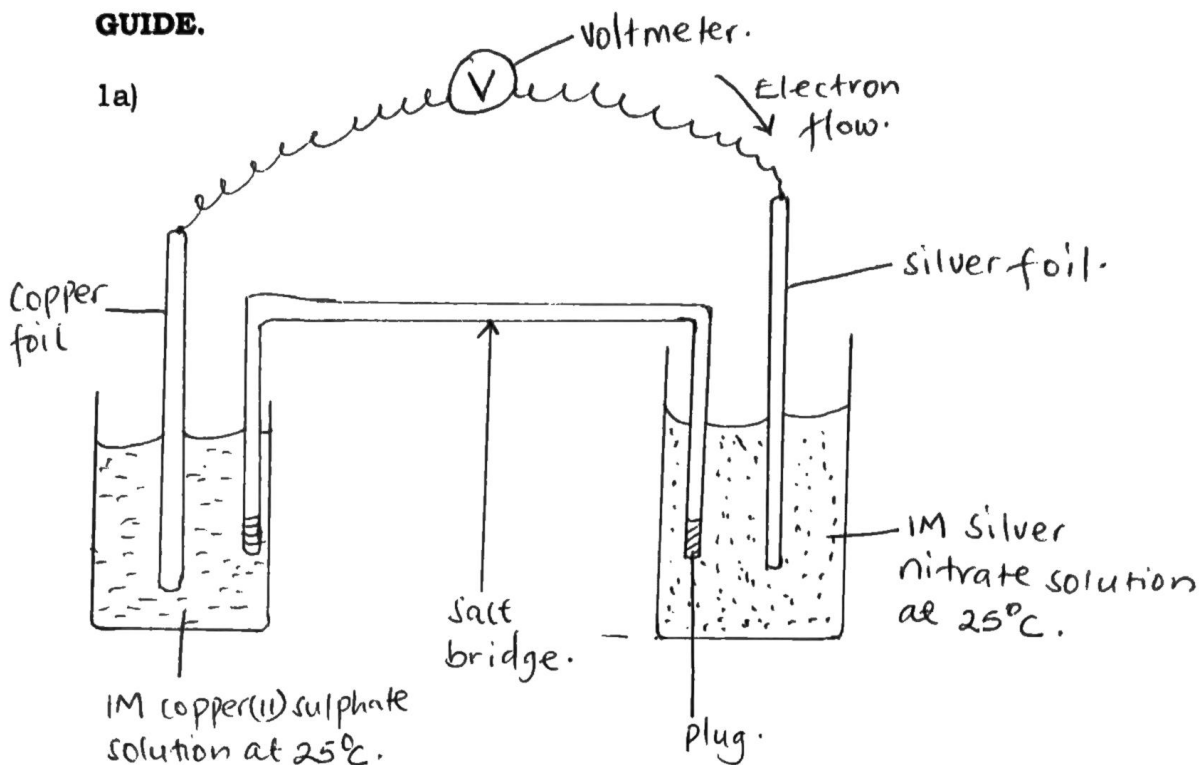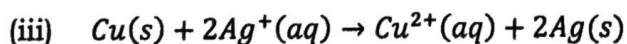# CHEMISTRY P525/2 NAMIREMBE DIOCESE MOCKS 2023 MARKING GUIDE.
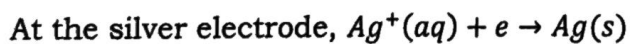
1a)

(b)(i) Cu(s)/Cu²⁺(aq)//Ag⁺(aq)/Ag(s)
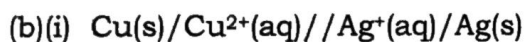
The positive pole (reduction) is written on the right-hand side and the negative pole (oxidation) is written on the left-hand side. The single vertical line represents the boundaries between phases, while the double line represents the salt bridge.

(ii)   At the copper electrode, $Cu(s) \rightarrow Cu^{2+}(aq) + 2e$.

