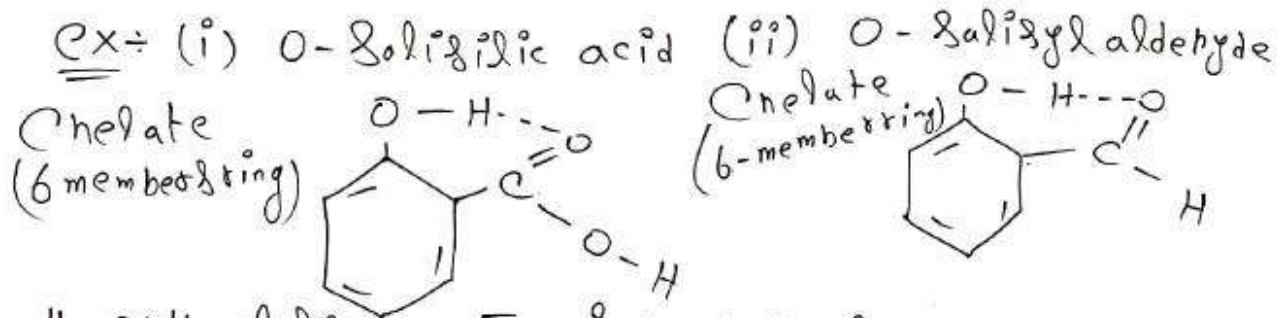


H-Bonding

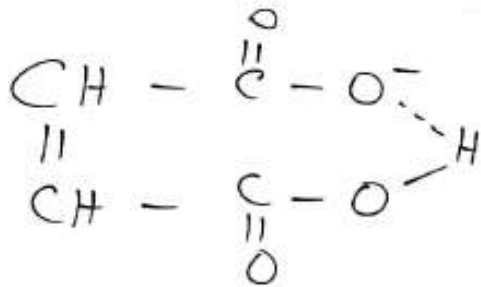
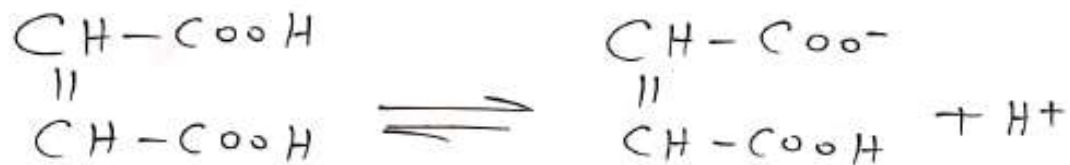
Intramolecular H-bonding



Ortho position \bar{u} intra H-bonding hoti hai.
because distance b/w molecules \bar{u} less.

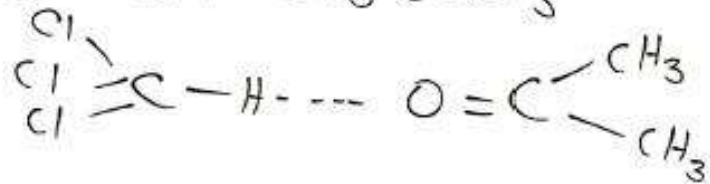
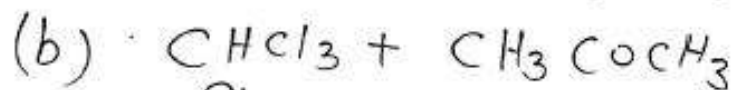
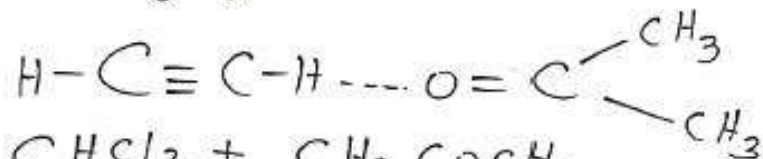
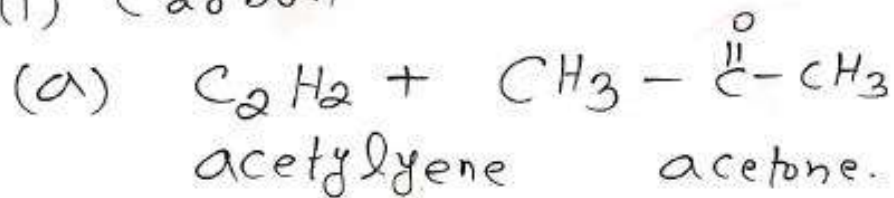
Meta & Para position \bar{u} inter H-bonding hogi.

(iii) Anion of Maleic acid



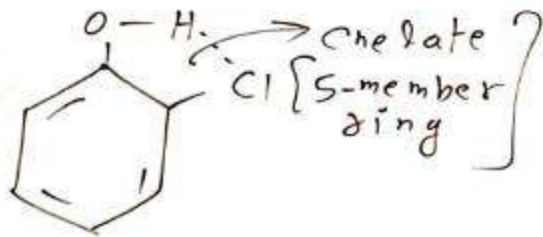
H-bonding in special case

(1) Carbon



(2) Chlorine (usually does not show H-bonding because more size and less charge density)

(a) O-chloro phenol



Strength of H-bonding \div

(1) H-bonds are found to be stronger when F is involve.

(2) But in the case of other atoms O & N.

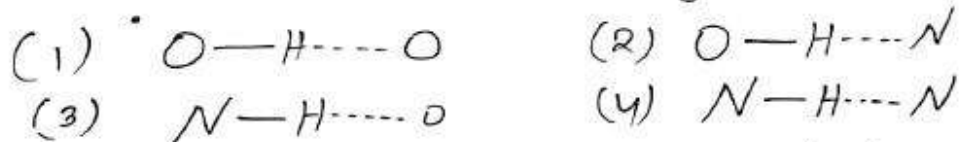
Stronger interaction $\xrightarrow{\alpha}$ A — H — $\xleftarrow{\beta}$ B \leftarrow Poor interaction
 less bond length greater bond length.

(i) $A, B \Rightarrow F$ (more stronger)

(ii) $A \Rightarrow O > N$ } Priority order

(iii) $B \Rightarrow N > O$

Ques. Compare H-bond strength in following -



Sol. (2) > (1) > (4) > (3)

Stronger interaction $A \overset{\alpha}{\downarrow} H \cdots \overset{\beta}{\leftarrow} B$ Poor interaction
 less bond length greater bond length.

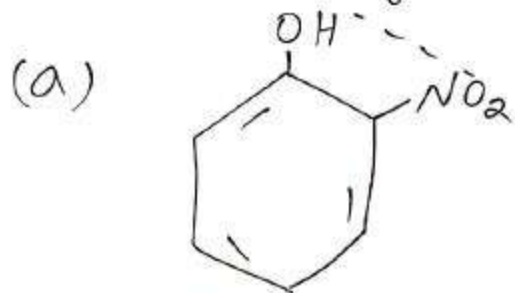
(i) $A, B \Rightarrow F$ (more stronger)

(ii) $A \Rightarrow O > N$ } Priority order
 (iii) $B \Rightarrow N > O$

Applications of H-bonding

Properties	Inter H-bonding (more attraction) m.wt ↑	Intra H-bonding.
(1) Boiling point	↑	↓
(2) melting point	↑	↓
(3) Solubility	↑	↓
(4) Vapour pressure	↓	↑

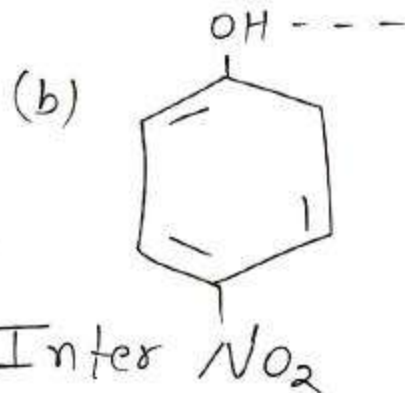
Ques. Compare boiling point and Volatility (v.p.) in following-



Intra

B.P. \div (b) > a

V.P. \div (a) > (b)



Inter NO₂

Vanderwall forces:

(1) Ion-dipole force

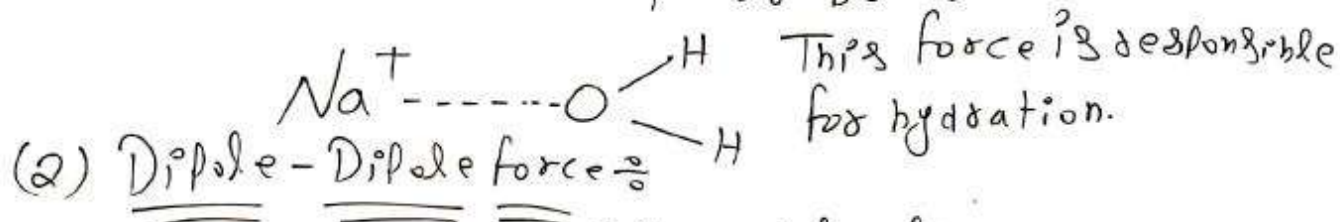
(2) Dipole-Dipole -||-

(3) Ion-Induced dipole -||-

(4) Dipole-Induced dipole -||-

(5) Induced Dipole - Induced dipole -||-

(1) Ion-dipole force \div Exist b/w ion and polar bond.

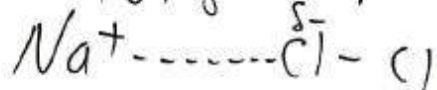


Exist b/w two polar molecule



(3) Ion-Induce dipole force \div

Exist b/w ion & non polar molecule



(4) Dipole - Ion dipole forces

Exist b/w polar & Non-polar molecule.



(5) Induce dipole - Induce dipole forces

Exist b/w two Non-polar molecule.



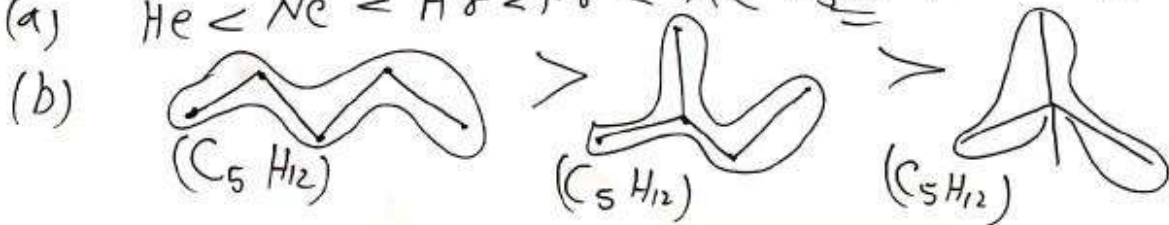
B.P. and m.p. in Covalent Compounds

Two factors (i) H-bonding
(ii) Vanderwall force.

