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Q1 (a)(i) Sc. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

(ii) Mn $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

(iii) Sc^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6$

(iv) Mn^{7+} $1s^2 2s^2 2p^6 3s^2 3p^6$

(b) Scandium loses two electrons of 4s-orbital and one electron from 3d-orbitals to form scandium (III) ion which has the outermost 3p subenergy level which is full and stable.

Manganese loses two electrons of the 4s orbital to form manganese (II) ion having half filled 3d-orbitals that are stable.

Manganese can also lose the two 4s orbital electrons and five electrons of the 3d-orbitals to form $3p^6$ subenergy level which is full and stable forming manganese (VII) ion.

(c) (i) Potassium manganate (VI)

$4KOH(s) + 2MnO_2(s) + O_2(g) \rightarrow 2K_2MnO_4(l) + 2H_2O(g)$

or $4OH^-(l) + 2MnO_2(s) + O_2(g) \rightarrow 2MnO_4^{2-}(s) + 2H_2O(l)$.

(ii) $3MnO_4^{2-}(aq) + 2CO_2(g) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 2CO_3^{2-}(aq)$

or $3MnO_4^{2-}(aq) + 4H^+(aq) \rightarrow MnO_2(s) + 2MnO_4^-(aq) + 2H_2O(l)$

or $3MnO_4^{2-}(aq) + 4CO_2(g) + 2H_2O(l) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 4HCO_3^-(aq)$

(d) Sulphur dioxide reduced manganate (VII) ions to manganese (II) ion

$2MnO_4^-(aq) + 5SO_2(g) + 2H_2O(l) \rightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 4H^+(aq)$

or $2MnO_4^-(aq) + 5SO_3^{2-}(aq) + 6H^+(aq)$

(e) (i) White precipitate turns brown on standing

$Mn^{2+}(aq) + 2OH^-(aq) \rightarrow Mn(OH)_2(s)$

$4Mn(OH)_2(s) + O_2(g) \rightarrow 2Mn_2O_3 \cdot 2H_2O$ or $2Mn_2O_3 + 4H_2O$

or $2MnO_2(s) + 2H_2O$

(ii) White precipitate

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

2 (a)(i) This is the ratio of the concentration of a solute btn two immiscible liquids solvents in the same container at constant temp ✓

(ii) - The temp of the entire system should be constant ✓
- The solute should be in the same molecular state in both solvents ✓
- The solute should not react with the solvents ✓
- The solution should not be saturated ✓

b) A known mass of iodine is dissolved in a known volume of ether. A known volume of water is added to the separating funnel, shaken for some time and left to stand at a fixed temp. After settling, a known volume of the ether layer is pipetted and titrated against a standard solution of sodium thiosulphate in the presence of starch indicator. The rxn is represented by the equation $I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$ ✓ The concentration of iodine in ether is calculated ✓. The concentration of iodine in water is determined by substraction ✓. The partition coefficient is obtained from the expression $KD = \frac{[I_2] \text{ in ether}}{[I_2] \text{ in water}}$ ✓

OR Iodine is introduced into a mixture of ether and water in a separating funnel. The mixture is shaken and allowed to settle at a constant temperature ✓. At equilibrium a known volume of the ether layer is pipetted and titrated with standard solution of sodium thiosulphate in the presence of starch indicator to calculate the conc of iodine in ether. The reaction is represented by the eqn $I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$ ✓
The same procedure is repeated ✓ for the aqueous layer to obtain the concentration of iodine in water. The partition coefficient is obtained from the expression $KD = \frac{[I_2] \text{ in ether}}{[I_2] \text{ in } H_2O}$ ✓

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(ii) - It's immiscible with water ✓✓
- It's a good organic solvent ✓✓
- It's a very volatile and hence can be distilled off or removed after use ✓✓
- It's generally inert, can't react with most organic compounds ✓✓

c (i) If xg of Z is extracted by ether, $(8-x)$g of Z remains in water.

$$\frac{x}{50} \times \frac{200}{8-x} = 12$$ ✓✓

$$x = 6g$$ ✓✓

(ii) If x_1g of Z is extracted by ether, $(8-x_1)$g remains in water.

$$\frac{x_1}{25} \times \frac{200}{8-x_1} = 12$$ ✓✓

$$x_1 = 4.8g$$ ✓✓

Mass remaining after 1st extraction $= (8-4.8) = 3.2g$ ✓✓

If x_2g of Z is extracted by ether $(3.2-x_2)$g remains in water

$$\frac{x_2}{25} \times \frac{200}{3.2-x_2} = 12$$ ✓✓

$$x_2 = 1.92g$$ ✓✓

Total mass extracted $= (4.8+1.92) = 6.72g$.