At the silver electrode, $Ag^+(aq) + e \rightarrow Ag(s)$

(iii) $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
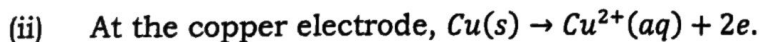
(c) E.m.f of the cell $= E^{\theta}_{RHS} - E^{\theta}_{LHS} = +0.81 - +0.35 = +0.46$ Volts.

Comment: The reaction is possible since emf of cell is positive

(d) The experimental arrangement is shown in the diagram below.

$$Pt(s)/H_2(g)/2H^+(aq)//Cu^{2+}(aq)/Cu(s)$$
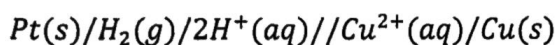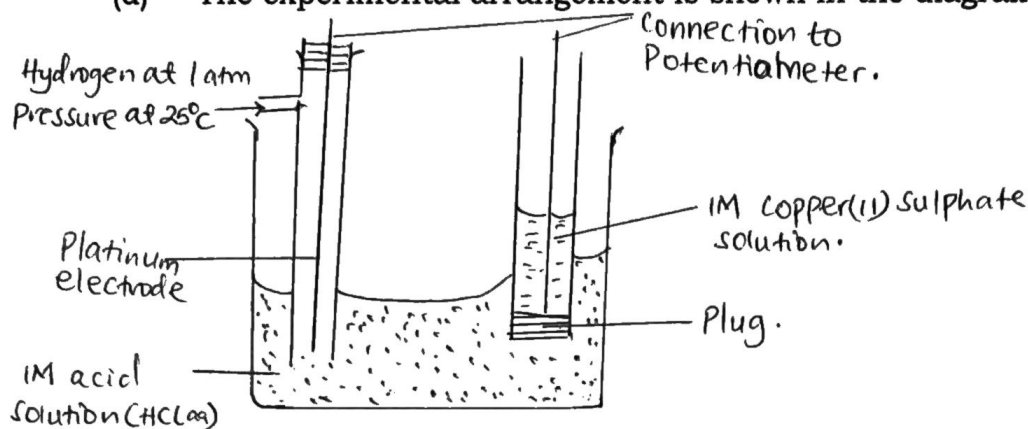
The measured potential of the cell is the standard electrode potential of copper.

2(a)(i) Number of moles of sodium hydroxide initially present $= \frac{25 \times 0.5}{100} =$ 0.0125 moles

Number of moles of HCl required to neutralize excess alkali $\frac{35 \times 0.1}{1000} =$ 0.0035 moles

But from the equation; $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

1 mole of HCl neutralized 1 mole of NaOH.

Therefore, number of moles of NaOH remaining after hydrolysis = number of moles of HCl = 0.0035 moles.

So moles of NaOH that reacted with alkyl iodide = 0.0125 – 0.0035 = 0.0090 moles.

0.0090 moles of $C_nH_{2n+1}I$ weigh 1.531g

1 mole will weigh $\frac{1.531}{0.0090} = 170g$

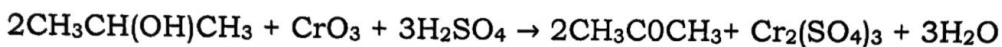(ii)   From $C_nH_{2n+1}I$
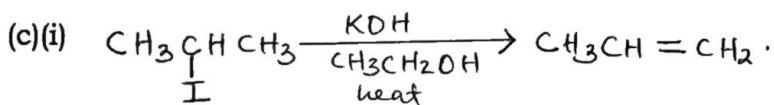
$12n + 2n + 1 + 127 = 170$
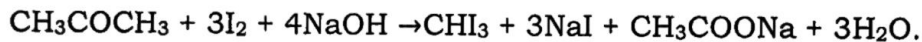
$14n = 42$

$n = 3$

Molecular formula is C_3H_7I

Possible isomers; $CH_3CH_2CH_2I$ and $CH_3CH(I)CH_3$

(b)(i) Colourless solution turns green.

$2CH_3CH(OH)CH_3 + CrO_3 + 3H_2SO_4 \rightarrow 2CH_3COCH_3 + Cr_2(SO_4)_3 + 3H_2O$

(iii)   Yellow precipitate

$CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CHI_3 + 3NaI + CH_3COONa + 3H_2O.$

(c)(i) $CH_3 \underset{I}{C}HCH_3 \xrightarrow[\text{heat}]{\substack{KOH \\ CH_3CH_2OH}} CH_3CH = CH_2$.

mechanism.

