Mark Scheme for JC2 H2 Chemistry (9729) Preliminary Examination Paper 2

- 1 (a) (i) Li⁺: **1s**² H^{-} : <u>1s²</u> [1m] for both
 - (ii) Both have same number of quantum shells and no shielding by inner shell electrons. Lit has a larger nuclear charge/more protons and hence smaller radius. [1m]
 - (iii) $\text{Li}A/H_4 \rightarrow \text{Li}A/ + 2H_2$ [1m]
 - (iv) LiAI has giant metallic structure. [1m]

Large amount of heat energy is required to overcome the strong electrostatic attraction between a lattice of cations and delocalised electrons. [1m]

(v) The effect of a smaller A_r is more significant than that of a smaller volume of Li atom due to its smaller (atomic) radius. [1m]



(ii) H is 2-hydroxybutanoic acid. [1m]

> NaBH₄ reduces ketone only while LiA/H₄ reduce both ketone and carboxylic acid, forming back butane-1,2-diol [1m]



iount/mol

	J	CO2	H₂O
Amount/mol	$\frac{4.32}{2} = 0.0225$	$\frac{5.94}{2}$ = 0.135	$\frac{1.62}{1.62} = 0.0900$
	192	44.0	18.0
Mol ratio	0.0225 - 1	0.135 - 6	0.0900 - 4
	0.0225	0.0225	0.0225

Mole ratio of J : C : H = 1 : 6 : 8 [1m] accept "3 : 4"

Let molecular formula of \mathbf{J} be $C_6H_8O_x$.

 $6(12.0) + 8(1.0) + 16.0x = 192.0 \Rightarrow x = 7$: molecular formula is <u>C₆H₈O₇</u>. [1m]

Since J : NaOH = 1 : 3, J has 3 – COOH groups. [1m] for any achiral C₆H₈O7 e.g.





- (iii) <u>Electron-withdrawing C=O in</u> the secondary <u>carbocation that forms Q</u> <u>intensifies the positive charge</u>, making it <u>less stable</u> and less readily formed than the primary carbocation that forms P. [1m]
- (c) (i) step 1: <u>hydrolysis/ nucleophilic substitution</u> [1m] step 2: <u>condensation</u> [1m]

2



(iii) When the reactants are <u>adsorbed on the catalyst surface</u> (✓), the <u>bonds in</u> <u>the reactants are weakened</u> (✓) which <u>lowers E_a</u>. Surface concentration of reactants also increases. Thus, the <u>rate</u> of the reaction <u>increases</u> (✓). The <u>products are desorbed</u> (✓) from the catalyst surface, making it available for adsorption of new reactant molecules. 4(✓): [2m]; 2-3(✓): [1m]



Cis-trans isomerism arises due to <u>restricted rotation about the C=N bond</u> which has <u>two different groups attached to each C and N</u> [1m]



Fig. 3.1

- (i) [1m] for 2 correctly read t₁ values clearly indicated on graph
 <u>Half-lives are</u> approximately <u>constant</u> so the reaction is first order wrt
 [C₆H₅N₂Cl] [1m]
 - (ii) rate = $k [C_6H_5N_2C_l]$ Average $t_{\frac{1}{2}} = \frac{1}{2} (720 + 700) = 710 s$ $k = \frac{\ln 2}{710} = \frac{9.76 \times 10^{-4}}{100} \frac{s^{-1}}{100} [1m] 3sf; ecf <math>t_{\frac{1}{2}} from (a)(i); [1m] units$
 - (iii) <u>Water is a solvent</u> so it is in <u>large excess</u>. Thus only a small proportion of water is reacted and hence <u>concentration of water remains</u> effectively <u>constant</u> throughout the progress of the reaction. [1m]

(b) (i)
$$n(N_2) = \frac{(101 \times 10^3)(252 \times 10^{-6})}{(8.31)(45 + 273)} = 9.63 \times 10^{-3} \text{ mol } [1m]$$

Since $HCl \equiv N_2$,

$$[H^{+}] = [HCl] = \frac{9.63 \times 10^{-3}}{100/1000} = 0.0963 \text{ mol dm}^{-3} [1m] \text{ ecf from n(N}_2)$$

pH = -lg 0.0963 = <u>1.02</u> [1m] ecf from [H⁺]

(ii) [1m] for any of the following methods

- Use an electronic weighing balance to <u>measure the mass of the solution at</u> various time intervals
- Use a conductivity meter to <u>measure the conductivity of the solution</u> due to production of H⁺ and Cl⁻ <u>at various time intervals</u>
- <u>Titrate quenched samples</u> taken from the main reaction mixture <u>at various</u> <u>time intervals with NaOH(aq)</u> of known concentration

(C)

$$k = Ae^{R/R}$$

 $-\frac{E_a}{DT}$

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T}\right)$$

gradient =
$$-\frac{E_a}{R} = \frac{(-6.60) - (-13.40)}{0.00310 - 0.00360} = -13600 \text{ K}^{-1}$$
 [1m]