(iii) Smaller successive portions of the same solvent extract more solute than one large volume used at once ✓

(d) - Determining formula of complex ions ✓✓
- Determination of equilibrium ~~complex~~ constants ✓✓
- Chromatography ✓✓

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(a) (i) Iodine has ~~SM~~ a bigger atomic radius than Chlorine. 2-Iodobutane has a higher molecular mass than 2-chlorobutane. Thus, 2-Iodobutane molecules are held by stronger Van der Waals forces than 2-chlorobutane. Hence more heat energy is required to overcome the stronger Vander Waal's forces in 2-Iodobutane.

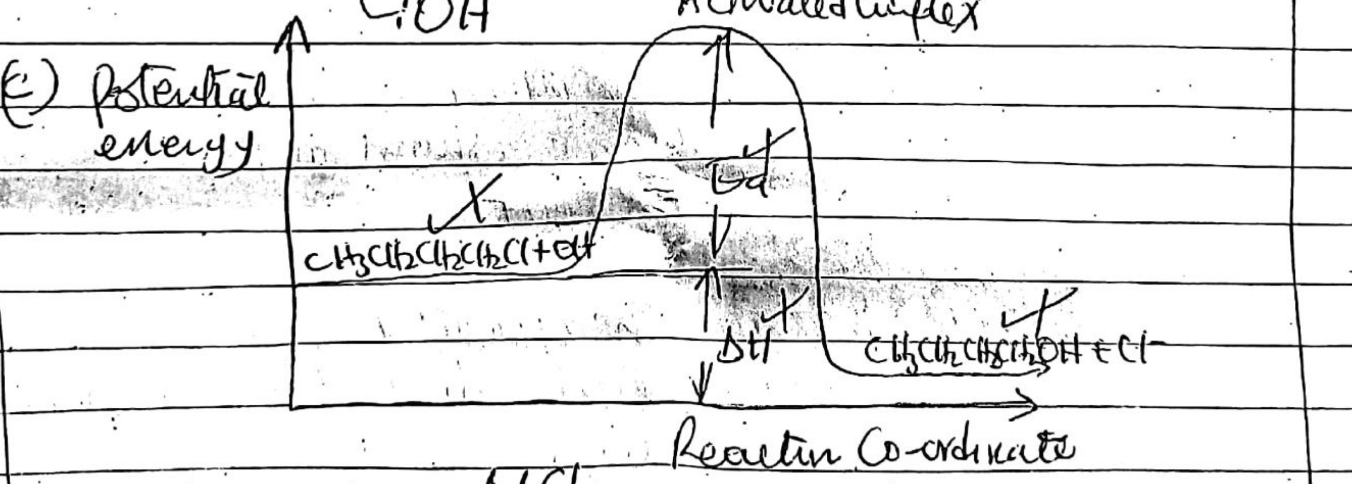
(ii) Iodine has a bigger atomic radius than chlorine. The Carbon-iodine bond is longer and weaker than the Carbon-Chlorine bond. Thus the iodine atom is more easily substituted by the hydroxide ion than the chlorine atom. Hence more time is taken by chloride ions to form the insoluble silver chloride than that ~~of~~ taken by the ~~bromide~~ iodide ions to form silver iodide.

