Section: Senior **Compounds of d-Block Elements** **Date: 26-06-2020**

I. Compounds of copper :

1) Cupric oxide (CuO):

Preparation: (i) $CuCO_3.Cu(OH)_2 \xrightarrow{\Delta} 2CuO + H_2O + CO_2$ (Commercial process)
Malachite Green

(ii) $2Cu + O_2 \xrightarrow{\Delta} 2CuO + Cu_2O$

$$Cu_2O + \frac{1}{2}O_2 \longrightarrow 2CuO$$

(iii) $Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$

(iv) $2Cu(NO_3)_2 \xrightarrow{250°C} 2CuO + 4NO_2 + O_2$

Properties: (i) CuO is a black powder insoluble in water.

(ii) It readily dissolves in dil. acids

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$HCl \longrightarrow CuCl_2$$

$$HNO_3 \longrightarrow Cu(NO_3)_2$$

(iii) It decomposes when, heated above 1100°C

$$4CuO \longrightarrow 2Cu_2O + O_2$$

(iv) CuO is reduced to Cu by H_2 or C

$$CuO + C \xrightarrow{\Delta} Cu + CO \text{ -}$$

$$CuO + H_2 \xrightarrow{\Delta} Cu + H_2O \text{ -}$$

(v) $CuO + NH_3 \longrightarrow Cu + N_2 + H_2O$

Uses :

i) As a pigment
ii) Abrasive
iii) Dry cells

2) Cupric chloride ($CuCl_2$) :

Preparation: $CuO + 2HCl \longrightarrow CuCl_2 + H_2O$

$Cu(OH)_2 \cdot CuCO_3 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$

$Cu + HCl + O_2 \longrightarrow CuCl_2 + H_2O$

$CuCl_2.2H_2O \xrightarrow[HCl\,gas]{150^0\,C} CuCl_2 + 2H_2O$

Anh. $CuCl_2$ is yellow brown mass obtained by heating $CuCl_2.2H_2O$ at 150^0C in presence of HCl vapour.

Properties: (i) It is crystallised as blue green $CuCl_2 \cdot 2H_2O$.

(ii) Dil. aq. solution is blue in colour due to formation of $[Cu(H_2O)_6]^{2+}$complex.

(iii) In conc. HCl or KCl the colour changes to yellow, owing to the formation of $[CuCl_4]^{2-}$

(iv) The conc. solution is green in colour having the two complex ions in equilibrium

$CuCl_2 \cdot 2H_2O + 6H_2O \rightleftharpoons [Cu(H_2O)_6]^{2+} + [CuCl_4]^{2-} + 4H_2O$

(v) $CuCl_2$ is converted to CuCl by no. of reagents

(a) $CuCl_2 + Cu \xrightarrow{\Delta} 2CuCl$

(b) $2CuCl_2 + H_2SO_3 + H_2O \longrightarrow 2CuCl + 2HCl + 2H_2SO_4$

(c) $CuCl_2 + SnCl_2 \longrightarrow CuCl + SnCl_4$

(vi) $CuCl_2 + NaOH \longrightarrow Cu(OH)_2\downarrow + NaCl$

$CuCl_2 + Cu(OH)_2 \longrightarrow CuCl_2.3Cu(OH)_2\downarrow$

pale blue

(vii) $CuCl_2 + NH_4OH \longrightarrow Cu(NH_3)_4Cl_2.xH_2O$

deep blue solution

☞ Copper (I) halides are insoluble in water. However they dessolve in solutions containing excess of halide ions due to complex formation $[CuCl_2]^-$, $[CuCl_3]^{2-}$, $[CuCl_4]^{3-}$

$CuF_2 \cdot 2H_2O \longrightarrow$ light blue

$CuCl_2 \cdot 2H_2O \longrightarrow$ blue-green

$CuBr_2 \longrightarrow$ almost black

CuI_2 does not exist

Uses : i) Co-catalyst in Wacker's process

ii) In pyrotechnics (gives blue-green colour)

3) Cupric sulphate ($CuSO_4.5H_2O$):

Preparation: $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$

(dil)

$$Cu(OH)_2 + H_2SO_4 \longrightarrow CuSO_4 + 2H_2O$$
(dil)

$$Cu(OH)_2 \cdot CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + 3H_2O + CO_2$$
(dil)

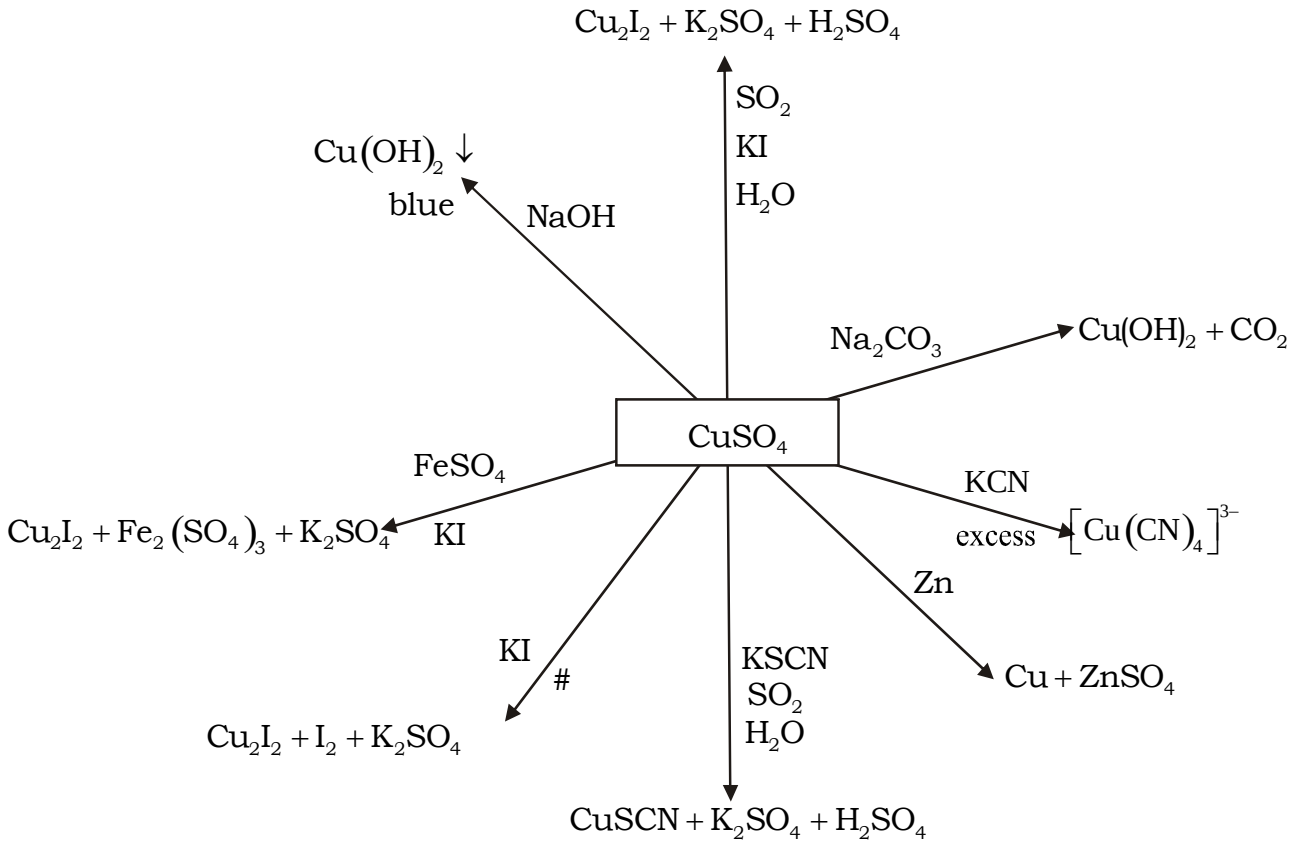
$$Cu + H_2SO_4 + \frac{1}{2}O_2 \longrightarrow CuSO_4 + H_2O$$ [Commercial scale]
(scrap)

