9647 TJC H2 Chemistry Prelim P3 Answers:

1 **(a)**

- $M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

- Charge density of the cation decreases down the group as charge of cation is constant and ionic radius increases.

- Polarising power of the cation decreases resulting in less distortion of the electron cloud of the NO_3^- ion, and the N-O covalent bond is weakened to a smaller extent.

  Therefore, ease of thermal decomposition decreases down the group.

(b) **(i)**

- $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$ **A**
- $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$
- $Al(OH)_3 + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$ **B**

(ii)

- When carbon dioxide is passed into Q, the following reaction occurs.
  $CO_2(g) + OH^-(aq) \rightarrow HCO_3^-(aq)$

- The concentration of OH^- decreases, causing the position of the equilibrium below to shift to the left according to Le Chatelier's principle. Thus $Al(OH)_3$ (white solid **C**) is precipitated.
  $Al(OH)_3 + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$

Or

- Carbon dioxide is an acidic gas, and there will be an acid/base reaction with the $Al(OH)_4^-$ complex to form salt and water.

- $CO_2(g) + Al(OH)_4^-(aq) \rightarrow HCO_3^-(aq) + Al(OH)_3(s)$ **C**

or $2CO_2(g) + 2Al(OH)_4^-(aq) \rightarrow 2HCO_3^-(aq) + Al_2O_3(s) + 3H_2O(l)$ **C**

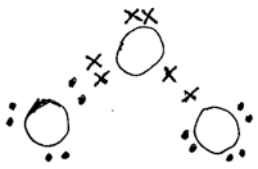
(iii) Residue **A** is $Mg(OH)_2$.

- Mass of Mg = 24.3/58.3 x 0.18 = 0.0750 g
  % by mass Mg = 0.075/1.75 x 100% = 4.29 %

After heating to constant mass, the residue is $Al_2O_3(s)$.

