Chapter - 3

General Principles and Processes of Isolation of Elements.

Metals are very important for us not in daily use but at industrial level as well.
Metals exist in nature in combined and in free state

Mineral : The compounds of Metal that occur in nature along with rocky and other impurities are called Minerals.

Ore : Those minerals from which metals can be extracted easily is called an ore.

Metallurgy : It is the process or study of getting metals from its ore. It can be done in several steps.

Concentration of the Ore : In this process Ore is dressed or benefation takes place. It is done to remove impurities.

The process of removal of gangue from the ore is known as concentration ore.

Methods of Concentration of Ore

1. Hydraulic Washing
2. Froth flotation
3. Electromagnetic Separation
4. Leaching

The basic Principle for Hydraulic Washing is density difference this method is used to get heavy metals like Sn, Pb, etc.

Froth flotation method is used for Sulphide ores of Cu, Zn, Fe & Pb. Gangue particles are wetted by water and settles down at bottom.

The Electromagnetic Separation is used if one of the ore or impurity is magnetic. Magnetic particles are attracted and fall nearer the magnetic roller, while other particles fall away from the roller

Leaching : When metal is more soluble than impurities present in its Ore. Ores of Al and Ag or Au can be Concentrated

Some ores of Aluminum
Alumina (Al_2O_3), Diaspore ($Al_2O_3 \cdot 1H_2O$), Bauxite ($Al_2O_3 \cdot 2H_2O$), Gibbsite ($Al_2O_3 \cdot 3H_2O$), Cryolite ($Na_3[AlF_6]$)

- Purification of Bauxite by Leaching method (Bayer's process).

Step 1
$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$

Step-2
$2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3 \cdot xH_2O(s) + 2NaHCO_3(aq)$

Step-3
$Al_2O_3 \cdot xH_2O(s) \xrightarrow{1470K} Al_2O_3(s) + xH_2O(g)$

Conversion of Ore into oxide
It is easier to reduce oxide than sulphide or carbonate ore. Therefore, the given ore should be converted into oxide by (i) Roasting
(ii) Calcination

Roasting: In this process, ore is in a regular supply of air at a temperature below melting point of the metal so that the given ore is converted into oxide ore.
Sulphide ores are converted into oxide by Roasting.
Calcination: heating ore in limited supply of air so as to convert carbonate ores into oxide

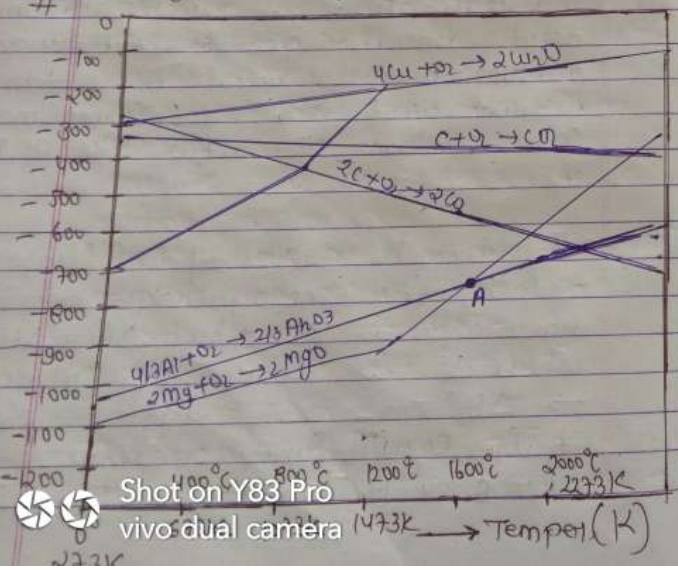
Reduction of Oxide to Metal:
Reduction needs a suitable reducing agent depending upon the reactivity or reducing power of metal. The common reducing agent used are Carbon or CO or any other metals like Al, Mg, etc.

Thermodynamic Principles of Metallurgy
→ Gibbs free energy change at any temperature is given by $\Delta G = \Delta H - T\Delta S$
where ΔS is change in entropy.
→ $\Delta G^\circ = -2.303RT \log K$ where K is equilibrium constant.
$R = 8.314\ JK^{-1}\ mol^{-1}$, T is Tem-

erature in Kelvin.
→ A -ve ΔG_f means +ve value of K. The rea^n will proceed in forward direction
→ If ΔS → +ve, on increasing the Temperature the value of $T\Delta S$ increases so that $T\Delta S > \Delta H$ and ΔG_f → -ve.

