# **METALLURGY**

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## **INTRODUCTION**

#### Metallurgy

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The branch of chemistry which deals with the method of extraction of metals from their ores.

## Metal

The element which tends to form positive ion is called a metal.

## Minerals

The various compounds of metals which occur in the earth's crust and are obtained by mining are called minerals. In earth crust order of abundance of elements is. O > Si > Al > Fe

A mineral may be single compound or a mixture of compounds having fixed chemical composition.

#### Ore

The mineral from which a metal can be profitably and easily extracted is called an ore.

#### **Gangue or Matrix**

The undesirable impurities present in an ore are called gangue.

#### **Mining Process**

Process of taking out ore from earth crust is called mining.

## **TYPES OF METALLURGY**

(a) **Pyro Metallurgy :** Extraction of metal from ore by using heat energy.

Steps involved are : Calcination, roasting, reduction etc.

**Ex.** Less reactive metals : Cu, Fe, CO, Ni, Zn, Sn, Pb etc.

- (b) Hydro Metallurgy : (Ag, Au, Cu) This is wet metallurgy process.
  - $Cu \longrightarrow Pyro + Hydro$

Ag and Au  $\longrightarrow$  By cynide process.

Steps are : (i) Complex formation (ii) Metal displacement

(i) AgCl or AuCl  $\xrightarrow{\text{NaCN}}$  Na[Ag(CN)<sub>2</sub>]

(Sodium argento cynide)

(ii)  $2\text{Na}[\text{Ag}(\text{CN})_2] \xrightarrow{\text{Zn}} \text{Ag} \downarrow + \text{Na}_2[\text{Zn}(\text{CN})_4]$ 

(Impure)

- (c) Electrical Metallurgy : This process used for highly electro positive metal (s-block and A●) metal obtained by electrolysis of fused salt/anhydrous medium.
- (d) Ion Exchange Metallurgy : Trans-Uranic (elements after Uranium in periodic table) elements are obtained by this method.

## STEPS INVOLVED IN THE EXTRACTION OF METALS

The extraction of a metal from its ore is completed in the following four steps.

- (a) Crushing and grinding
- (b) Pulverisation
- Concentration of the ore

- (d) Reduction to the metal
- (e) Refining of the metal.

**(c)** 

#### **CONCENTRATION OF THE ORE**

The removal of impurities from the ore is called its concentration. It is carried out in one or more of the following steps. These undesired impurity are gangue or matrix.



## **BY PHYSICALS SEPARATION**

#### (a) Gravity Separation (Lavigation)

This method of concentration of the ore is based on the difference in the specific lavigation gravities of the ore and the gangue particles.

Powdered ore is agitated with a running stream of water. The lighter gangue particles are taken away by water while heavier ore particles settle down. Ex. Oxygenated Ores.

#### (b) Froth Floatation Method

This method is mainly employed for the concentration of sulphide ores.

The method is based on the different wetting characteristics of the gangue and the sulphide ore with water and oil. The gangue preferentially wetted by water and the ore by oil.

The crushed ore along with water is taken in a floatation cell. Various substances are added depending on the nature of the ore and a current of air is blown in. The substances added are usually of three types.

#### (i) Frothers

They generate a stable froth which rises to the top of the tank. Example of frother is pine oil, Eucalyptus oil, etc.

#### (ii) Collectors or Floating Agents

These attach themselves by polar group to the grains of the ores which then become water repellant and pass on into the froth. Example: sodiumethyl /ethyly xanthate.

#### (iii) Activators or Depressants

These reagents activate or depress the flotation properly and help in the separation of different sulphide ores present in a mixture.

An example of depressant is NaCN. An activator is CuSO<sub>4</sub>.

#### (c) Magnetic Separation

If the ore and not the gangue or the gangue and not the ore is attracted by a magnet, the two can be separated by this method.

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is concentrated by this method, (FeWO<sub>4</sub>) wolframite removed from SnO<sub>2</sub>, FeO removed from chromite (FeCr<sub>2</sub>O<sub>4</sub> $\Rightarrow$ Cr<sub>2</sub>O<sub>3</sub>·FeO).

## **BY CHEMICAL SEPARATION**

Some of the ores are concentrated by means of chemical treatment.

**Leaching :** It involves the treatment of the ore with a suitable reagent. as to make it soluble while impurity remain insoluble. The ore is recovered from the solution by suitable chemical method.

(i) Bayer's Process

Ex. Bauxite ore contain impurity  $Fe_2O_3$ ,  $TiO_2$ ,  $SiO_2$  when it dissolve in aq. NaOH/pressure + 150°C T bauxite is dissolve but other are not dissolve.

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH$$

$$Al_2O_3 + 3H_2O$$

(ii) Cyanide Process : Their process used for Au, Ag by (Mac-Arthur forrest cyanide process).



## CALCINATION

Calcination is a process in which ore is heated, generally in the **absence of air**, to expel water from a hydrated oxide or carbon dioxide from a carbonate at temperature below their melting points.

For Example

(i) 
$$Al_2O_3$$
.  $2H_2O \longrightarrow Al_2O_3 + 2H_2O$ ,  $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$ 

(ii) 
$$2Fe_2O_3. 3H_2O \longrightarrow 2Fe_2O_3 + 3H_2O$$

(iii) 
$$CaCO_3 \longrightarrow CaO + CO_2$$

(iv) 
$$CaCO_3$$
. MgCO<sub>3</sub>  $\longrightarrow$  CaO + MgO + 2CO<sub>2</sub>  $\uparrow$ 

(v) 
$$MgCO_3 \longrightarrow MgO + CO_2^{\uparrow}$$

(vi) 
$$ZnCO_3 \longrightarrow ZnO + CO_2$$

(vii) 
$$FeCO_3 \longrightarrow FeO + CO_2^{\uparrow}$$

## **Advantages of Calcination**

- (i) Moisture is removed.
- (ii) Organic matter is destroyed
- (iii) The hydroxide and carbonates ores are converted into their oxides.
- (iv) The metal become porous and easily workable

## ROASTING

## (Metal sulphides $\longrightarrow$ Metal oxide + SO<sub>2</sub>)

The removal of the excess sulphur contained in sulphide ores by heating in an excess of air is called roasting.