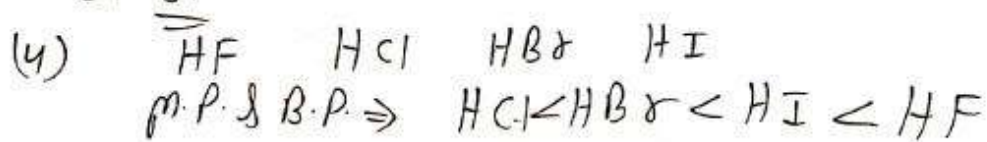
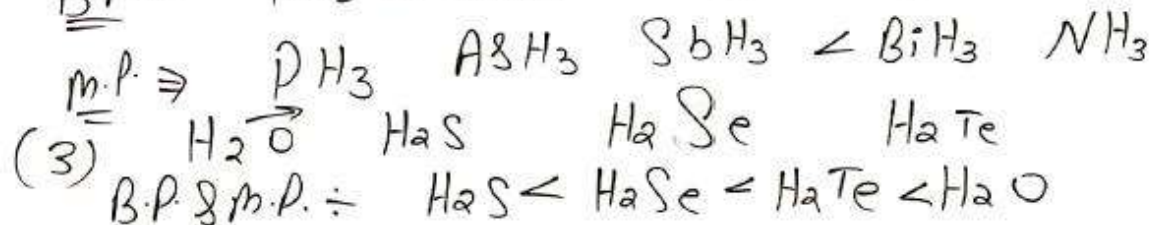
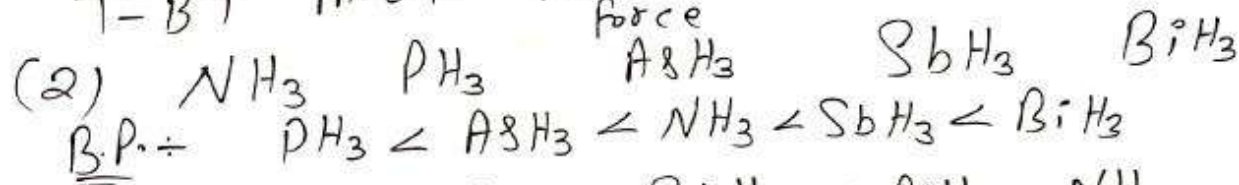
Magnitude of Vanderwall force \propto M.W.

If M.W. is same
Magnitude of Vanderwall force \propto Surface area $\propto \frac{1}{\text{Branching}}$

Ques. Compare B.P.
(a) $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$ sol. m.w. ↑ B.P.



Hydrides of 14th, 15th, 16th & 17th group



1.7.19

Metallurgy

→ Extraction and purification of metals. is k/a^l metallurgy

* Ore → Mineral from which metal can be extracted profitably.

* ~~Geo~~ Minerals → Metal containing compound obtained by mining.

* ~~Geo~~

→ All ores are water insoluble.

* ~~Nitrates~~ ^{salts} do not form water soluble, that is why they do not form ores.

* Generally nitrates do not form ores as they are water soluble.

* Gangue/Matrix - Impurities associated with ore particles.

* Flux - Chemical substance added to remove impurities.

(i) Acidic flux - used for basic impurities.
→ e.g. SiO_2

(ii) Basic flux - used for acidic impurities
→ e.g. CaO , FeO

* Slag → Flux + impurities
Use: → It prevents further oxidation of metals.
Property: → Density ↓, M.P ↓ as compared to metals.

Types of Metallurgy

(i) Pyro Metallurgy
→ Heating effect is used.

(ii) Hydro Metallurgy
Solvent is used.

(iii) Electro metallurgy
Electrolysis is used.

* Imp # Some important ores

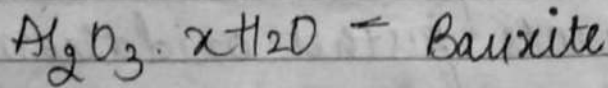
* Cu

- Cu_2O - Cuprite
- Cu_2S - Copper glance
- $CuFeS_2$ - Copper pyrites* (JEE-2019)
- $CuCO_3.Cu(OH)_2$ - Malachite* (NEET-2019)

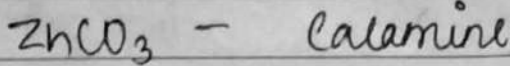
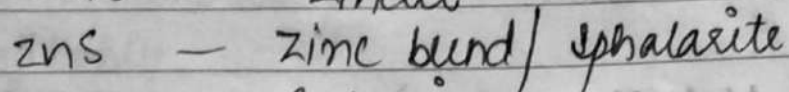
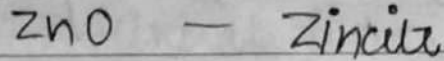
* Fe

- Fe_2O_3 - Haemetite
- Fe_3O_4 - Magnetite
- $FeWO_3$ - Siderite
- FeS_2 - Iron pyrite

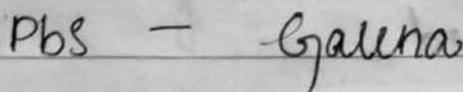
* Al



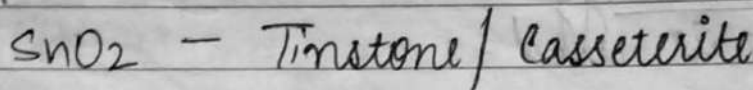
* Zn



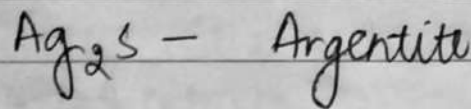
* Pb



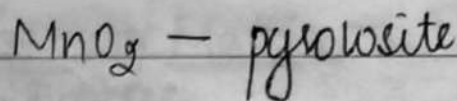
* Sn



* Ag



* Mn



Crushed Ore

Concentration
Dressing

Conc. Ore

→ Gravity separation

→ magnetic separation

→ Froth Flotation
(used for sulphide ores)

→ Leaching
(chemical process)

(used for native ores)

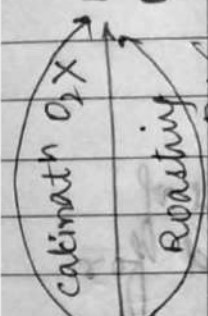
[Eg Al_2O_3 in presence of NaOH
(Hall Heroult process)

→ Froth's process

& Ags in presence of Zn
(Mc Arthur Forest cyanide process)

[Eg Al_2O_3 in presence of NaOH
(Hall Heroult process)

Metal Oxide



Reduction

→ Carbon Fe, Sn, Pb, Zn
Redⁿ

→ Aluminos Cr, Mn, Fe
thermite redⁿ

→ Thermal redⁿ
Ag₂S, HgS

→ self redⁿ
Cu₂S, HgS, PbS

→ HMR (Hydro
metallurgical redⁿ)
→ Mc Arthur
→ Low grade Cu
→ Electrolytic
redⁿ

→ Au s-block
& Al

(impure metal)

→ Liquefaction
Sb, Sn, Pb, Bi

→ Distillation
Zn, Cd, Hg

→ Palling
Ag, Sn, Pb
(impurities of oxides)

→ Cupellation
Ag, Au

→ Zone refining
(semi-conductor)

→ Vapour phase
refining
(Al Back)

→ Electrolytic
Refining

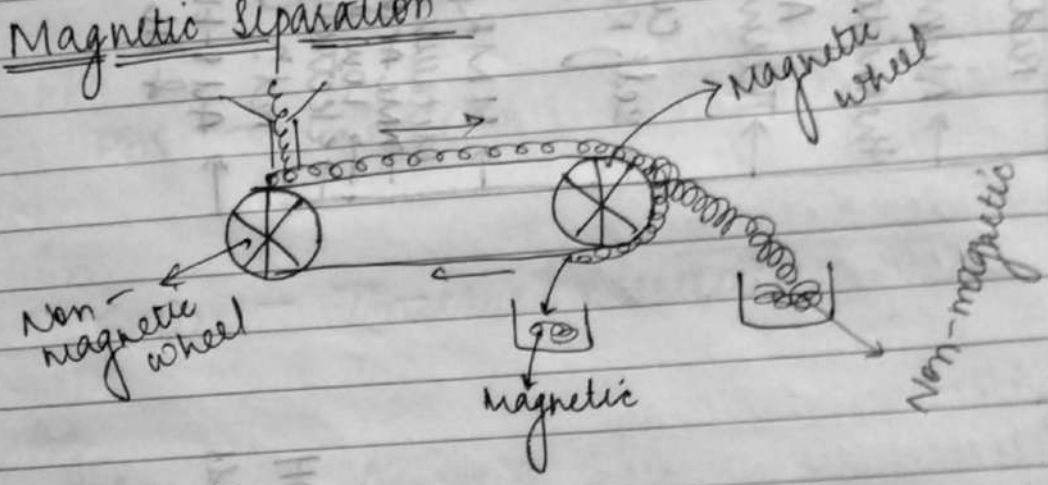
for all metals
(Al, Fe, Zn, Sn, Pb, Ag, Au, Cu)

Date: _____
Page No: _____

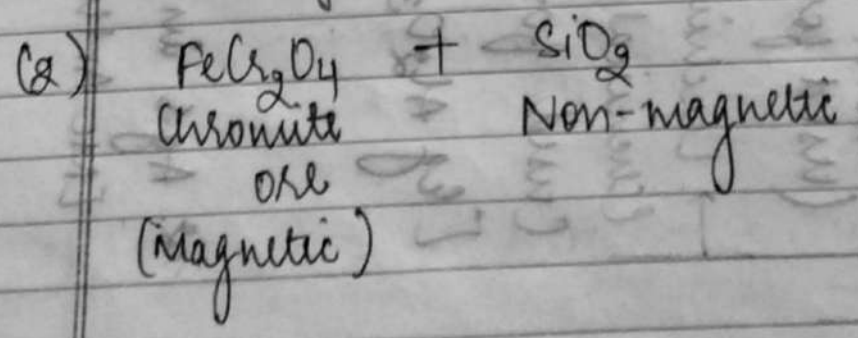
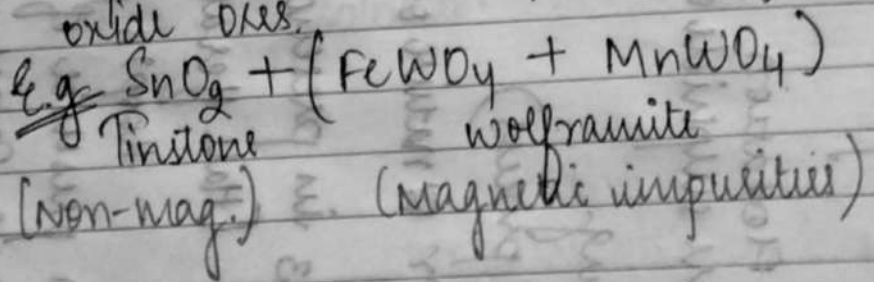
Step-I (A) Concentration/Dressing

(i) Gravity separation/Lavigation/Hydrolic washing
 → It is based on differences in density of ore particles and impurities generally used for oxide ores.