- Mass of Al = 54/102 x 3.16 = 1.67 g
  % by mass Al = 1.67/1.75 x 100% = 95.4%

(c) **(i)**

- 

(ii) $2O_3 \longrightarrow 3O_2$

At t = 0 s, vol. of O_3 = 38 cm^3 and vol. of O_2 = 762 cm^3

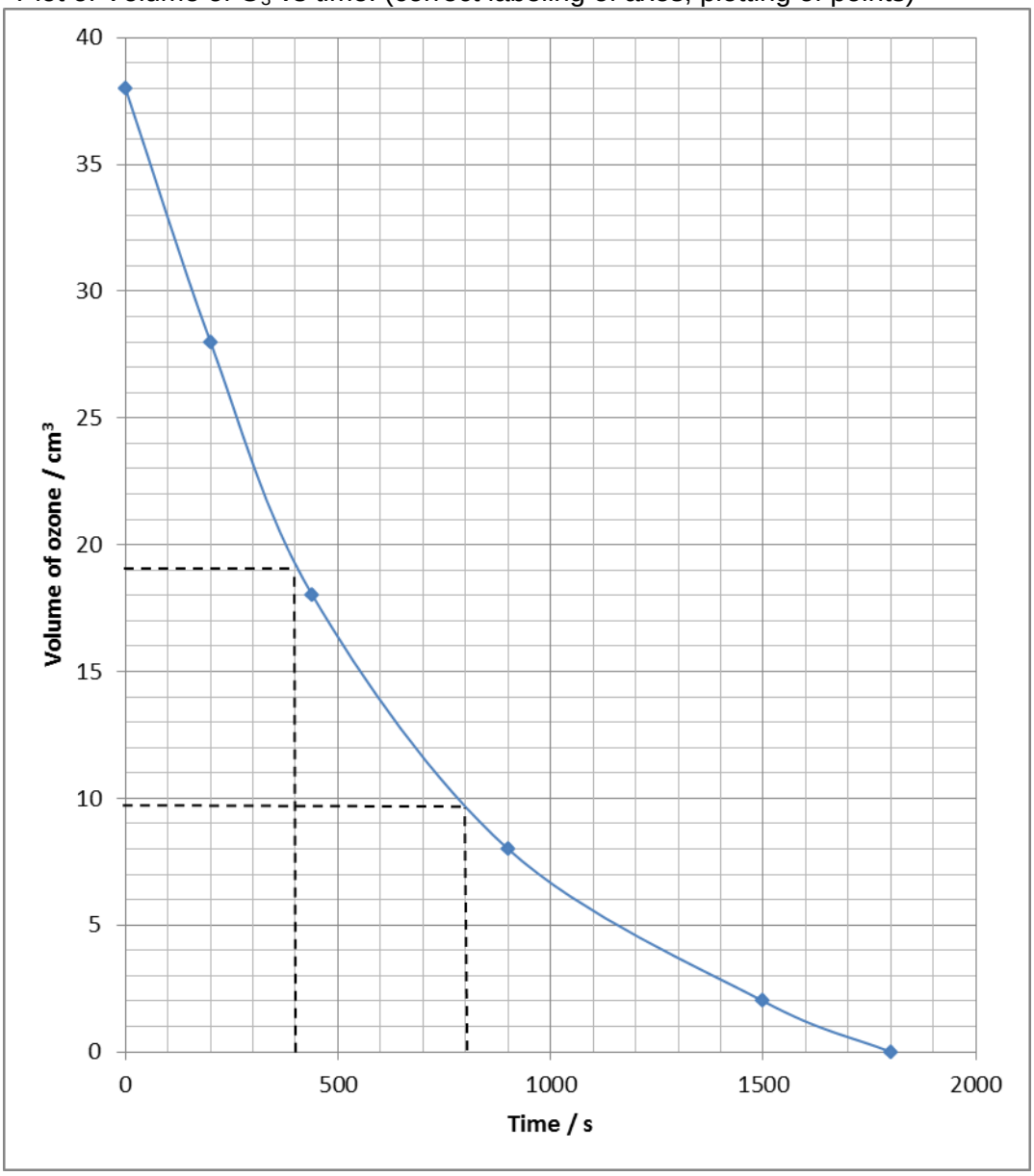
At t = 1500 s, let vol. of O_3 = (38 – y) cm^3 and vol. of O_2 = (3y/2 + 762) cm^3

(38 – y) + (3y/2 + 762) = 818

y = 36.0

• Volume of O_3 = 38 – 36 = 2.00 cm^3

(iii) •Plot of Volume of O_3 vs time. (correct labeling of axes, plotting of points)



- Both half-lives are <u>constant</u> = 400 s (indicate at least 2 $t_{1/2}$ on graph)
- Therefore, the reaction is <u>first order</u> with respect to ozone.

(iv) $k = \ln 2 / t_{1/2}$

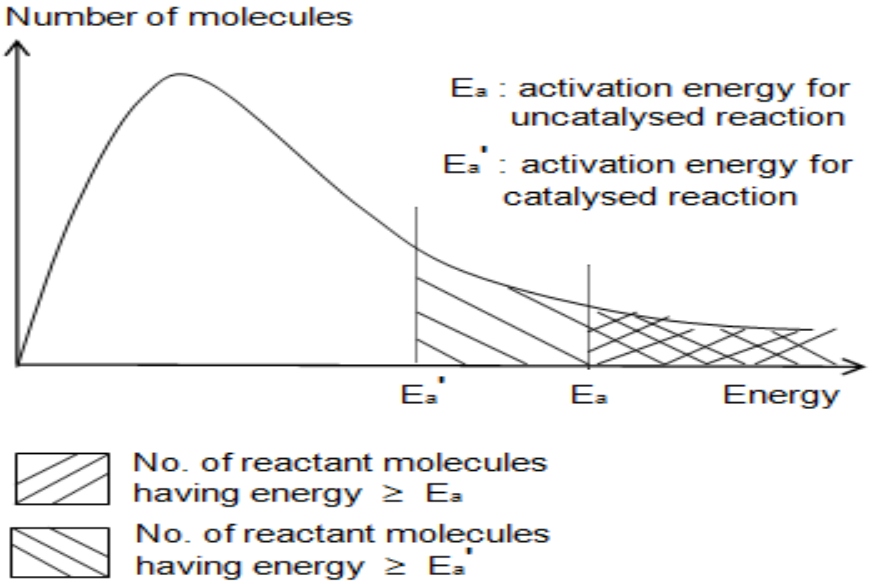
•$k = 1.73 \times 10^{-3}\ s^{-1}$

•Rate = $k[O_3]$

(v)

- A catalyst provides <u>alternative pathway of lower activation energy</u>, which is the <u>minimum amount of energy the particles must collide with for reaction to take place</u>.