The concentrated sulphide ore is heated in reverberatory furnace, below its melting point or fusion temperature in the presence of an excess of air with or without the addition of an external substance.

In roasting definite chemical like oxidation, chlorination etc. take place but in calcination does not occur any major chemical changes.

(i)  $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$ 

(ii) 
$$ZnS + 2O_2 \longrightarrow ZnSO_4$$

(iii) 
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + SO_2$$

(iv) 
$$4\text{FeS}_2 + 11\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$$

(v) 
$$HgS + O_2 \longrightarrow HgO + SO_2$$

(vi) 
$$2As_2S_3 + 9O_2 \longrightarrow 2As_2O_3 + 6SO_2$$

## Advantages of Roasting

(i) Excess of sulphur is removed as volatile oxide.

$$S + O_2 \rightarrow SO_2 \uparrow$$
  
(air)

(ii) The metal sulphide is converted into metal oxide.

(iii) Impurities of arsenic and antimony are removed as their volatile oxides.

$$Sb_4 + 3O_2 \rightarrow 2Sb_2O_3$$
  
 $As_4 + 3O_2 \rightarrow 2As_2O_3$ 









e.g. Manufacture of metallic sodium (Down's process)

Molten NaCl containing a little  $CaCl_2$  is electrolyzed between graphite anode and iron cathode. The various reactions that take place are

**On Fusion :** NaCl  $\implies$  Na<sup>+</sup> + Cl<sup>-</sup> (Ions become mobile)

**On Electrolysis :** At Cathode :  $Na^+ + e^- \rightarrow Na$  (reduction)

(Metallic sodium)

At Anode:  $2Cl^- \rightarrow Cl_2(g) + 2e^-$ 



#### (e) Reduction by Al

This process is employed in the case of those metals which have very high melting points and are to be extracted from their oxides

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$
$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$$

#### **Purification or Refining of Metals**

Metals obtained by reduction processes still contain some objectionable impurities and have to be refined. Numerous techniques are available, including the following :

#### **PHYSICAL METHODS**

These methods include the following processes :

(I) Liquation Process : This process is used for the purification of the metal, which itself is readily fusible, but the impurities are infusible.

**Examples:** (a) Purification of impure tin metal

(b) Purification of crude zinc

- (II) Fractional Distillation Process : This process is used to purify those metals which themselves are volatile and the impurities in them are nonvolatile and vice-versa. Zn, Cd and Hg are purified by this process.
- (III) Zone Refining Method (Fractional Crystallisation Method): This process is used when metals are required in very high purity. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.
- (IV) Chromatographic Methods : This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent.

## **CHEMICAL METHODS**

These methods include the following methods :

#### (I) OXIDATIVE REFINING:

The method is used when the impurities present in the metal have a greater affinity for oxygen and are more readily oxidized than the metal.

#### (i) Bessemerisation (Purification of iron) :

The iron obtained from a blast furnace is a brittle material called cast iron or pig iron. Molten iron from blast furnace is exposed to a jet of pure  $O_2$  gas for about 20 minutes in a furnace that is lined with basic oxide such as CaO. The impurities in the iron are oxidized and the acidic oxides that form react with basic CaO to yield a molten slag that can be poured off. Phosphorous, for example, is oxidized to  $P_4O_{10}$ , which then reacts with CaO to give molten Ca<sub>3</sub> (PO<sub>4</sub>)<sub>2</sub>.

$$P_4(l) + 5 O_2(g) \longrightarrow P_4 O_{10}(l)$$

 $6 \operatorname{CaO}(g) + \operatorname{P}_4 \operatorname{O}_{10}(l) \longrightarrow 2 \operatorname{Ca}_3(\operatorname{PO}_4)_2(l)$ 

Basic oxide acidic oxide slag

#### (ii) Cupellation (Removal of Lead) :

In this process the molten impure metal is heated in a cupel, which is boat-shaped dish made of bone ash or cement, and a blast of air is passed over the molten metal. The impurities are oxidized and the volatile oxides thus produced escape with the blast of air. The pure metal remains behind in the cupel. Pb present in silver is removed by cupellation process.

$$2 \operatorname{Pb}(g) + O_2 \longrightarrow 2 \operatorname{PbO}(g)$$



#### (II) **PARTING PROCESS :**

Crude gold obtained by MacArthur-Forrest cyanide and chlorination process contains Ag, Cu, Zn, and sometimes Pb as impurity. Zn and Pb are removed by cupellation process. Cu and Ag are removed by parting process.

- (i) Parting with sulfuric acid or nitric acid: Gold is not attacked by these acids while Cu and Ag dissolve. If, however, the Au content in an impure sample is more than 30%, the Cu and Ag are also not attacked by the acid of any strength. Hence, before the acid treatment, the impure sample is melted with necessary amount of Ag to reduce its gold content to about 25% (quartation). The resulting alloy, after being granulated in water, is boiled with  $H_2SO_4$  or nitric acid when Cu and Ag pass into solution, leaving Au undissolved . Au is separated and fused again with borax and nitre when 100% Au is obtained.
- (ii) Parting with  $CI_2$ : Sometimes chlorine is used for the purification of Au. The impure sample of Au is fused with borax and  $CI_2$  gas is forced through it. The base metals are converted into chlorides that pass out as fumes at this high temperature, and AgCI forms a separate layer between the fused layer of Au and borax, which is skimmed off and the Au left behind cast into ingots.

#### (III) POLING PROCESS :

This process is used for the purification of copper and tin.