$$Cu + \text{dil. } H_2SO_4 \longrightarrow \text{no reaction}$$

Properties: (i) It is crystallised as $CuSO_4 \cdot 5H_2O$

(ii) $CuSO_4 \cdot 5H_2O \underset{\text{effloresence}}{\rightleftharpoons} CuSO_4 \cdot 3H_2O \overset{100°C}{\rightleftharpoons} CuSO_4 \cdot H_2O$

Blue Pale blue Bluish white



The reaction is used to estimate Cu^{2+} in solution by volumetric analysis. Excess KI is added to an acidified solution and I_2 produced is estimated by acidified solution and I_2 produced is estimated by titrating with standard Hypo.

$$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$$

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

Uses :

i) Fehling's & Benedict's reagent ii) Electroplating iii) Bordeaux mixture

II Compounds of Silver

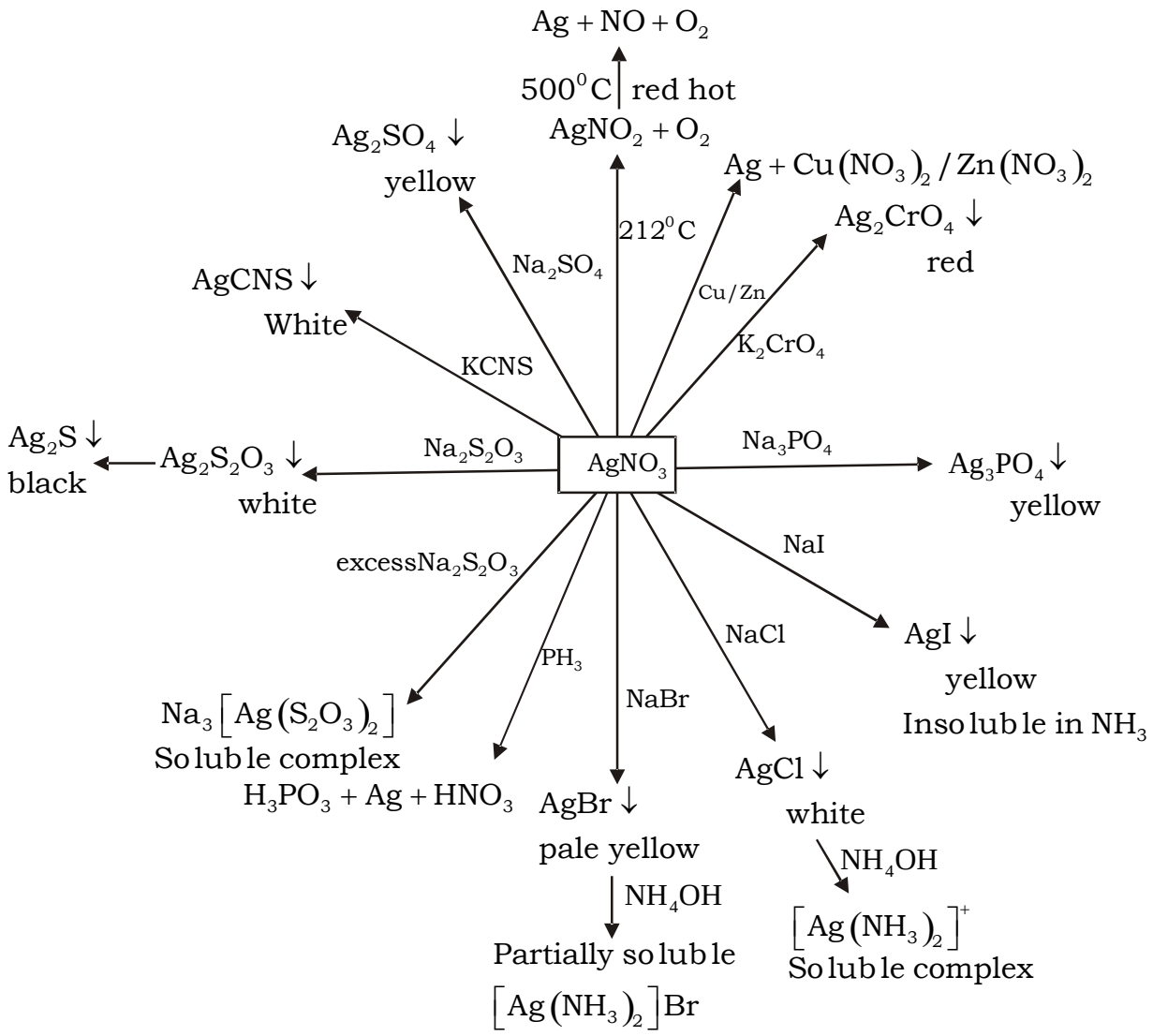
1) Silver nitrate ($AgNO_3$)

Preparation: $Ag + HNO_3 \longrightarrow AgNO_3 + NO + H_2O$

dil.

