



# METALLURGY

## 1. INTRODUCTION :

The compound of a metal found in nature is called a mineral. The minerals from which metal can be economically and conveniently extracted are called **ores**. An ore is usually contaminated with earthy or undesired materials known as gangue. So all minerals are not ores but all ores are minerals. Ores may be classified mainly into following four classes.

- (a) **Native ores** : They contain the metal in free state. Silver, gold, platinum etc, occur as native ores.
- (b) **Oxidised ores** : These ores consist of oxides or oxysalts (e.g. carbonates, phosphates, sulphates and silicates ) of metals.
- (c) **Sulphurised ores** : These ores consist of sulphides of metals like iron, lead, zinc, mercury etc.
- (d) **Halide ores** : These ores consist of halides of metals.

## 2. SECTION (A) : ORES & METHOD OF CONCENTRATION

**Important ore :**

### 2.1. Oxide ore :

- (i) Bauxite  $\rightarrow$   $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  (Major ore of Al)
- (ii) Haematite  $\rightarrow$   $\text{Fe}_2\text{O}_3$
- (iii) Zincite =  $\text{ZnO}$
- (iv) \*\*\*Cassiterite or tin stone  $\rightarrow$   $\text{SnO}_2$  (Black Tin = 60 – 70%  $\text{SnO}_2$ )

### 2.2. Carbonate ore :

- (i) Lime stone  $\rightarrow$   $\text{CaCO}_3$
- (ii) Dolomite  $\rightarrow$   $\text{CaCO}_3 \cdot \text{MgCO}_3$
- (iii) Siderite  $\rightarrow$   $\text{FeCO}_3$
- (iv) Malachite  $\rightarrow$   $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
- (v) Azurite  $\rightarrow$   $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
- (vi) \*\*\*Calamine  $\rightarrow$   $\text{ZnCO}_3$
- (vii) \*\*\*Cerussite  $\rightarrow$   $\text{PbCO}_3$

### 2.3. Sulphate ore :

Epsom salt  $\rightarrow$   $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

### 2.4. Silicate ore :

Feldspar  $\rightarrow$   $\text{KAlSi}_3\text{O}_8$

### 2.5. Sulphurised ore :

Consist of sulphides of metal like Iron, lead, zinc & mercury.

- (i) Iron pyrites  $\rightarrow$   $\text{FeS}_2$
- (ii) Copper glance  $\rightarrow$   $\text{Cu}_2\text{S}$
- (iii) Copper pyrite or chalcopyrite  $\rightarrow$   $\text{CuFeS}_2$
- (iv) Zinc Blende  $\rightarrow$   $\text{ZnS}$
- (v) Galena  $\rightarrow$   $\text{PbS}$
- (vi) Cinnabar  $\rightarrow$   $\text{HgS}$



## 2.6. Halide ore :

- (i) Cryolite  $\rightarrow \text{Na}_3\text{AlF}_6$
- (ii) Sylvine  $\rightarrow \text{KCl}$
- (iii) \*\*Carnallite  $\rightarrow \text{KCl} \cdot \text{MgCl} \cdot 6\text{H}_2\text{O}$
- (iv) Fluorspar  $\rightarrow \text{CaF}_2$
- (v) Horn silver  $\rightarrow \text{AgCl}$

**Note :** Mg obtained from both sea water & earth crust.

### Solved Example

**Example 1.** Which metals are supposed to occur in the native state in nature ?

**Solution:** Elements below hydrogen in the electrochemical series like Cu, Ag, Au etc, exist native ores.

**Example 2.** Match the ores listed in Column-I with their correct chemical formula listed in Column-II.

	Column I		Column II
(A)	Cassiterite	(p)	$\text{FeCO}_3$
(B)	Siderite	(q)	$\text{SnO}_2$
(C)	Cerussite	(r)	$\text{PbSO}_4$
(D)	Anglesite	(s)	$\text{PbCO}_3$

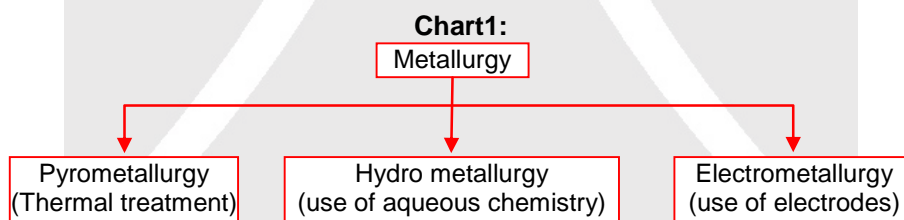
**Solution:**  $\text{SnO}_2$  is called as cassiterite or tin stone,  $\text{FeCO}_3$  is called as siderite,  $\text{PbCO}_3$  is called as cerussite and  $\text{PbSO}_4$  is called anglesite. So correct match is (A)  $\rightarrow$  (q), (B)  $\rightarrow$  (p), (C)  $\rightarrow$  (s) and (D)  $\rightarrow$  (r).

