# METALLURGY

**Mineral** → Naturally occuring chemical substance, which contain some % of metal in it.

**Ore** → Minerals from which, metal can be extracted profitably/economically.

**Gangue (matrix)** → Non-metallic impurities (clay, sand, quartz).

**Flux** → Additional substance added to ore to remove infusible impurity.

**Slag** → It is lighter than metal, and hence floats over metal.
It prevents further oxidation of liquid metal.

## Ores →

### ① Sulphide Ore →
- Iron pyrite – $FeS_2$
- Copper pyrite – $CuFeS_2$
- Silver glance – $Ag_2S$
- Copper glance – $Cu_2S$
- Zinc blende – $ZnS$
- Galena – $PbS$
- Cinnabar – $HgS$

### ② Oxide Ore →
- Haematite → $Fe_2O_3$
- Magnetite → $Fe_3O_4$
- Pyrolusite → $MnO_2$
- Bauxite → $Al_2O_3 . xH_2O$
- Casseterite → $SnO_2$
- Litharge → $PbO$
- Cuprite → $Cu_2O$
- Zincite → $ZnO$
- Limonite → $Fe_2O_3 . 3H_2O$

### ③ Carbonate Ore →
- Malachite – Green – $CuCO_3 . Cu(OH)_2$
- Azurite – Blue – $2CuCO_3 . Cu(OH)_2$
- Siderite – $FeCO_3$
- Magnesite – $MgCO_3$
- Limestone – $CaCO_3$
- dolomite – $MgCO_3 . CaCO_3$
- Cerrusite – $PbCO_3$

### ④ Halide Ore →
- Fluorspar → $CaF_2$
- Cryolite → $Na_3AlF_6$

### Copper Ore →
- Cuprite → $Cu_2O$
- ★ Copper pyrite → $CuFeS_2$
- Copper glance → $Cu_2S$
- Malachite → $CuCO_3 . Cu(OH)_2$ – green
- Azurite → $2CuCO_3 . Cu(OH)_2$ – Blue

### Iron Ore →
- Haematite → $Fe_2O_3$ ★
- Magnetite → $Fe_3O_4$
- Limonite → $Fe_2O_3 . 3H_2O$
- Iron pyrite → $FeS_2$
- Siderite → $FeCO_3$

### Zinc Ore →
- Zincite → $ZnO$
- Zinc blende → $ZnS$
- Calamine → $ZnCO_3$

### Aluminium Ore →
- Bauxite → $Al_2O_3 . xH_2O$
- Cryolite → $Na_3AlF_6$

### Mercury ore →
- Cinnabar → $HgS$
- Florospar → $CaF_2$

## Metallurgy
1. Concentration of Ore
2. Roasting / Calcination
3. Reduction
4. Refining

## Metallurgical Process →
1. Hydrometallurgy → Aquous solution is used in extraction.
2. pyrometallurgy → Heat is used in extraction.
3. Electrometallurgy → Electrolysis is used in extraction.

## Steps in Metallurgy →

Ore → powdered Ore

↓

Concentration of ore / Benefication of ore / dressing of ore

- → Hydrolautic Washing
- → Froth Floatation
- → Magnetic Separatic

} physical method

- → Leaching ] → Chemical Method

↓

Concentrated Ore → Reduction

- → Roasting
- → Calcination

Reduction:
- → Smelting
- → Reduction with Aluminium

↓

Crude Metal

→ Refining

## ① Concentration Of Ore

### ① Gravity Separation / Hydraulic Washing / Levigation →

↳ Difference in gravity of ore particle and gangue particle.

→ Powdered Ore is passed with steam of water

(Heavy particle of ore – Settles down)

(Light gangue particle – Washes away)

e.g. → Oxide ore, Carbonate Ore

Cassiterite, Haematite

$SnO_2$ $Fe_2O_3$

### ② Magnetic Separation →

→ Difference in magnetic property of ore particle and impurity.