(ii) Magnetic Separation

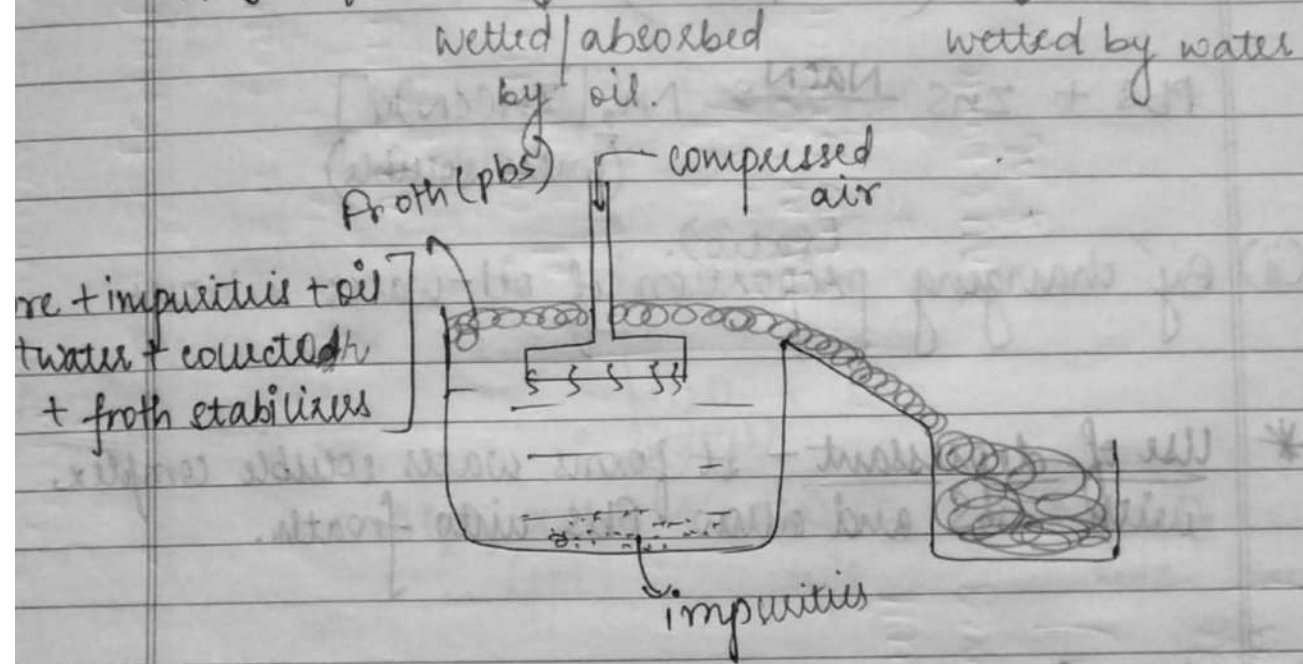


→ It is based on difference in magnetic properties of ore particles and impurities generally used for oxide ores.

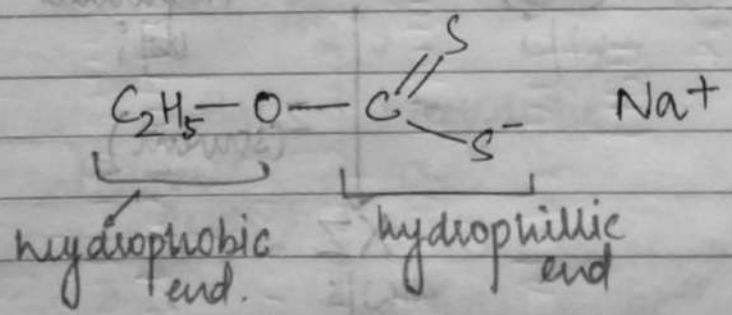


Froth Flotation

- Generally, used for sulphide ores.
- It is based on different ~~absorption~~ adsorption ppty of sulphide ores and gangue.



- oil → Pine oil
- Collector → Sodium ethyl Xanthate



Use of collector - It enhance non-wettability of ore particles with water.

Froth stabilizers - Aniline, cresol.

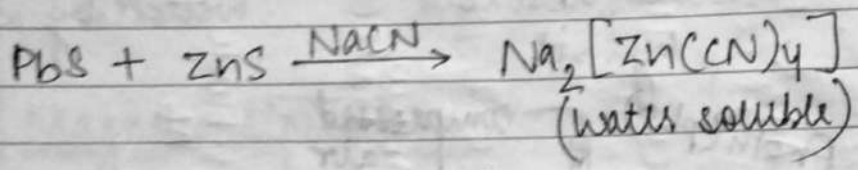
* When Fe_2O_3 is major \rightarrow Bauxite c/d red bauxite.
 (Red)

* When SiO_2 is major \rightarrow White Bauxite.

Date: / /
 Page No.

Separation of two different Sulphide ores

(i) By using Depressant
 \downarrow
 (NaCN / KCN)

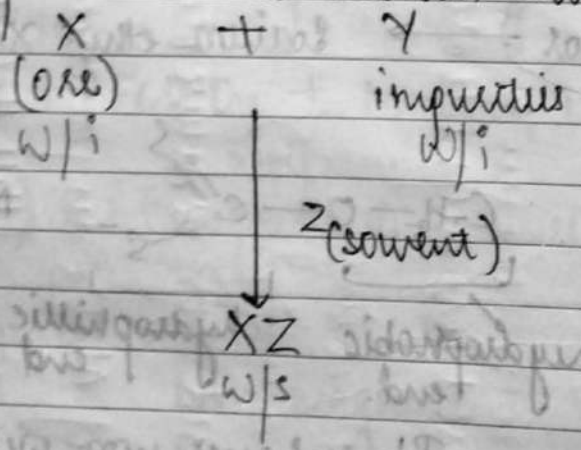


(ii) By changing ^(ratio) proportion of oil-water mixture.

* Use of depressant - It forms water soluble complex with ZnS and allow PbS into froath.

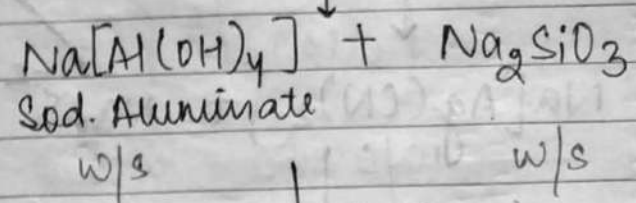
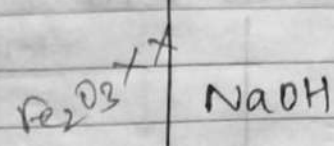
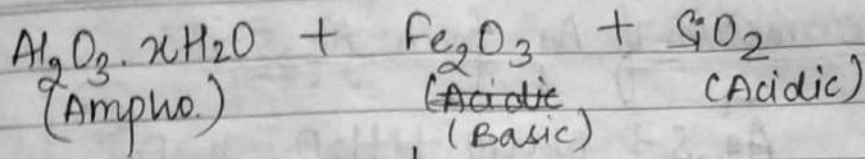
(iv) Leaching

\rightarrow When ore particle is soluble in solvent



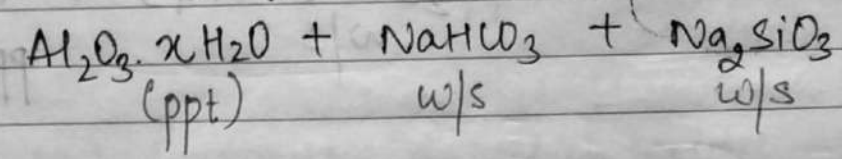
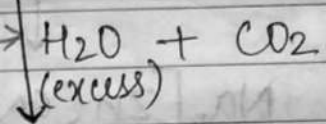
(A) Concn of Bauxite ore

~~Also~~

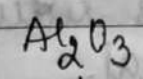
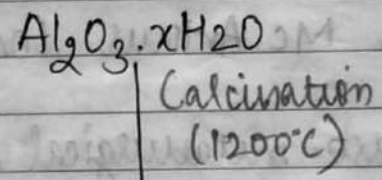


Acidification

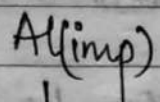
Seeded with freshly prepared Al_2O_3



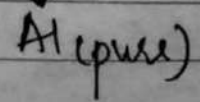
⇒



Hall Herault process | Electrolytic red.