$KOH + CH_3CH_2OH \longrightarrow CH_3CH_2OK + H_2O$.

$CH_3CH_2OK \longrightarrow CH_3CH_2\bar{O} + K^+$.

$CH_3 \overset{H}{\underset{H}{C}} \overset{H}{C} - H \longrightarrow CH_3CH = CH_3$.

$\overset{HK}{\underset{O CH_2CH_3}{}}$

ii) $CH_3 CH = CH_3$ + $\xrightarrow{H_3PO_4}$ $\xrightarrow{O_2}$

 + $CH_3 COCH_3$ $\xleftarrow{\text{Dilute } H_2SO_4}$
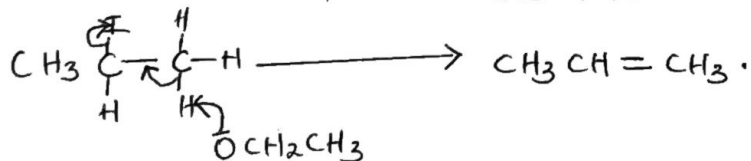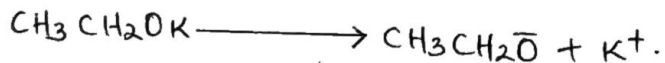
3(a)(i) Azeotropic mixture is a constant boiling mixture of two or more miscible components which distills without any change in its composition at a given pressure. It behaves to all intents and purposes like as pure compound would, but it is clearly not.
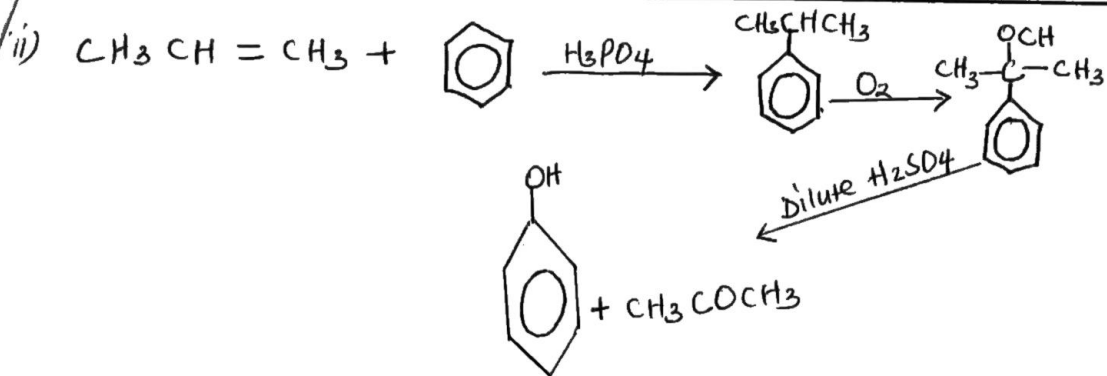
(ii)
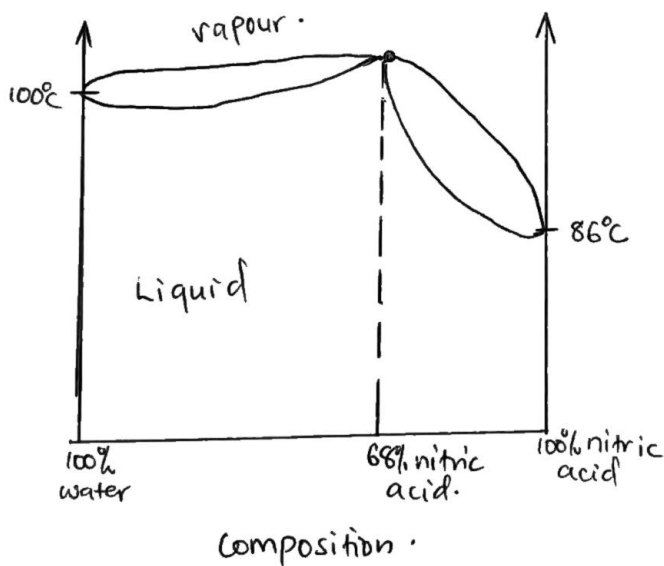
(iii) The mixture boils at a constant temperature forming a vapour which contains a greater percentage of water and when cooled forms a liquid of same composition. With continued distillation,

water is obtained as the distillate and the residue is the azeotropic mixture which can't be separated by fractional distillation.