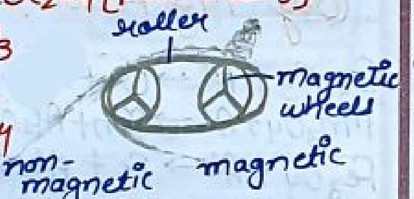
→ powdered ore is dropped on belt moving on rollers (magnetic). magnetic particle in ore are attracted by magnet and fall inside.

→ Chromite Ore = $FeCr_2O_4$ [$FeO \cdot Cr_2O_3$]

Haematite = $Fe_2O_3$

Magnetite = $Fe_3O_4$

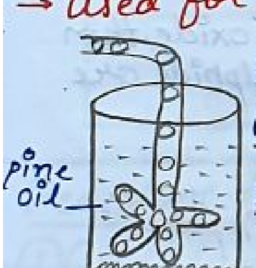
Wolframite = $FeWO_4$




### ③ Froth Floatation → (O loves O)

↳ Based on preferitial wetting of ore particle by oil and gangue particle.

→ Used for sulphide ores.




Froth agent → Pine Oil.

Collector → Pottasium ethyl Xanthate.

Froth Stabilizer → Phenol, Cresol, Aniline

Depressent → Separate two Sulphide Ores

$\boxed{ZnS + PbS}$ → depressent → NaCN

depress → ZnS

activator → $CuSO_4$ (promote froth floatation)

→ powdered ore is added to water containing pine oil

→ air is passed to create froth

→ Sulphide ore sticks to oil droplet → and rise to surface and floats with air bubble.

→ Impurity settle down

### ④ Leaching →

It is used if ore is soluble in suitable Solvent.

→ Leaching of Alumina from Bauxite Ore

→ Bauxite ore → $Al_2O_3 \cdot xH_2O$.

→ Impurity → $SiO_2$, $TiO_2$, Iron Oxide.

**Bayer's Process** →

$$Al_2O_{3(s)} + \underbrace{\text{conc } NaOH}_{\text{Suitable solvent}} \rightarrow \underbrace{Na[Al(OH)_4]}_{\text{Soluble}}$$

$$Na[Al(OH)_4] + CO_2 \rightarrow Na_2CO_3 + Al_2O_3 \cdot xH_2O$$

$$Al_2O_3 \cdot xH_2O \xrightarrow{\Delta} \underset{(\text{pure})}{Al_2O_3} + xH_2O$$

$$\underbrace{\text{Impurity} \rightarrow \text{Iron Oxide} \rightarrow \text{conc. } NaOH}_{\text{Bayer's Process}}$$

Impurity → Silicon Oxide → Serpeck process

↳ Ore is heated to 1800°C with Carbon and nitrogen.

→ It forms $AlN \xrightarrow{\text{hydrolysis}} Al(OH)_3 + NH_3$

Solvent → Conc. NaOH → Bayer's process

Solvent → Conc. $Na_2O_3$ → Hall's process.

### Mac Arthur Cyanide process (leaching) →

↳ Ag, Au

oxidation

$$Ag + NaCN + O_2 + H_2O \rightarrow Na[\overset{+}{Ag}(CN)_2] + NaOH$$

$$Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + Ag\downarrow$$

oxidation

$$Au + NaCN + O_2 + H_2O \rightarrow Na[Au(CN)_2] + NaOH$$

$$Na[Au(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + Au\downarrow$$

## Step 2 → Concentrated Ore → Oxide

### Calcination →

Heating (absence of air), below M.P.

Hydroxide, Hydrated Oxide, Carbonate

$Al_2O_3 \cdot xH_2O \xrightarrow{\Delta} Al_2O_3 + xH_2O$

$Fe_2O_3 \cdot 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$

$PbCO_3 \xrightarrow{\Delta} PbO + CO_2$

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

$FeCO_3 \xrightarrow{\Delta} FeO + CO_2$

$CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + CO_2$

## Roasting →

Heating (presence of air) below M.P.