## 3. METALLURGY :

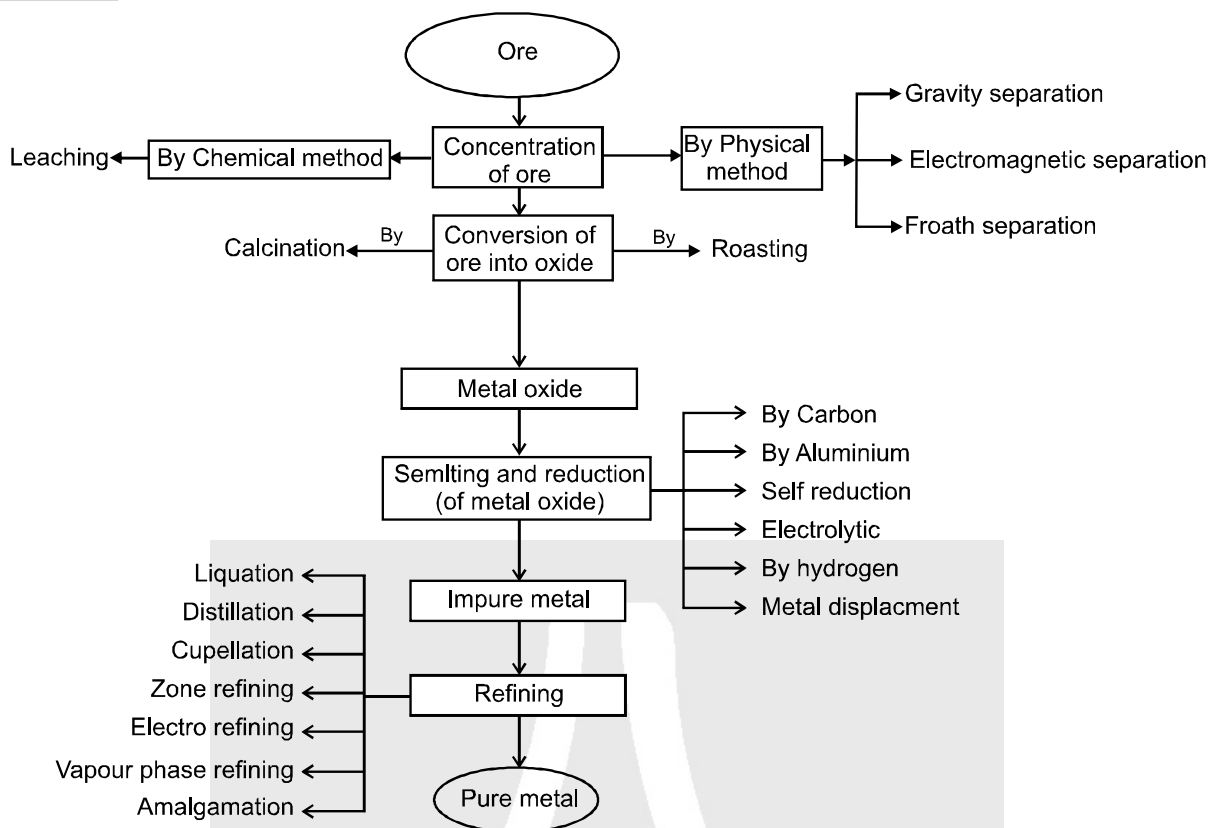
The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

The isolation and extraction of metals from their ores involve the following major steps:

- (A) Crushing of the ore.
- (B) Dressing or concentration of the ore.
- (C) Isolation of the crude metal from its ore
- (D) Purification or refining of the metal.



**Chart2: Steps involved in metallurgy.**



### 3.1. Physical Method :

#### 3.1.1 Crushing and Grinding :

The ore is first crushed by jaw crushers and ground to a powder (pulverisation of the ore) in equipments like ball mills and stamp mills.