(iv) Negative deviation from Raoults law means the mixture has a vapour pressure lower than that predicated by Raoults law. This is due to the intermolecular forces of attraction between nitric acid and water molecules being stronger than those between water molecules or nitric acid molecules alone. Therefore, the escaping tendency of these molecules into the vapour phase decreases, lowering the vapour pressure.

- There is heat and volume change during the mixing of water and nitric acid molecules.
- Boiling point of the mixture is above boiling point of an ideal mixture.
- Total vapour pressure of the mixture is below total vapour pressure of the ideal mixture.

(b)(i) Liquid isolated must be immiscible with water.

Liquid must exert high vapour pressure near 100°C.

(or equivalent)

(ii) $$\frac{mass\ of\ water\ in\ the\ distillate}{mass\ of\ Z\ in\ the\ distillate} = \frac{vapour\ pressure\ of\ water \times its\ RMM}{vapour\ pressure\ of\ Z \times its\ RMM}$$

$$\frac{25.5}{7.4} = \frac{720 \times 18}{40 \times RMM\ of\ Z}$$

RMM of Z is 94.

4(a)(i) +2 and +4

+2 as in CO, SnO, PbO
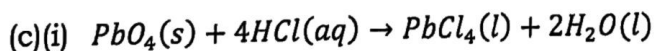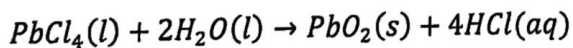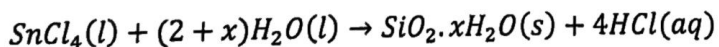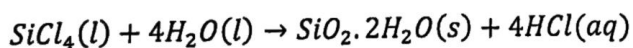
+4 as in CO_2, CH_4, SiO_2, SnH_4, $PbCl_4$

(ii)   The stability of +2 oxidation state increases down the group from carbon to leads, which is in line with increasing metallic character and increasing inert pair effect.

Lead invariably forms more stable compounds in +2 oxidation state than in +4 oxidation state. For example lead(IV) oxide as exemplified by decomposition reaction below

$$PbO_2(s) \xrightarrow{heat\ (>300^0C)} PbO(s) + O_2(g)$$
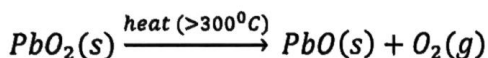
The stability of +4 oxidation state decreases down the group from carbon to lead. For example; with carbon, right at the top of the group, the dioxide, oxidation state +4, is the more stable oxide over the monoxide, oxidation state +2 as exhibited by the combustion of carbon monoxide in oxygen. $2CO(g) + O_2(g) \rightarrow 2CO_2(g), \Delta H = -ve$

(b)   All the tetra chlorides with exception of tetra chloromethane are hydrolyzed by water. This is because the other elements show covalency greater than 4 due to the availability of empty d-orbitals. Silicon(IV) chloride and tin(IV) chloride are completely hydrolyzed by water and lead(IV) chloride is only partially hydrolyzed.

$$SiCl_4(l) + 4H_2O(l) \rightarrow SiO_2.2H_2O(s) + 4HCl(aq)$$

$$SnCl_4(l) + (2+x)H_2O(l) \rightarrow SiO_2.xH_2O(s) + 4HCl(aq)$$

$$PbCl_4(l) + 2H_2O(l) \rightarrow PbO_2(s) + 4HCl(aq)$$

(c)(i) $PbO_4(s) + 4HCl(aq) \rightarrow PbCl_4(l) + 2H_2O(l)$

Cold concentrated acid required

(ii)   Ionic bond.

(iii)   Has high melting point.

