**NJC 2018 SH2 H2 Chemistry Prelim Paper 3 Solutions:**

| **Question 1** | |
|---|---|
| **(a)(i)** | **Suggested solution**<br><br>Both octan-1-ol and iodine have simple covalent structure<br>Strength of Td-Id in iodine due to its large electron cloud size is comparable to the stronger hydrogen bonding between octan-1-ol molecules. |
| **(ii)** | **Suggested solution**<br><br>Graphite has a giant molecular structure with strong covalent bonds between carbon atoms to be overcome during melting.<br>Fullerene has a simple covalent structure with weaker td-id interactions between fullerene molecules to be overcome during melting.<br>Hence, more energy is required to melt graphite and a higher temperature is required. |
| **(b)** | **Suggested solution**<br><br>Step 1: reaction 1 ;(-COCHO)<br>Step 2: $K_2Cr_2O_7$/$KMnO_4$ with $H_2SO_4$(aq) and heat; (-COCOOH)<br>Step 3: $NaBH_4$ in ethanol or $H_2$ with Nickel/Pt ; (compound B) |
| **c(i)** | **Suggested solution**<br><br>$P_{CO2} = \frac{0.035}{100} \times 101.3kPa$<br>$= 0.03546kPa$<br><br>$K_H = \frac{[CO_2(aq)]}{P_{CO2}}$<br>$[CO_2(aq)] = 1.17 \times 10^{-5}$ mol $dm^{-3}$ |
| **c(ii)** | **Suggested solution**<br><br>$K_c = \frac{[H_2CO_2(aq)]}{[CO_2]}$<br>$[H_2CO_3] = 1.52 \times 10^{-8}$ mol $dm^{-3}$ |
| **(iii)** | **Suggested solution**<br><br>$Ka_1$ is larger than $Ka_2$. $H_2CO_3$ will dissociate accordingly to eqm 1 first and $[H^+]$ from eqm 1 suppresses the dissocation of $HCO_3^-$ in eqm 2.<br><br>OR<br><br>$HCO_3^-$ from eqm 1 is low as $Ka_1$ is small. Hence $[H^+]$ from $HCO_3^-$ is negligible. $[H^+]$ is largely from eqm 2. |
| **c(iv)** | **Suggested solution**<br><br>$K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$<br><br>$[H^+] = 1.915 \times 10^{-6}$ $moldm^{-3}$<br>pH = 5.71 |
| **d** | **Suggested solution** |