(i) **Purification of Impure Copper :** Impure copper is remelted in a reverberatory furnace lined with SiO<sub>2</sub> and a blast of O<sub>2</sub> is blows into the furnace. O<sub>2</sub> oxidises S, Sb and As to their respective oxides which, being, volatile, get volatilised and are thus removed. Fe is oxidised to FeO which forms a slag of FeSiO<sub>3</sub> with SiO<sub>2</sub> lining of the furnace. Molten copper left behind contains CuO as impurity. This molten copper is treated with powdered anthracite and then stirred with a pole of green wood. Green wood, at high temperature, liberates hydrocarbon gases, which are converted into methane (CH<sub>4</sub>). Methane thus obtained reduces CuO to free Cu–metal, which is about 99.5% pure and is called tough pitch copper.

Green wood  $\rightarrow$  Hydrocarbons  $\rightarrow$  CH<sub>4</sub>

 $4\text{CuO} + \text{CH}_4 \rightarrow 4\text{Cu} \text{ (pure metal)} + \text{CO}_2 + 2\text{H}_2\text{O}$ 

(ii) Purification of Impure Tin : Impure tin metal contains the impurities of Cu, Fe, W and SnO<sub>2</sub>. The impurity of SnO<sub>2</sub> is due to the incomplete reduction of tin stone ore (SnO<sub>2</sub>) during smelting. In order to remove these impurities, the impure molten tin metal is taken in a big pot and stirred with a pole of green wood. Green wood, at high temperature liberates hydrocarbon gases, which are converted into methane CH<sub>4</sub>. Methane thus obtained reduces SnO<sub>2</sub> to pure metal while the impurities of Cu, Fe, W etc. come up to the surface, where they come in contact with air and are oxidised to their respective oxides. The oxides form a scum on the surface of pure tin metal. This scum is removed from the surface. Tin metal obtained by this method is 99% pure.

$$\begin{array}{ll} \text{Green wood} & \rightarrow & \text{Hydrocarbon} \rightarrow \text{CH}_4 \\ 2\text{SnO}_2 + \text{CH}_4 & \rightarrow & 2\text{Sn} + \text{CO}_2 + 2\text{H}_2\text{O} \end{array}$$

#### (IV) ELECTROLYTIC REFINING:

Some metals such as Cu, Ni, and Al are refined electrolytically. The Hooper process is a process for the electrolytic refining of aluminum. Impure Al forms the anode and pure Al forms the cathode of the Hooper's cell which contains three liquid layers. The bottom layer is molten impure Al, the middle is a fused salt layer containing aluminum fluoride, and the top layer is pure Al. At the anode (bottom layer), Al passes with solution as aluminum ion (Al<sup>3+</sup>), and at the cathode (top layer), these ions are reduced to the pure metal. In operation, molten metal is added to the bottom of the cell and pure aluminum is drawn off the top.

At anode : Al  $\longrightarrow$  Al<sup>3+</sup> + 3e<sup>-</sup> At cathode : Al<sup>3+</sup> + 3e<sup>-</sup>  $\longrightarrow$  Al

Copper obtained from the reduction of ores must be purified for use in making electrical wiring because impurities increase its electrical resistance. The method used is electro-refining.

Impure Cu obtained from ores is converted to pure Cu in an electrolyte cell that the impure copper as the anode an



## **CHEMISTRY FOR JEE MAIN & ADVANCED**

pure copper as the cathode. The electrolyte is an aqueous solution of  $CuSO_4$ . At the impure Cu anode, Cu is oxidized along with the more easily oxidized metallic impurities such as Zn and Fe. The less easily oxidized impurities such as Ag, Au, and Pt fall to the bottom of the cell as anode mud, which is reprocessed to recover the precious metals. At the pure Cu cathode,  $Cu^{2+}$  ions get reduced to pure copper metal, but the less easily reduced metal ions (Zn<sup>2+</sup>, Fe<sup>2+</sup> etc.) remain in the solution.

Anode (oxidation):  $M(s) \longrightarrow M^{2+}(aq) + 2e^{-}$  (M = Cu, Zn, Fe)

Cathode (reduction) :  $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$ 

Thus, the net cell reaction simply involves transfer of Cu metal from the impure anode to the pure cathode, Cu obtained by this process is 99.95% pure.

## (V) KROLL'S PROCESS :

 $TiCl_4 + 2 Mg \_ 1000-1500^{\circ}C \rightarrow Ti + 2 MgCl_2$  (Kroll's process)

TiCl<sub>4</sub>+4 Na \_\_\_\_\_\_ Ti+4 NaCl (Imperial metal industries (IMI) process)

NaCl is leached with H<sub>2</sub>O. Ti is in the form of small granules. Zr is also produced by Kroll's process.

## (VI) VAPOUR PHASE REFINING:

#### (i) Extraction of Nickel (Mond's process) :

 $Ni(s) + 4CO(s) \xrightarrow{50^{\circ}C} [Ni(CO_4)](g)$ 

 $[Ni(CO)_4](g)$  200°C Ni + 4CO(g)

## (ii) Van Arkel-De Boer Process :

Small amounts of very pure metals (Ti, Zr, or Bi) can be produced by this method.

Impure  $Ti + 2I_2 \xrightarrow{50 - 250^{\circ}C} TiI_4 \xrightarrow{1400^{\circ}C} TiI_2 \xrightarrow{1400^{\circ}C} Ti + 2I_2$ 

## (VII) PARKES PROCESS :

The removal of the impurities of Ag from the commercial lead is called desilverisation of lead and is done by **Parkes Process**. Thus, Parkes process is the desilverisation of lead.