- The <u>number of molecules having energy greater than or equal to activation energy increases</u>, resulting in an <u>increase in frequency of effective collisions</u> and the rate of decomposition.



[Total: 20]

2 (a) (i)

- The primary structure of a protein refers to the number and sequence of amino acids in the polypeptide chains.

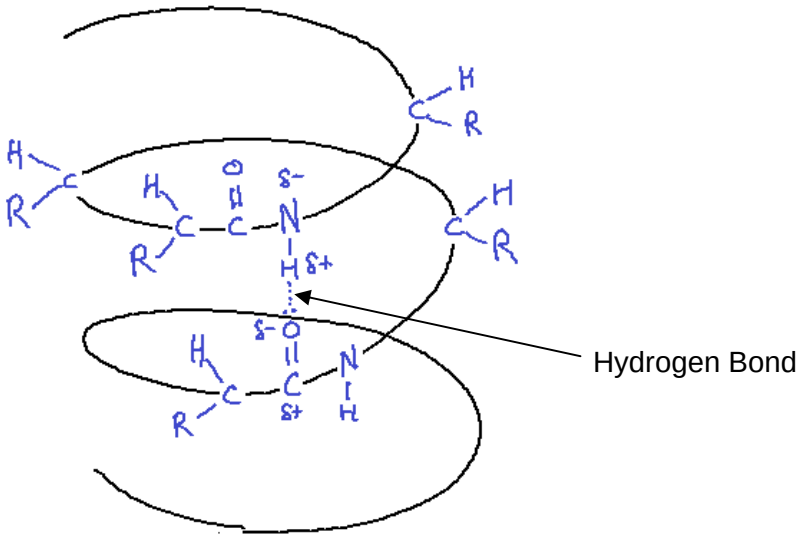
- The amino acids are bonded by peptide bonds in the polypeptide chain.

(ii)

- The α-helix takes the shape of an extended spiral spring that is held in place by hydrogen bonds between the -C=O of each amino acid the –NH of the amino acid 4 amino acids away.

- The hydrophobic R groups of the amino acid point out of the helix and are perpendicular to the main axis of the helix.

- Drawing of alpha helix with hydrogen bond:



(iii)
- The formation of a disulphide bond requires 2 cysteine residues within the polypeptide chain but the α-sub-unit only has one.

(iv)
- When the pH is decreased, the histidine residue can be protonated. This causes ionic bonds to form between the positively charged –R group of the histidine residue and negatively charged –R groups on other amino acid residues in the polypeptide chain.

- This results in a change in the conformation and folding of the sub-units which decreases the affinity that haemoglobin has on oxygen.

(v)
- In the lungs, the concentration of O_2 is high. By Le Chatelier's principle, the position of equilibrium for the reaction shift to the right causing oxygen to bind to haemoglobin and increasing the concentration of oxyhaemoglobin.

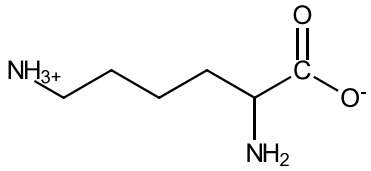
- Oxyhaemoglobin travels to the tissues in the body where the concentration of O_2 is low. By Le Chatelier's principle the position of equilibrium for the reaction shift left, releasing oxygen to the surrounding tissues.

(b) **(i)**
- –COOH group in lysine is a carboxylic acid group and thus has the lowest pK_a value of 2.15. The $–CO_2H$ group can deprotonate easily as the carboxylate ion is stable as the negative charge can be delocalised over the 2 O atoms.