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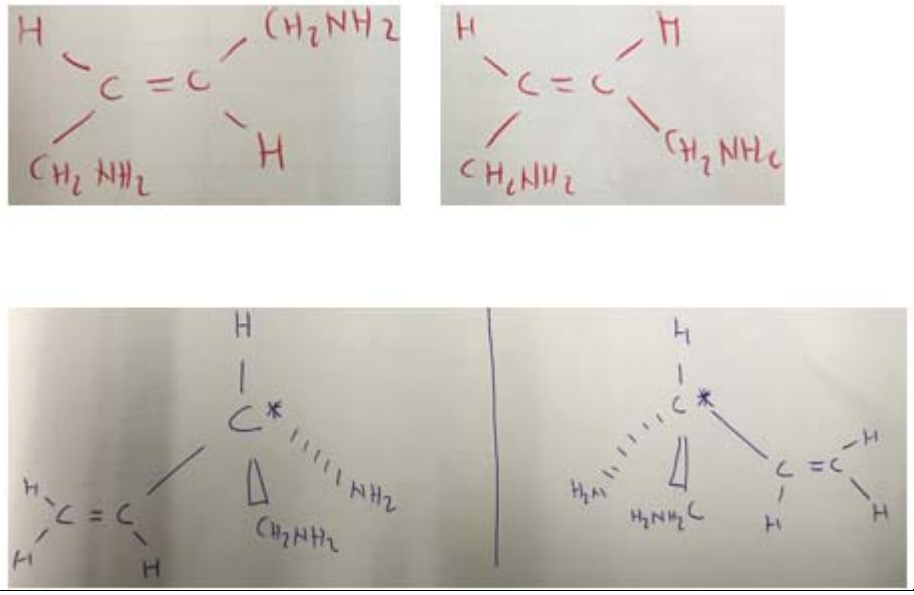
| |  |
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| Question 2 | |
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| **(a)** | **Suggested solution:**<br><br>At anode: Co has $E^{\ominus}_{ox}$ ($Co/Co^{2+}$) = +0.28V more positive that $E^{\ominus}_{ox}$ ($Cu/Cu^{2+}$) = –0.34V, hence Co will be oxidised together with Cu and dissolve as $Co^{2+}$, becoming part of the electrolyte. Ag on the other hand has more negative $E^{\ominus}_{ox}$ ($Ag/Ag^{+}$) of –0.80V, hence will not be oxidised. It will fall below anode as sludge.<br>At cathode: $Co^{2+}$ has a more negative $E^{\ominus}_{red}$($Co^{2+}/Co$) = –0.28 V than $E^{\ominus}_{red}$($Cu^{2+}/Cu$) = 0.34 V, hence $Co^{2+}$ is not reduced at the cathode, remain dissolved as electrolyte. |
| **(b)**<br>**(i)** | **Suggested solution**<br>• mass of Ag = 0.07 g<br>• No of moles of Co oxidised at anode = no of moles of $Co(C_4H_7N_2O_2)_2$<br><br>$= \frac{0.55}{58.9+2(4\times12+7+2\times14+2\times16)}$<br><br>= 0.0019038 mol<br><br>Mass of Co in alloy (anode) = 0.0019038 x 58.7 = 0.112 g<br>Mass of Cu = 1.25 – 0.07 – 0.112 = 1.068 g |
| **b(ii)** | % purity = 1.068 /1.25 x 100 = 85.4% |
| **b(iii)** | **Suggested solution:**<br>**Any one of the suggestion below is acceptable:**<br>(i) Mass of Ag and $Co(C_4H_7N_2O_2)_2$ should be heated to consistent mass to ensure all water is driven off, so that mass measured is that of dry mass of Ag and $Co(C_4H_7N_2O_2)_2$.