- (iii) 8E(Al-Cl) = -(+116) (-1401) + 2(+326) + 3(+244) [1m] ecf from multiplier<math>E(Al-Cl) = +334 kJ mol⁻¹ [1m] 3sf
- (iv) $A_{l_2}C_{l_6}$ dissolves in water to form $[A_l(H_2O)_6]^{3+}$ in water. $A_{l_2}C_{l_6} + 12H_2O \rightarrow 2[A_l(H_2O)_6]^{3+} + 6C_l^{-\Box}$

Since <u>Al³⁺ has a high charge density</u> (\checkmark), <u>Al₂Cl₆/[Al(H₂O)₆]³⁺ undergoes</u> partial <u>hydrolysis</u> (\checkmark) in water. <u>Al³⁺ polarises the coordinated H₂O molecule</u> and weakens the O-H bond (\checkmark) which breaks to release H⁺, giving rise to a

weakly acidic solution of pH 3 (
$$\checkmark$$
).
[AI(H₂O)₆]³⁺ \ll [AI(H₂O)₅(OH)]²⁺ + H⁺
OR AI₂CI₆ + 12H₂O \ll 2[AI(H₂O)₅(OH)]²⁺ + 2H⁺ + 6CI⁻ [1m]

OR
$$Al_2Cl_6$$
 + 12H₂O \ll 2[Al(H₂O)₅(OH)]Cl₂ + 2HCl

6

7

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(b) (i) CI^{-} anion and H_2O molecules are attracted to the anode.

$$C_{2} + 4H^{+} + 4e^{-} \ll 2H_{2}O + 1.23$$

$$C_{2} + 2e^{-} \ll 2CI^{-} + 1.36 - -- (1)$$

<u>High [C/] shifts the position of equilibrium (1) to the left (\checkmark), making <u>E(Cl_2/Cl^)</u> less positive (or more negative) than <u>E (O_2/H_2O)/+1.23V</u> (\checkmark).</u>

So <u>Ct is more easily oxidised than H_2O </u>, producing Cl_2 gas instead of O_2 gas. (\checkmark) award only with mention of shift in position of equilibrium

4(√): [2m]; 2-3(√): [1m]

square planar (1)



5 (a) CFCs are <u>non-toxic</u> / <u>non-flammable</u>. [1m]

T-shape (✓

shape: ..

(b) <u>R-11 / CCI₃F is a better refrigerant. [1m]</u>

From Table 5.1, CCl_3F has a higher boiling point than NH₃ so CCl_3F has stronger IMF. Both CCl_3F and NH₃ have simple covalent structures.

shape:

Due to greater number of electrons per (CCl₃F) molecule (\checkmark), more energy (\checkmark^*) is needed to overcome the stronger (\checkmark^*) instantaneous dipole-induced dipole interaction between CCl₃F molecules (\checkmark) than the weaker <u>hydrogen bonds</u> between NH₃ molecules (\checkmark). Thus, CCl₃F is less easily vaporised and has lower vapour pressure than NH₃. 4(\checkmark): [2m]; 2-3(\checkmark): [1m]

 (\checkmark^*) stronger + more energy

(c) (i) A radical is a species with <u>unpaired electron(s) [1m]</u>

(ii)
$$C_{l} \xrightarrow{C_{l}} C_{l} \xrightarrow{C_{l}}$$

Name the type of bond breaking: homolytic fission [1m]

(iii) First propagation step: $Cl \bullet + O_3 \rightarrow Cl O \bullet + O_2$ [1m] Second propagation step: $Cl O \bullet + O_3 \rightarrow 2O_2 + Cl \bullet$ [1m]

(iv)
$$2Cl \bullet \rightarrow Cl_2$$

OR $ClO \bullet + Cl \bullet \rightarrow ClO - Cl$ (or Cl_2O)
OR $2ClO \bullet \rightarrow ClO - OCl$ (or Cl_2O_2) [1m]

(v) $E(C-F) = +\frac{485}{100} \text{ kJ mol}^{-1}$; $E(C-Cl) = +\frac{340}{100} \text{ kJ mol}^{-1}$ (\checkmark)

Since E(C-F) > E(C-Cl), <u>C-F bond is stronger</u> (\checkmark) than C-Cl bond and will <u>not</u> <u>be broken</u> by UV light (\checkmark). Thus, <u>no F radical will be produced</u> (\checkmark) and hence no depletion of ozone layer by R-32.

OR

Atomic radius of F = 0.072 nm; atomic radius of Cl = 0.099 nm (\checkmark)

Since F has a smaller radius than Cl, <u>C-F bond is shorter and stronger</u> (\checkmark) than C-Cl bond and will <u>not be broken</u> by UV light (\checkmark). Thus, <u>no</u> <u>F radical will be produced</u> (\checkmark) and hence no depletion of ozone layer by R-32. $4(\checkmark): [2m]; 2-3(\checkmark): [1m]$

- (v) p-p orbital overlap results in the <u>delocalisation of lone pair</u> of electrons <u>on</u> <u>Cl into</u> the adjacent π electron cloud of the <u>C=C bond</u>. This imparts a <u>partial</u> <u>double bond character in C-Cl bond and strengthens C-Cl bond</u>. Thus, it will not break under UV light to give a Cl radical. [1m]
- (d) advantage: Propane is easy to produce/ readily available/ inert. [1m]
 potential hazard: It is highly flammable. [1m]