(b) (i) $CH_3CH_2CH_2CH_2Cl \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CH_2CH_2CH_2OH + Cl^-$

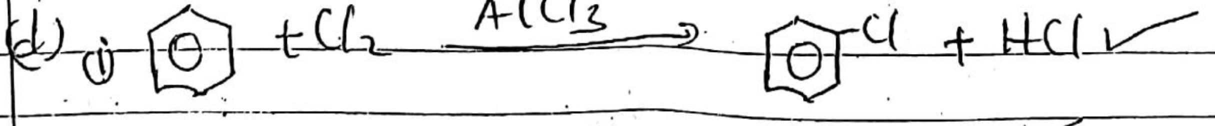
(ii) $CH_3CH_2CH_2CH_2-Cl \longrightarrow CH_3CH_2CH_2CH_2OH + Cl^-$

$:OH$

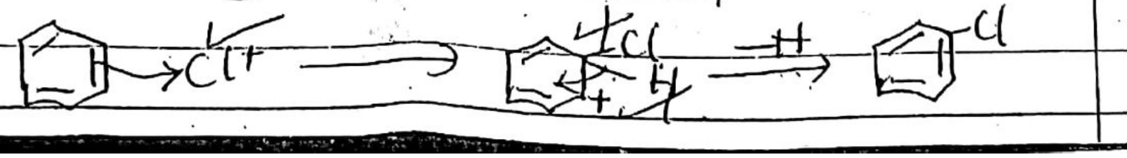
(c)



(d) (i)



(ii) $Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$



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(e) $CH_3CH(Br)CH_2CH_3 \xrightarrow[\text{heat}]{\bar{O}H(aq)} CH_3CH(OH)CH_2CH_3$

$\downarrow MnO_4^-/H^+$, heat

$CH_3COCH_2CH_3$

or $CH_3CH(Br)CH_2CH_3 \xrightarrow[\text{heat}]{KOH(aq)/C_2H_5OH} CH_3CH=CHCH_3$

$CH_3CH=CHCH_3 \xrightarrow{Cl_2/CCl_4} CH_3CHClCHClCH_3 \xrightarrow[\text{heat}]{KOH/C_2H_5OH} CH_3C\equiv CCH_3$

$CH_3CH=CHCH_3 \xrightarrow[\text{heat}]{H_2O/H^+} CH_3CH(OH)CH_2CH_3 \xrightarrow[\text{Heat}]{MnO_4^-/H^+} CH_3COCH_2CH_3$

$CH_3C\equiv CCH_3 \xrightarrow[HgSO_4, 60°C]{H^+/H_2O} CH_3COCH_2CH_3$

f (i) 2,4 - dinitrophenylhydrazine solution / Brady's reagent

(ii) yellow precipitate

(iii) $CH_3COCH_2CH_3$ + 2,4-$(NO_2)_2C_6H_3NHNH_2$ $\xrightarrow{H^+}$ $CH_3CH_2C(CH_3)=NNH-C_6H_3(NO_2)_2$

(y) yellow precipitate

(4) (a) (i) Is the enthalpy change when a reaction takes place in molar quantities as shown in the equation under standard conditions (1atm and 298K)

(ii) A known volume (V_1) of a standard solution of nitric acid (M_1) is placed in a plastic beaker (insulated calorimeter) and its initial temperature t_1°C is recorded. A known volume (V_2) of a standard solution of sodium hydroxide (M_2) is placed in another container and its initial temperature t_2°C is recorded. The amount of the alkali must be equal to or more than that of acid. The alkali is added to the acid and the mixture stirred and the highest steady temperature t_3°C

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Assumptions

Density of solution = $1 g cm^{-3}$

S.H.C of the solution = $4.2 J g^{-1} {}^{0}C^{-1}$

Heat capacity of the container is negligible.

Average ~~temp~~ initial temp $= \frac{t_1 + t_2}{2} = t_i {}^{0}C$

Temp change $\Delta T = (t_3 - t_i) {}^{0}C$

Mass of soln $= (V_1 + V_2) \times 1 g cm^{-3} = (V_1 + V_2) g$

Heat change $= ((V_1 + V_2) \times 4.2 \times \Delta T) J$

Moles of acid $= \left(\frac{M_1 V_1}{1000}\right)$ moles

~~Heat evolved = $(V_1 + V_2) \times 4.2$~~

$\frac{M_1 V_1}{1000}$ moles of acid liberated $((V_1 + V_1) \times 4.2 \times \Delta T) J$

1 mole of acid liberated $\frac{(V_1 + V_2) \times 4.2 \times \Delta T \times 1000}{M_1 V_1}$

Heat of neutralisation of nitric acid

$= -\left[\frac{(V_1 + V_2) \times 4.2 \times \Delta T}{M_1 V_1}\right] kJ mol^{-1}$.