<br>(ii) As mass of Ag (sludge) is rather small, use electronic balance of higher precision in order to reduce % uncertainty in mass measurement.<br>(iii) Repeat the experiment using fresh samples so that an average of the mass measurements can be taken to reduce random error. |
| **b(iv)** | **Suggested solution:** |

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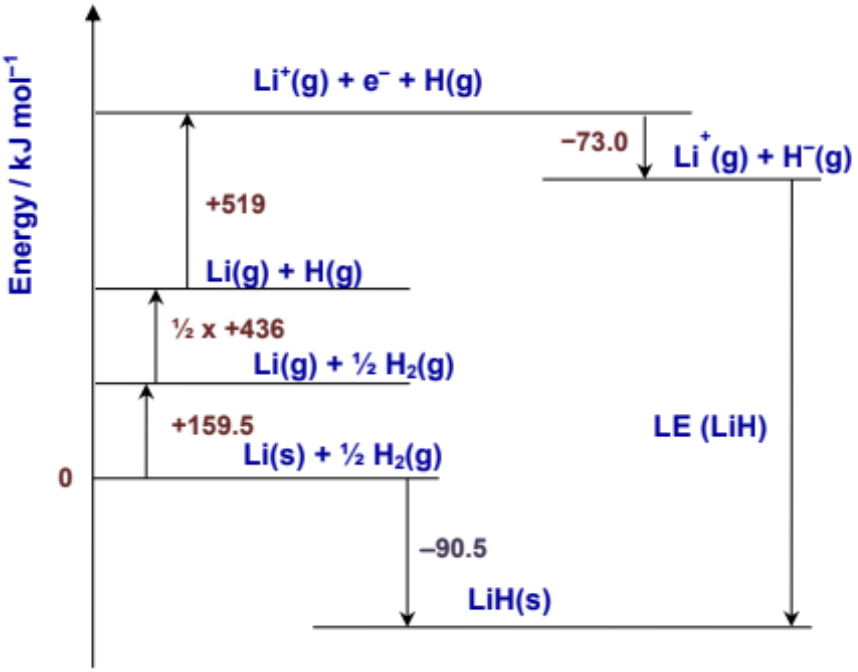
| | Total no of moles of e used for electrolysis = 2.15 x 28.0 x 60 ÷ 96500<br>= 0.03743<br><br>No of moles of Cu expected to be discharged = 0.043523 ÷ 2<br>= 0.018715<br><br>Mass expected = 0.018715 x 63.5<br>= 1.19 g (3sf) |
| **(c)** | **Suggested solution:**<br><br>$Co(C_4H_7N_2O_2)_2$ + aq ⇌ $Co^{2+}$ + 2 $C_4H_7N_2O_2^-$<br>$-1.23 \times 10^{-4}$ $+1.23 \times 10^{-4}$ $+ 2 \times 1.23 \times 10^{-4}$<br><br>$K_{sp} = [Co^{2+}][C_4H_7N_2O_2]^2$<br><br>$= (1.23 \times 10^{-4})(1.23 \times 10^{-4} \times 2)^2$<br><br>$= 7.44 \times 10^{-12}\ mol^3dm^{-9}$ |
| **(d)(i)** | **Suggested solution**<br><br>  <br><br><br>By Hess' law:<br>L.E. = 73.0 – 519 – (½ x 436) – 159.5 – 90.5 = **– 914 kJ mol$^{-1}$** |
| **d(ii)** | **Suggested solution:**<br><br>$$\|LE\| = \left\|\frac{q^+q^-}{r^+ + r^-}\right\|$$<br>Ionic radii of $Cl^-$ = 0.181, ionic radii of $H^-$ = 0.208nm<br>They have the same product but LiH has a larger interionic distance than LiCl, therefore LE magnitude of LiH is smaller. |
| **(e)** | **Suggested solution:**<br>Amt of $AlCl_3$ = $\frac{5}{27+35.5\ x\ 3)}$ = 0.037453 mol |