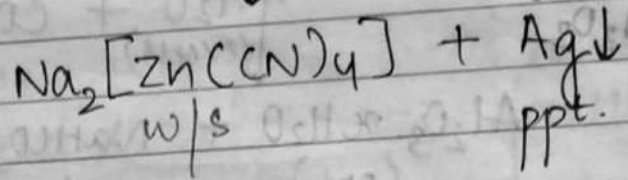
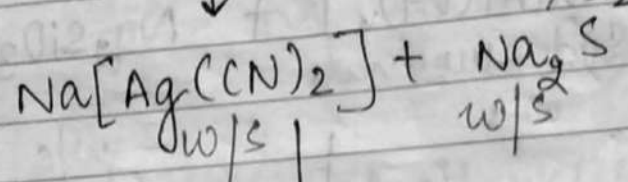
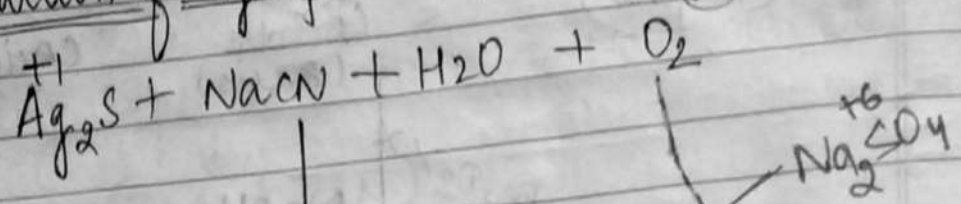


Hoop's Process | Electrolytic Refining

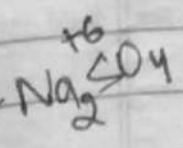


(B)

Extraction of Ag from Ag_2S



(O.A)



Zn (RA)

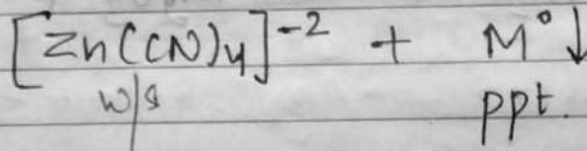
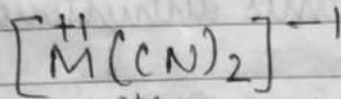
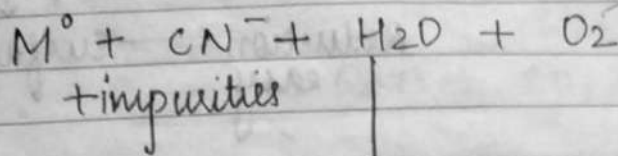
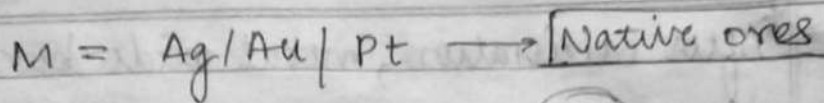
Hydro-metallurgy
HMCR

→ This is k/a Mc. Arthur Forest cyanide process.

→ It is a hydro-metallurgical redⁿ in which less reactive metal is reduced & replaced by more reactive metal.

→ O_2 is used as oxidising agent which convert Na_2S^{-2} to $Na_2SO_4^{+6}$ and prevent reaction from backward direction.

→ This process can also be used for native ores.



Step-I (B) Formation of Metal Oxides

(i) Calcination

→ Heating ore in absence of O_2 (below melting point of metal).

→ Generally used for oxygenated ores

O_2 not in any form

→ Carried out in Reverberatory Furnace.

→ Organic & volatile impurities are removed.

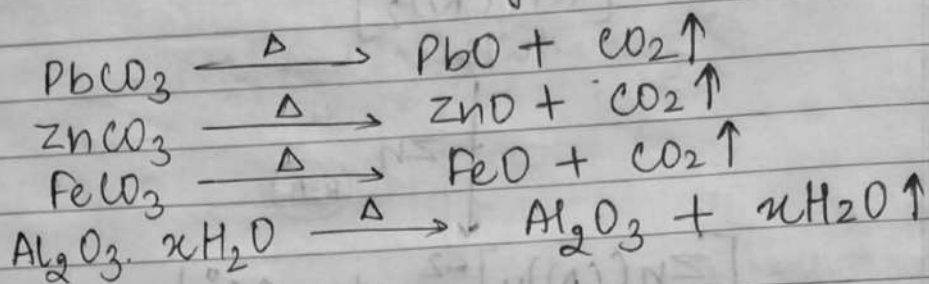
→ Impurities of P, S, and Arsenic are removed in elemental state.

melting point
low
P, S, As
3.5

booz method
metal becomes
more reactive

→ After calcination, metal oxide become porous
 ↓
 Reduction easy ← surface area ↑

→ Hydrated oxes becomes anhydrous.



(ii) Roasting

→ Heating of ore in the presence of O_2 (below the melting point of metals).

→ Generally used for sulphide ores.

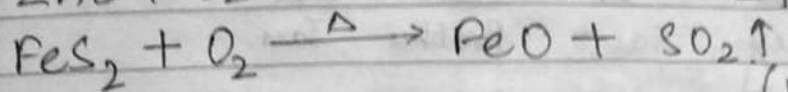
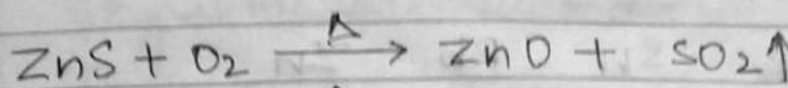
→ Carried out in Reverberatory furnace.

→ Organic & volatile impurities are removed.

→ Impurities of P, S, and As are removed in their oxide forms.

→ After roasting, metal oxide become porous
 ↓

Reduction easy ← surface area ↑



used in
In contact

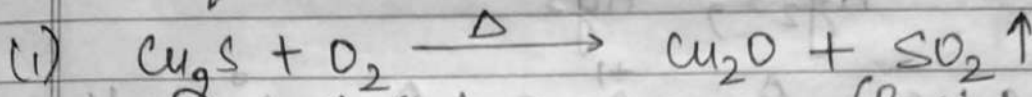
process.

(Formatⁿ of H₂SO₄)

* Partial Roasting

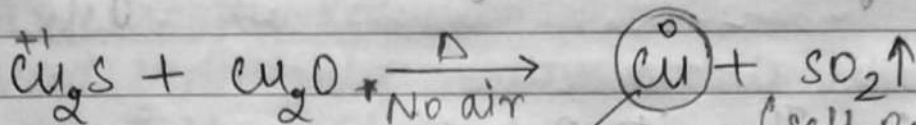
Reductⁿ (Cu₂S, HgS, PbS)

Reductⁿ in the absence of solvent is self Redⁿ.



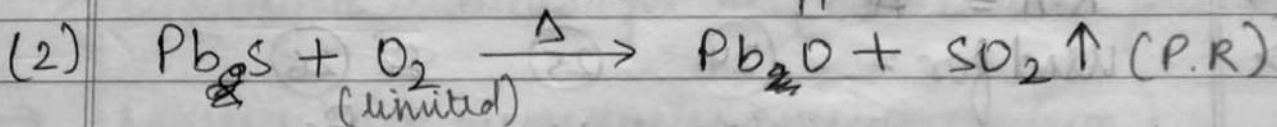
excess A limited

(Partial Roasting)

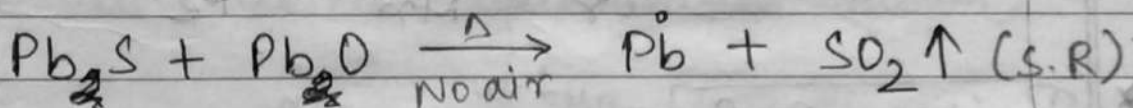


(self Reductⁿ)

98% pure
blistered copper.



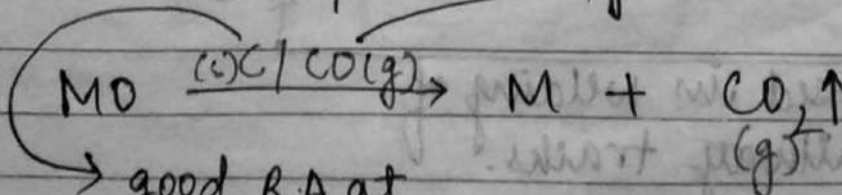
(limited)



Step-II Reduction

(i) Carbon Reduction

R.A \Rightarrow C/CO \rightarrow good R.A at low temp



good R.A at
high temp.

Metals which can be reduced,

Car se Fe Sn Pb Zn
Fisley Sant Prabhu Jan.

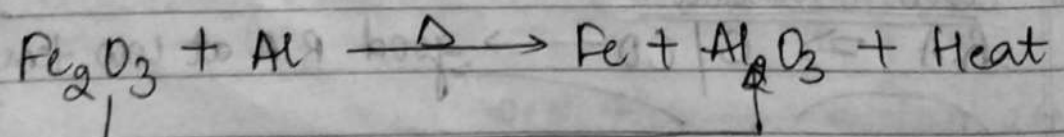
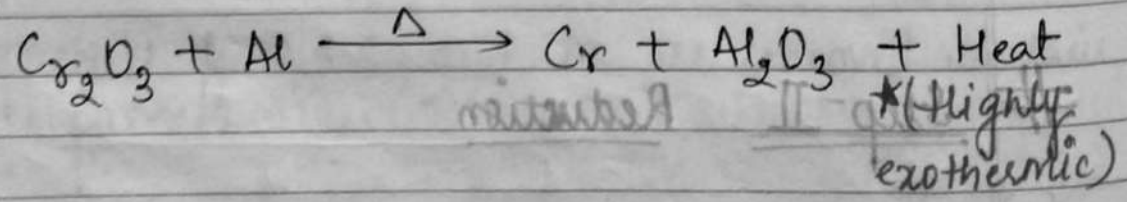
(ii) Self Reduction (cinnabar) *
 Cu_2S, HgS, PbS

(iii) Thermal Reduction
 Ag_2S, HgS
 $Ag_2S \xrightarrow{\Delta} Ag_2O \xrightarrow{\Delta} Ag + \frac{1}{2}O_2$

(iv) Alumino Thermite Reduction
→ Gold smith Alumino Thermite Reduction.
→ R.A = Al.

→ Used for = $\textcircled{24}$ $\textcircled{25}$ $\textcircled{26}$
Cr Mn Fe

* Ignitor = BaO_2 → used to initiate the rxn.



* used in welding of railway tracks.