- $–NH_3^+$ group on the α-carbon is a stronger acid than the $–NH_3^+$ group at the end of the carbon chain. The $–NH_3^+$ group on the α-carbon is closer to the electron withdrawing –COOH group and experiences a stronger inductive effect, the N–H bond is more polarised and a proton is lost more readily.

- Hence the $–NH_2$ group on the α-carbon has a pK_a of 9.16 and the $–NH_2$ group at the end of the carbon chain, being the strongest base, has a pK_a of 10.67.

(ii)

- Isoelectric point occurs at pH = 9.92 (i.e. $\frac{(9.16 + 10.67)}{2}$)
- 

(c) **(i)**

- Concentration of O_2 in solution = $\frac{0.2 \times 1}{769}$ = 2.60 x 10^{-4} mol dm^{-3}
- Concentration of CO in solution = $\frac{0.03 \times 1}{1052}$ = 2.85 x 10^{-5} mol dm^{-3}

(ii) Let initial concentration of $Hb(O_2)$ = n mol dm^{-3}

	$Hb(O_2)(aq)$ +	$CO(aq)$ $\rightleftharpoons$	$Hb(CO)(aq)$ +	$O_2(aq)$
Initial conc. / mol dm^{-3}	n		0	
Change in conc. / mol dm^{-3}	$-\frac{23n}{24}$		$+\frac{23n}{24}$	
Equil conc. / mol dm^{-3}	$\frac{n}{24}$		$\frac{23n}{24}$	

- $K_c = \frac{[Hb(CO)][O_2]}{[Hb(O_2)][CO]}$

$= \frac{\left(\frac{23n}{24}\right)\left(2.60 \times 10^{-4}\right)}{\left(\frac{n}{24}\right)\left(2.85 \times 10^{-5}\right)}$

- = 210

(iii) At toxic levels of carbon monoxide,

$\frac{[Hb(CO)]}{[Hb(O_2)]} = \frac{10}{90}$

$K_c = \frac{[Hb(CO)][O_2]}{[Hb(O_2)][CO]}$

$210 = \frac{(10)(2.60 \times 10^{-4})}{(90)[CO]}$

- $[CO] = 1.38 \times 10^{-7}$ mol dm^{-3}

$P_{CO} = 1052 \times (1.38 \times 10^{-7})$
$= 1.45 \times 10^{-4}$ atm

- Percentage of CO in air to cause toxicity $= \frac{0.000145}{1} \times 100$
$=$ **<u>0.0145 %</u>**

[Total: 20]

3 **(a)** **(i)** Anode: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$
Cathode: $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$ ●

Overall: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ ●

(ii) ● $E^{\theta}_{O2/H2O} = +1.23$ V

$E^{\theta}_{cell} = E^{\theta}_{O2/H2O} - E^{\theta}_{CO2/C2H5OH}$
$1.61 = 1.23 - E^{\theta}_{CO2/C2H5OH}$
● $E^{\theta}_{CO2/C2H5OH} = -0.38$ V

(iii) ● Ethanol is more energy-efficient than methanol.
Or
● Ethanol can be obtained in great quantity (or easily obtained) from a fermentation process.

(b) **(i)** Number of moles of copper deposited = 0.5 mol
Since Cu ≡ 2 mol of e^-
Number of moles of electrons passed = 1 mol ●

Since CO_2 ≡ 6 mol of e^-
Number of moles of CO_2 produced = 1/6 mol
Volume of CO_2 produced = 1/6 x 24 000
= 4000 cm^3 ●

(ii) Since number of moles of electrons passed = 1 mol
Amount of charge passed = 96500 c ●

$Q = I\,t$
$96500 = I \times 8 \times 60 \times 60$
$I = 3.35$ A ●

(c) **(i)** Amount of carbon dioxide = 2300/44
= 52.27 mol ●

(ii) $PV = nRT$
$P = nRT/V$
$= (52.27 \times 8.31 \times 298)/(2.5 \times 10^{-3})$
$= 5.18 \times 10^7$ Pa ●

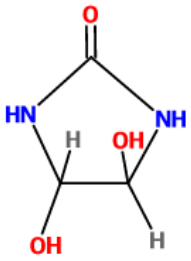
(iii)

- The calculation in (ii) assumes that CO_2 behaves ideally i.e. there are no forces of attraction between the molecules.

