METALLURGY

(Concentration + Extraction + Refining)

1. Occurrence of metals - Free State, Combined

   Free State (Less Reactive metals) Ex: Gold

   Combined (More Reactive metals) Ex: Alkali metals

2. Minerals and ores :

Minerals - Naturally occuring substance - mining
- free ; combined state - oxides, sulphid
etc. - Less % metal

ores - minerals that contain high % metal -
metals extracted commercially, conveniently

All ores are minerals. But ....

Example: Bauxite - $Al_2O_3 \cdot nH_2O$ - High % Al - ore
china clay - $Al_2O_3 \cdot SiO_2 \cdot 2H_2O$ - Less % Al - mineral

3. **Metallurgical Process**: Concn + Extraction + Refining

Concentration: i) Removal of impurities (gangue)
ii) several methods - nature of the ore, type of impurity.

Gravity separation or **Hydraulic wash:**

ore - High specific gravity, Gangue - low sp. Gravity simply washing with running water. Lighter particles (gang washed away. suitable - oxide ores.

Froth flotation : Sulphide ores

ore + water + Pine oil (or) Eucalyptus oil

Sodium ethyl xanthate - collector - water Repellent

Leaching

- * Based on the solubility of the ore
- * suitable solvent
- * aqueous medium

crushed ore + suitable solvent ⟶ metal salt (or) complex
(metal + impurities)

(metal → soluble in solvent, while impurities → insoluble)

Types: **cyanide leaching:**

Example: Concn of Gold ore

Gold ore + Aerated dil. soln of NaCN ⟶ Gold cyanide complex
(NaCN + O_2 + H_2O)

(Gangue → Remains Insoluble)

entation

Gold cyanide complex + deoxygenated leached solution with Zn ⟶ Au (Gold) + zinc cyanide
↓
(without O_2)

Alkali leaching:

Al_2O_3 + alkali + H_2O ⟶ sodium meta Aluminate
(Bauxite) NaOH

(Impurities (FeO_2 and TiO_2) → Remove

AMMONIA LEACHING:

Crushed ore + $NH_{3\,(aq)} \longrightarrow$ cationic complex + Gangue
(Ni, Cu, Co)
$[Ni(NH_3)_6]^{2+}$
Hexaammine nickel(II)ion

Extraction of crude metal:

(Concentrated ore) → Extraction of crude metals

* Conversion of the ore into oxide

* Reduction of the metal oxide to metal

Conversion of ore into oxide: (Roasting) (oxidation)

$$\underset{\text{(Galena)}}{PbS} + O_2 \xrightarrow{\Delta} PbO + SO_2\uparrow$$

* usually applied for Sulphide ores

* Roasting removes Impurities by converting into volatile oxides

Calcination:

Concentrated ore heated strongly in the absence of air

Hydrated ore $\xrightarrow{\text{calcination}}$ Oxides escapes as moisture.
(Hydrated)

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

$$Fe_2O_3\cdot 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O_{(g)}\uparrow$$

Reduction of metal oxides: (smelting) (Reduction)

metal oxides - Reduced to - crude metal - using a suitable Reducing agent - C, CO, H_2, Al, Na etc - choice of Reducing agent depend upon the nature of the metal.

Smelting :

Concentrated ore + flux + Reducing agent $\xrightarrow{\overset{\Delta}{\text{High temp}}}$ Crude metal

Flux :- a chemical substance that forms easily fusible slag with gangue.