Properties.: (i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely divided silver (black colour)

(ii) Soluble in water



Uses :

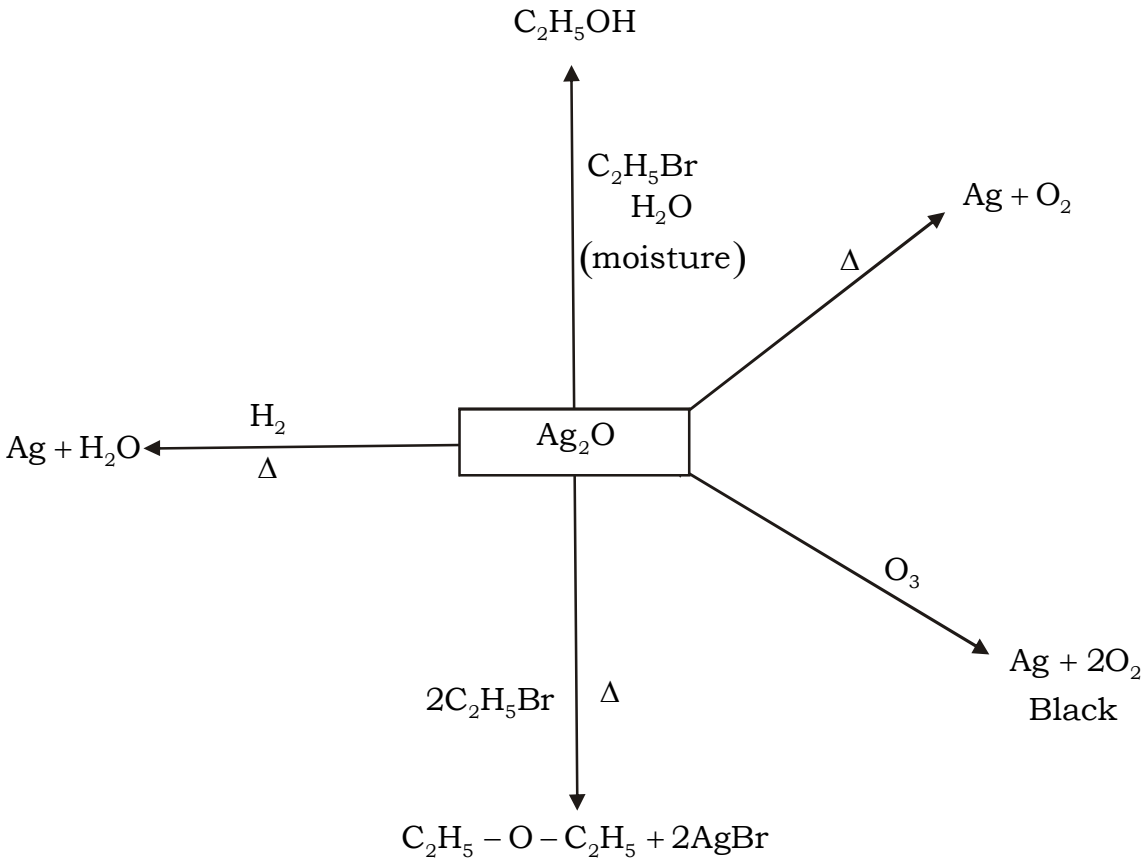
i) $AgNO_3$ is used in the detection of halide ions

ii) Ammonical $AgNO_3$ (Tollen's reagent) is used in Analysis of organic compounds.

2) Silver oxide (Ag_2O)

Preparation : $2AgNO_3 + 2NaOH \longrightarrow Ag_2O + 2NaNO_3 + H_2O$

Properties : Brown solid – sparingly soluble in water



Uses :

i) Batteries

ii) mild oxidant in organic syntheisis

$$R-CHO \xrightarrow{Ag_2O} RCOOH$$

III. Compounds of Iron.

1) Ferrous oxide (FeO):

Preparation: $FeC_2O_4 \xrightarrow[\text{in absence of air}]{\Delta} FeO + CO + CO_2$

Properties : Black powder. Non-stoichiometric

It is stable at high temperature and on cooling slowly disproportionates into Fe_3O_4 and iron

$4FeO \longrightarrow Fe_3O_4 + Fe$

2) Ferric oxide (Fe_2O_3):

Preparation : (i) $Fe(OH)_3 \longrightarrow Fe_2O_3 + H_2O$

(ii) $FeSO_4 \longrightarrow Fe_2O_3 + SO_2 + SO_3$

(iii) $FeS + O_2 \longrightarrow Fe_2O_3 + SO_2$

Properties : Deep red powder - Insoluble in water-slightly amphoteric oxide (largely basic)

Reactions : (i) $Fe_2O_3 + HCl \longrightarrow FeCl_3 + H_2O$

(ii) $Fe_2O_3 + NaCO_3$ (or) $NaOH \xrightarrow{\text{fusion}} NaFeO_2$

(iii) $2Fe_2O_3 + 3C \longrightarrow Fe_3O_4 + CO_2$

(iv) $Fe_2O_3 + CO \longrightarrow Fe_3O_4 + CO_2$

(v) $Fe_2O_3 \xrightarrow{1400^0C} Fe_3O_4 + O_2$

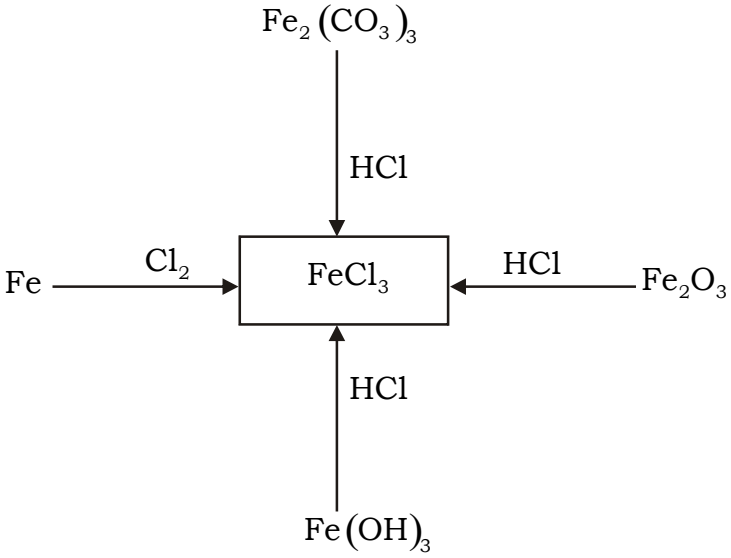
(vi) $Fe_2O_3 + H_2 \longrightarrow Fe + H_2O$

☞ $NaFeO_2$ is better considered as mixed oxide rather than ferrite($Na_2O.\ Fe_2O_3$)

Uses : i) Pigment
ii) Removes phosphates in aquaria
iii) As Jeweler's rogue
iv) Production of Iron & steel.