- However, due to the van der Waals' forces of attraction between the CO_2 molecules, this resulted in the molecules colliding against the cylinder wall with a smaller force. As a result, the pressure of the gas is smaller than expected.

(d) **(i)**

- **D** has both O and N atoms but is neutral ➔ **D** is <u>neither a carboxylic acid nor an amine</u>, and is likely an amide. (insufficient to just state the **D** is neither acidic nor basic, nor to only suggest that **D** is likely an amide with stating what are impossible.)
- **D** gives white fumes with PCl_5 ➔ **D** contains <u>alcohol group</u> (incomplete if student only mentions –OH group)
- **D** does not react with Br_2 ➔ **D** <u>does not contain >C=C< bond (or not an alkene)</u>
- **D** exhibits geometric isomerism but is not an alkene ➔ **D** is a <u>cyclic structure</u>.
- **E** readily dissolves in HC*l*(aq) ➔ **E** is <u>basic</u>, i.e. **E** is an <u>amine</u>.
-



D

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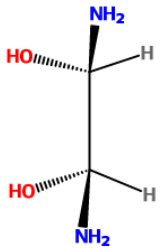
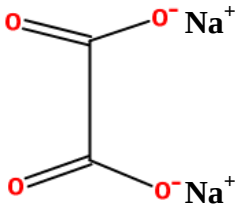


E

-

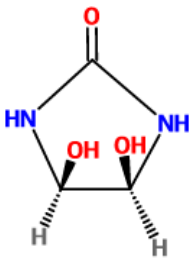


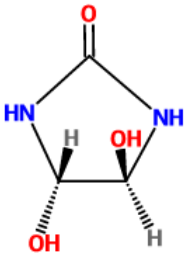
F

1 – 2 • → 1 mark
3 – 4 • → 2 marks
5 – 6 • → 3 marks
7 – 8 • → 4 marks

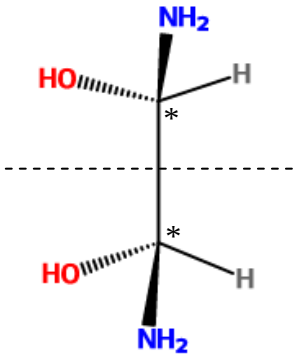
(ii)

- Due to the presence of a <u>ring structure</u>, there is <u>restricted rotation about the C-C bond bearing the 2 –OH groups</u>. There are <u>two different groups on each of those two adjacent carbon atoms</u>. Thus, **D** can exhibit geometrical isomerism.





(iii)



Plane of symmetry

Although **E** has 2 chiral centres, it has a plane of symmetry within the molecule. As such, **E** will not display optical isomerism.

[Total: 20]

4 **(a)** ●Transition metals have higher melting points than typical s-block metals due to availability of 3d and 4s electrons, smaller metallic radius and closely packed structures for stronger metallic bonds.

(Other physical properties with adequate explanations are acceptable.)

(b) For **I**:

From Data Booklet:
$E^{\ominus}(MnO_2/Mn^{2+})$ = + 1.23 V ; $E^{\ominus}(Cl_2/Cl^-)$ = + 1.36 V

With a higher $[Cl^-]$ from concentrated HCl, value of $E(Cl_2/Cl^-)$ decreases to be less positive than +1.23 V.
Also due to the higher $[H^+]$, value of $E(MnO_2/Mn^{2+})$ becomes more positive.

$E_{cell} = E^{\ominus}(MnO_2/Mn^{2+}) - E(Cl_2/Cl^-) > 0$ and MnO_2 will reduce to Mn^{2+} while Cl^- will oxidise to yellow-green Cl_2 gas.