Fairly soluble especially in hot water. (OR EQUIVALENT)

5(a)   Zinc blend, ZnS.

(b)(i)   The ore is first concentrated by froth floatation. In principle the powdered ore is agitated with water containing certain chemicals (slaked lime, potassium cyanide and a frothing agent)

The impurity, lead(IV) sulphide or Gelena, is removed in the froth when air is blown, then in slightly altered condition Zinc sulphide is removed in a more concentrated state.

(ii)   The concentrated blende is roasted in air when zinc sulphide is oxidized by oxygen of air to zinc oxide.

$$ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$
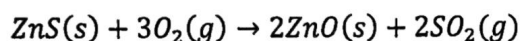
(c)   Reduction of Zinc Oxide

The zinc oxide is mixed with limestone and coke and the mixture fed into the blast furnace. Air is blasted through. Zinc oxide is reduced to the metal.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

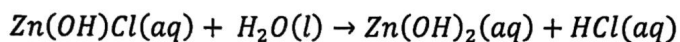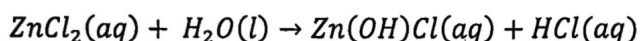$$ZnO(s) + CO(g) \rightarrow Zn(s) + CO_2(g)$$
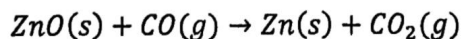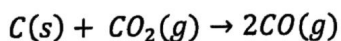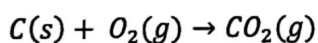
Zinc distills off and slag runs to the base of furnace. Zinc vapour is cooled in a spray of lead and then separated on cooling to form zinc of 99% purity.

(d)   A transition element is a d-block element that has unfilled d-orbitals either in its atoms or its ion. Zinc $[Ar]3d^{10}$, is also a d-
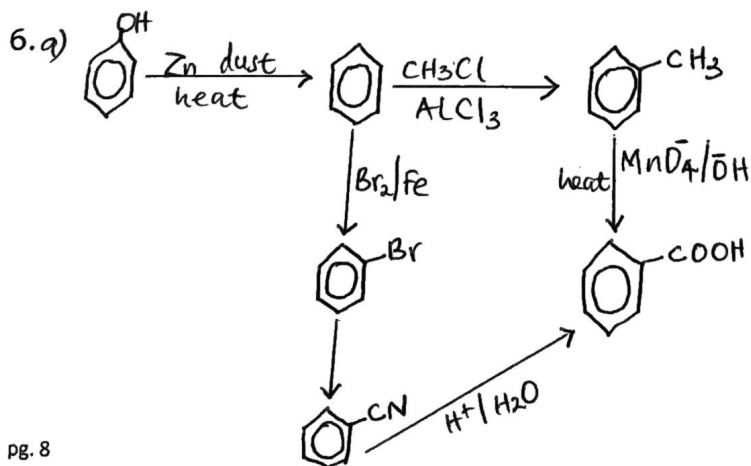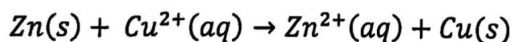
block element but does not have atoms or ions with unfilled d-orbitals, so it is not regarded fully as a true transition element and has little in common with them, for example zinc exercises only one common oxidation state of +2, the ion is not paramagnetic and is not coloured. Zinc because of lack of variable oxidation states, shows little catalytic activity.

(e) Zinc chloride has a low melting point, is a poor conductor of electricity in aqueous solution and is soluble in some non-aqueous solvents. All of these indicates that zinc chloride structure possesses considerable covalent character small wonder then that the zinc chloride hydrolyses in aqueous solution forming aa basic salt or even zinc hydroxide.

$$ZnCl_2(aq) + H_2O(l) \rightarrow Zn(OH)Cl(aq) + HCl(aq)$$

$$Zn(OH)Cl(aq) + H_2O(l) \rightarrow Zn(OH)_2(aq) + HCl(aq)$$

The hydrolysis produces hydrochloric acid in the solution and the Ph becomes less than 7.