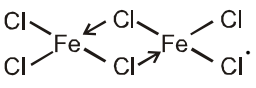
3. FERRIC CHLORIDE ($FeCl_3.6H_2O$)

Preparations:



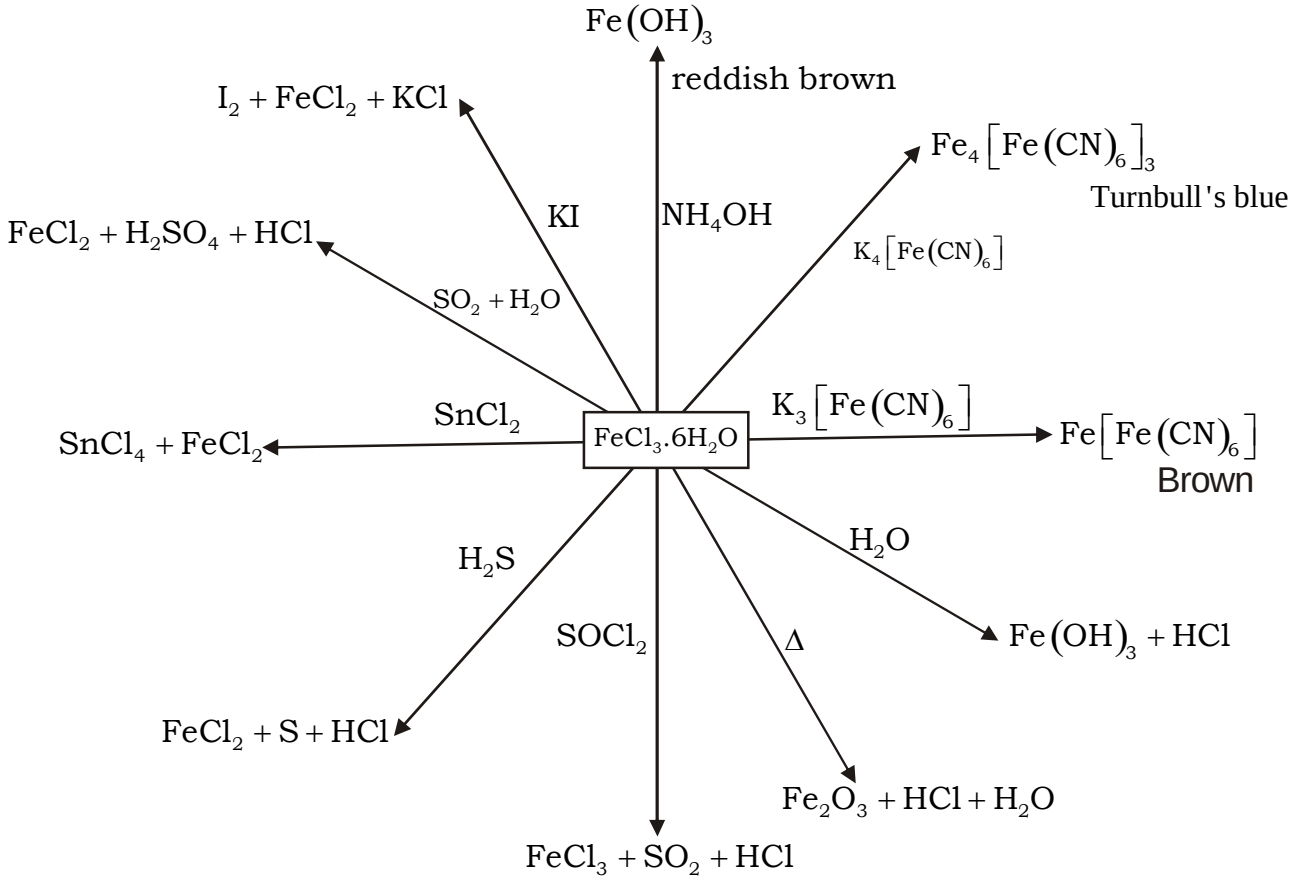
Anhydrous ferric chloride is dark black solid while hydrated salt, $FeCl_3 . 6H_2O$ is yellowish-brown deliquescent crystalline solid and exists as trans-$[Fe(H_2O)_4Cl_2]Cl.2H_2O$. Both are soluble in water as well as in ether forming solvated species,

$[Fe(H_2O)_4Cl_2]Cl . 2H_2O$ and $(C_2H_5)_2O \longrightarrow FeCl_3$ respectively.

It is sublimed at 300°C giving a dimeric gas,  .

☞ $FeCl_3$ gives blood red colour with SCN^-, colour is due to formation of mixture of

$\left[Fe(SCN)_4\right]^-$, $Fe(SCN)_3$ & $[Fe(SCN)\ (H_2O)_5]^{+2}$



Uses :

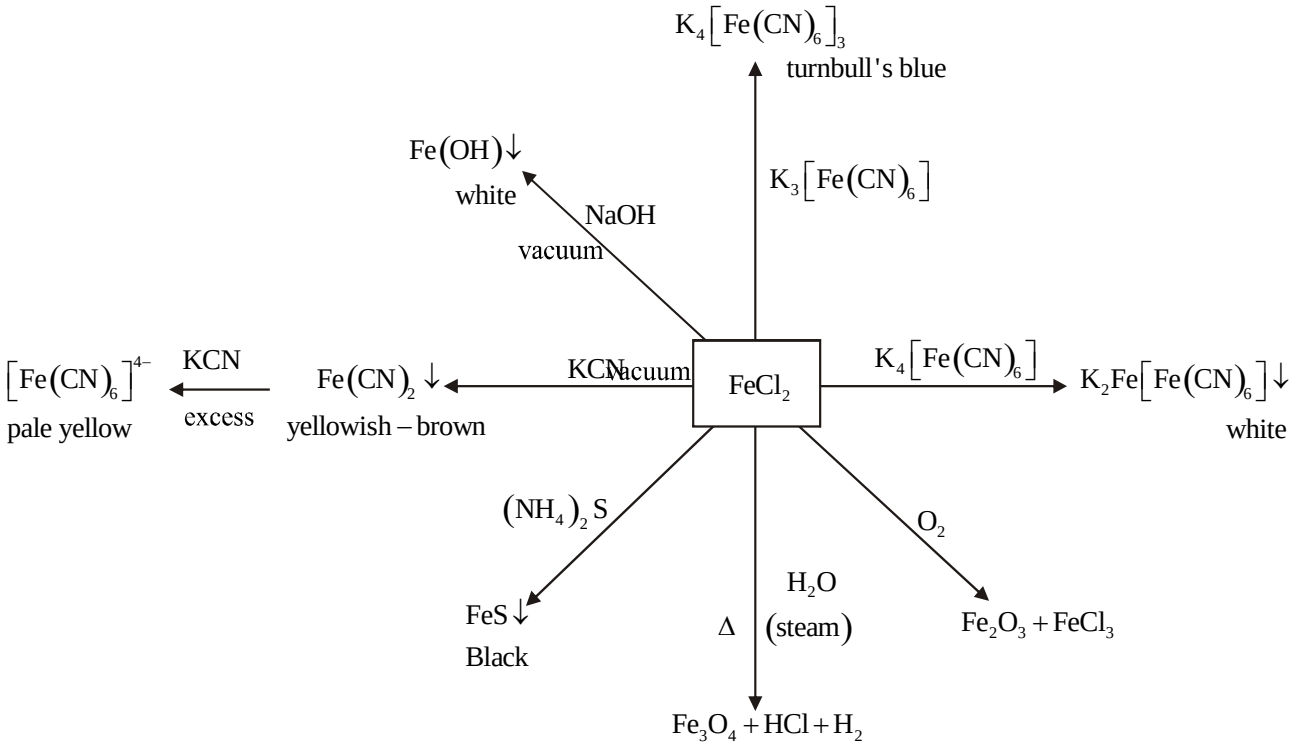
i) Flocculating agent ii) etching copper in PCBs
iii) As a Lewis Aci iv) Detection of phenols