Equation: $MnO_2 + 2HCl + 2H^+ \longrightarrow 2H_2O + Cl_2 + Mn^{2+}$

For **II**:

From Data Booklet:
$E^{\ominus}(H^+/H_2)$ = 0.00 V ; $E^{\ominus}(Cr^{2+}/Cr)$ = –0.91 V ;
$E^{\ominus}(Cr^{3+}/Cr^{2+})$ = –0.41 V ; $E^{\ominus}(O_2/H_2O)$ = +1.23 V

When Cr is dissolved in sulfuric acid, Cr will be oxidised to blue $Cr^{2+}(aq)$ and H^+ is reduced to H_2 gas (acid–metal reaction).

$E^{\ominus}_{cell}$ = 0.00 – (–0.91) = + 0.91 V > 0
Thus reaction is energetically feasible.

When left to stand, $Cr^{2+}(aq)$ is oxidised by O_2 to form green $Cr^{3+}(aq)$ and O_2 is reduced to H_2O.

$E^{\ominus}_{cell}$ = +1.23 – (–0.41) = + 1.64 V > 0
Thus reaction is energetically feasible.

Equations: $Cr + 2H^+ \longrightarrow H_2 + Cr^{2+}$

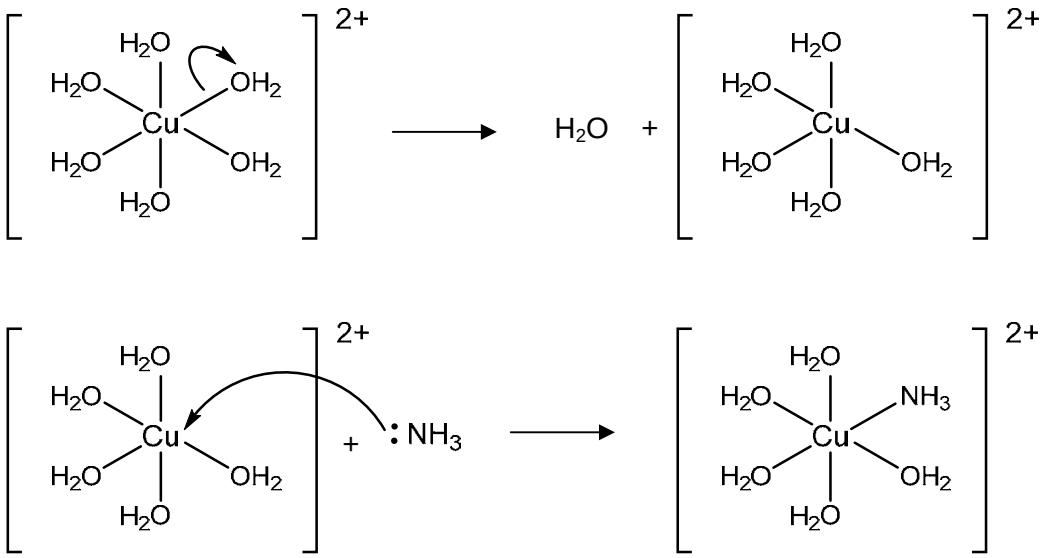
$O_2 + 4Cr^{2+} + 4H^+ \longrightarrow 2H_2O + 4Cr^{3+}$

●● 3 balanced equations / ● 1–2 balanced equation(s)
● 3 correct identities
●● Quoting of data from Data Booklet and explanations *(accept explanation if student explains by comparing $E^{\ominus}$ qualitatively instead of calculating $E^{\ominus}_{cell}$. e.g. $E^{\ominus}(Cr^{2+}/Cr)$ <u>less positive</u> than $E^{\ominus}(H^+/H_2)$, thus Cr can be oxidised Cr^{2+})*

(c) **(i)** ● Equation: $[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 2H_2O$
● Coordination number: 6

(ii) ●Dissociative: S_N1(unimolecular nucleophilic substitution)
Associative: S_N2 (bimolecular nucleophilic substitution)

(iii)