* M.P of $Al_2O_3 = 2200^\circ C$ (approx)

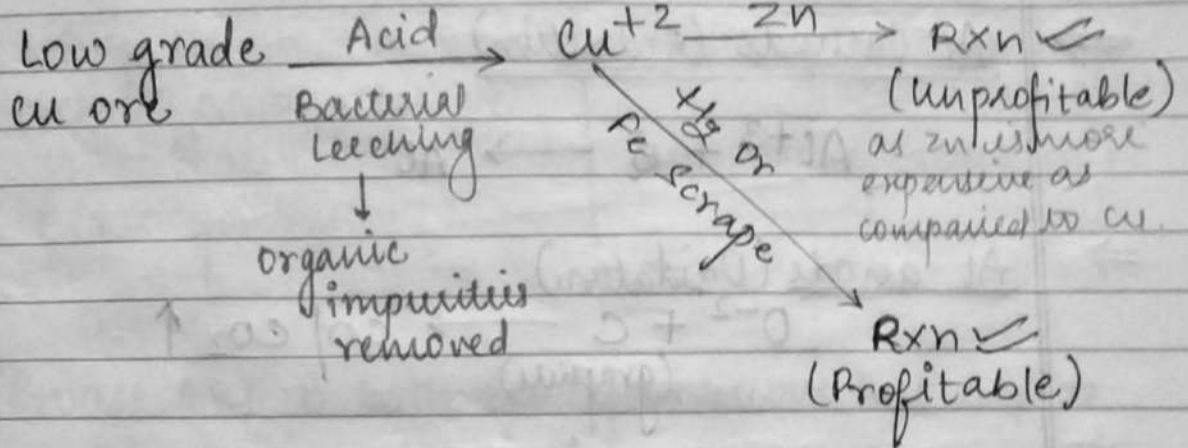
Date: / /

Page No.

(V) HMR - Hydrometallurgical Reduction.

E.g. (i) Mc. Arthur Forest.

(2)



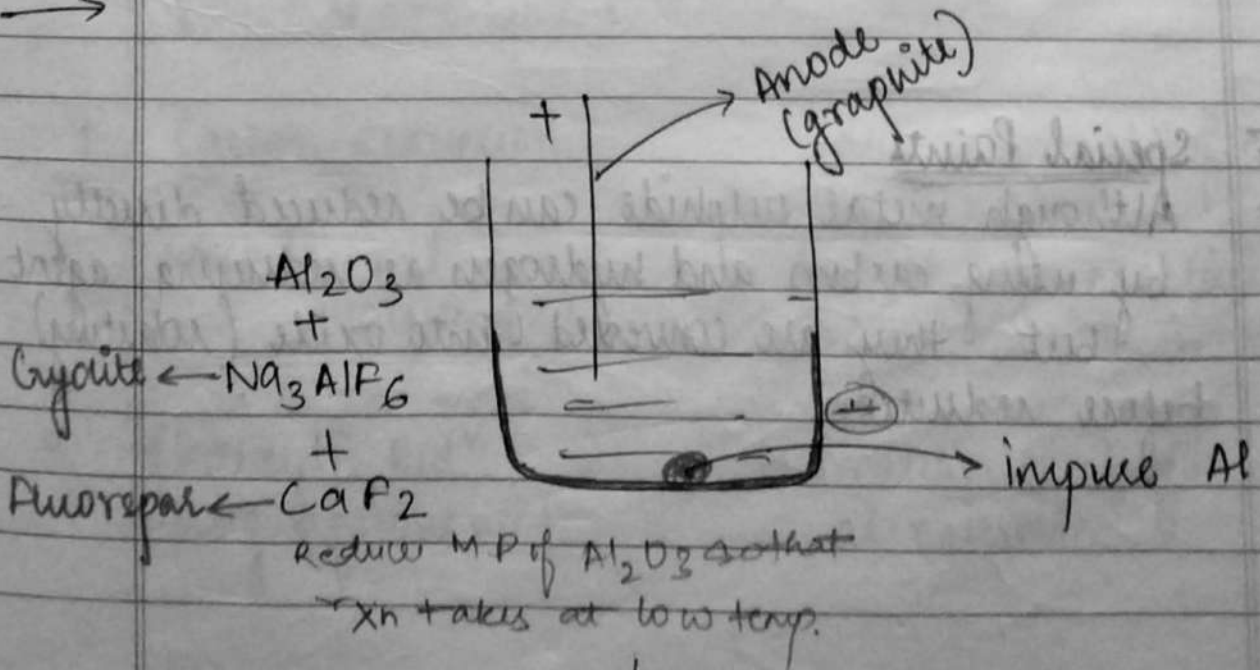
(vi) Electrolytic Reduction

\rightarrow Used for highly reactive metals like s-block and Al.

\rightarrow Electrolytic reduction for Al. (Hall Herault process)

\rightarrow Molten salt electrolysis (~~aqueous medium~~)

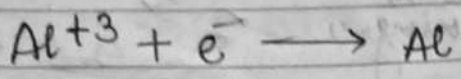
\rightarrow



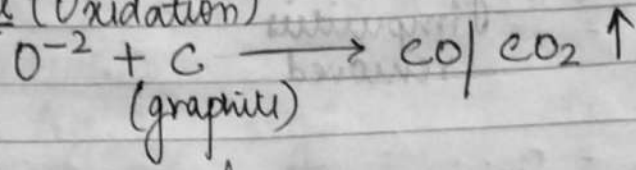
Use:-

- * Cryolite } * M.P of Al_2O_3 ↓
- * Fluorspar } * conductance ↑

⇒ At Cathode (Reduction)



⇒ At anode (Oxidation)



→ Anode gets ^{degraded} due to formation of CO & CO₂, so, it should be changed after regular intervals.

⇒ Total Reaction



(R.A) X X
(Anode)

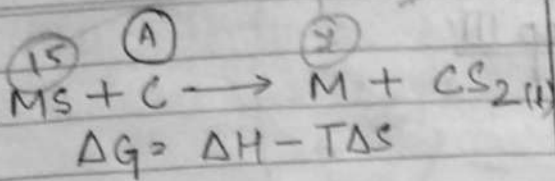
Special Points

→ Although metal sulphide can be reduced directly by using carbon and hydrogen as reducing agent but they are converted into oxide (roasting) before reduction.

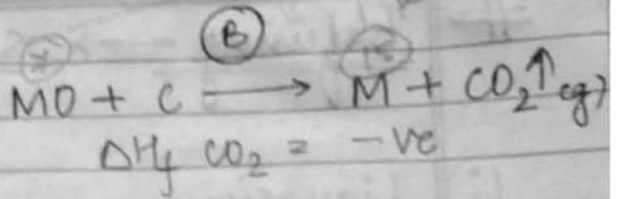
* If aqueous medium not in redn or refining, then
 ↓ H or S-block elements cannot be extracted.

Date: _____
 Page No. _____

* Reduction can



$\Delta H_f CS_2 = +ve$
 Overall ΔG_f less -ve
 of CS_2 (less stable)
 (Less spontaneous)



Overall $\Delta G_f =$ More -ve
 of CO_2 (more stable)
 (More spontaneous)

* Process A & B both are spontaneous but ΔG_f is
 more -ve in case of B

→ * ΔG_f of metal sulphide can^{not} be overcome by
 ΔG_f of H_2S & CS_2 .

→ Metal oxides are less stable than metal sulphides.

** TRICK

Process not used
 for Al & S-block

Reason

1. Carbon Reduction

due to formatⁿ of carbide

2. HMR (Metal displacement)

due to high reactivity
 (Al & S-block elements stable
 zada reactive)

3. Electrolytic Redⁿ
 using aqueous med^m

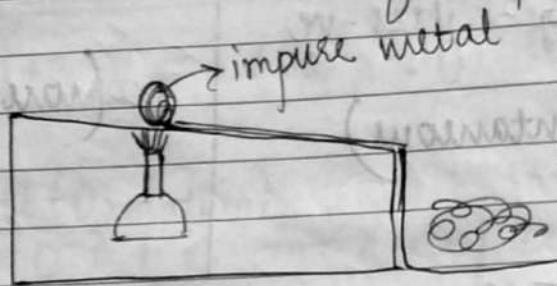
Formation of H_2 gas
 at cathode.

(Purification)

Refining → Step III

(i) Liquation

→ M.P of metal < M.P of impurities so metals convert into liq. & gets collected



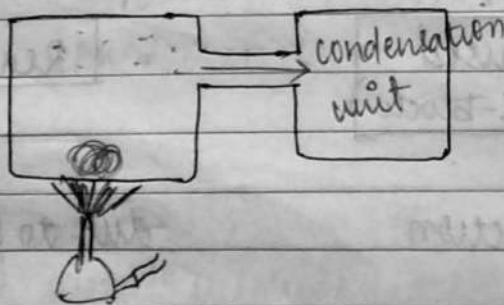
* Liquid like

Sb Sb Pb Bi
sabhi sant Prabhu Bigde

(ii) Distillation

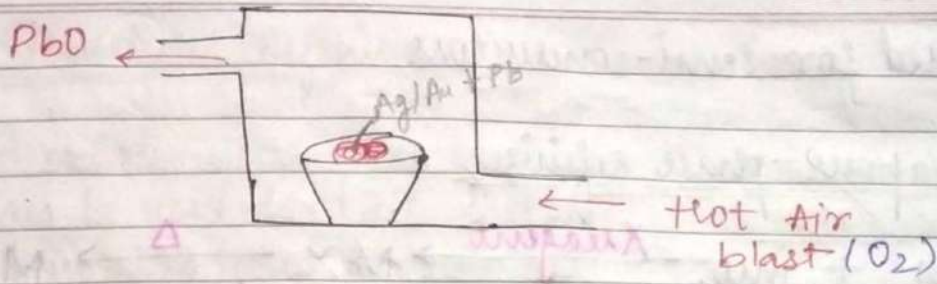
→ B.P of metal < B.P of impurities

→ Zn, Cd, Hg



(iii) Cupellation (NCERT X X)

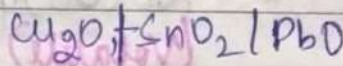
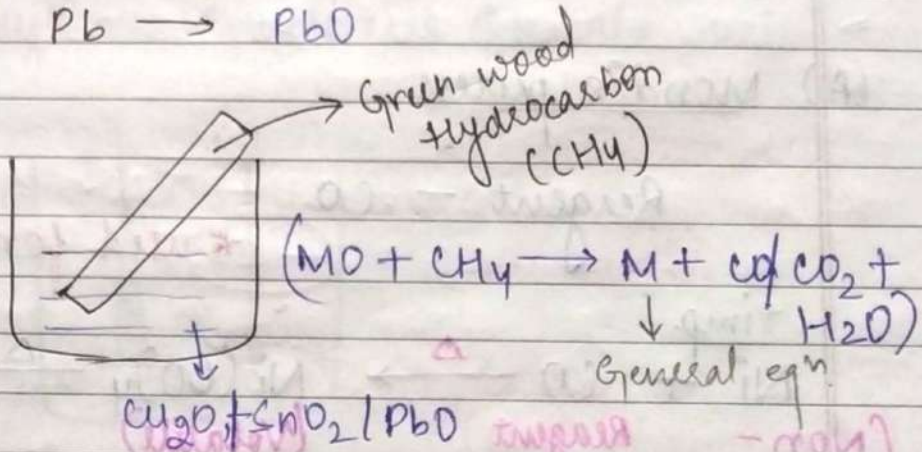
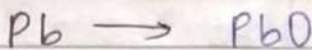
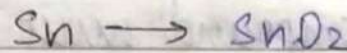
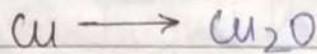
→ Removal of lead impurity from Ag & Au.