(iii) Nitric acid is a strong acid and sodium hydroxide is a strong base. The only reaction involved is between hydrogen ions and hydroxide ions to form water. $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$.

Hydrocyanic acid is a weak acid. The reaction involves further ionisation of weak acid which is endothermic. $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$ $\Delta H = +Q\ kJ mol^{-1}$

The overall enthalpy change $= -57.1 + Q = -12 kJ mol^{-1}$

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(b) Ionic radius. When ionic radius is small, the forces of attraction of the ions for water molecules is strong and the hydration energy is therefore higher.
Ionic Charge. When ionic charge is high, the force of attraction of the ions for water molecules is strong and therefore the hydration energy is high.

(c) (i) For LiCl ; $\Delta H_{soln} = \Delta H_{Lattice} + \Delta H_{hydration}$

$= +718 + -695 = +23 kJmol^{-1}$

For KCl $\Delta H_{soln} = \Delta H_{lattice} + \Delta H_{hydration}$

$= +862 + -883$

$= -21 kJmol^{-1}$

(ii) Potassium chloride is more soluble in water because the enthalpy of solution is exothermic or the magnitude of the hydration energy is more than lattice energy

(d)

$Na(s) + \frac{1}{2}Cl_{2}(g) \xrightarrow{-411.3} NaCl(s)$

$Na(s) \xrightarrow{108} Na(g) \xrightarrow{500} Na^{+}(g)$

$\frac{1}{2}Cl_{2}(g) \xrightarrow{\frac{242.2}{2}} Cl(g) \xrightarrow{-364} Cl^{-}(g)$

$Na^{+}(g) + Cl^{-}(g) \xrightarrow{\Delta H\ Lattice} NaCl(s)$

$-411.3 = 108 + 500 + \frac{242.2}{2} + -364 + \Delta H_{Lattice}$

$\Delta H_{Lattice} = -776.4 kJmol^{-1}$

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5. (i) Heated Carbon reacts with steam to form carbonmonoxide and hydrogen.

$C(s) + H_2O(g) \xrightarrow{heat} CO(g) + H_2(g)$

Heated silicon reacts with steam to form silicon(IV)oxide and hydrogen

$Si(s) + 2H_2O(g) \rightarrow SiO_2(s) + 2H_2(g)$

Lead reacts with soft water in the presence of oxygen to form lead (II)hydroxide ~~and~~ $2Pb(s) + 2H_2O(l) + O_2(g) \rightarrow 2Pb(OH)_2(s)$.

Silicon reacts with hot concentrated (cold dilute) sodium hydroxide solution to form sodium silicate and hydrogen gas

$Si(s) + 2OH^-(aq) + H_2O(l) \rightarrow SiO_3^{2-}(aq) + 2H_2(g)$

Tin reacts with hot concentrated sodium hydroxide solution to form sodium stannate(IV) and hydrogen gas

$Sn(s) + 2OH^-(aq) + H_2O(l) \rightarrow SnO_3^{2-}(aq) + 2H_2(g)$

Lead reacts with hot concentrated sodium hydroxide solution to form sodium plumbate (II) and hydrogen gas

$Pb(s) + 2OH^-(aq) \rightarrow PbO_2^{2-}(aq) + H_2(g)$

(ii) Carbon reacts with hot concentrated sulphuric acid to form Carbondioxide and sulphur dioxide and water.

$C(s) + 2H_2SO_4(l)(aq) \rightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$

Tin reacts with hot concentrated sulphuric acid to form tin (IV) sulphate, sulphur dioxide and water

$Sn(s) + 4H_2SO_4(aq) \rightarrow Sn(SO_4)_2(aq) + 2SO_2(g) + 4H_2O(l)$

Lead reacts with hot concentrated sulphuric acid to form lead(II) sulphate, sulphur dioxide and water