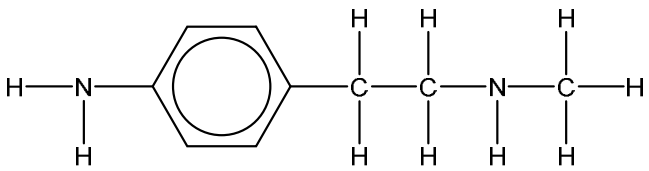
(d) **(i)**

$C_6H_5CH_2OH \xrightarrow[\text{cold / room temperature}]{\bullet\ PCl_5(s)} \bullet\ C_6H_5CH_2Cl \xrightarrow[\text{heat under reflux}]{\bullet\ \text{ethanolic (or alcoholic) NaCN}} C_6H_5CH_2CN$

(ii) ●Step **3**: Sn, concentrated HC*l*, heat; followed by NaOH(aq) (room temperature)

(iii) ● Ni acts as a <u>heterogeneous catalyst</u>. Ni has <u>partially filled d subshell</u>. (vacant orbitals can act as electron acceptors; filled orbitals can act as electron donors)

(iv) ● Drawing the <u>displayed formula</u> of the compound **G**:

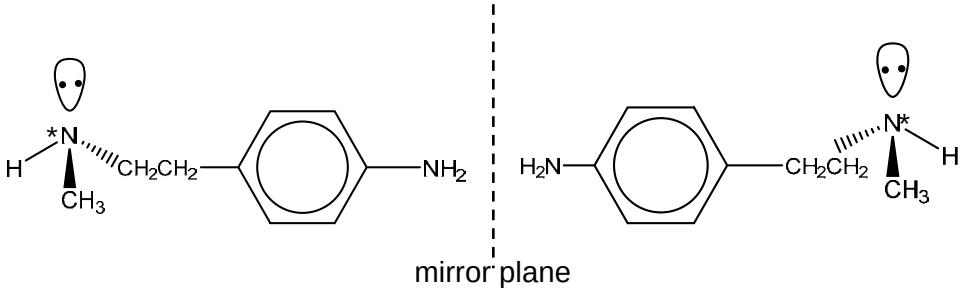


●The electron density around N atom in primary amine group is higher than the electron density around N atom in phenylamine group*. The lone pair of electrons on N atom in the primary amine group is more available for nucleophilic attacks, making the primary amine group more nucleophilic and the primary amine group undergoes nucleophilic substitution with CH_3Cl.

(*as the lone pair of electrons around N in phenylamine group can delocalise into the benzene ring)

(v) (N atom in the secondary amine group is sp^3 hybridised with three different substituent groups and a lone pair of electrons)

- Indicate chiral N
- Illustration of the two enantiomers:



[Total: 20]

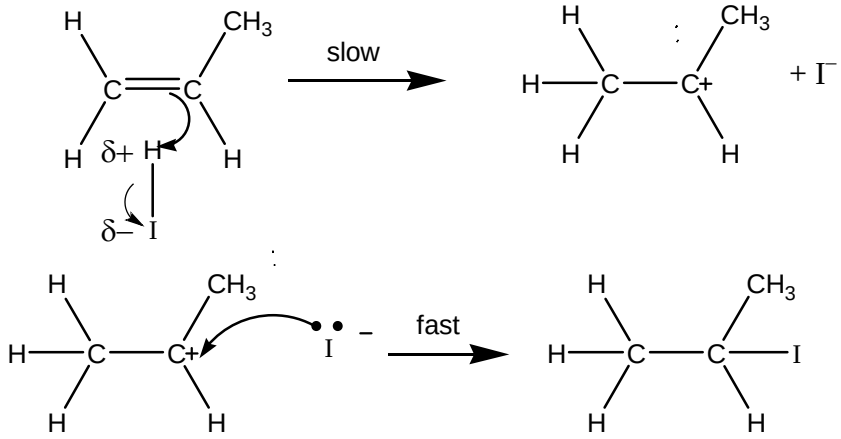
5 (a) (i) ● Use concentrated H_2SO_4. NaCl reacts with concentrated H_2SO_4 to give steamy white fumes of HCl gas.

- $NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$

(ii) ● Not suitable because reducing power of HI > HCl. HI is easily oxidised by conc H_2SO_4 to form I_2. Yield of HI is very poor.