(iv) Poling (NCERT XX)

→ It is used when metal contains impurities of its own oxides.

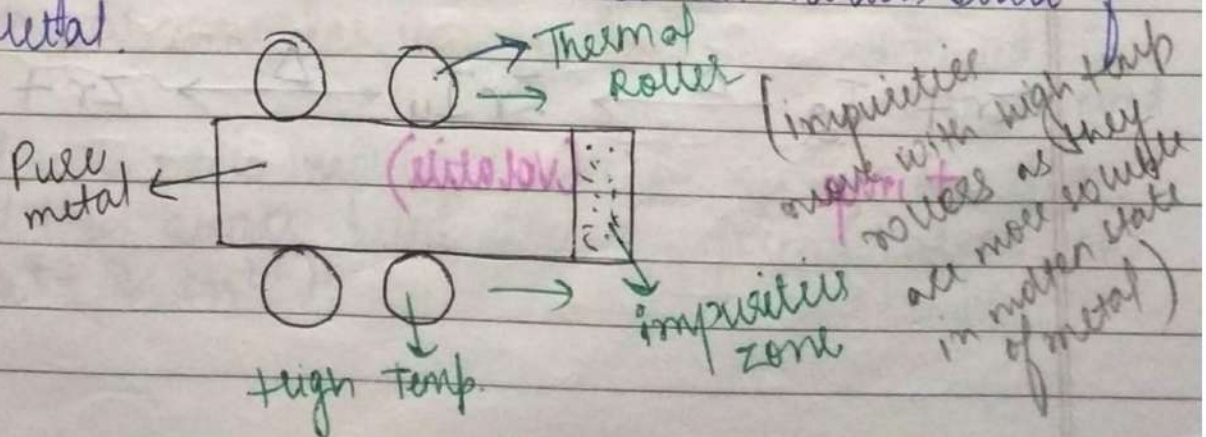
Volatiles impurities are removed by itself *



volatile nature wali impurities udh jayegi baki scumming process se remove hogi.

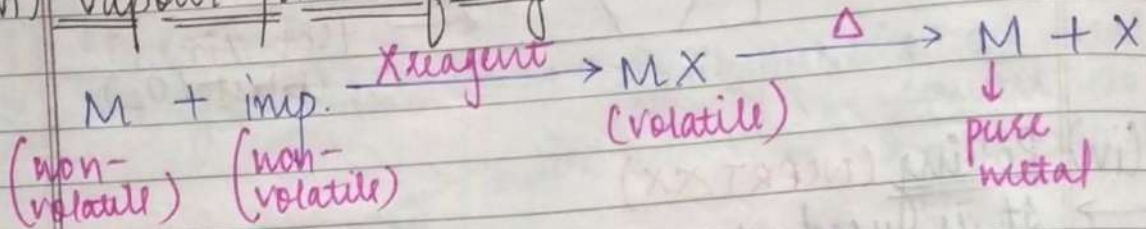
(v) Zone Refining

→ Impurities are more soluble in molten state of metal.



→ Used for semi-conductors.

(vi) Vapour-phase refining



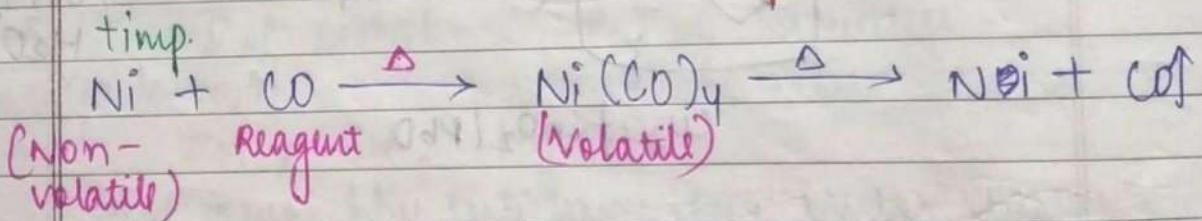
→ Reagent should form volatile compound with metal.

→ Formed volatile compound must be decomposable.

(A) Mond's process

Reagent - CO

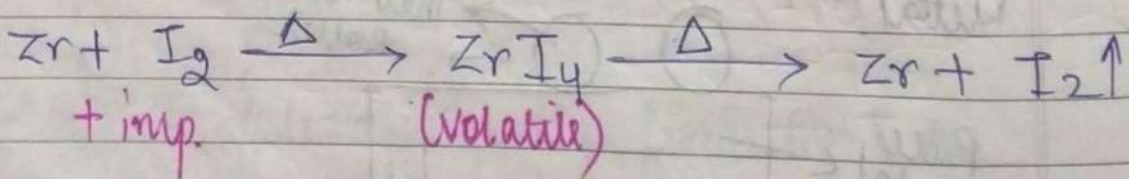
* used for Ni



(B) Van arkel

→ Reagent → I₂

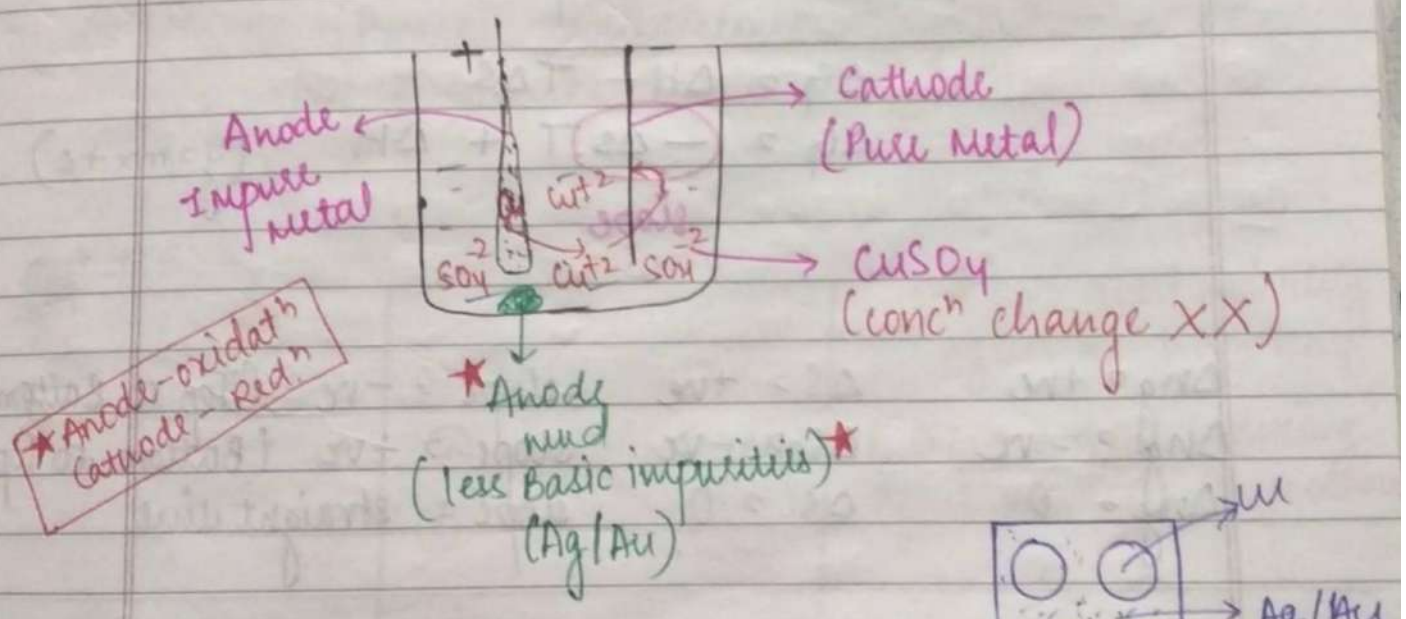
→ Ti, Zr, Hf



(vii) Electrolytic Refining

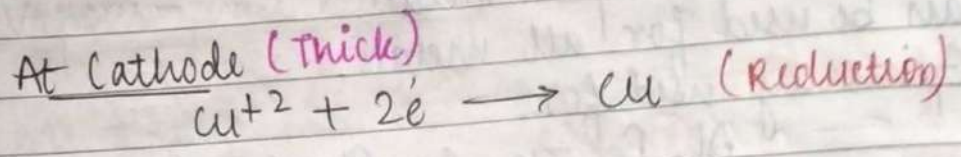
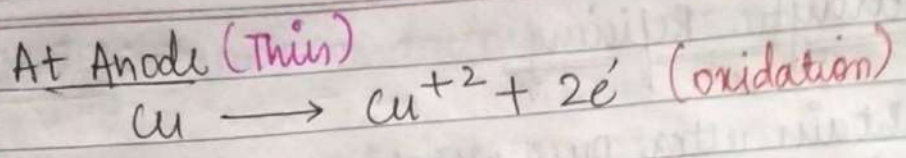
- To obtain ultra pure metals.
- Can be used for all metals.
- Generally used for:
Al, Fe, Zn, Sn, Pb, Ag, Au, Cu.

⇒ Electrolytic refining of Cu *(impurities)* #
 Anode - impure metal
 Cathode - metal
 Electrolyte - soluble salt of metal.



* Anode mud is formed as Ag/Au does not come as ions in solⁿ.