Sulphide Ores

$ZnS + O_2 \rightarrow ZnO + SO_2$

$PbS + O_2 \rightarrow PbO + SO_2$

$Cu_2S + O_2 \rightarrow Cu_2O + SO_2$

*If ore contains Fe →

$CuFeS_2 \rightarrow \underbrace{Cu_2S + FeS}_{\text{Copper matte}} + \underbrace{FeO}_{\text{Basic}} + SO_2$ → $H_2SO_4$ preparation

$\underbrace{FeO}_{} + \underbrace{SiO_2}_{\text{acidic flux}} \rightarrow \underbrace{FeSiO_3}_{\text{slag}}$

## Partial Roasting →

क्या होगा प्रभु ? → $Cu_2S$, $HgS$, $PbS$

## Step 3 → Reduction of Oxide to Metal →

① **Smelting** → Extracting a metal from metal oxide by Reduction, with Carbon (Coke, coal, CO)

$M_xO_y + yC \rightarrow xM + yCO$

### Reactivity Series →

Please — Potassium — K
Stop — Sodium — Na
Calling — Calcium — Ca
Me — Magnesium — Mg
A — Aluminium — Al
Cute — Carbon — C
(electrolytic reduction)

Zebra — Zinc — Zn
I — Iron — Fe
Never — Nickel — Ni
Today — Tin — Sn
Like — Lead — Pb
Her — Hydrogen — H
call — Copper — Cu
(smelting se reduce hote)

smart — Silver — Ag
goat — Gold — Au
poor — platinum — Pt
(pyrometallurgy reduction)

example →

$ZnO + C \rightarrow Zn + CO$

$Fe_2O_3 + C \rightarrow Fe + CO_2$

$Fe_3O_4 + C \rightarrow Fe + CO_2$

$CuO + C \rightarrow Cu + CO$

$NiO + C \rightarrow Ni + CO$

$SnO_2 + C \rightarrow Sn + CO_2$

$PbO + C \rightarrow Pb + CO$

② **Pyrometallurgy** → Extraction of metal using heat.

$HgO \xrightarrow{\Delta} Hg + O_2$

$Ag_2O \xrightarrow{\Delta} Ag + O_2$

$Au_2O \xrightarrow{\Delta} Au + O_2$ ($Au_2O_3$)

③ **Reduction By Aluminium / Gold Schmidt aluminothermic process / Thermite process** →

↳ Oxide of Chromium, iron, manganese, are reduction using aluminium

Cr, Mn, Fe → Al

(Cry My Fellow) → (Alia)

$Cr_2O_3 + Al \rightarrow Cr + Al_2O_3$

$Mn_3O_4 + Al \rightarrow Mn + Al_2O_3$

$Fe_3O_4 + Al \rightarrow Fe + Al_2O_3$

④ **Auto reduction / Self Reduction**

क्या होगा प्रभु ? → Cu, Hg, Pb

→ Cu, Hg, Pb → partial roasting

→ A part of ore converts to oxide, then react with remaining sulphide ore to give metal and $SO_2$

$Cu_2S + Cu_2O \rightarrow Cu + SO_2\uparrow$

Blister Copper, (98% pure)

⑤ **Electrolytic Reduction** →

Highly reactive metals (alkali + alkaline + Al)

Pure Metal → Cathode

(molten) $NaCl \rightarrow \underbrace{Na}_{\text{(Metal)}} + Cl_2$

(molten) $MgCl_2 \rightarrow \underbrace{Mg}_{\text{(metal)}} + Cl_2$

→ Cathode

## ⑥ Hydrometallurgy →

Ag, Au (dissolve in suitable reagent, then react with more electropositive metal)

$Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + Ag$

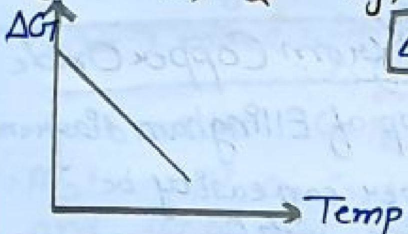
$Na[Au(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + Au$

## Thermodynamic principle of Metallurgy →

→ **Ellingham Diagram** →

plot b/w ΔG and Temp. →

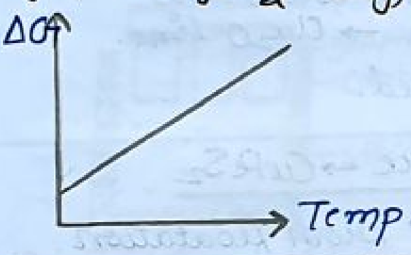
e.g. → $C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$




$\boxed{\Delta G = \Delta H - T\Delta S}$

$\boxed{\Delta S = +ve}$

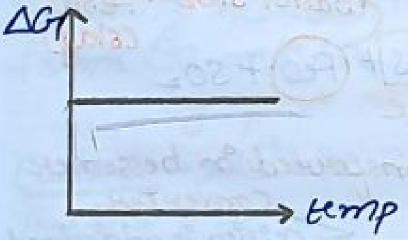
eg. → $CO_{(g)} + \frac{1}{2}O_{2}(g) \rightarrow CO_{2(g)}$




$\boxed{\Delta G = \Delta H - T\Delta S}$

$\boxed{\Delta S = -ve}$

eg → $C_{(s)} + O_{2}(g) \rightarrow CO_{2(g)}$




$\boxed{\Delta S = 0}$

y = constant

### Reactions for ellingham diagram →

① $Cu_{(g)} + O_{2(g)} \rightarrow CuO_{2(s)}$ ($\Delta S = (-ve)$)

② $Fe_{(s)} + O_{2(g)} \rightarrow FeO_{(s)}$ ($\Delta S = (-ve)$)

③ $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ ($\Delta S = 0$)

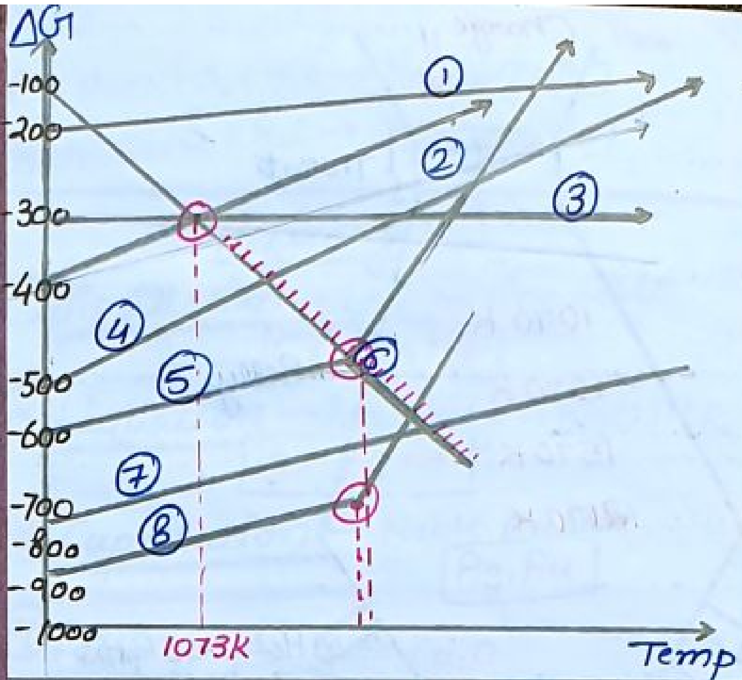
④ $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$ ($\Delta S = (-ve)$)