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| | Amt of LiH = $\frac{5}{7.9}$ = 0.6329 mol<br><br>$AlCl_3$ is limiting since 0.037453 mol of $AlCl_3$ requires 0.037453 x 4 mol of $LiH_4$ = 0.14981 mol < 0.6329 mol.<br><br>No of moles of $LiAlH_4$ formed = 0.037453 mol<br>0.037453 x $\Delta H_{reaction}$ = – 1.24 x 8.4<br><br>$\Delta H_{reaction}$ = – 1.24 x 8.4 ÷ 0.037453<br>= –278 $kJmol^{-1}$ |
| **(f)(i)** | **suggested solution**<br><br>$\Sigma n\Delta Hf(products) - \Sigma n\Delta Hf(reactants)$ = –454 – 3(–152.5)<br>= +3.5 $kJmol^{-1}$ |
| **f(ii)** | **Suggested solution**<br><br>$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$<br>–27.7 = +3.5 – 298 x $\Delta S^{\ominus}$<br>$\Delta S^{\ominus}$ = +0.105 $kJmol^{-1}K^{-1}$<br>$\Delta S$ is positive as there is an increase of 3 moles of gas molecules after the reaction; there are more ways to distribute the molecules and their energies, increasing entropy level of the system at the end of reaction. |
| **f(iii)** | **Suggested solution**<br><br>Temp at which decomposition becomes spontaneous is the cross over temperature.<br><br>$\Delta G = 0$<br>+3.5 = 0.105 x T<br>T = 33.3 K |