Example: $Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)}\uparrow$

flux : CaO (limestone)

Gangue : SiO_2 (silica)

$CaO_{(s)} + SiO_{2(s)} \longrightarrow CaSiO_{3(s)}$

Calcium Silicate

(slag) Removed

of Copper from Copper Pyrites ($CuFeS_2$)

$$\text{Concentrated ore}_{(s)} + O_{2(g)} \xrightarrow{\Delta} 2\,FeS_{(l)} + Cu_2S_{(l)} + SO_2\uparrow$$

$$2\,FeS_{(l)} + 3O_{2(g)} \longrightarrow 2\,FeO_{(l)} + 2SO_2\uparrow$$

$$\underset{\text{(flux)}}{FeO} + \underset{\text{(gangue)}}{SiO_2} \longrightarrow \underset{\text{(slag)}}{FeSiO_3}$$

The matte ($FeS + Cu_2S$) is separated from the slag

FeS from Matte is oxidised to FeO

$$FeS \xrightarrow{(O)} FeO$$

Cu_2S from Matte is oxidised to Cu_2O

$$Cu_2S \xrightarrow{(O)} Cu_2O$$

Then, Cu_2O is mixed with Cu_2S to convert it into metallic copper.

$$Cu_2O + Cu_2S \longrightarrow Cu_{(l)} + SO_2\uparrow$$

The metallic copper is solidified and it has blistered (கொப்புள appearance due to the evolution of SO_2.

(v) Blister copper → 2% impurities + 98% Copper (Pure)

Reduction by carbon:

$$\text{Oxide ore} + \text{coal} \xrightarrow{\Delta} \text{metal}_{(s)} + CO_{(g)}\uparrow$$

$$ZnO + C \xrightarrow{\Delta} Zn + CO_{(g)}$$

This Process can be applied to the metals which do not form carbides with carbon at the reduction temperature.

Reduction by Hydrogen:

$$\text{metallic oxide}_{(s)} + H_{2(g)} \longrightarrow \text{metal}_{(s)} + H_2O_{(l)}$$

This process can be applied to the metals which have less electro positive character than Hydrogen.
(Donating electrons)

Reduction by metal: (Aluminothermite Process) ⊗ Repeated Question

Cr_2O_3 (Chromic oxide) + Aluminium Powder

To initiate the reduction process, An ignition mixture ($Mg + BaO_2$) is used.

$$BaO_2 + Mg \longrightarrow BaO + MgO$$

Large amount of heat is liberated which facilitates the Reduction of Cr_2O_3 with Aluminium powder.

$$Cr_2O_3 + 2Al \xrightarrow{\Delta} 2Cr + Al_2O_3$$

Auto Reduction :

$$\text{~~Simple~~ ore} \xrightarrow{\text{Roasting}} \text{Crude metal.}$$

In such cases, the use of Reducing agents is not necessary.

$$\underset{\text{(Cinnabar)}}{HgS_{(s)}} + O_{2(g)} \longrightarrow Hg_{(l)} + SO_2\uparrow$$

Thermodynamic Principle of metallurgy : (ΔG value)

ΔG - change in Gibbs free energy

$\Delta G = \Delta H - T\Delta S$

$$\text{metal oxide} \xrightarrow[\text{Reducing agent}]{\text{Different}} \text{metal}$$

$$M_xO_{y\,(s)} \longrightarrow M_{(s)} + O_{2\,(g)} \quad \text{①}$$

The above reduction may be carried out with Carbon.

Carbon may be oxidised to either CO or CO_2

$$C + O_2 \longrightarrow CO_{2\,(g)} \quad \text{②}$$

$$2C + O_2 \longrightarrow 2CO_{(g)} \quad \text{③}$$

If Carbon monoxide is used as Reducing agent,

$$2CO_{(g)} + O_2 \longrightarrow 2CO_{2\,(g)} \quad \text{④}$$

Coupled Reaction

Eq. 1, 2

Eq. 1, 3

Eq. 1, 4

A suitable reducing agent is selected based on Thermodynamic Conditions.

(x) For spontaneous Reaction, ΔG is -ve

Hence, the reducing agent is selected in such a way that it provides a large negative ΔG value for the coupled reaction.

Ellingham diagram

It is a Graphical Representation - variation of ΔG_f° (y-axis) - formation of various metal oxides - Temperature (x-axis)

It helps us to select a suitable reducing agent and appropriate Temperature range for reduction.