$Pb(s) + 2H_2SO_4(aq) \rightarrow PbSO_4(s) + SO_2(g) + 2H_2O(l)$

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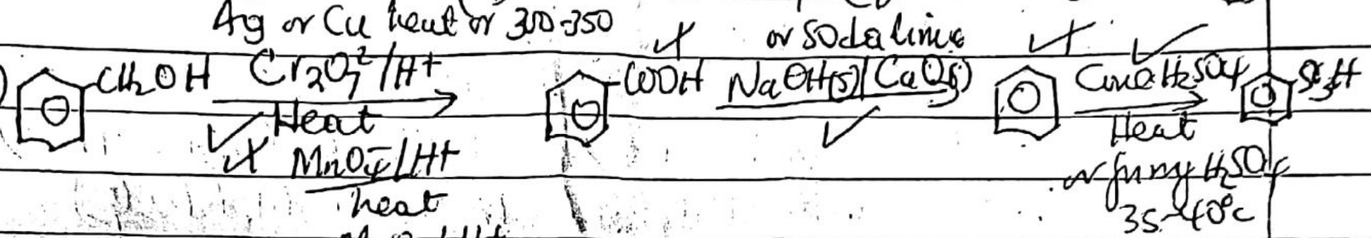
(b) Brown solid dissolves with effervescence of a greenish yellow gas to form a colourless solution

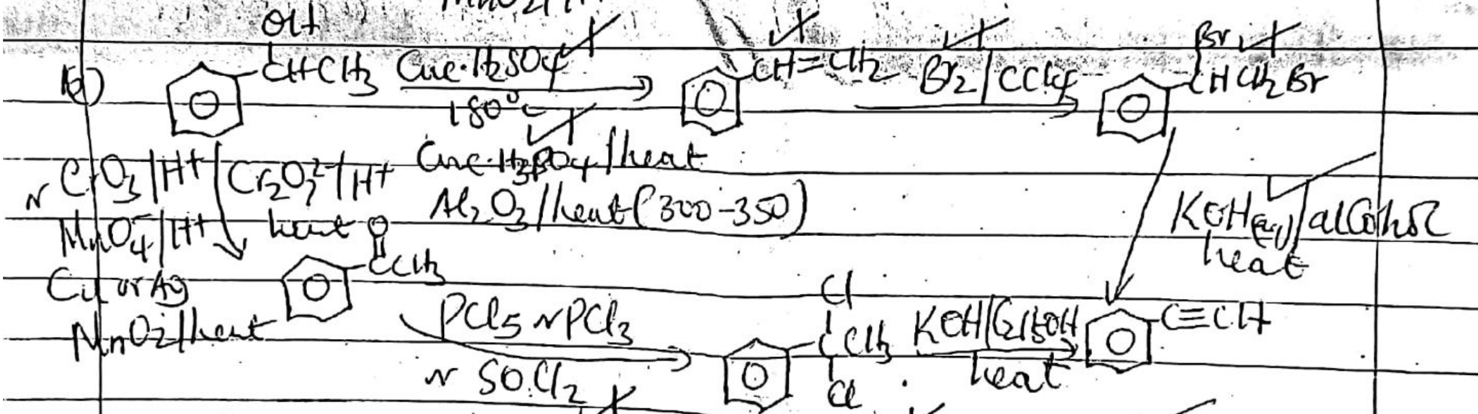
$PbO_2(s) + 6HCl(aq) \rightarrow PbCl_4^{2-}(aq) + 2H_2O(l) + Cl_2(g) + 2H^+(aq)$

or $PbO_2(s) + 6HCl(aq) \rightarrow H_2PbCl_4(aq) + 2H_2O(l) + Cl_2(g)$

6(a)



(b)



(c) $CH_3CH_2COOH \xrightarrow[\text{or } B_2H_6]{LiAlH_4/\text{Dry ether}} CH_3CH_2CH_2OH \xrightarrow[170-180^\circ c]{\text{Conc. } H_2SO_4} CH_3CH=CH_2$