In Parkes process, the commercial lead, which contains Ag as impurities, is melted in iron pots and 1% of Zn is added to it. The molten mass is thoroughly agitated. Since Ag is about 300 times more soluble in Zn than in Pb, most of the Ag present in the commercial lead as impurity mixes with Zn, to form Zn–Ag alloy. When the whole is cooled, two layers are obtained. The upper layer contains Zn–Ag alloy in the solid state, while the lower layer has lead in the molten state. This lead contains only 0.0004% of Ag and hence is almost pure. Lead obtained after removing most of Ag from it (desilverisation of lead) by Parkes process, is called desilverised lead. This lead contains the impurities of metals like Zn, Au, Sb etc. These metal impurities are removed from desilverised lead by **Bett's Electrolytic Process.** 



Zn–Ag alloy, formed in the upper layer, is skimmed off from the surface of the molten lead by perforate ladles. This alloy contains lead as impurity. This impurity of Pb is removed from the alloy by **liquation process**, in which Zn–Ag alloy is heated in a slopping furnace, when the impurity of Pb melts and hence drains away from the solid alloy. Thus purified Zn–Ag is obtained. Now Ag can be obtained from this purified Zn–Ag alloy by **distillation process**, in which the alloy is heated strongly in presence of little carbon in a fire–clay retort. Zn, being more volatile, distills off while Ag remains in the retort, carbon used in the process reuses the oxide of Zn, if formed. Ag obtained from Zn–Ag alloy is contaminated with a little of Pb as impurity. This impurity of Pb placed in a cupel (cupel is a boat–shaped) dish made of bone ash which is porous in nature) in a reverberatory furnace and heated in the presence of air. By doing so, lead (impurity) is oxidised to PbO (litharge) which volatilises and pure Ag is left behind in the cupel. Last traces of PbO are absorbed by the porous mass of the cupel.

#### (VIII) PUDDING PROCESS :

This process is used for the manufacture of wrought iron from cast iron. We know that cast iron contains the impurities of C, S, Si, Mn and P. When these impurities are removed from cast iron, we get wrought iron. In this process the impurities are oxidised to their oxides not by blast of air but by the hematite (Fe<sub>2</sub>O<sub>3</sub>) lining of the furnace.

## **EXTRACTION OF SOME METALS**

## (A) EXTRACTION OF COPPER

Copper is mainly extracted from copper pyrites. After the concentration of its ore by froth flotation process, the ore is roasted in a current of air to remove arsenic, antimony and much of sulphur. The reactions occuring are

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2 \uparrow \text{ (major reaction)}$$
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2 \text{ (minor reactions)}$$

The ore is then mixed with a little coke and sand and smelted in a water-jacketed blast furnace. The minor reactions that occured during roasting continue here. Ferrous oxide combines with sand to form a fusible slag. Cuprous oxide formed combines with ferrous sulphide to give ferrous oxide and cuprous sulphide. This is because iron has more affinity for oxygen than copper.

$$FeO + SiO_2 \longrightarrow FeSiO_3$$
;  $Cu_2O + FeS \longrightarrow Cu_2S + FeO$ 



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The molten matte is finally transferred to Bessemer converter. A blast of sand and air is blown in the converter through tuyeres which are situated a little above the bottom. This causes removal of S and As oxides and ferrous oxide as slag. At the same time  $Cu_2S$  is oxidized mostly into  $Cu_2O$  and partly into CuO and  $CuSO_4$ . All these react with  $Cu_2S$  giving copper.

The reactions are

$$2Cu_{2}S + 3O_{2} \longrightarrow 2Cu_{2}O + 2SO_{2} \uparrow$$
  

$$2Cu_{2}S + 5O_{2} \longrightarrow 2CuSO_{4} + 2CuO$$
  

$$2Cu_{2}O + Cu_{2}S \longrightarrow 6Cu + SO_{2} \uparrow$$
  

$$CuSO_{4} + Cu_{2}S \longrightarrow 3Cu + 2SO_{2} \uparrow$$
  

$$Cu_{2}S + 2CuO \longrightarrow 4Cu + SO_{2} \uparrow$$

Finally, copper may be refined electrolytically (electrolyte; copper sulphate : anode; impure copper and cathode; pure copper).

#### (B) EXTRACTION OF LEAD

Lead is mainly extracted from galena. After the concentration of the ore by froth flotation process, the ore is roasted in a reverberatory furnace for about six hours at a moderate temperature in a current of air. Part of galena is converted into lead oxide and lead sulphate. After this, the supply of air is stopped and small quantities of carbon, quicklime and cheap iron ore are added along with increase of temperature. At this stage, unreacted sulphide reacts with the lead oxide and sulphate giving metallic lead :

 $PbS + 2PbO \longrightarrow 3Pb + 2SO_{2}$  $PbS + PbSO_{4} \longrightarrow 2Pb + 2SO_{2}$ 

The obtained lead contains impurities such as Cu, Ag, Bi, Sb and Sn. Silver is removed by Parke's process where molten zinc is added to molten impure lead. The former is immiscible with the latter. Silver is more soluble in molten zinc than in molten lead. Zinc-silver alloy solidifies earlier then molten lead and thus can be separated. After this, crude lead is refined electrolytically (Electrolyte; lead silicofluoride,  $PbSiF_6$  and hydrofluosilicic acid,  $H_2SiF_6$  with a little gelatin, anode, crude lead and cathode; pure lead).



(C) EXTRACTION OF IRON





Iron is extracted from its principal ore, heamatite. After the preliminary washing, concentration and roasting, the ore is smelted in the presence of coke and limestone in a blast furnace.

Roasted ore (8 parts) with desulphurized coke (4 parts) and limestone pieces (1 part) is fed into the blast furnace from the top. (Preheated air is blown in through water - jacketed pipes called tuyeres fixed in the lower part of the furnace). There is a temperature gradient as we move from the bottom (temperature about 2000K) to the top (temperature about 500K) of the blast furnace.

The blast furnace may be broadly divided into three main parts as described in the following.



#### (a) Zone of Fusion

The lower portion where coke burns and produced carbon dioxide and a lot of heating is known as zone of fusion:

 $C + O_2 \longrightarrow CO_2$   $\Delta H = -406 \text{ kJ mol}^{-1}$ 

Here the temperature is about 1775 K. A little above this, where temperature is above this, where temperature is about 1475 K - 1575 K, iron coming from above melts.