Gibbs free energy, $\Delta G = \Delta H - T\Delta S$

ΔH = change in Enthalpy (Heat Content)

T = Temperature

ΔS = change in Entropy (Randomness of molecules)

ΔG° (std. free energy change)

$$\Delta G^0 = -RT \ln K_p$$

R = Gas Constant

K_p = Equilibrium Constant (in Constant pressure)

OBSERVATIONS FROM THE ELLINGHAM DIAGRAM:

* for most of the metal oxide, the slope is positive

<u>Explaination</u> : oxygen combines with metal - metal oxide - decrease in Randomness (ΔS value). so ΔS is -ve.

$$\Delta G = \Delta H - T\Delta S$$
$$= \Delta H - T(-\Delta S)$$
$$= \Delta H + T\Delta S \quad (\therefore \Delta G \text{ value is +ve})$$

* formation of Carbom monoxide (CO) is a straight line with negative slope. so ΔS is +ve. <u>2 moles</u> of CO gas is formed by consuming <u>one mole</u> of O_2

so, CO is <u>more stable</u> at <u>higher</u> temperature.

* As the temperature increases, ΔG value becomes less -ve and becomes zero at a particular temperature.

· metal oxide - more stable - High -ve value of ΔG

X metal oxide - Less stable - ΔG is +ve

If ΔG is +ve - metal oxide will be easily decomposed.

* sudden change in the slope at a particular temperature for some metal oxides like MgO, HgO - Due to Phase Transition.

Applications :

- * Ag_2O and HgO is at upper Part of the diagram (ΔG is +ve). So easily decomposed at moderate Temperatures (600 and 700 K). It will decompose in the absence of Reducing agent.

- * It is used to Predict thermodynamic feasibility (able to work) of Reduction of oxides of one metal by another metal.

Example: why Al Powder is used as Reducing agent for the Reduction of Cr_2O_3? ⓧ

In Ellingham diagram, the formation of Cr_2O_3 lies above that of Al, meaning that Al_2O_3 is more stable than Cr_2O_3. Hence Al can be used as Reducing agent.

Al is not used to reduce MgO or CaO which occupy lower position than Al_2O_3.

- * Carbon line cuts across the lines of many metal oxides, so it can reduce all those oxides at high temperature.

Example: Reduction of FeO by carbon

From the diagram, formation of FeO and CO intersects around 1000K.

Below this temperature, the carbon line lies above the Iron line which Indicates that feo is more stable than CO and hence at this temperature range, the reduction is not feasible.

But above this temperature (1000K), the carbon line lies below the Iron line and hence, the reduction is feasible above 1000K.

from the diagram at 1500K,

$2fe_{(s)} + O_{2(g)} \longrightarrow 2feO_{(g)}$ $\Delta G_1 = -350$ kJ/mol —①

$2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)}$ $\Delta G_2 = -480$ kJ/mol —②

Reverse eqn from ①

$2feO_{(s)}\cancel{(g)} \longrightarrow 2fe_{(s)} + O_{2(g)}$ $-\Delta G_1 = +350$ kJ/mol —③

Couple ② and ③

$2feO_{(s)} + 2C \longrightarrow 2fe_{(s)} + 2CO_{(g)}$ $\Delta G_3 = -130$ kJ/mol

for 2 moles of feo → ΔG is -130 kJ/mol

for 1 mole of feo → ΔG is -65 kJ/mol. ($-130/2$)

Limitations of Ellingham diagram:

* It gives only the feasibility of a reaction, it does not tell anything about the Rate of a reaction.

* ΔG value is based on the assumption that Reactants $\rightleftharpoons$ Products which is not always true.

⊛ Electrochemical Principle of metallurgy

$$\Delta G^\circ = -nfE^\circ$$

ΔG° = std. Gibbs free energy change, n = no. of electrons, f = faraday (96485 c/mol.)

E° = Emf of the cell (or) Electrode potential

If E° value is +ve then the reduction reaction is spontaneous

(note: If ΔG is -ve the reaction is spontaneous - Thermodynamic Principle)

The metal oxide is reduced to metal by some reducing agent (suitable) or by electrolysis.