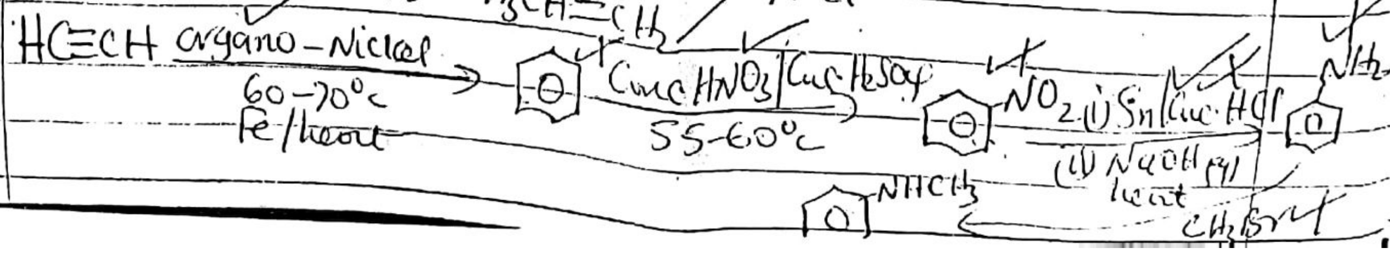
$CH_3CH=CH_2 \xrightarrow[\text{heat}]{\text{Conc } H_2SO_4/H_2O} CH_3CH(OH)CH_3$

$CH_3CH=CH_2 \xrightarrow{HCl} CH_3CHClCH_3 \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CH(OH)CH_3$

(d) $CH_3CH(OH)CH_3 \xrightarrow[ZnCl_2/\text{Conc. } HCl]{PCl_5, PCl_3 \text{ or } SOCl_2} CH_3CHClCH_3 \xrightarrow[\text{heat}]{NH_3(\text{alcohol})} CH_3CH(NH_2)CH_3$

$CH_3CH(OH)CH_3 \xrightarrow[180^\circ c]{\text{Conc. } H_2SO_4} CH_3CH=CH_2 \xrightarrow{HCl} CH_3CHClCH_3$

(e)



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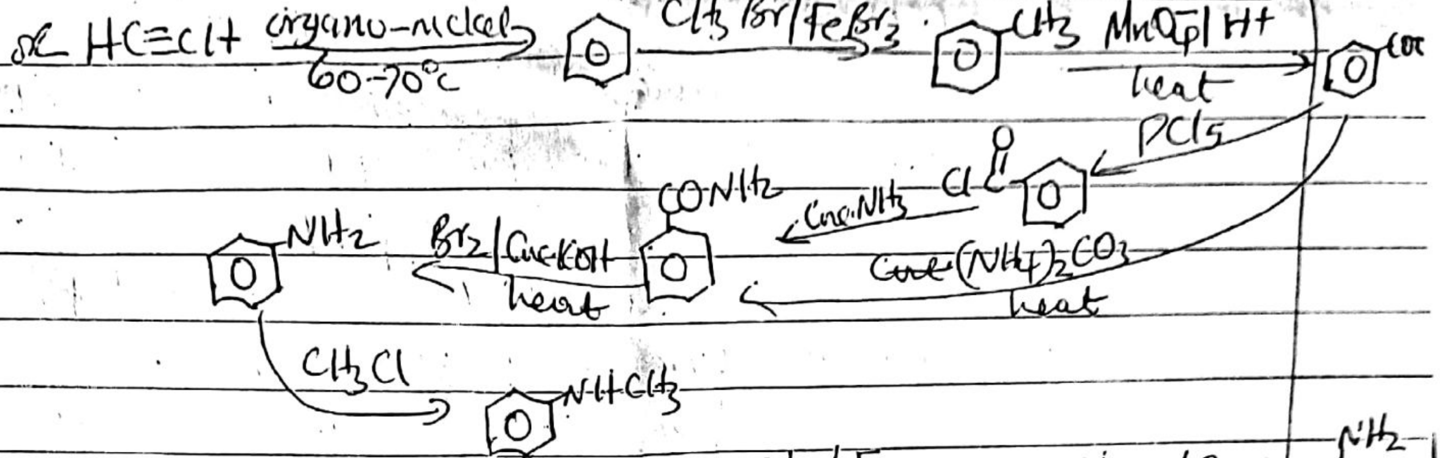