## (b) Zone of Heat Absorption

The middle portion (temperature 1075 K – 1275 K), CO<sub>2</sub> rising up is reduced to CO with the absorption of heat: CO<sub>2</sub> + C  $\longrightarrow$  2CO  $\Delta H = 163 \text{ kJ mol}^{-1}$ 

In this portion, limestone coming from above is decomposed and the resultant lime (CaO), which acts as flux, combines with silica (present as impurity - gangue) to form calcium silicate (fusible slag) :

$$CaCO_3 \longrightarrow CaO + CO_2$$

 $CaO + SiO_2 \longrightarrow CaSiO_3$ 



## (c) Zone of Reduction

The upper portion (675K - 975 K) where iron oxide is reduced to spongy iron by carbon monoxide rising up to furnace

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

The reduction is believed to take place in stages :

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

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$$
  

$$FeO + CO \longrightarrow Fe + CO_2$$

At the bottom of the furnace the molten iron sinks down while above this floats the fusible slag which protects the molten iron form oxidation. These two can be removed from different holes (fig.). Waste gases escaping at the top consists of about 30% CO, 10% CO<sub>2</sub> and the rest nitrogen.

Iron obtained from the blast furnace is known as pig iron.

Pig iron contains about 2–5% carbon as well as other impurities (usually Si, Mn, S and P). Pig iron is converted into cast iron by remelting in a vertical furnace heated by coke. Cast iron expands on solidification and is used for casting various articles. Wrought iron, which is the purest form of iron can be obtained by heating cast iron in a reverberatory furnace lined with iron oxide. Wrought iron contains about 0.2% carbon.

#### (D) MANUFACTURE OF STEEL

Different method are used :-

(a) Bessemer Process

This process is based on the fact that impurity of the pig iron are completely oxidised in presence of hot air blast.

This process involves the use of a large pear- shaped furnace (vessels) called Bessemer converter.

## (b) BOP Method (Basic Oxygen Process)

The process is carried out in a steel vessel with a refractory lining (usually made of dolomite,  $CaCO_3$ ,  $MgCO_3$ ). Oxygen gas at about 10 atm pressure and a stream of powdered limestone are fed through a water-cooled lance and discharged above the molten pig iron.

$$2C + O_{2} \longrightarrow 2CO$$

$$2FeO + Si \longrightarrow 2Fe + SiO_{2}$$

$$FeO + Mn \longrightarrow Fe + MnO$$

$$FeO + SiO_{2} \longrightarrow FeO. SiO_{2}$$

$$MnO + SiO_{2} \longrightarrow MnO.SiO_{2} (slag)$$

$$4P + 5O_{2} \longrightarrow 2P_{2}O_{5}$$

$$3CaO + P_{2}O_{5} \longrightarrow Ca_{3} (PO_{4})_{2}$$

The properties of steel depend on its chemical composition but also on heat treatment. At high temperatures, iron and carbon in steel combine to form iron carbide,  $Fe_3C$ , called cementite :

 $3Fe(s) + C(s) \rightarrow Fe_3C(s)$ 

The forward reaction is endothermic, so that the formation of cemetite is favoured at high temperatures. When steel containing cemetite is cooled slowly, the above equilibrium shifts to the left, and the carbon separates as small particles of graphite, which give the steel a gray colour. If the steel is cooled rapidly, equilibrium is not attained and the carbon remains large in the form of cementite, Fe<sub>3</sub>C. Steel containing cementite is light in colour, and is harder and more brittle than that containing graphite.



#### (c) Heat Treatment of Steel

#### **Quenching or Hardening**

Steel is heated to red hot temp. and is then cooled suddenly by plunging into either cold water or oil. It makes steel hard and brittle.

#### Annealing

The steel is heated to red hot temp. and then cooled slowly.

It makes steel soft.

#### Tempering

If quenched steel is heated to temp. between 500 to 575 K and then cooled slowly, it becomes quite hard but brittleness disappears. The process is called tempering.

#### **Surface Treatment of Steel**

(i) Nitriding - Process of heating steel at 1000 K in an atmosphere of  $NH_3$ .

This gives hard coating of iron nitride on the surface.

- (ii) Case hardening Process of giving a thin coating of hardend steel, by heating steel in contact with charcoal followed quenching in oil.
- It is used for axles of railway wagons.
- (d) Types of Iron

#### **Cast Iron or Pig Iron**

It is most impure form of Iron and contains the higest proportion of carbon (2.5 - 4 %) along with traces of S, P, Mn and Si. Cast iron contain 2.5 to 4.3 & pig contain 2.5 to 5%.

#### Wrought Iron (Fibrous Iron) or Malleable Iron

It is the purest form of iron and contains minimum amount of carbon (0.12 - 0.25%) and less than 5% of other impurities.

#### Steel

It is the most important form of iron and finds extensive applications. As far as carbon content (impurity) is concerned it is mid-way between cast iron and wrought iron, it contains 0.25- 2% carbon.

Thus all the three forms of iron differ in their carbon contents, both iron and steel are obtained from cast iron.

Order of M.P. WI > Steel > CI or PI

#### (E) EXTRACTION OF ZINC (Zn)

 $ORE \longrightarrow Zinc blende or Black jack (ZnS)$ 



#### USES

- (a) Zn-Cu couple, Zn-Hg, zinc dust etc. are used as reducing agent in organic reactions.
- (b) large amounts of zinc are used for galvanizing iron. Zinc is deposited on the surface of iron articles. This process is called galvanization.
- (c)  $ZnSO_4$  .7H<sub>2</sub>O (White vitrol) issued as eye lotion.