Electrolysis - chemical reaction is carried out by applying current.

Electrodes - cathode (-ve) and anode (+ve)

Electrolyte - The solution used in electrolysis.

Displacement Reaction - more reactive element displaces the less reactive element for Example: $\underset{\text{(metal)}}{Cu_{(s)}} + \underset{\text{(solution)}}{2Ag^+_{(s)}} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$

Refining Process:

Ore → Concentrated ore ⟶ Extraction of crude metal → Refining

(Removal of Gangue)

- * Gravity separation
- * froth flotation
- * Leaching
- * magnetic separation

Extraction of crude metal:

Conversion of ores into oxides

- * Roasting
- * Calcination

Reduction of oxides to crude metal

- * Smelting
- * Reduction by
  - ⇒ Carbon
  - ⇒ Hydrogen
  - ⇒ metal
- * Auto Reduction

Electrolytic Refining:

* Crude metal is Refined (Purified by electrolysis).

* It is carried out in an electrolytic cell containing aqueous solution of the salts of the metal.

* cathode - Thin pure metal

Anode - Impure metal

Electrolyte - acidified aqueous solution of metal salt.

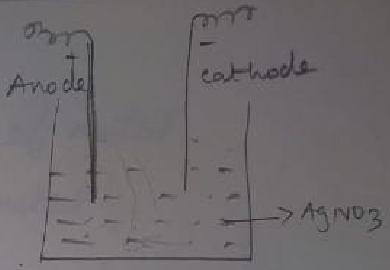
* On passing electric current, pure metal will be deposited at the cathode.

Example: Electrolytic Refining of silver

Cathode : Pure silver (Thin)

Anode : Impure silver

Electrolyte : Acidified aq. soln of $AgNO_3$.



On passing Electric current,

$$\text{Anode} : Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + 1e^{-}$$

$$\text{cathode} : Ag^{+}_{(aq)} + 1e^{-} \longrightarrow Ag_{(s)}$$

Zone Refining :

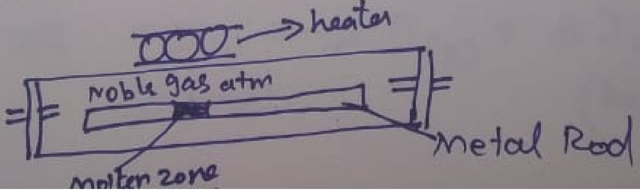
* When an impure metal is melted and allowed to solidity, the impurities will Prefer to be in the molten region.

* Impurities are more soluble in the melt than in the solid state

* Impure metal is taken in the form of a rod. One end of the rod is heated using a mobile induction heater.

* When the heater is moved to the other end, the impurities (molten zone) also moves along with it. The Process is repeated for several times.

* Process is carried out in an inert gas atmosphere.



vapour Phase method :

metal + Suitable Reagent → volatile compound of metal.

volatile compound is decompose to give pure metal.

Mond Process

✪ Im

This Process is used for Refining of **Nickel**

$$Ni_{(s)} + 4\,CO_{(g)} \xrightarrow[350K]{\Delta} Ni(CO)_{4\,(g)}$$

Nickel tetra carbonyl
(Highly volatile)

$$Ni(CO)_{4\,(g)} \xrightarrow[\Delta]{460K} Ni_{(s)} + 4\,CO_{(g)}$$

Decompose

Van-Arkel method

Titanium and zirconium canbe purified by this method.

$$Ti_{(s)} + 2I_{2\,(s)} \xrightarrow[550K]{\Delta} TiI_4 \text{ (vapour)}$$

Titanium Tetra Iodide.

TiI_4-passed over Tungsten filament around 1800k - it is decomposed.

~~Fit~~. $TiI_4 \longrightarrow Ti_{(s)} + 2I_{2}(s)$

(vapour) (Reused)