4) Ferrous chloride ($FeCl_2$):

Preparation: i. $Fe + 2HCl \xrightarrow[\text{a current of HCl}]{\text{heated in}} FeCl_2 + H_2$

ii. $FeCl_3 + H_2 \xrightarrow{\Delta} 2FeCl_2 + 2HCl$

Reactions :



Properties: (i) Paramagneitc, off white solid, tetrahydrate is greenish.

(ii) It is deliquescent like $FeCl_3$

(iii) It is soluble in water, aq. solution is acidic.

(iv) It volatilises at about 1000°C and vapour density indicates.

(v) It undergoes oxidation when heated in air.

$$12FeCl_2 + 3O_2 \longrightarrow 2Fe_2O_3 + 8FeCl_3$$

(vi) H_2 evolves on heating in steam.

$$3FeCl_2 + 4H_2O \longrightarrow Fe_3O_4 + 6HCl + H_2$$

(vii) It can exist in different hydrated forms.

$FeCl_2 \cdot 2H_2O$: colourless

$FeCl_2 \cdot 4H_2O$: pale green

$FeCl_2 \cdot 6H_2O$: green

5. FERROUS SULPHATE ($FeSO_4.7H_2O$)

Preparation:

i) $Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2O$

ii) $2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$

Pyrite

- Light green & soluble in water
- Exists as $[Fe(H_2O)_6]SO_4.H_2O$
- Hydrated ferrous sulphate is a green crystalline compound, effloresces on exposure to air. Anhydrous $FeSO_4$ is colourless.
- Diffcult to obtain pure as it undergoes aerial oxidation.
- Reaction with NO :

$FeSO_4 + NO \longrightarrow FeSO_4.NO$
(brown)

$\left[Fe(H_2O)_6\right]SO_4 + NO \longrightarrow \left[Fe(H_2O)_5\,NO\right]SO_4$

- The above reaction is used for identification of nitrite and nitrate radicals (Brown Ring test)
- Impure NO is passed into $FeSO_4$ to get the adduct [$FeSO_4$.NO], NO is recovered by heating the adduct.
- Mohr's salt {$FeSO_4(NH_4)_2SO_4.6H_2O$} is preferred over $FeSO_4$ in volumetric analysis as Mohr's salt prevents aerial oxidiation of $FeSO_4$. Unlike simple $FeSO_4$.

Uses :

i) Treatement of Iron deficiency
ii) Mordant

IV. Compounds of Zinc

1) Zinc oxide (ZnO):

It is called as philospher's wool due to its wooly flock type appearance

Preparation: i) $2Zn + O_2$ ¾® $2ZnO$

ii) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

iii) $2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$

iv) $Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$

v) $Zns + O_2 \longrightarrow ZnO + SO_2$

vi) $4ZnSO_4 + 4Na_2CO_3 + 3H_2O$ ¾® $ZnCO_3{\cdot}3Zn(OH)_2$ ¯ $+ 4Na_2SO_4 + 3CO_2$
white basic zinc carbonate

$\downarrow \Delta$

$4ZnO + 3H_2O$ - + CO_2 -
pure

Properties: i)$ZnO \underset{\text{(cold)}}{\overset{\Delta}{\rightleftharpoons}} \underset{\text{(hot)}}{ZnO}$ - Colour is due to crystal defect
white yellow

ii) It is insoluble in water
iii) It sublimes at 400°C
iv) It is amphoteric oxide

Reactions :

i) $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$

ii) $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

iii) $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$

iv) ZnO is reduced by heating with H_2 & C.

$ZnO + H_2 \xrightarrow{>400°C} Zn + H_2O$

$ZnO + C \longrightarrow Zn + CO$

v) It forms Rinmann's green with $Co(NO_3)_2$

$2Co(NO_3)_2 \longrightarrow 2CoO + 4NO_2 + O_2$

$CoO + ZnO \longrightarrow CoZnO_2$ or $CoO{\cdot}ZnO$

Rinmann's green

Uses: i) As white pigment, it is superior than white lead because it does not turn into black.

ii) Rinmann's green is used as green pigment

iii) It is used as zinc ointment in medicine

2) **ZINC CHLORIDE ($ZnCl_2$):**

Preparation: i) $ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$

ii) $ZnCO_3 + 2HCl \longrightarrow ZnCl_2 + H_2O + CO_2$ } It crystallises as $ZnCl_2{\cdot}2H_2O$

iii) $Zn(OH)_2 + 2HCl \longrightarrow ZnCl_2 + 2H_2O$

Anhyd. $ZnCl_2$ cannot be made by heating $ZnCl_2{\cdot}2H_2O$ because

$ZnCl_2{\cdot}2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$

$Zn(OH)Cl \xrightarrow{\Delta} ZnO + HCl$

Anhydrous $ZnCl_2$is obtained by following methods

i) $Zn + Cl_2 \longrightarrow ZnCl_2$

ii) $Zn + 2HCl(dry) \longrightarrow ZnCl_2 + H_2$

iii) $Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg$

Properties: i) It is deliquescent white solid (when anhydrous)

ii) $ZnCl_2 + H_2S \longrightarrow ZnS + 2HCl$

iii) $ZnCl_2 + NaOH \longrightarrow Zn(OH)_2 \xrightarrow{excess} Na_2[Zn(OH)_4]$

iv) $ZnCl_2 + NH_4OH \longrightarrow Zn(OH)_2 \xrightarrow{excess} [Zn(NH_3)_4]^{2+}$