Coupled reactions: If reactant and Product are put together in a system the net ΔG_f → -ve. These reactions are called Coupled reactions.

Ellingham diagrams



The plots b/w $\Delta_f G^\circ$ of formation of Oxides of element vs temperature are called Ellingham diagrams. It provides a sound idea about selecting a reducing agent in reduction of Oxides. Such diagrams help in predicting the feasibility of a thermal reduction of an ore. ΔG_f must be -ve at a given temperature for a rea^n to be feasible.

Limitations: It doesn't take kinetics of reduction into consideration, i.e., how fast reduction will take place can't be determined.

Reduction of iron Oxide in blast furnace: It takes place in different Zones

(a) At 500-800 K

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$

$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

(b) At 900-1500 K

$C + CO_2 \rightarrow 2CO$

$FeO + CO \rightarrow Fe + CO_2$

(c) Limestone decomposes to CaO and CO_2
$CaCO_3 \xrightarrow{Heat} CaO + CO_2$

(d) Silica (impurity) reacts with CaO to form calcium silicate which forms slag. It floats over molten iron and prevents oxidation of iron.

- Types of iron
  (i) Pig iron
  (ii) Cast iron
  (iii) Wrought iron.

- Electrolytic Reduction: Purified bauxite ore is mixed with Na_3AlF_6 or CaF_2 which lowers its melting point and increases electrical conductivity. Molten mixture is electrolysed using a number of graphite rods as anode and carbon lining as cathode.
  The graphite anode is useful for reduction of metal oxide to metal.
  $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$
  $Al_2O_3 \xrightarrow{Electrolysis} 2Al^{3+} + 3O^{2-}$

At cathode: $Al^{3+}(melt) + 3\bar{e} \rightarrow Al(l)$
At anode: $C(s) + O^{2-}(melt) \rightarrow CO + 2\bar{e}$

$C(s) + 2O^{2-}(melt) \rightarrow CO_2(g) + 4\bar{e}$

Graphite rods get burnt forming CO and CO_2. The Aluminium thus obtained is refined electrolytically using Al as anode, pure Al as cathode and molten cryolite as electrolyte.

At anode: $Al_{(impure)} \longrightarrow Al^{3+} + 3\bar{e}$
At cathode: $Al^{3+} + 3\bar{e} \rightarrow Al(pure)$

Electrolysis of NaCl gives 'Na' metal at cathode and $Cl_2(g)$ is liberated at anode.

Refining: It is the process of converting an impure metal into pure metal depending upon the nature of metal.

Distillation: It is the process used to purify those metals which have low boiling points. Impure metal is heated so as to convert it into vapours which changes into pure metal on

condensation and is obtained as distillate.

Liquation: Those metals which have impurities whose melting points are higher than metal can be purified by this method. In this method, Sn metal can be purified. Tin containing iron as impurities heated on the top of sloping furnace. Tin melts and flows down the sloping surface where iron is left behind and pure tin is obtained.

→ Electrolyte refining:- In this method impure metal is taken as anode, pure metal is taken as cathode, and a soluble salt of metal is used as electrolyte. When electric current is passed, impure pure metal forms metal ions which are discharge at cathode forming pure metal.

At anode: $M_{(impure)} \longrightarrow M^{n+} + ne^-$

At Cathode: $M^{n+} + ne^- \rightarrow M_{(pure)}$

Zone refining: It is based on the principle that impurities are more soluble in the melt than in the solid state of Metal. The impure metal is heated with the help of circular heaters at one end of the rod of impure metal. The molten zone moves forward along with the heater with impurities and reaches the other end and is discharged. Pure metal crystallizes out of the melt. The process is repeated several times & heater is moved in same direction. It is used for purifying Semiconductors like B, Ge, Si, Ga and In.

Vapour phase refining:- Nickle when heated in stream of carbon monoxide forms volatile $Ni(CO)_4$ which on further subjecting to higher temperature decomposes to give pure metal.

$$Ni_{(impure} + 4CO \xrightarrow{330-350K} Ni(CO)_4 \xrightarrow{450-470K} Ni_{(Pure)} + 4CO$$

Van-Arkel method: It is used to purify ultra pure metals. Zr and

Ti are purified by this process. Zr and Ti are heated in iodine vapours at about 870 K to form volatile ZrI_4 or TiI_4 which are heated over a tungsten filament at 1800 K to give pure Zr and Ti.