⑤ $Zn_{(s)} + O_2 \rightarrow ZnO_{(s)}$ ($\Delta S = (-ve)$)

⑥ $C + O_{2(g)} \rightarrow 2CO_{(g)}$ ($\Delta S = (+ve)$)

⑦ $\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3$ ($\Delta S = (-ve)$)

⑧ $Mg + O_2 \rightarrow MgO$ ($\Delta S = (-ve)$)

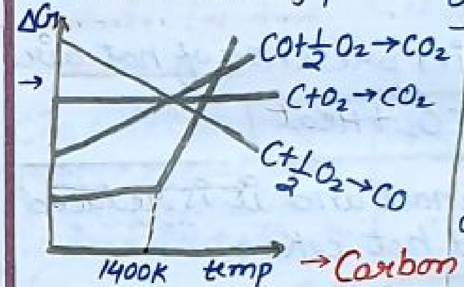



### Important Points →

→ lower line metal reduces upper line metal oxide.

(metal have more (-ve) ΔG) (have less (-ve) ΔG)

→ Sharp turn in ellingham diagram → shows melting point of metal.




→ melting point → 1400K

$\boxed{\text{after 1400K}}$

Both 'C' and 'CO' are reducing agent

→ Carbon is good reducing agent

→ In Ellingham diagram →

$\boxed{\text{Below 1073K}}$ 'CO' is reducing agent

for $Fe + O_2 \rightarrow FeO$

→ $C + \frac{1}{2}O_2 \rightarrow CO$ → line above

$CO + \frac{1}{2}O_2 \rightarrow CO_2$ → line below

$\boxed{\text{after 1073K}}$

C is a good reducing agent (coke)

## Smelting Of Iron

→ Carried Out in blast furnace

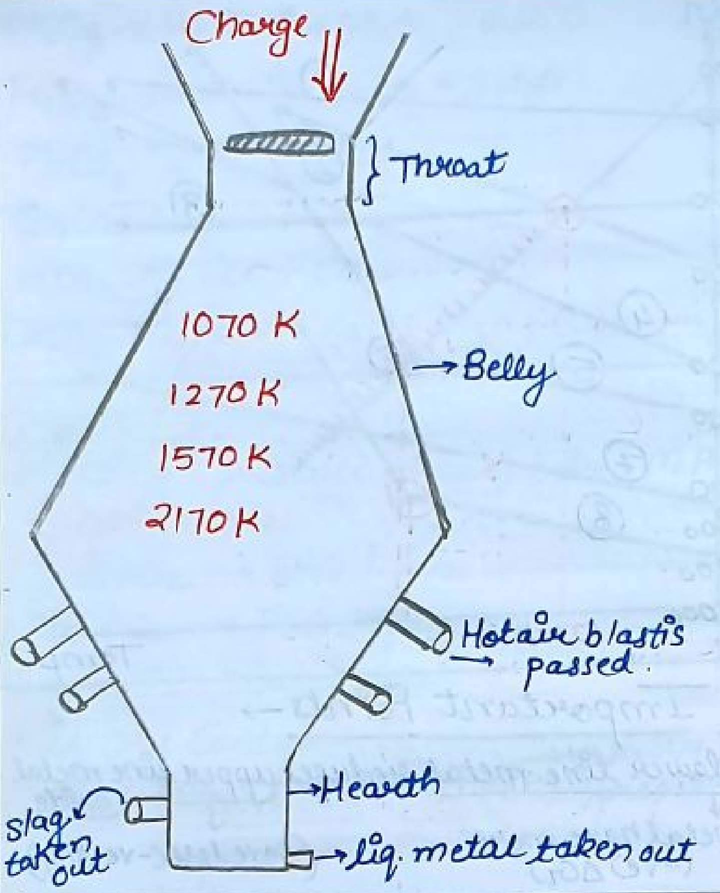
→ Charge → $(Fe_2O_3 + C + CaCO_3)$

① Combustion Zone (1500° - 1600°C)