(f) The blue colour of the solution fades and turns colourless, the zinc metal slowly reduces in size and a brown red solid is deposited.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

6.a)

c) $CH_3C\equiv CH \xrightarrow[1\% \ HgSO_4]{40\% \ H_2SO_4} CH_3\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{CH_3MgI} CH_3\underset{\underset{OMgI}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 .$

$\xrightarrow[warm]{H^+/H_2O}$ $CH_3\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3 .$

b) $CH_3CH_2COOH \xrightarrow{NH_3} CH_3CH_2COONH_4 \xrightarrow{heat} CH_3CH_2CONH_2$

$\downarrow heat \quad Br_2/ conc. \ NaOH .$

$CH_3COOH \xleftarrow[H^+_{(aq)}]{excess \ Cr_2O_7^{2-}} CH_3CH_2OH \xleftarrow[0°C]{NaNO_2/HCL} CH_3CH_2NH_2$

d) $+ HNO_3$ conc. $\xrightarrow[60°C]{conc. \ H_2SO_4}$ $-NO_2 \xrightarrow[NaOH, heat]{Sn/HCL}$ $-NH_2 \xrightarrow[HCl, <5°C]{NaNO_2/}$ $\overset{+}{N}\equiv NCL \xrightarrow[OH]{\overset{OH}{\bigcirc}}$ $-N=N-$ $-OH$

e) $CH_3\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow[heat]{KOH/alcohol} CH_3CH=CH_2 \xrightarrow[Peroxide]{HBr} CH_3CH_2CH_2Br \xrightarrow[heat]{NaOH} CH_3CH_2CH_2OH .$

f) $\overset{COOH}{} \xrightarrow[heat]{NaOH(aq)}$ $\overset{COONa}{} \xrightarrow[80°C]{soda \ lime}$ $\xrightarrow[heat]{conc. \ H_2SO_4}$ $-SO_3H \xrightarrow[300°C]{NaOH}$ $-ONa \xrightarrow{H^+/H_2O}$ $-OH .$

7(a)(i) The atomic radius of magnesium is taken to be half the inter nuclear distance between two magnesium atoms in the metallic lattice.

(ii) The ionic radius of magnesium is the space occupied by the magnesium ion in any direction in the crystal lattice of any ionic compound of magnesium, usually an oxide MgO or a fluoride, MgF_2.

(b)(i) Each of the elements forms divalent ions by loss of two s-electrons from the outermost shell. The ratio of protons to electrons for a cation is greater than that in the neutral atom, consequently the

remaining electrons are attracted more strongly by the nucleus causing a shrinkage in the size.

(ii) Atomic radius increases on descending the group because electrons are being added to a shell with higher energy. Each successive element has one more shell than the preceding element, also there are more inner complete shells of electrons shielding the outermost electrons from the increasing nuclear charge.

(iii) Each ion has 18 electrons the Ca^{2+} with 20 protons in the nucleus attracts these electrons more strongly than the K^+ ion with 19 protons.

(c)(i) Potassium chromate solution followed by ethanoic acid.

(ii) Magnesium ion – No observable change.

Barium ion – Yelow precipitate insoluble in the acid.

(iii) $Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$
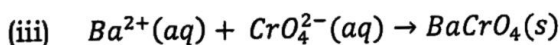
(d)(i) Beryllium forms an amphoteric oxide, BeO and hydroxide Be(OH)$_2$ where as all the oxides and hydroxides of the rest of the alkaline earth metals are basic in character.

- Beryllium forms a volatile covalent chloride, BeCl$_2$ whereas all the other chlorides of the alkaline earth metals are ionic and non-volatile.
- Beryllium does not form a nitrate. All the other alkaline earth metals form a nitrate of the type M(NO$_3$)$_2$. (OR EQUIVALENT)

(ii) The beryllium atom electronic configuration $1s^2 2s^2$, is a small atom and the beryllium ion, Be^{2+} is even smaller. All the alkaline earth

metals form ions of this type, M^{2+} with ionic size increasing down the group.

Beryllium ion, Be^{2+} being the smallest in the group possesses a very high charge /radius ratio or polarizing power. This creates a high degree of of covalency in all its compounds.