| **Question 3** | |
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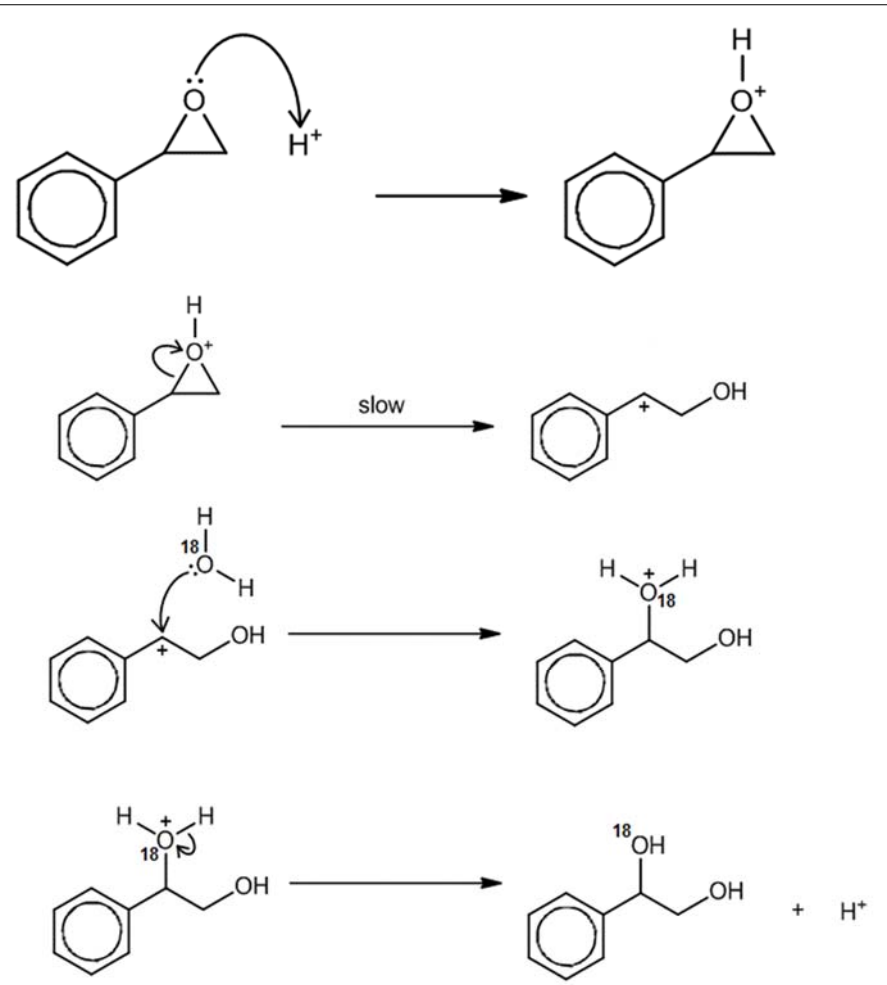
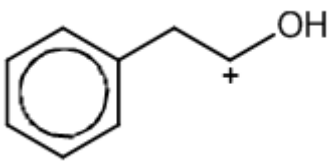
| **(a)(i)** | **Suggested solution:** |




**(ii)** **Suggested solution:**

A is formed from the primary carbocation as shown.




This primary carbocation is less stable due to the positive charge not being resonance stabilised by the aromatic ring. Hence, the carbocation is formed in trace amounts, leading to trace amounts of A being formed.

**(iii)** **Suggested solution:**

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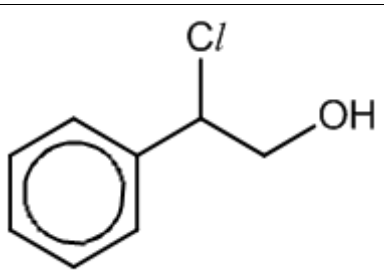
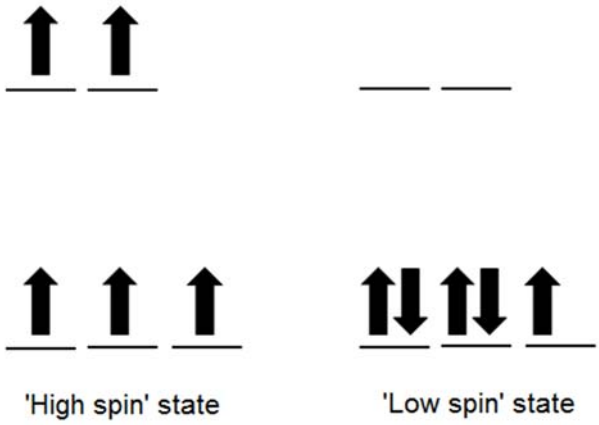
| |  |
| **(b)(i)** | **Suggested solution:**<br><br>In the presence of ligands, d-orbitals of $Fe^{3+}$ are split into two different energy levels with small energy gap. d-d transition, where the electron is promoted from a lower energy d orbital to a higher energy d orbital, is possible.<br><br>Energy that corresponds to the wavelength of light in the visible region of the electromagnetic spectrum is absorbed. Colour observed is complementary to the wavelength of visible light absorbed. |
| **(ii)** | **Suggested solution:**<br><br>  |
| **(iii)** | **Suggested solution:**<br><br>G has a larger energy gap. Since the electronic configuration of $Fe^{3+}$ in G is in a 'low spin' state, energy required to overcome the energy gap in adding subsequent electrons to higher energy d-orbitals is more than that required to overcome inter-electronic repulsion when electrons paired up in the lower energy d-orbitals. |
| **(c)(i)** | **Suggested solution:**<br><br>Oxidation number of C in carbon dioxide: +4<br><br>Oxidation number of C in methanol: -2 |
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| **(ii)** | **Suggested solution:**<br><br>Electrode 1 : $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$<br><br>Electrode 2 : $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$<br><br>Overall: $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$ |
| **(iii)** | **Suggested solution:**<br><br>When $[CH_3OH]$ is decreased, oxidation of methanol becomes less favoured OR by LCP, the position of equilibrium for $CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^-$ shifts to the left to partially increase $[CH_3OH]$. Thus, $E_{ox(CH3OH/CO2)}$ becomes less positive.<br><br>A less positive $E_{ox(CH3OH/CO2)}$ will cause $E_{cell}$ to be less positive since $E_{cell} = E + E_{ox}$. |
| **(iv)** | **Suggested solution:**<br><br>$CH_3OH$ is a liquid at room temperature and thus can be easily transported and stored than hydrogen gas<br><br>OR<br><br>$CH_3OH$ is less explosive than $H_2$ gas<br><br>OR<br><br>$CH_3OH$ is less expensive to maintain than $H_2$ gas |