Anhydrous $ZnCl_2$ absorbs ammonia gas to from $ZnCl_2.4NH_3$

Uses:

i) Used for impregnating timber to prevent destruction by insects

ii) As dehydrating agent when anhydrous

iii) $ZnO{\cdot}ZnCl_2$ used in dental filling

3) Zinc Sulphate ($ZnSO_4.7H_2O$):

Preparation:

i) $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$
(dil)

ii) $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$
(dil)

iii) $ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$

dil

iv) $ZnS + 2O_2 \longrightarrow ZnSO_4$

$ZnS + \frac{3}{2}O_2 \longrightarrow ZnO + SO_2$

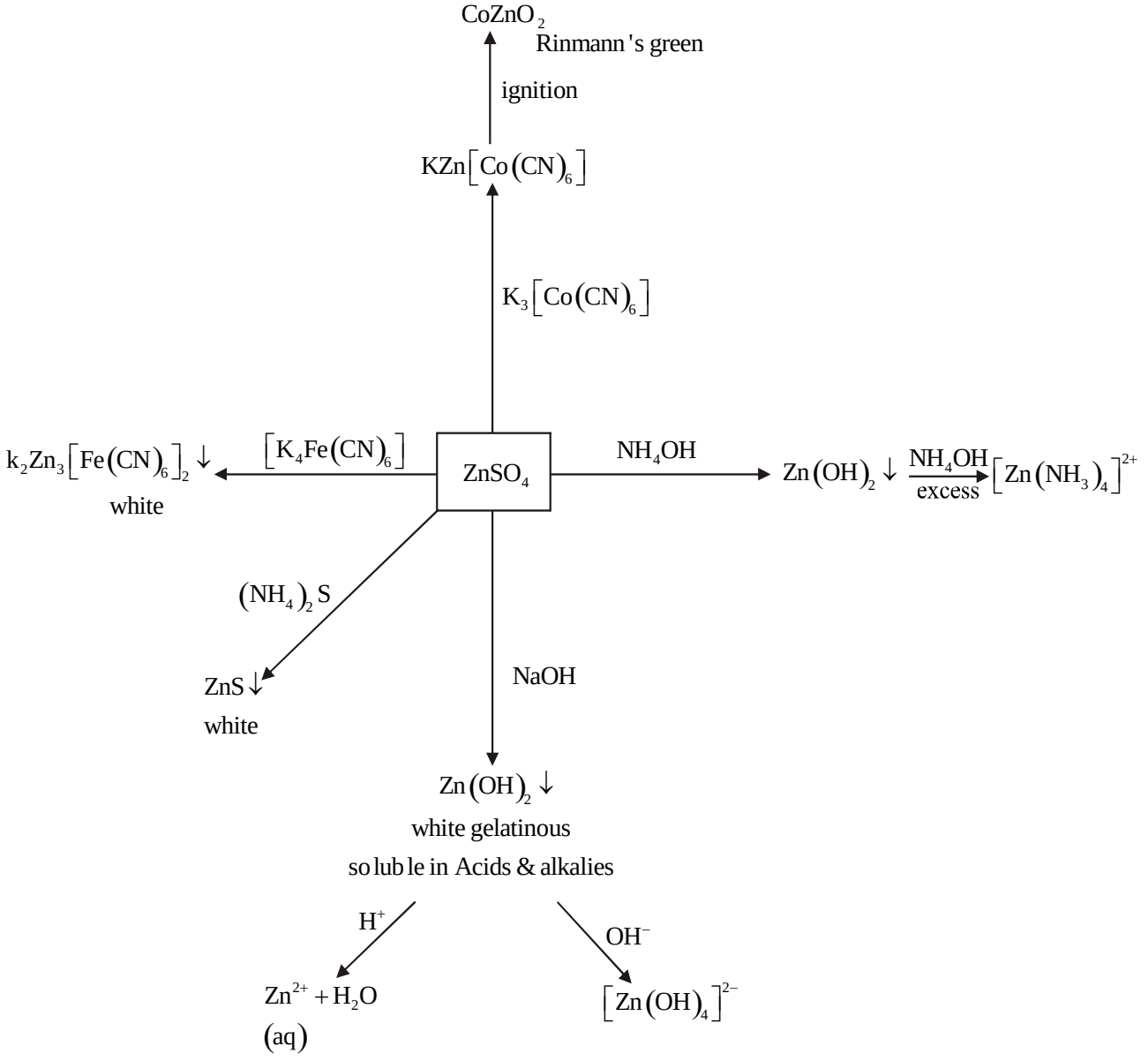
v) $ZnS + 4O_3 \longrightarrow ZnSO_4 + 4O_2$

Properties: white, crystalline, efflorescent solid & soulble in water. It is isomorphous with Epsom salt ($MgSO_4 \cdot 7H_2O$), exists as $[Zn(H_2O)_6]SO_4.H_2O$.

Reactions :

i) $ZnSO_4 \cdot 7H_2O \xrightarrow{39-70°C} ZnSO_4 \cdot 6H_2O \xrightarrow{>70°C} ZnSO_4 \cdot H_2O \xrightarrow{>280°C} ZnSO_4$

$\frac{1}{2}O_2 + SO_2 + ZnO \xleftarrow{>800°C}$



Uses: i) In eye lotion

ii) Lithophone ($ZnS + BaSO_4$) as white pigment

V. POTASSIUM DICHROMATE ($K_2Cr_2O_7$)

Preparation:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{red hot in presence of air}]{1000°–1300°C} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