8(a) 4-nitrophenol forms intermolecular hydrogen bonds , between -OH group of one molecule and $-NO_2$ group of another molecule that are very strong and so need extra energy to overcome these force hence higher boiling point.

On the other hand 2-nitrophenol possesses an intra-molecular hydrogen bond formed between -OH group and $-NO_2$ group of the same molecule so there are weaker forces of attraction between its molecules hence low boiling point.

Intramolecular H-bond in 2- nitro phenol.

Intermolecular hydrogen bonds in 4-nitrophenol.
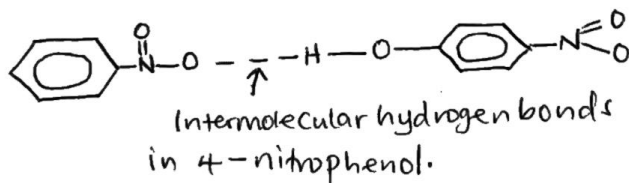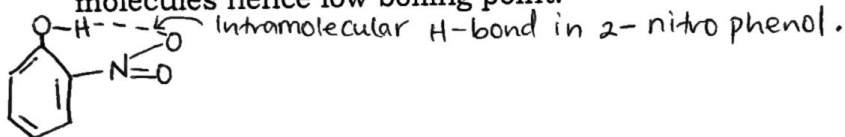
(b) Lithium atom forms a very small cation, Li^+ compared to potassium ion K^+ . Hydration of the cation is proportional to the ratio of the charge to ionic radii. Therefore, lithium ion is heavily hydrated compared to potassium ion. Since electrode potential is the measure of the ease with which an ion is hydrated in aqueous

solution therefore lithium has a higher standard electrode potential.

(c)   The strength of any hydrochloric acid is determined by the tendency of the reaction.

$$H_2O(l) + H\text{-}X \rightarrow H_3O^+(aq) + X^-(aq)$$
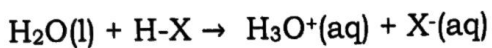
In the forward direction. This tendency is governed by the enthalpy required to break H-X bond. The lesser the bond enthalpy of the H-X bond the strongest the acid. Since fluorine is more electronegative than chlorine, then H-F bond is stronger than H – Cl bond hence hydrogen fluoride is a much weaker acid than hydrogen chloride in aqueous solution.

(d)   The boiling points of compounds increase with increase in molecular mass and polarity of the molecule. The molecular mass of the hydrides are in the order,

$SnH_4 > GeH_4 > SiH_4 > CH_4$.
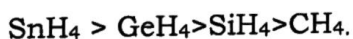
Therefore, boiling points increase in the same order.

(e)   Both bromine and potassium manganate(VII) undergo rapid electrophilic addition to the alkylene-cyclohexene since it is unsaturated.

Benzene reacts with bromine under comparatively harsh conditions by electrophilic substitution rather than by addition due to its relative stability compared to alkenes e.g with bromine a reaction requires presence of iron or aluminium tribromide as catalyst.
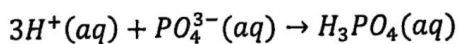
$$\text{C}_6\text{H}_6 + Br_2 \xrightarrow[\text{or } AlBr_3]{\text{Fe}} \text{C}_6\text{H}_5Br + HBr.$$
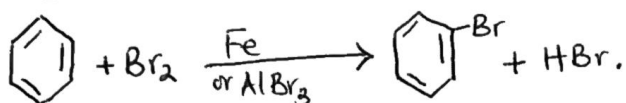
Benzene is resistant to oxidation so does not react with potassium manganate(VII) solution.

(f) The solubility equilibrium of calcium phosphate is

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$
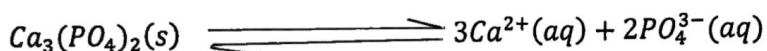
In dilute hydrochloric acid, the hydrogen ions of the acid react with phosphate ions to form phosphoric acid.

$$3H^+(aq) + PO_4^{3-}(aq) \rightarrow H_3PO_4(aq)$$

This acid is weak and is only partially ionized. The formation of phosphoric acid lowers the concentration of the phosphate ions in the solution and so displaces the equilibrium to the right causing calcium phosphate to dissolve.