#### (F) EXTRACTION OF SILVER AND GOLD

**Cyanide Process :** Silver and gold are extracted by the cyanide process (Mac Arthur - Forrest process). After the preliminary crushing and concentration by forth floatation process, the ore (crushed auriferous rocks in the case of gold) is leached with dilute (0.4 - 7%) solution of sodium cyanide made alkaline by adding lime kept agitated by a current of air. Silver (or gold) pass into solution as argentocyanide (or aurocyanide) :

$$Ag_2S + 4NaCN \ddagger 2Na[Ag(CN)_2] + Na_2S$$

The air blown in remove  $Na_2S$  and  $Na_2S_2O_3$  and  $Na_2SO_4$  causing the above reaction to proceed to completion.

$$2Na_{2}S + 2O_{2} + H_{2}O \longrightarrow Na_{2}S_{2}O_{3} + 2NaOH$$

$$Na_{2}S_{2}O_{3} + 2NaOH + 2O_{2} \longrightarrow 2Na_{2}SO_{4} + H_{2}O$$

$$4Au + 8NaCN + 2H_{2}O \ddagger^{\uparrow} \uparrow^{\downarrow} 4Na[Au(CN)_{2}] + 4NaOH$$

The solution obtained above is filtered and treated with scrap iron or zinc when silver (or gold) get precipitated:

$$2Ag(CN)_{2}^{-} + Zn \longrightarrow Zn(CN)^{2}_{4} + 2Ag$$
$$2Na[Au(CN)_{2}] + Zn \longrightarrow Na_{2}[Zn(CN)_{4}] + 2Au$$

The obtained silver is purified electrolytically (eletrolyte : silver nitrate solution containing 1% nitric acid, anode : impure silver, cathode : pure silver). The impurities like zinc and copper pass into the solution while gold falls down as anode mud.

Gold thus obtained is contaminated by zinc which is dissolved out by sulphuric acid. The dried residue of gold is then fused under borox (flux) in graphite crucible and the melted down gold (bullion) which invariably contain silver, is set for refining.

## (G) EXTRACTION OF MERCURY (HYDRAGYRUM) (Hg)

Short Chart of Hg (Hydragyrum) by HgS (Cinnabar or Vermilon)



- (a) Pb & Zn remove as oxide.
- (b) Basic metal remove as nitrate in HNO<sub>3</sub>
- (c) Final purification done by vacuum distillation.



#### **PROPERTIES**

- (a) It vigorously combines with  $Cl_2$  slowly with  $Br_2$  and  $I_2$ .
- (b) Hot conc.  $H_2SO_4$ , dil. & conc. HNO<sub>3</sub> dissolve it.
- (c) Mercury is acted upon by HI on account of the formation of a complex ion(HgI<sub>4</sub>)<sup>2-</sup>

 $Hg + 2HI \rightarrow HgI_2 + H_2$ 

 $HgI_2 + 2HI \rightarrow H_2HgI_4$ 

(d) Hg dissolves many metals and the combinations are called **amalgams**. Au, Ag, Sn, Pb,Mg, Cu, Na, K etc. rubbed with mercury form amalgams. Co, Fe and Ni do not form amalgam directly.

#### USES

#### Mercury is used :

- (a) In thermometers, barometers and other physical apparatus.
- (b) In the extraction of Ag and Au. In amalganation process.
- (c) In the form of amalgams as reducing agents.
- (d) In mercury vapour lamps.
- (e) In manufacture of vermilon (HgS).

#### (H) EXTRACTION OF ALUMINIUM





(c) Serpeck's Process : (Used for white bauxite in which main impurity is silica)

Bauxite ore + coke 
$$\xrightarrow{1800^{\circ}C}$$
 AlN  $\xrightarrow{H_2O}$  Al(OH)<sub>3</sub> + NH<sub>3</sub>  
+ ppt

(Nitrogen) N<sub>2</sub>

$$C + SiO_2$$
 (gangue)  $\rightarrow CO_2 \not F + Si \not F$ 

#### CALCINATION

Al(OH)<sub>3</sub> 
$$\xrightarrow{1500^{\circ}\text{C}}$$
 Al<sub>2</sub>O<sub>3</sub>

#### **Electrolytic Reduction**

Electrolyte Al<sub>2</sub>O<sub>3</sub> dissolved in Na<sub>3</sub>AlF<sub>6</sub> and CaF<sub>2</sub>

Cathode-Carbon lining

Anode – Graphite rods

$$Al_2O_3 \xrightarrow{Electrolysis} Al + O_2$$

↓ 99.8% pure

#### **Electrolytic Refining**

(Hoop's process)

Pure Al (99.98 % pure)

## **IMPORTANT POINTS**

- (a) Useful gas  $NH_3$  is evolved in the leaching of bauxite by Serpeck's process.
- (b) In the electrolytic reduction of  $Al_2O_3$  cryolite (Na<sub>3</sub>AlF<sub>6</sub>) is added along with CaF<sub>2</sub> (fluorspar) to-
  - decrease m.p. of Al<sub>2</sub>O<sub>3</sub>
  - decrease viscosity of electrolyte ( $CaF_2$  is used)
  - increase conductivity
- (c) In the electrolytic reduction graphite anode get corrode or finished due to reaction with O<sub>2</sub> liberates at anode, hence it had to be changed periodically.
- (d) In the electrolytic refining (4th step) no electrodes are used. In the Hoop's process molten pure Al is used as cathode and molten impure Al is used as anode.
- (e) In the Hoop's process carbon dust is sprayed over molten Al to
  - avoid heat lose

- minimise metallic lusture (glaze) which is harmful for the eyes.

## (I) EXTRACTION OF MAGNESIUM

Magnesium is commonly obtained by the electrolysis of fused magnesium chloride containing a little (25%) sodium chloride and sodium fluoride at  $700^{0}$ C in an air-tight iron pot which itself serves as the cathode, the



anode being a graphite rod which dips into the electrolyte. The anode is surrounded by a perforated porcelain tube for the exit of chlorine. The electrolysis is carried out in the atmosphere of coal gas so as to prevent the attack of atmospheric oxygen and nitrogen on magnesium. Molten magnesium being lighter then the electrolyte, it floats over the fused electrolyte and is withdrawn



In Dow process, magnesium is recovered from seawater as magnesium chloride which is then electrolysed using cell described above.