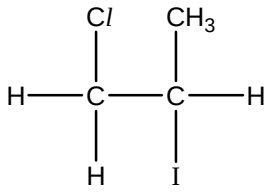
- $NaI + H_2SO_4 \rightarrow HI + NaHSO_4$
  $8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$

(i) ●Electrophilic Addition



- Equations, structure of the carbocation
- arrows, partial charges and fast slow step

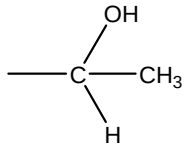
(ii)
- C*l* is withdrawing and reduces the electron density on the >C=C< hence the electrophile is less attracted to the >C=C<.
- Carbocation formed is relatively unstable as the electron withdrawing chlorine atom intensifies the positive charge on the carbocation, hence it is less likely to be formed.

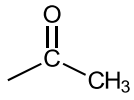


(c)
- Reaction I: Both gives H_2 with Na metal → Both have –OH groups. As the molecular formula of **J** and **K** is $C_{10}H_{13}OCl$, both are either alcohols or phenols. *(Note: carboxylic acids are not accepted)*

- Reaction II: **J** forms white ppt with aq Br_2, while **K** does not. Hence, **J** is a phenol and **K** does not contain a phenol functional group.

- Reaction III: Both do not react with aqueous alkaline iodine hence do not contain



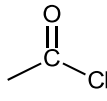


(Note: is not accepted as Reaction I and II has already shown that –OH group is present in $C_{10}H_{13}OCl$.)

- Reaction IV: **J** heated with NaOH undergoes nucleophilic substitution reaction where C*l* is substituted with –OH, hence **J** is a halogenoalkane. **K** has no reaction with NaOH. Hence C*l* not substituted→C*l* directly bonding on benzene ring (halogenoarenes are present).

- **K** is not oxidized by dichromate hence contains a tertiary alcohol. Product of hydrolysis of **J** is oxidized by dichromate hence contains a primary or secondary alcohol, thus **J** contains a primary or secondary halogenoalkane.

- Reaction V: Product of oxidation of **J** formed from (IV) gives yellow ppt with aqueous alkaline iodine hence contains



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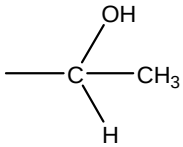
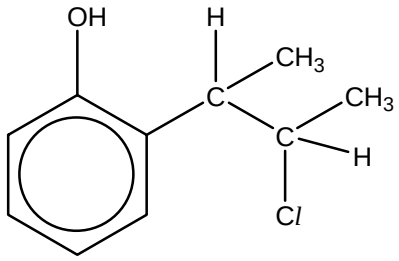
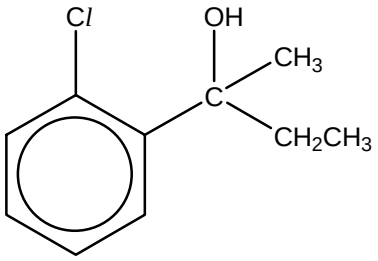


(Note: not accepted because Reaction V involves product of oxidation of J)

●**J**



●**K**



(Different positions of substituents on the benzene ring are acceptable.)

(c) **(i)** $I_2O_5 + 5CO \rightarrow 5CO_2 + I_2$

- 5 mol of CO reacts with I_2O_5 to form 5 mol of CO_2 and solid I_2 thus there is no change in the volume of gas.

OR CO reacts to form the same number of moles of CO_2. Total number of moles of gas remains the same hence total volume of gas remains the same.

(ii) $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

●No of moles of I_2 = ½ x Number of moles of $Na_2S_2O_3$

$$= \frac{1}{2} \times \frac{16.6}{1000} \times 0.05 = 4.15 \times 10^{-4} mol$$

$I_2O_5 + 5CO \rightarrow 5CO_2 + I_2$

● No of moles of CO required $= 4.15 \times 10^{-4} \times 5 = 2.075 \times 10^{-3} mol$

Volume of CO used = $= 2.075 \times 10^{-3} \times 24000 = 49.8\ cm^3$

●Total volume of gaseous mixture, **V** = 49.8 x 2 = 99.6 cm^3

[Total: 20]