② Reduction Zone (250° - 700°C)

③ Slag formation Zone (800° - 1000°C)

④ Melting Zone (1200°C - 1500°C)




**Combustion Zone** → Lower part of furnace

Carbon burns in presence of hot air.

$$\boxed{C + O_2 \rightarrow CO_2 + \text{Heat}}$$

$CO_2$ rises in furnace and it is reduced to CO, with red hot coke.

$$\boxed{CO_2 + C \rightarrow CO}$$

**Reduction Zone** → Upper most part in furnace

Metal oxide → metal

$$\left.\begin{array}{l} Fe_2O_3 + CO \rightarrow Fe_3O_4 + CO_2 \\ Fe_2O_4 + CO \rightarrow FeO + CO_2 \\ FeO + CO \rightarrow Fe + CO_2 \end{array}\right\} \text{below } 1073K$$

$FeO + C \rightarrow Fe + CO$ → above 1073 K

↳ Iron formed is spongy iron

**Slag Formation Zone** → Central part of furnace

$$CaCO_3 \xrightarrow{\Delta} \underset{\text{Basic}}{\underline{CaO}} + CO_2$$

$$CaO + SiO_2 \rightarrow \underline{CaSiO_3}$$

**Melting Zone** → above combustion zone.

Spongy iron → 1300°C → molten iron

Iron Obtained → $\boxed{\text{Pig Iron}}$ → 4% Carbon

impure form of iron

→ impurities - S, P, Si, Mn

→ not of any industrial use.

$\boxed{\text{Cast Iron}}$ melting pig iron with scrap iron. Carbon - 3%

Lining with $Fe_2O_3$

$Fe_2O_3 + C \rightarrow Fe + CO$

$\boxed{\text{Wrought Iron}}$ oxidizing impurities in reverberatory furnace

# purest form of iron

**Extraction of Cu from Copper Oxide**

$Cu + O_2 \rightarrow Cu_2O$ (top of Ellingham diagram)

So, oxides of Copper can easily be reduced by heating with C.

$$\left.\begin{array}{l} C \rightarrow CO \\ CO \rightarrow CO_2 \end{array}\right\} \text{These lines are below } Cu + O_2 \rightarrow Cu_2O \text{ line.}$$

So, easily reduced.

Copper → Main ore → $CuFeS_2$

Concentration → Froth floatation

Step-2 → Roasting (Reverberatory furnace)

$$CuFeS_2 \rightarrow \underbrace{\boxed{Cu_2S + FeS}}_{\text{Copper matte}} + FeO + SO_2$$

Basic + $SiO_2$ → $FeSiO_3$ (slag)

Copper matte is transferred in bessemer convertor. ← (Silica is added and blast of air) (Sand)

$$Cu_2S + O_2 \xrightarrow{\text{Partial roasting}} Cu_2O + SO_2$$

$$Cu_2S + Cu_2O \rightarrow Cu + SO_2\uparrow$$

Blister Copper, 98% pure

**Extraction of Zinc from Zinc blend (ZnS)** →

1. Froth floatation
2. Roasting $ZnS + O_2 \rightarrow ZnO + SO_2\uparrow$

This 'ZnO' is mixed with coke and clay

→ bricketts are formed

↓

Heat

↓

Zn

$ZnO + C \xrightarrow{1673K} Zn + CO\uparrow$

## ElectroChemical principles of Metallurgy →

↳ electrolysis → Molten Salt.

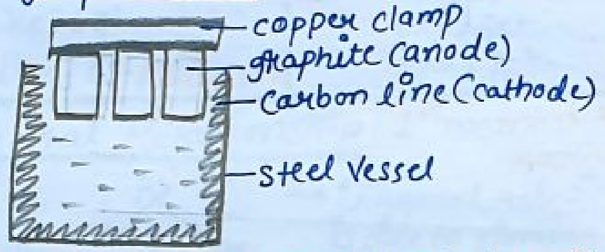
→ Cations are collected at Cathode.