#### 3.1.2 Concentration :

The removal of unwanted useless impurities from the ore is called **dressing, concentration or benefaction of ore.**

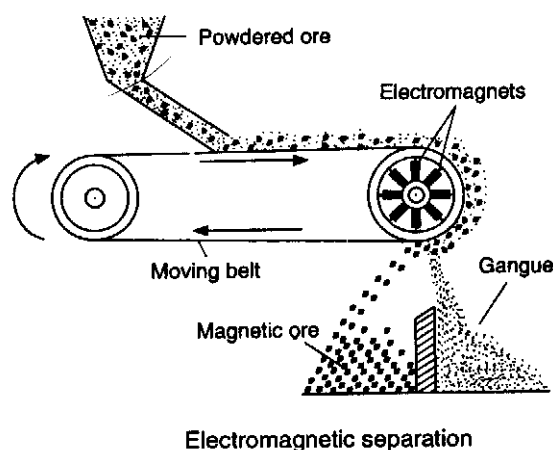
It involves several steps and selection of these steps depends upon the difference in physical properties of the compound of metal and that of gangue. Some of the important procedures are described below.

- (i) **Hydraulic washing or Gravity separation or Levigation method :** It is based on the difference in the densities of the gangue and ore particles. In this, the powdered ore is agitated with water or washed with a upward stream of running water, the lighter particles of sand, clay etc. are washed away leaving behind heavier ore particles. For this either hydraulic classifier or Wilfley table is used. This method is generally used for the concentration of oxide and native ores.
- (ii) **Electromagnetic separation :** It is based on differences in magnetic properties of the ore components.



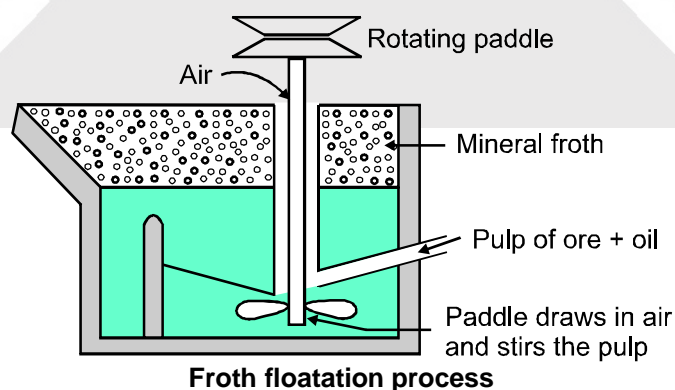
It is used when either the ore or the impurities associated with it are magnetic in nature. A magnetic separator consists of a belt (of leather or brass) moving over two rollers, one of which is magnetic. When the powdered ore is dropped on the belt at the other end, magnetic component of the ore is attracted by the magnetic roller and falls nearer to the roller while the non-magnetic impurities fall away from it.

**Examples :** Chromite ore ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ) is separated from non-magnetic silicious impurities and cassiterite ore ( $\text{SnO}_2$ ) is separated from magnetic Wolframite ( $\text{FeWO}_4 + \text{MnWO}_4$ ).



(iii) **Froth floatation process :** This method is commonly used for the concentration of the low grade sulphide ores like galena,  $\text{PbS}$  (ore of  $\text{Pb}$ ) ; copper pyrites  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$  or  $\text{CuFeS}_2$  (ore of copper) ; zinc blende,  $\text{ZnS}$  (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil. In this process one or more chemical frothing agents are added.

- (a) **Frothers :** These form stable froth which rises to the top of the flotation cell. Oils like pine oil, camphor oil etc., are used as frothers. These are added in small quantity. The stabiliser are added to the frothers so that the froth can last for longer period.
- (b) **Collectors :** Potassium or sodium ethyl xanthate is used as a collector. These get attached with the particles of the sulphide ore and thus make them water-repellant. Consequently the ore particles pass on into the froth. Collectors are always added in small quantity.
- (c) **Activating and depressing agents :** When a mineral contains other minerals as impurities. The addition of these agents activates or depresses the flotation property of other minerals present as impurities and thus helps in separating the impurities. For example galena ( $\text{PbS}$ ) usually contains the minerals namely zinc blende ( $\text{ZnS}$ ) and pyrites ( $\text{FeS}_2$ ) as impurities. Flotation is carried out by using potassium ethyl xanthate (used as a collector) along with  $\text{NaCN}$  and  $\text{Na}_2\text{CO}_3$  (used as depressing agent). The addition of  $\text{NaCN}$  and  $\text{Na}_2\text{CO}_3$  depresses the flotation property of  $\text{ZnS}$  and  $\text{FeS}_2$  grains, so mainly  $\text{PbS}$  passes into the froth when air is blown in. After  $\text{PbS}$  has been collected with the froth, the process is repeated by adding  $\text{CuSO}_4$  (activator) which activates the flotation property of  $\text{ZnS}$  grains which are now removed with the froth. The acidification of the remaining material left in the flotation cell leads to the flotation of  $\text{FeS}_2$ .