⇒ If more basic impurities like Fe & Zn are there then anode mud does not form. (but as ions Fe⁺² & Zn⁺²)

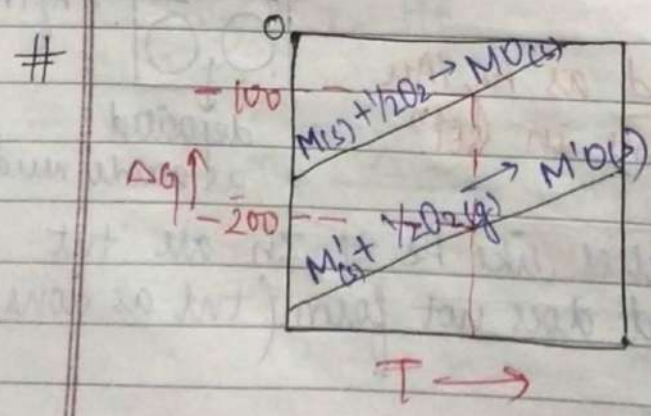


Ellingham diagram (Graph में नीचे आने वाले Metals upper wall metals ko reduce kar sakte hai kuki more reactive metals are placed downward in graph)

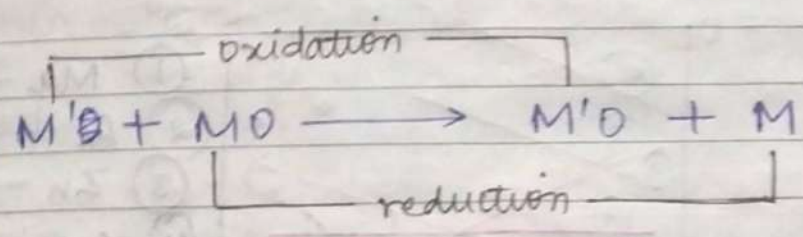
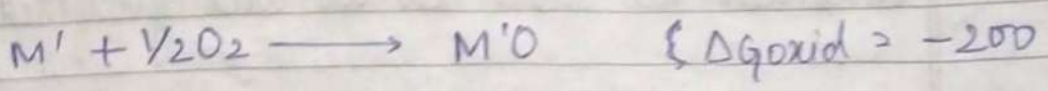
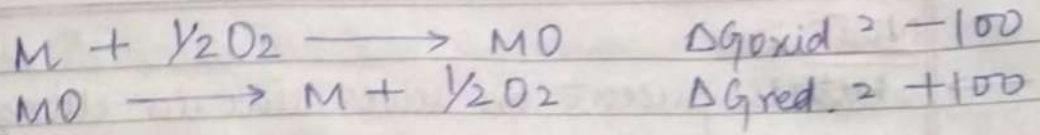
- Curve of metal oxide formation.
- Curve b/w ΔG and Temp.

$\Delta G = \Delta H - T\Delta S$
 $\Delta G = -\Delta S \cdot T + \Delta H$ (y = mx + c)
 slope

$\Delta G = +ve$	$\Delta S = +ve$	slope = -ve (Top to Bottom)
$\Delta G = -ve$	$\Delta S = -ve$	slope = +ve (Bottom to Top)
$\Delta G = 0$	$\Delta S = 0$	slope = straight line



$\Delta H = -ve$, $\Delta S = -ve$
 slope = +ve
 (B → T)



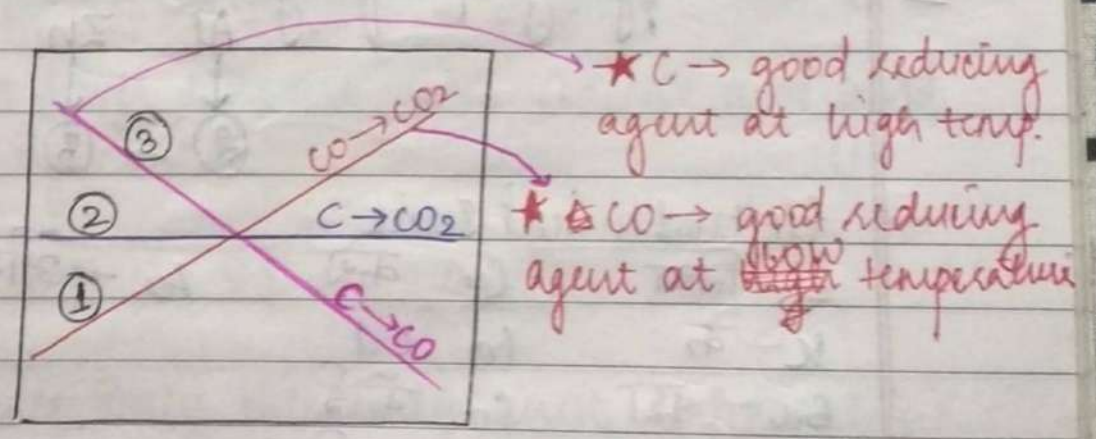
$$\Delta G_{overall} = \Delta G_{oxid} + \Delta G_{red}$$

$$= -200 + 100$$

$$= \boxed{-100}$$

∴ Process spontaneous
~~M'~~ M' can reduce MO

~~Ans~~ #

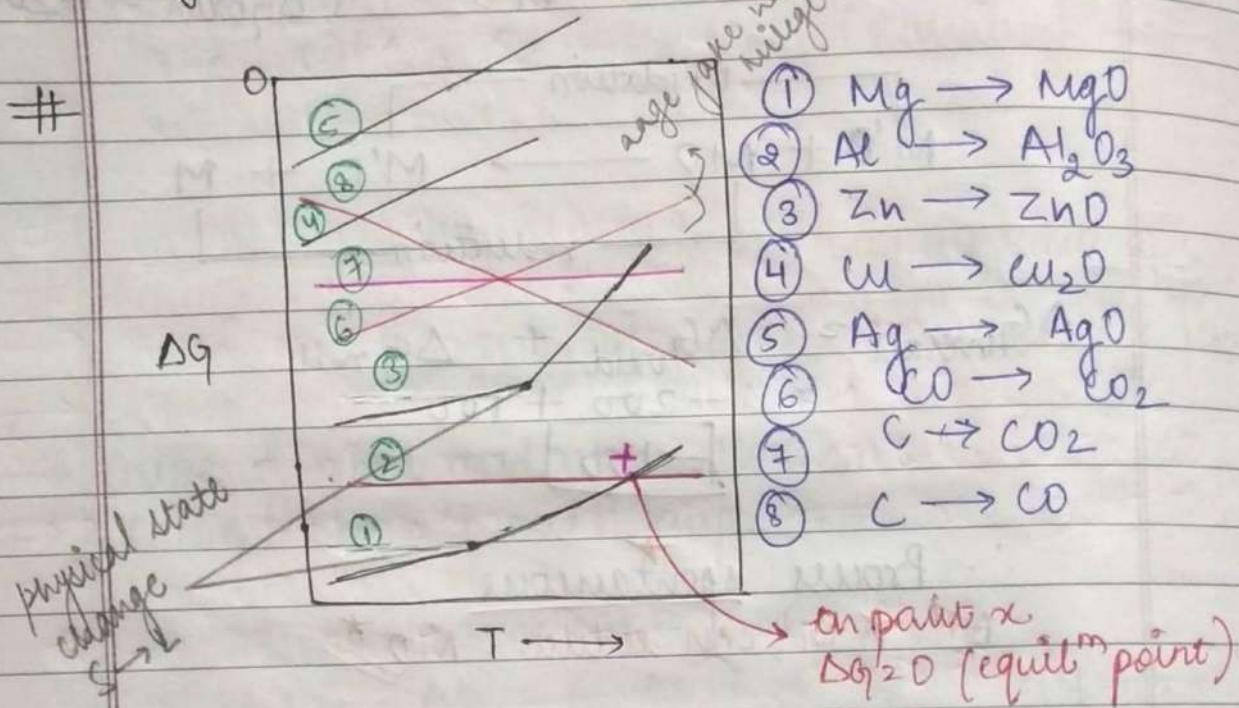


Ans Identify graph ①, ② & ③ from given reactions.

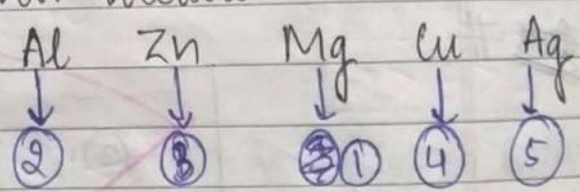
- (A) $C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H_g = 0 \longrightarrow \textcircled{2}$
 - (B) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \quad \Delta H_g = +ve \longrightarrow \textcircled{3}$
 - (C) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H_g = -ve \longrightarrow \textcircled{1}$
- slope = st. line
 slope = -ve
 slope = +ve

NOTE :->

Metals present on lower line in Ellingham diagram are more reactive and good reducing agents.



Ques) Identify graph for given metals:-



Electrochemical series

Li - लिख	Cr - करे	Au - और
K - के	Cd - कद	
Ba - बडा	Co - कोई	
Sr - सरकार	Ni - नी	
Ca - का	Sn - सुन्ता	
Na - नाम	Pb - पंजाब	
Mg - Maggie	H - भरियाणा से	
Al - Aaloo	Cu - क्यु	
Mn - मन मे	Ag - आज	
Zn - जान से	Hg - होगी	
Pb - पेका	Pt - पियई	

- (2) Can Al_2O_3 be reduced by Mg - Yes (Below X)
- (3) Can MgO be reduced by Al - Yes (Above X MgO can be reduced by Al)
- (4) Can ZnO be reduced by C - Yes (at very high temp.)
- (5) Can ZnO be reduced by CO - Never
- (6) Can Cu_2O be reduced by C - Yes (very easily)
- ★ $Ag_2O \rightarrow$ reduction is spontaneous as ΔG (+ve) for
 \downarrow
 ΔG (-ve)
 \downarrow
 spontaneous
 \therefore Oxidation \rightarrow non-spontaneous

Some important points about E.D

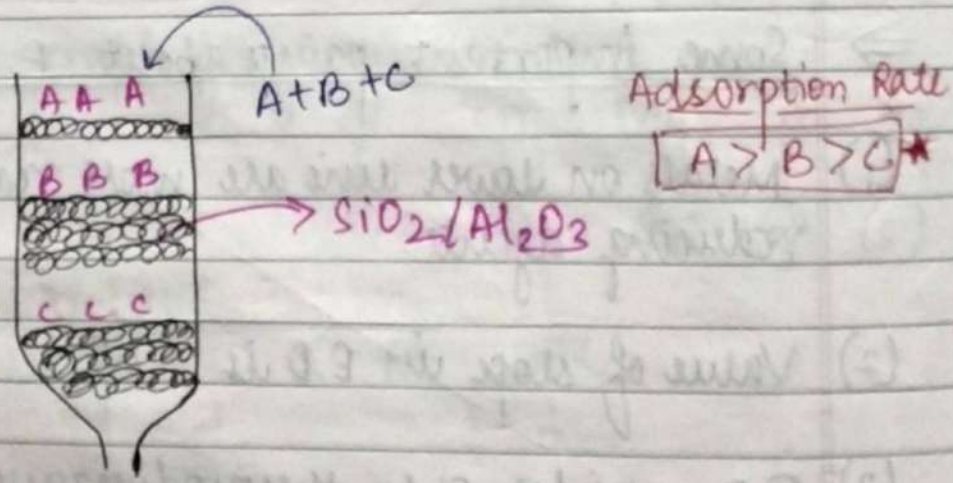
- (1) Metals on lower line are more reactive and good reducing agents.
- (2) Value of slope in E.D is $-\Delta S$.
- (3) E.D provides only thermodynamic information. not ~~dynamic~~ kinetics.
- (4) Carbon is good reducing agent in lower part of blast furnace, while CO is good reducing agent in ~~low~~ upper part (C good reducing at high temp, CO good reducing at low temp)

(5) ED can also be plotted for metal sulphide and metal halides.