| **Question 4** | |
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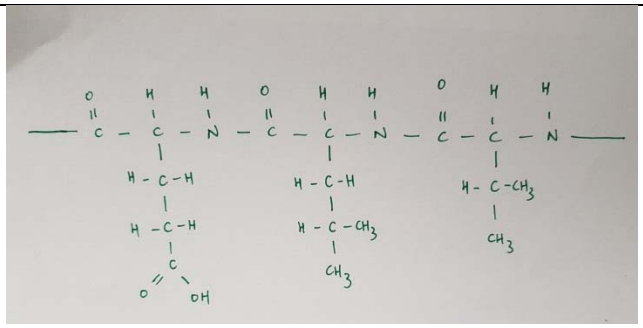
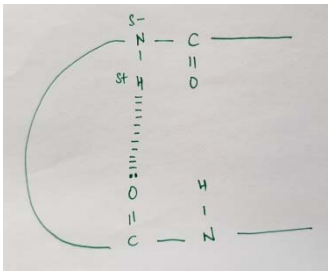
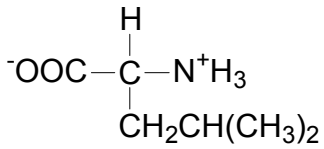
| **(a)(i)** |  |
| **(ii)** | **Suggested solution:**<br><br>  <br><br>Hydrogen bonding<br><br>- lone pair |

<table>
<tr><td></td><td>- δ+ / δ-<br>- dotted lined to show bond</td></tr>
<tr><td>(iii)</td><td>Suggested solution:<br><br>Leucine and Valine.<br><br>Their side chains consist of hydrocarbon chains which are able to form temporary dipole-induced dipole interactions with hydrophobic groups to transport them in the blood stream.</td></tr>
<tr><td>(b)(i)</td><td>Suggested solution:<br><br>  </td></tr>
<tr><td>(ii)</td><td>Suggested solution:<br><br><u>Melting point</u><br><br>Unionised form: Hydrogen bonding<br>Zwitterionic form: Ionic bonding<br>More energy is required to overcome the stronger ionic bonding compared to the hydrogen bonds. Hence the zwitterionic form will have a higher melting point.<br><br><u>Solubility:</u><br><br>Unionised form: Hydrogen bonds with water<br>Zwitterionic form: ion-dipole interactions with water<br>Stronger ion-dipole interactions produce more energy to overcome the hydrogen bonds between water molecules and the interactions between the solute. Hence the zwitterionic form will be more soluble in water.</td></tr>
<tr><td>(c)</td><td>Suggested solution:<br><br>
<table>
<tr><td>Observation</td><td>Deductions</td></tr>
<tr><td>Compound A, $C_8H_{10}O_2$, reacts with $Br_2$(aq) to form a white precipitate compound B with molecular formula, $C_8H_7O_2Br_3$</td><td>A contains phenol (reacts without halogen carrier)<br><br>B is 2,4,6- trisubstituted</td></tr>
<tr><td>Compound A also reacts with dilute nitric acid to give compound C, $C_8H_9NO_4$</td><td>Mononitration of A to give C<br><br>Confirm presence of phenol</td></tr>
<tr><td>Compound C with tin in concentrated hydrochloric acid, followed by hot aqueous sodium hydroxide gives compound D, $C_8H_{10}NO_2Na$.</td><td>$NO_2$ group in C is reduced to $-NH_2$<br><br>phenol in C is converted to sodium phenoxide in D</td></tr>
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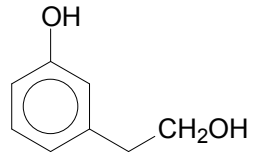
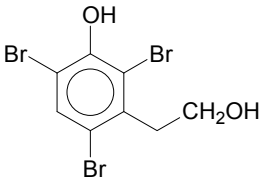
| Compound **D** turns hot acidified potassium dichromate solution green and forms compound **E,** $C_8H_9NO_3$. | **D** undergoes oxidation to form carboxylic acid<br><br>primary alcohol present in **D,**<br><br>phenoxide in **D** is acidified to phenol in **E** |
| 1 mole of compound **E** reacts with 2 moles of aqueous sodium hydroxide. | 2 acidic groups present<br><br>Carboxylic acid and phenol confirmation |
| Compound **E** reacts with phosphorus pentachloride to give compound **F**, $C_8H_7NO_2$. | -$CO_2H$, in **E** is converted into an acyl chloride, –COC*l*,by $PCl_5$.<br><br>Amine undergoes internal nucleophilic substitution),with loss of C*l*–, to yield the cyclic amide **F**<br><br>Carboxymethyl group, –$CH_2CO_2H$, must be adjacent to amine – $NH_2$ group in **A** to enable ring formation |