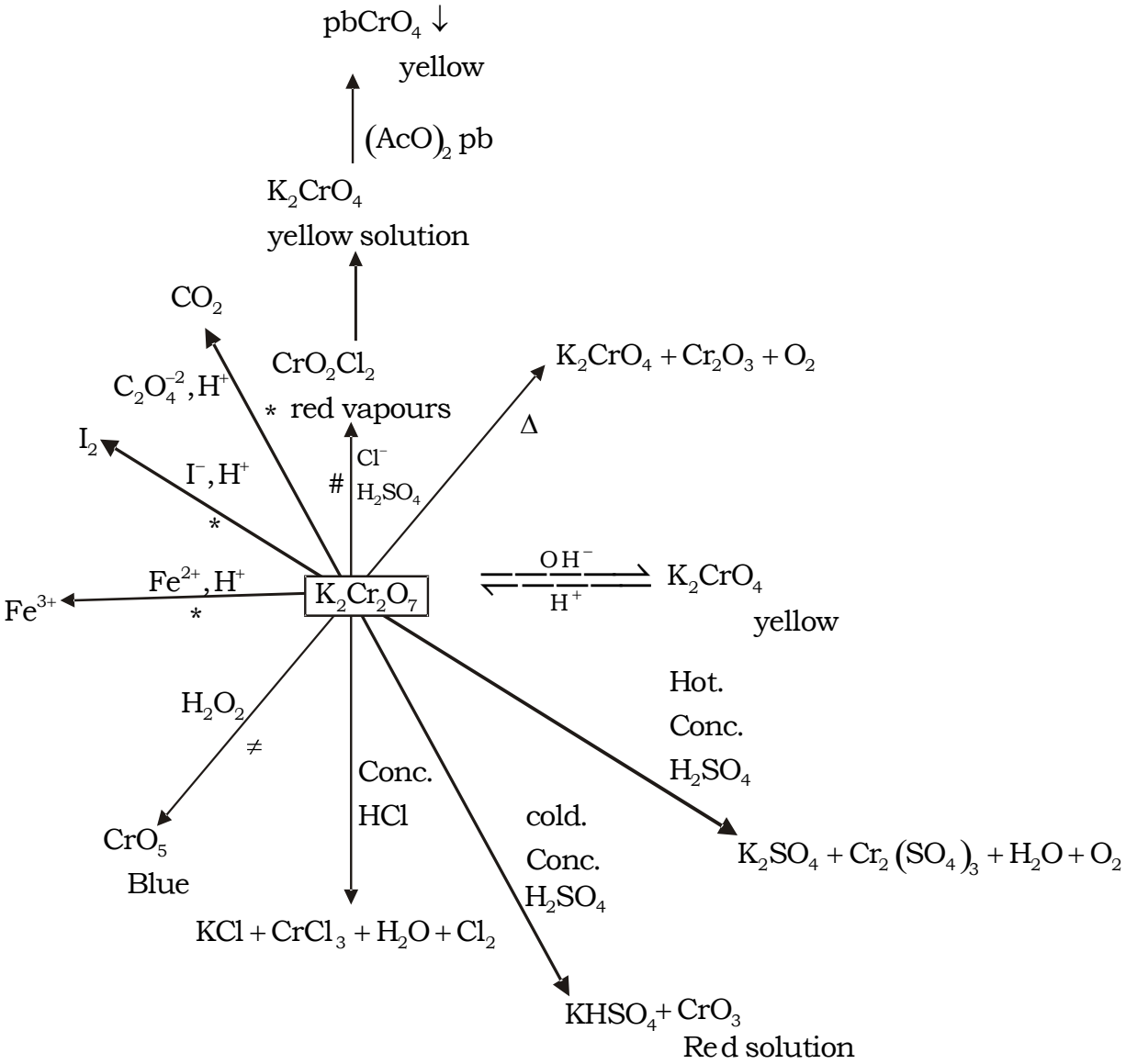
$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2SO_4 + Na_2Cr_2O_7 + H_2O$$

☞ Solubility of Na_2SO_4 increases upto 32°C and then decreases

Hence, suitable temperature is to be employed to crystallise out Na_2SO_4 first. Then $Na_2Cr_2O_7$ is crystallised out as $Na_2Cr_2O_7 \cdot 2H_2O$ on evaporation.

$$\underset{\text{hot conc.}}{Na_2Cr_2O_7} + KCl \xrightarrow[\text{decomposition}]{\text{double}} K_2Cr_2O_7 + 2NaCl$$

NaCl crystallises out first and filtered off. Then $K_2Cr_2O_7$ crystallises out on cooling



Chromyl chloride test: It is given by ionic chlorides which are soluble in water
Eg : $HgCl_2$ does not give this test

* Oxidising properties :

K_2CrO_7 acts as a good oxidant in acidic medium in inorganic and organic reactions.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O; E^o = 1.33V$$

or

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4) + 4H_2O + 3(0)$$

Its n-factor is taken as six as it accepts $6e^-$ (or) produces three nascent oxygens.

≠ Reaction of $K_2Cr_2O_7$ with H_2O_2 gives different products at different p^H values

(i) Acidic condition $\Rightarrow$ $CrO(O_2)_2$ - Chromium diperoxide gives blue colour in ether layer

(ii) neutral condition $\Rightarrow$ $\left[CrO(O_2)OH\right]^-$ diperoxychromate (violet)

(iii) Alkaline solution :

$(NH_4OH) \Rightarrow (NH_4)_3\left[Cr(O_2)_4\right]$

VI. POTASSIUM PERMANGANATE ($KMnO_4$)

Preparation : i) $3K_2MnO_4 + 2H_2SO_4$ ¾® $2KMnO_4 + MnO_2 \downarrow + 2K_2SO_4 + 2H_2O$

ii) $3K_2MnO_4 + 2H_2O + 4CO_2$ ¾® $2KMnO_4 + MnO_2 + 4KHCO_3$

In the above method $\frac{1}{3}$ of Mn is lost as MnO_2 but when oxidised either by Cl_2or by o_3 unwanted MnO_2 does not form.

$_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$

$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$

Properties :

i) MnO_4^- is coloured due to charge-transfer phenomenon (purple colour)

ii) MnO_4^- is unstable in acidic solution

$MnO_4^- + H^+ \longrightarrow MnO_2 + H_2O + O_2$

above reaction is catalysed by sunlight

$\therefore$ It is stored in dark bottles

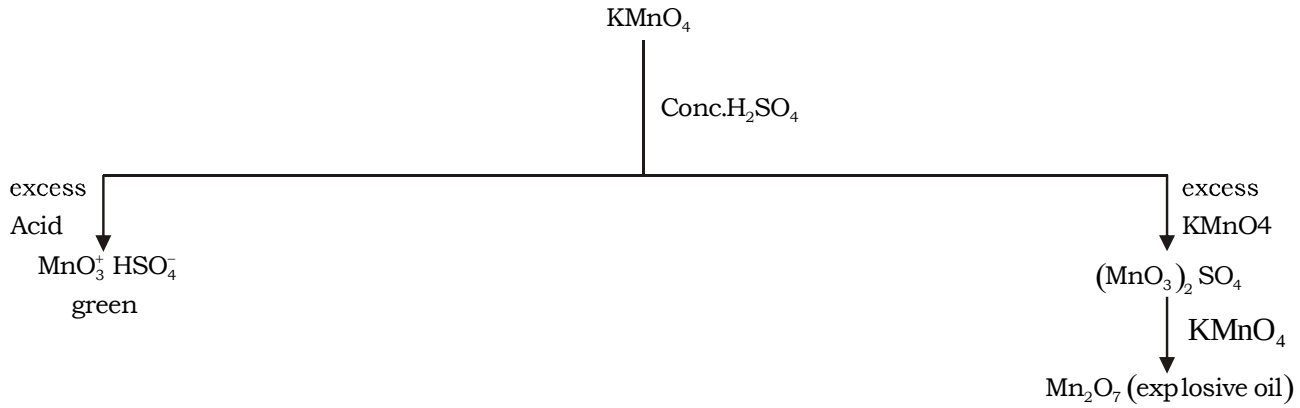
iii) moderately soluble in water

Reactions of $KMnO_4$:

i) Action of Heat :

$KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

ii) Action of conc. H_2SO_4 :

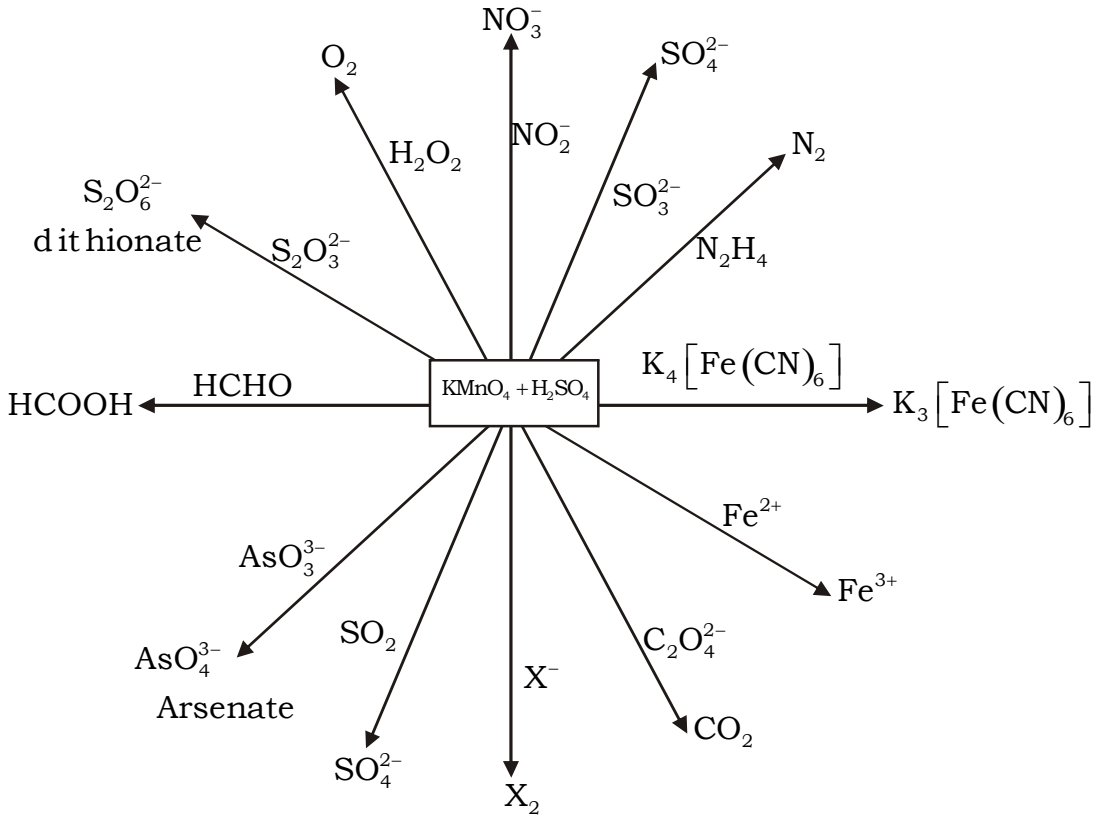


iii) Oxidising properties:

A) In Acidic medium

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(0)$$

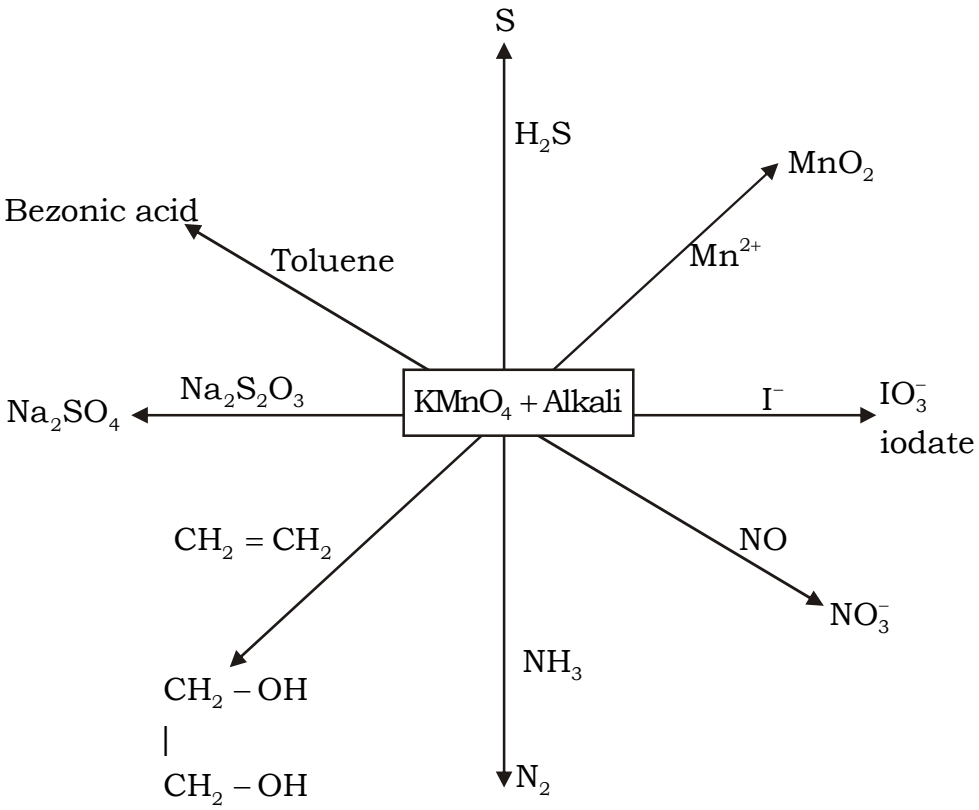
$$MnO_4^1 + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O;\ E^\circ = 1.51V$$



B) In alkaline medium

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-;E = 1.23V$$

* Alkali is formed in the reaction, this makes the medium alkaline even if we start with neutral solution



Uses :

i) Oxidising agent

ii) Alk. $KMnO_4$ (Baeyer's reagent) used in detection of unsaturation.

iii) As an oxidant in Redox titrations.