Dow's Sea Water Process: Sea water contains 0.13% Mg ions.

 $Mg^{2+}(seawater) + Ca(OH)_{2}(from oyster shells) \rightarrow Mg(OH)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickened in Dorr Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} \xrightarrow{\text{Thickeners}} MgCl_{2} \cdot 2H_{2}O(H)_{2} + CaCl_{2} +$ 

 $MgCl_2.2H_2O \xrightarrow{spray drying} MgCl_2.1.5H_2O \xrightarrow{dry HCl} MgCl_2$ 

**Dow's Natural Brine Process** 

$$MgCO_{3}.CaCO_{3} \xrightarrow{heat} MgO.CaO \xrightarrow{dil. HCl} CaCl_{2}(aq) + MgCl_{2}(aq) \xrightarrow{CO_{2}} MgCl_{2}(aq) + CaCO_{3}$$

(dolomite)

(calcined dolomite)

The reaction is :  $CaCl_2$ .  $MgCl_2(aq) + MgO.CaO + 2CO_2 \longrightarrow MgCl_2(aq) + 2CaCO_3 \downarrow$ 

**Electrolysis:** Anhydrous carnallite (KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O) may also be employed as the starting material of magnesium chloride. The cathode may be a layer of molten lead on the floor of the cell and anode may be graphite rods which are suspended above the molten lead. Magnesium liberated at the cathode dissolves in molten lead. The alloy of lead-magnesium is subjected to electrolysis to obtain pure magnesium (electrolyte: fused carnallite, anode : lead-magnesium alloy and cathode-steel rods.)

## THERMODYNAMICS OF EXTRACTION : ELLINGHAM DIAGRAM OF A METAL

Some basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations. Gibbs energy is the most significant term here. The change in Gibbs energy,  $\Delta G$  for any process at any specified temperature, is described by the equation:

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

.....(1)



where,  $\Delta H$  is the enthalpy change and  $\Delta S$  is the entropy change for the process. For any reaction, this change could also be explained through the equation:

 $\Delta GV = -RT lnK$ 

.....(2)

where, K is the equilibrium constant of the 'reactant – product' system at the temperature T. A negative  $\Delta G$  implies a +ve K in equation (2) And this can happen only when reaction proceeds towards products. From these facts we can make the following conclusions:

- 1. When the value of  $\Delta G$  is negative in equation (1) only then the reaction will proceed. If  $\Delta S$  is positive, on increasing the temperature (T), the value of T $\Delta S$  would increase ( $\Delta H < T\Delta S$ ) and then  $\Delta G$  will become –ve.
- 2. If reactants and products of two reactions are put together in a system and the net  $\Delta G$  of the two possible reactions is -ve, the overall reaction will occur. So the process of interpretation involves coupling of the two reactions, getting the sum of their  $\Delta G$  and looking for its magnitude and sign. Such coupling is easily understood through Gibbs energy ( $\Delta G^{-}$ ) vs T plots for formation of the oxides

## **ELLINGHAM DIAGRAM**

The graphical representation of Gibbs energy was first used by H.J.T. Ellingham. This provides a sound basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham Diagram. Such diagrams help us in predicting the feasibility of thermal reduction of an ore. The criterion of feasibility is that at a given temperature, Gibbs energy of the reaction must be negative.

(a) Ellingham diagram normally consists of plots of  $\Delta_t G^-$  vs T for formation of oxides of elements i.e., for the reaction,

$$2xM(s) + O_{2}(g) \rightarrow 2M_{2}O(s)$$

In this reaction, the gaseous amount (hence molecular randomness) is decreasing from left to right due to the consumption of gases leading to a –ve value of  $\Delta S$  which changes the sign of the second term in equation (1) Subsequently  $\Delta G$  shifts towards higher side despite rising T (normally,  $\Delta G$  decreases i.e., goes to lower side with increasing temperature). The result is +ve slope in the curve for most of the reactions shown above for formation of Mx O(s).

- (b) Each plot is a straight line except when some change in phase (s → liq or liq → g) takes place. The temperature at which such change occurs, is indicated by an increase in the slope on +ve side (e.g., in the Zn, ZnO plot, the melting is indicated by an abrupt change in the curve).
- (c) There is a point in a curve below which  $\Delta G$  is negative (So Mx O is stable). Above this point, Mx O will decompose on its own.
- (d) In an Ellingham diagram, the plots of  $\Delta G^-$  for oxidation (and therefore reduction of the corresponding species) of common metals and some reducing agents are given. The values of  $\Delta_f G^-$ , etc.(for formation of oxides) at different temperatures are depicted which make the interpretation easy.
- (e) Similar diagrams are also constructed for sulfides and halides and it becomes clear why reductions of Mx S is difficult. There, the  $\Delta_{f}GV$  of M<sub>x</sub> S is not compensated.





## LIMITATIONS OF ELLINGHAM DIAGRAM :

- 1. The graph simply indicates whether a reaction is possible or not i.e., the tendency of reduction with a reducing agent is indicated. This is so because it is based only on the thermodynamic concepts. It does not say about the kinetics of the reduction process (Cannot answer questions like how fast it could be ?).
- 2. The interpretation of  $\Delta G^-$  is based on K ( $\Delta GV = -RT \ln K$ ). Thus it is presumed that the reactants and products are in equilibrium:

$$M_x O + A_{red} \longrightarrow xM + AO_{or}$$

This is not always true because the reactant/product may be solid. [However it explains how the reactions are sluggish when every species is in solid state and smooth when the ore melts down. It is interesting to note here that  $\Delta H$  (enthalpy change) and the  $\Delta S$  (entropy change) values for any chemical reaction remain nearly constant even on varying temperature. So the only dominant variable in equation (1) becomes T. However,  $\Delta S$  depends much on the physical state of the compound. Since entropy depends on disorder or randomness in the system, it will increase if a compound melts (s  $\rightarrow$  1) or vapourises (1  $\rightarrow$  g) since molecular randomness increases on changing the phase from solid to liquid or from liquid to gas].