A:




B:

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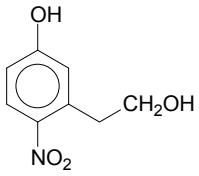


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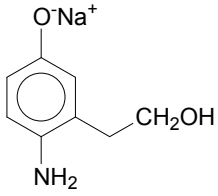
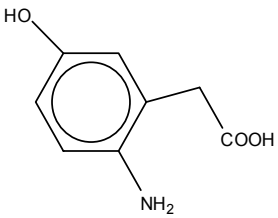
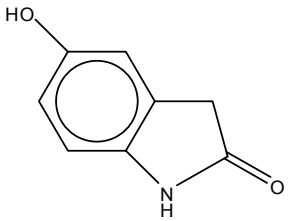



E:




F:




| **Question 5** | |
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| **(a)(i)** | **Suggested solution:** |

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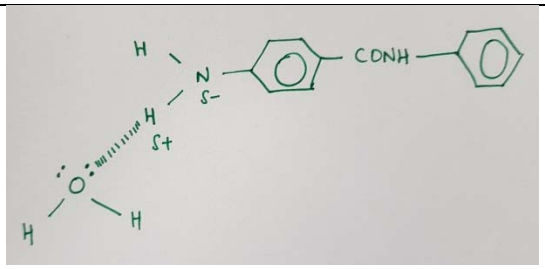
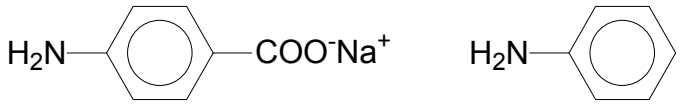
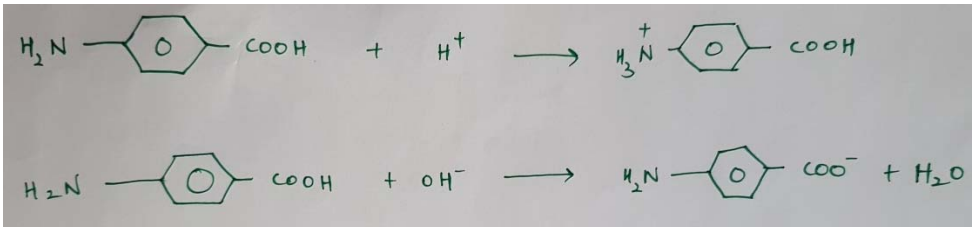
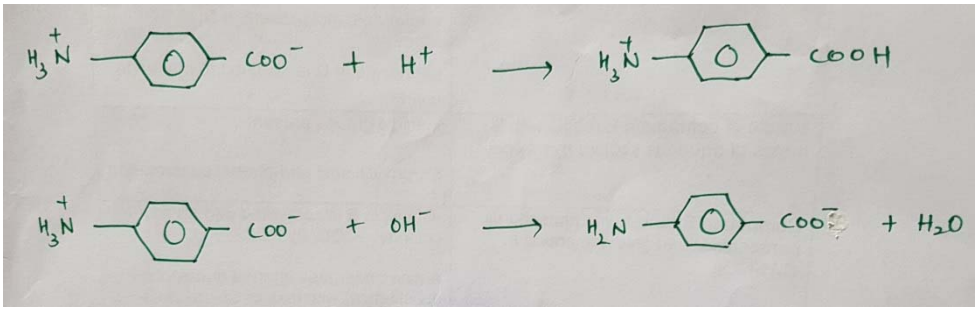
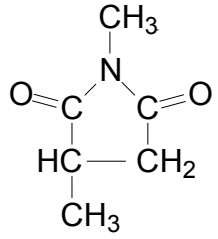
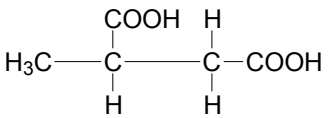
| |  <br><br>Hydrogen bond<br>- lone pair<br>- δ+ / δ-<br>- dotted lined to show bond |
| **(ii)** | **Suggested solution:**<br>Energy given out when hydrogen bonds are formed between water molecules and 4-amino-N-phenylbenzylamide is insufficient to overcome the extensive temporary dipole-induced dipole interactions between 4-amino-N-phenylbenzylamide molecules. Hence solubility is low. |
| **(b)(i)** | **Suggested solution:**<br>  <br> |
| **(ii)** | **Suggested solution:**<br>Phenylamine is a simple covalent molecule with weak intermolecular attractions between them whereas the other product is an ionic compound with strong electrostatic forces of attraction between ions. Phenylamine thus has a lower boiling point of the 2 and will distil out first to be the distillate. |
| **(iii)** | **Suggested solution:**<br>  <br><br>OR<br>  <br> |

**(c)** **Suggested solution:**

| Information / Type of reaction | Deductions |
|---|---|
| Compound **G**, $C_6H_9O_2N$, is a neutral compound with the ability to rotate plane polarised light. | As **G** contains N and is neutral, **G** is likely to be an amide.<br><br>**G** contains at least 1 chiral carbon. |
| **G** reacts with aqueous sodium hydroxide to form pungent gas **H** that turned moist red litmus blue.<br><br>Upon acidification with aqueous hydrochloric acid, **J** $C_5H_8O_4$. | Alkaline hydrolysis<br>Alkaline gas **H**: $CH_3NH_2(g)$.<br>(**J** has 1 less carbon than **G**)<br><br>**J** has 2 carboxylic acid groups.<br>**G** is cyclic amide. |
| **J** reacts with LiA/$H_4$ to form **K**, $C_5H_{12}O_2$. | **K** has 2 is primary alcohol groups. |
| On heating with excess concentrated $H_2SO_4$, **K** forms **L**, $C_5H_8$. **L** does not exhibit cis-trans isomerism. | **K** undergoes elimination of $H_2O$ to form **L**, $C_5H_8$, with 2 alkene groups.<br>Most likely terminal alkenes as no cis-trans isomerism. |
| When **L** is heated with acidified $KMnO_4$ solution, **M,** $C_3H_4O_3$ is formed. | **L** undergoes oxidative cleavage to form **M,** $C_3H_4O_3$ |
| **M** reacts with aqueous $Na_2CO_3$ to produce effervescence that forms a white precipitate in limewater. | acid-base reaction<br>**M** contains a carboxylic acid. |
| **M** also forms a yellow precipitate when warmed with alkaline aqueous $I_2$. | **M** contains $CH_3CO$- group.<br>(must be ketone as it is a product of oxidative cleavage of a C=C) |

| G | H | J |
|---|---|---|
|  | $CH_3NH_2$ |  |

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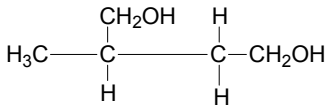
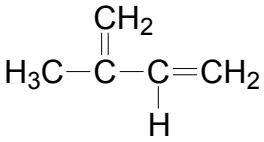
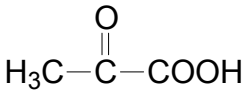
|---|---|---|---|
| K  | L  | M  | |