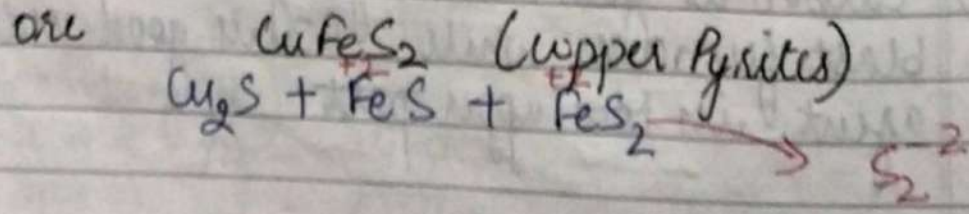
(6) ΔG_f° of metal sulphide cannot overcome by ΔG_f° of CS_2 & H_2S .

Chromatography (Refining process)

- Based on different adsorption rate.
- It is used when minute quantity of sample is available and impurities have very less difference in chemical props. from the element to be purified.
- ★ Adsorbant used - SiO_2 & Al_2O_3 .

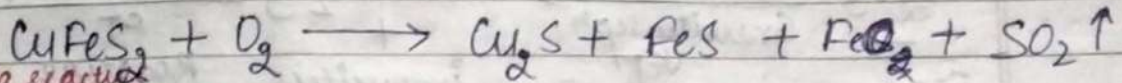


Individual Metallurgy of Cu

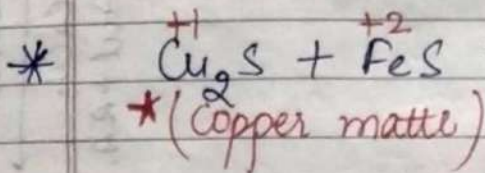
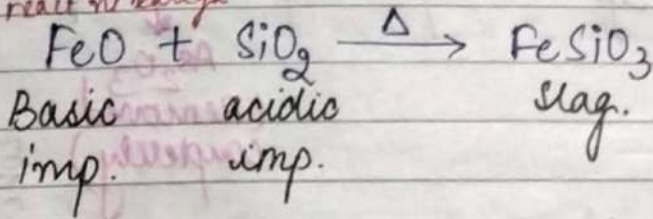


Concentration - By Froth Flotation

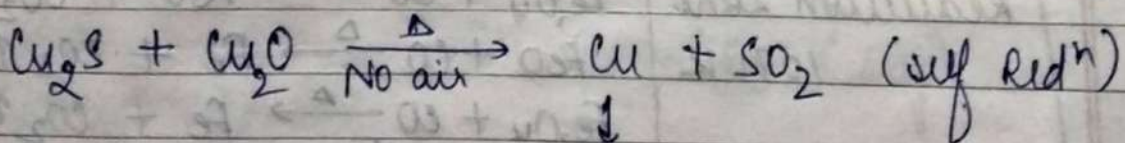
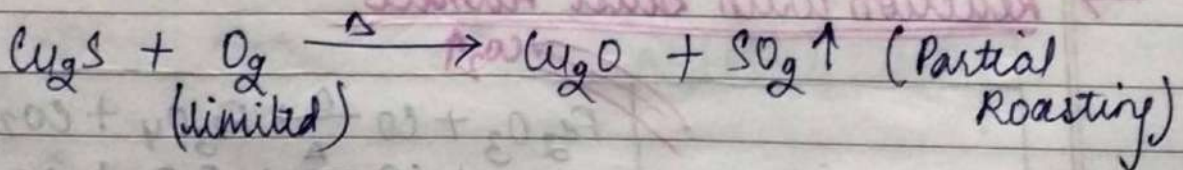
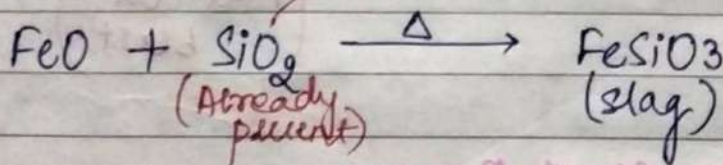
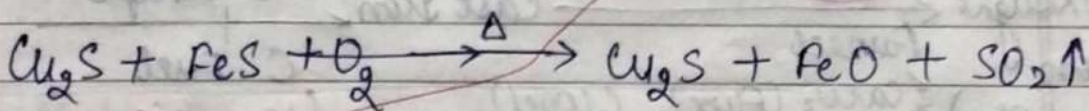
Roasting with smelting (in Reverberatory Furnace)



Iron gets oxidised
to Cu react ni karega



→ Bessemerisation
in Bessemer converter
* Modified Reverberatory
* SiO_2 lined
(Silica)

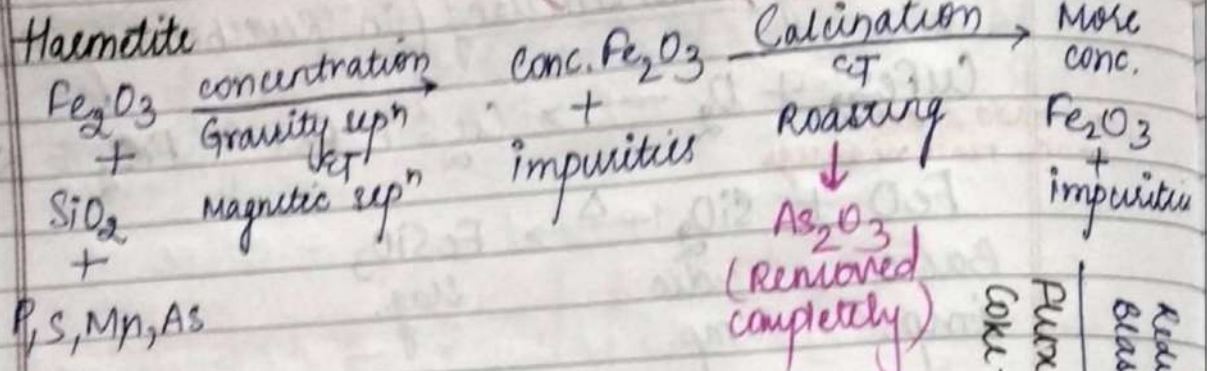


98% pure
For more purely
electrolytic
refining

Individual Metallurgy of Fe

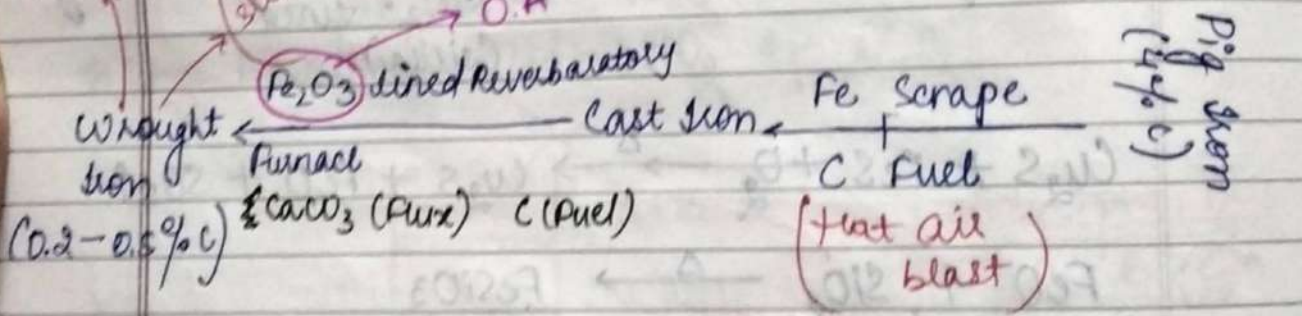
(In Reverberatory)

moisture & volatile impurity removed



Reductⁿ in Blast Furnace
 Pure $\rightarrow CaCO_3$
 Coke \rightarrow Pur + R.A.

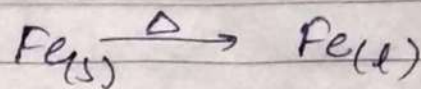
* Purest form of iron
 (steel / stainless steel formed from this)



Reaction with Blast Furnace

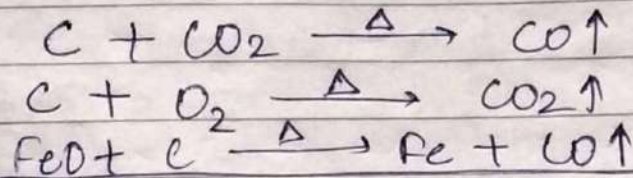
Reduction zone 1070 K	$Fe_2O_3 + CO \xrightarrow{\Delta} Fe_3O_4 + CO_2 \uparrow$
	$Fe_3O_4 + CO \xrightarrow{\Delta} FeO + CO_2 \uparrow$
	$FeO + CO \xrightarrow{\Delta} Fe + CO_2 \uparrow$
	$Fe_3O_4 + CO \xrightarrow[\text{excess}]{\Delta} Fe + CO_2 \uparrow$
slag zone 1270 K	$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$
	$CaO + SiO_2 \xrightarrow{\Delta} CaSiO_3$ Purx imp. slag

Fusion zone
1570K



Combustion
zone

2170K



* Cast Iron $\xrightarrow{\text{Riverbatory Furnace}}$ Wrought Iron
* Fe_2O_3 lined
work as O.A.