The reducing agent forms its oxide when the metal oxide is reduced. The role of reducing agent is to provide  $\Delta G^-$  negative and large enough to make the sum of  $\Delta G^-$  of the two reactions (oxidation of the reducing agent and reduction of the metal oxide) negative.

As we know, during reduction, the oxide of a metal decomposes:

$$M_x O(s) \rightarrow xM \text{ (solid or liq)} + \frac{1}{2} O_2 \text{ (g)}$$
 .....(3)

The reducing agent takes away the oxygen. Equation (3) can be visualised as reverse of the oxidation of the metal. And then, the  $\Delta_{f}G^{-}$  value is written in the usual way:

$$xM(s \text{ or } l) + \frac{1}{2}O_2(g) \rightarrow M_xO(s) [\Delta G^-(M, M_xO)]$$
 .....(4)

If reduction is being carried out through equation (3), the oxidation of the reducing agent (e.g., C or CO) will be there

$$C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g) \qquad [\Delta G_{(C,CO)}]$$
$$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g) \qquad [\Delta G_{(C,CO)}]$$

If carbon is taken, there may also be complete oxidation of the element to CO<sub>2</sub>:

$$\frac{1}{2}C(s) + \frac{1}{2}O_2(s) \to \frac{1}{2}CO_2(g) \qquad \qquad [\frac{1}{2}\Delta G_{(C,CO_2)}]$$

On subtracting equation (4) [it means adding its negative or the reverse form as in equation (3) from one of the three equations, we get:

$$M_{x}O(s) + C(s) \rightarrow xM(s \text{ or } 1) + CO(g)$$
$$M_{x}O(s) + CO(g) \rightarrow xM(s \text{ or } 1) + CO_{2}(g)$$
$$M_{x}O(s) + \frac{1}{2}C(s) \rightarrow xM(s \text{ or } 1) + \frac{1}{2}CO_{2}(g)$$

These reactions describe the actual reduction of the metal oxide,  $M_x O$  that we want to accomplish. The  $\Delta_r G^-$  values for these reactions in general, can be obtained by similar subtraction of the corresponding  $\Delta_r G^-$  values.

As we have seen, heating (i.e., increasing T) favours a negative value of  $\Delta_r G^-$ . Therefore, the temperature is chosen such that the sum of  $\Delta_r G^-$  in the two combined redox process is negative. In  $\Delta_r G^-$  vs T plots, this is indicated by the point of intersection of the two curves (curve for M<sub>v</sub>O and that for the oxidation of the reducing substance).

After that point, the  $\Delta_r G^-$  value becomes more negative for the combined process including the reduction of  $M_x O$ . The difference in the two  $\Delta_r G^-$  values after that point determines whether reductions of the oxide of the upper line is feasible by the element represented by the lower line. If the difference is large, the reduction is easier



## Mettallurgy at a Glance





## METALLURGY



Hot conc.  $H_2SO_4$  dissolves lead with evolution of  $SO_2$  but the reaction becomes lower due to formation of insoluble  $PoSO_5$ .

 $Pb + 2H_2SO_4 \longrightarrow PbSO_4 + SO_2 + 2H_2O$ 

HNO<sub>3</sub> is the best solvent for load. With dill HNO<sub>3</sub>, NO is evolved while with one, HNO<sub>3</sub>, NO<sub>2</sub> is liberated.

 $\begin{array}{l} 3[\mathrm{Pb}+2\mathrm{HNO}_3\,(\mathrm{dil}_2)\longrightarrow 2\mathrm{Pb}(\mathrm{NO}_3)_2+2\mathrm{H}]\\ \\ \hline 2[\mathrm{HNO}_3\dashv 3\mathrm{H} \longrightarrow \mathrm{NO}+2\mathrm{H}_2\mathrm{O}]\\ \hline 3\mathrm{Pb}+8\mathrm{HNO}_3\,(\mathrm{dil}_2)\longrightarrow 3\mathrm{Pb}(\mathrm{NO}_3)_2+2\mathrm{NO}+1 \end{array} \overset{\mathrm{A}}{\longrightarrow} \end{array}$ 











Some Important Compound and their	formulae
Lunar caustic (Highly photo sensensitive)	AgNO <sub>3</sub>
Monozite	ThO <sub>2</sub>
Calomal	Hg <sub>2</sub> Cl <sub>2</sub>
I●imanite	TiO <sub>2</sub>
Corrosive sublimate	HgCl <sub>2</sub>
(does not give chromyl chloride test)	
Type metal	Pb+Sn+Sb
Constantan	Cu(60%)+Ni(40%)
Litharge	РЬО
Red Lead (OR) Sindhur	Pb <sub>3</sub> O <sub>4</sub>
Butter of tin	SnCl <sub>4</sub> .5H <sub>2</sub> O
Spelter	(Impure Zn during extraction of Zn) Crude zinc metal called spelter which contain nonfusible impurities and the impurities of Pb, Fe, Cd.
Green vitrol	FeSO <sub>4</sub> . 7H <sub>2</sub> O
Blue vitrol	CuSO <sub>4</sub> .5H <sub>2</sub> O
White vitrol	ZnSO <sub>4</sub> .7H <sub>2</sub> O
Lithopone	BaSO <sub>4</sub> +ZnS
Nessler Reagent in basic medium	K <sub>2</sub> HgI <sub>4</sub>
Mohr salt (ferrous Ammonium sulphate)	$\textbf{FeSO}_4 \cdot (\text{NH}_3)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$
Ignition mixture	Mg powder + $BaO_2$
Fusion mixture	$Na_2CO_3 + K_2CO_3$
Freezing mixture	NaCl is used with ice
Electron	Mg (95%) + Zn (5%) used in aircraft

