = excess V_{O2} – 3nx – 7x + nx + 5x + 2nx

= excess V_{O2} – 2x

(Volume before combustion) – (Volume after combustion) = 1st volume contraction

(excess V_{O2} + x + nx) – (excess V_{O2} – 2x) = 1st volume contraction

x + nx + 2x = 70

3x + nx = 70

(n + 3)x = 70 ------- (1)

Volume of CO_2 and SO_2 in resultant mixture = 2nd volume contraction

5x + nx + 2nx = 170

(3n + 5)x = 170 ------ (2)

$\frac{(1)}{(2)}$: $\frac{n+3}{3n+5} = \frac{70}{170}$ **[3]**

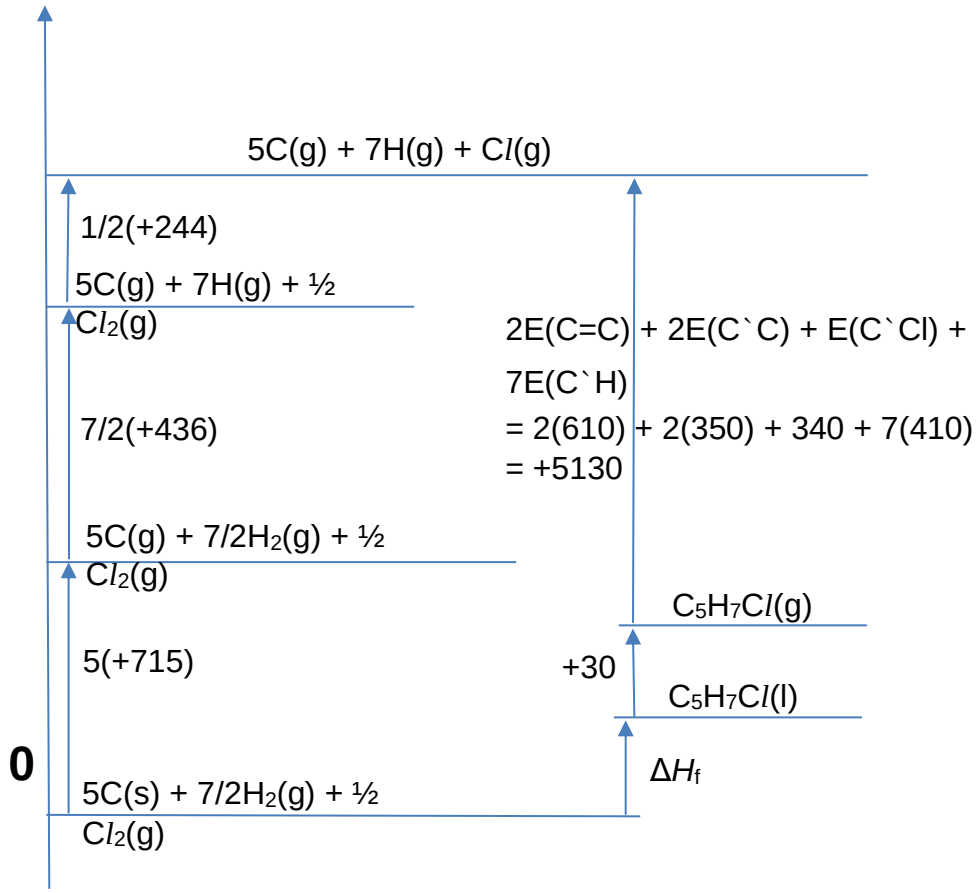
170n + 510 = 210n + 350

210n – 170n = 510 – 350

40n = 160 ➔ **n = 4**

(d) (i) **[4]**

Energy / kJ mol^{-1}



ΔH_f = +(5223 – 5160) = <u>+63</u> kJ mol^{-1}

(d) (ii) constitutional / structural / functional group isomerism. **[1]**

(iii) The C`C*l* bond in compound **N** has a partial double bond character due to the delocalisation of lone pair on C*l* into the neighbouring C^C π electron system.

Hence the C`C*l* bond energy will be larger than +340 kJ mol^{-1} and will in turn decrease the magnitude of compound **N**'s enthalpy change of formation. **[1]**

[Total: 20]

5 (a) MgO(s) reacts with water to form $Mg(OH)_2$(s), which dissolves sparingly in water to give a weakly alkaline (pH = 8) solution. **[5]**

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

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

SiO_2(s) is insoluble in water as a large amount of energy is required to break the many strong covalent bonds in the giant covalent structure. Since the oxide does not dissolve in water, it will not affect the pH (*i.e.* pH = 7).

P_4O_{10}(s) react violently/vigorously with water to give an acidic solution (pH = 2).

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$
OR $P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$

(b) (i) $SO_2(aq) + 2H_2O(l) + I_2(aq) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2I^-(aq)$ **[1]**

(ii) **[2]**

Amount of $I_2 = \frac{17.70}{1000} \times 0.0100 = 1.77 \times 10^{-4}$ mol

Amount of SO_2 in 50 $cm^3 = 1.77 \times 10^{-4}$ mol

$[SO_2] = \frac{1.77 \times 10^{-4}}{50 \times 10^{-3}} = 3.54 \times 10^{-3}$

Concentration of SO_2 in mg $L^{-1} = 3.54 \times 10^{-3} \times 64.1 = 227$ mg L^{-1}

Amount of SO_2 per kg $= \frac{227 \times \frac{400}{1000}}{70} = 1.30 > 0.7$

Exceeded the maximum daily intake of SO_2 so it is not advisable.

(c) (i) Lithium and magnesium are highly electropositive, polarised the bond towards carbon. **[1]**

(ii) It is used to avoid prolonged exposure to the moisture in the air/ as a dehydrating agent. **[1]**

(iii) Hydrolysis/ nucleophilic substitution **[2]**

Accept OH^- $MgBr^+$

(iv) Acidification of benzoate/4-toluate ion is a highly exothermic process as O–H bonds are formed and no bonds are broken. **[1]**

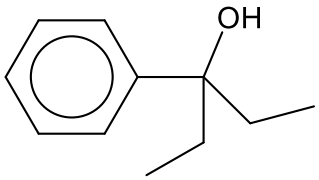
(v) $R_f = \frac{0.85}{4.35} = 0.195$ **[1]**

(vi) **F**: 4-toluic acid, **G**: 4-bromotoluene **[2]**

4-toluic acid forms <u>stronger hydrogen bonding</u> with the hydroxyl group of the silica surface, hence, 4-bromotoluene travels further than 4-toluic acid.

(vii) The R_f value will increase. **[1]**

(viii)



[1]

(ix) Test: Acidified $K_2Cr_2O_7$, heat **[2]**

Observation: Orange dichromate turned green for Compound **K** but not **J**.

Or

Test: 2,4-DNPH

Observation: Orange ppt is formed for Compound **J** but not **K**.

Or

Test: PCl_5 or PCl_3 or $SOCl_2$

Observation: White fumes of HCl evolved for Compound **K** but not **J**.

[Total: 20]