$\underset{(molten)}{NaCl} \rightarrow \underset{cathode}{Na} + Cl_2$

## Extraction Of Aluminium from Alumina →

- $Al_2O_3$ is mixed with $Na_3AlF_6$, $CaF_2$ and heated
  - ↳ ↓se M.P. of mixture (2KC-900)
  - ↳ ↑se conductivity

↳ Molten $Al_2O_3$ is taken is steel vessel and lined with carbon → act as cathode and graphite rod → acts as anode.




$Al_2O_3 + C \rightarrow Al + CO_2$ ) Hall Heroult process

↳ during reduction of $Al_2O_3$ → Carbon forms CO and $CO_2$.

(graphite rod burns out)

Cathode → $Al^{+3} + 3e^- \rightarrow Al_{(s)}$

Anode → $C + O \rightarrow CO$

$C + O \rightarrow CO_2$

## Extraction of Cu from low grade Ore →

↳ Hydrometallurgy

→ Leaching → Bacteria and acid

## Oxidation / Reduction →

↳ Some metallurgy also involves oxidation

eg. → Chlorine gas from Brine Sol.$^n$

molten $NaCl \xrightarrow{electrolysis} Na + Cl_2$

eg. 2 →

$Au + NaCN + O_2 + H_2O \rightarrow Na[\overset{+1}{Au}(CN)_2]$

$Ag + NaCN + O_2 + H_2O \rightarrow Na[\overset{+1}{Ag}(CN)_2]$

## Refining

① Distillation → Low boiling point

Cd, Zn, Hg

② Liquation → impurity → high M.P.

Sn, Pb, Bi

③ Cupellation → Noble Metals

Ag, Au

④ Poling → Cu from $Cu_2O$

Sn from $SnO_2$

⑤ Electrolytic refining →

Cu, Ag, Au, Ni, Cr, Al.

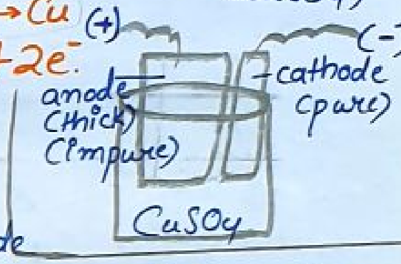
Anode → Impure Metal (Cu) thick.

Cathode → Pure Metal (Cu) thin.

Electrolyte Sol.$^n$ → Soluble salt of metal ($CuSO_4$)

Cathode: $Cu^{+2} + 2e^- \rightarrow Cu$

Anode: $Cu \rightarrow Cu^{+2} + 2e^-$




Electric Current pass → metal ion from electrolyte is deposited at cathode

↳ same amount of metal breaks from anode and goes into solution.

After Some time, → anode gets finished.

↳ impurities → collected as anode mud

antimony, Selenium, Tellurium, Silver, Gold, Platinum

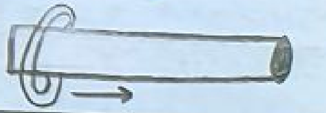
⑥ Zone Refining →

Difference in solubility of impurity in molten state and solid state.

↳ Highly pure metal is required.

→ Semiconductors.

Si, Ge, B, Ga, In



⑦ Vapour phase refining →

Van-Arkel Method → Ultra pure metal

Ti, Zr

$Zr + 2I_2 \rightarrow ZrI_4 \xrightarrow{heat} Zr + 2I_2$.

Mond's Process → Mo, Ni, CO

$Ni + 4CO \rightarrow Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO$

## Chromatography

Principle → Different component of mixture are differently adsorbed on adsorbent.

Column Chromatography → Used for elements present in minute quantity.

Lanthanides → purify → ion exchange as adsorbent.

NEET
SLAYER