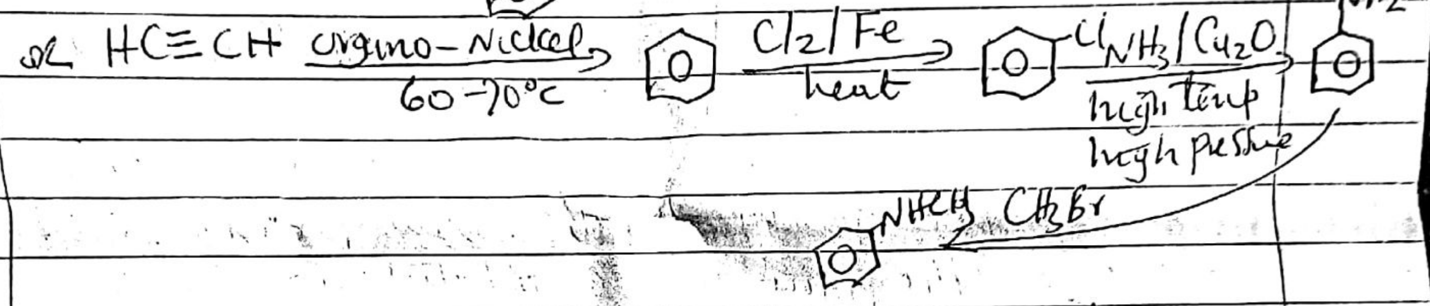

(7) (a) A solid mixture which melts at constant temperature to form a liquid of the same composition ✓

or

A liquid mixture which freezes / solidifies at constant temperature without change in composition.

(b) – Mixtures of various compositions of solid naphthalene and biphenyl are prepared ✓

– Each mixture is heated separately until it melts ✓

– Each mixture is allowed to cool while stirring and the constant temperature at which it solidifies / freezes is recorded. ✓

– The melting points of pure naphthalene and pure biphenyl are determined in the same way ✓

– A graph of melting points against compositions is plotted and phase diagram drawn.

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(c)(i) Axes ✓ Title ✓ Plots ✓ Shape ✓ Regions ✓

(ii) Eutectic temperature is 35-37 °c (36 ± 1 °c)
Eutectic Composition is 0.4 ± 0.01 Naphthalene

(d) From 85°c, the mixture cools to 53°c (point p) without change in phase or (Composition).
At point P biphenyl begins to solidify as the mole fraction (or Composition) of Naphthalene increases in the liquid mixture.
The Melting point / freezing point decreases up to the eutectic point (temp) as further cooling is done.
At the eutectic point the temperature and Composition remains constant until the whole System solidifies and then the solid mixture cools with no change in phase (Composition) up to 30°c.

(e) The Melting point of naphthalene reduces up to the eutectic point
At the eutectic point, the melting point is constant and further addition of biphenyl increases the Melting point towards that of pure biphenyl.

(8) (a) Oxygen has small atomic radius and high electronegativity compared to Sulphur.
The O-H bond is strongly polar whereas the S-H bond is not.
Water molecules are held together by hydrogen bonds whereas hydrogen sulphide molecules are held by Van der Waals forces

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which are weaker than hydrogen bonds. Hence water has a higher boiling point than hydrogen sulphide.

(b) ~~Ethylamine~~ Ethylamine reacts with cold solution of sodium nitrite and concentrated hydrochloric acid to form ethanol and nitrogen.

$CH_3CH_2NH_2 \xrightarrow[<10^\circ C]{NaNO_2/Conc.HCl} CH_3CH_2OH + N_2$

~~Ethyl~~ Phenylamine reacts with a cold solution of nitrous acid at a temperature below $10^\circ c$ ~~to~~ form Benzene diazonium salt which is more stable.

$C_6H_5NH_2 \xrightarrow[<10^\circ c]{NaNO_2/Conc.HCl} C_6H_5\overset{+}{N}\equiv N$

(c) Hydrazine reduces acidified manganate (VII) ions to manganese (II) ions and is oxidized to nitrogen.

$4MnO_4^-(aq) + 5NH_2NH_2(g) + 12H^+(aq) \rightarrow 4Mn^{2+}(aq) + 16H_2O(l) + 5N_2(g)$.

(d) Chlorine oxidises excess sodium thiosulphate solution to sulphate ions with formation of sulphur.

$Cl_2(g) + S_2O_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + S(s) + 2H^+(aq) + 2Cl^-(aq)$

or Chlorine reacts with water to form hydrochloric acid and hypochlorous acid (an acidic solution)

$Cl_2(g) + H_2O(l) \rightarrow HCl(aq) + HOCl(aq)$

Sodium thiosulphate disproportionates in the acidic solution to form sulphur.

$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + H_2O(l) + S(s)$