### Solved Example

**Example 1.** How does  $\text{NaCN}$  act as a depressant in preventing  $\text{ZnS}$  from forming the froth?

**Solution:**  $\text{NaCN}$  reacts with  $\text{ZnS}$  and forms a layer of  $\text{Na}_2[\text{Zn}(\text{CN})_4]$  complex on the surface of  $\text{ZnS}$  and thus prevents it from the formation of froth.



**Example 2.** What is the role of stabiliser in froth floatation process ?

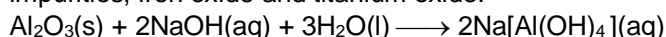
**Solution:** Froth can last for a longer period in presence of stabiliser.

### 3.2. Chemical Method :

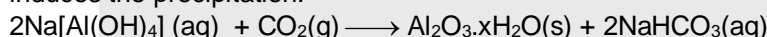
(iv) **Leaching** : Leaching is often used if the ore is soluble in some suitable solvent, e.g, acids, bases and suitable chemical reagents. e.g. Al ore, Ag ore, Au ore, low grade copper ore.

#### Leaching of alumina from bauxite :

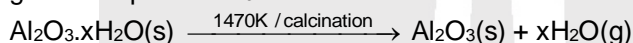
The principal ore of aluminium, bauxite, usually contains  $\text{SiO}_2$ , iron oxide and titanium oxide ( $\text{TiO}_2$ ) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of  $\text{NaOH}$  at 473-523 K and 35-36 bar pressure. This way,  $\text{Al}_2\text{O}_3$  is leached out as sodium aluminate (and also  $\text{SiO}_2$  as sodium silicate) leaving behind the impurities, iron oxide and titanium oxide.



The aluminate in solution is neutralised by passing  $\text{CO}_2$  gas and hydrated  $\text{Al}_2\text{O}_3$  is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated  $\text{Al}_2\text{O}_3$  which induces the precipitation.

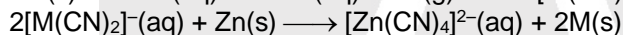
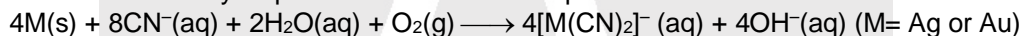


The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure  $\text{Al}_2\text{O}_3$  :



These steps comprises the **Bayer's process**.

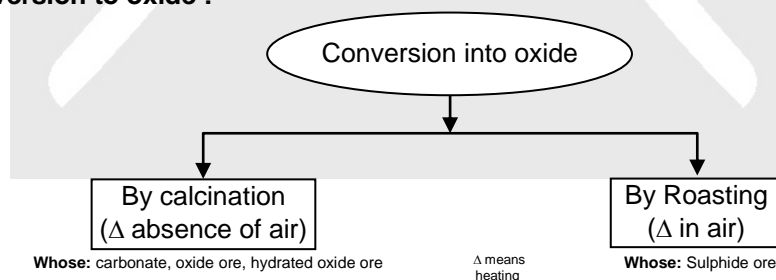
**Other examples** : In the metallurgy of **silver** and that of **gold**, the respective metal/ore is leached with a dilute solution of  $\text{NaCN}$  or  $\text{KCN}$  in the presence of air (or  $\text{O}_2$ ) from which the metal is obtained later by displacement with zinc scrap.



#### 3.2.1 Extraction of crude metal from concentrated ore :

The concentrated ore must be converted into a form which is suitable for reduction. Usually the sulphide ore is converted to oxide before reduction. Oxides are easier to reduce. Thus isolation of metals from concentrated ore involves two major steps as given below.

- (i) Conversion to oxide
  - (ii) Reduction of the oxide to metal.
- (i) **Conversion to oxide :**



Conversion of ore into oxide is carried out in two ways depending upon the nature of ore.

**Calcination.** It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of calcination brings about the following changes :

- (a) The carbonate ore gets decomposed to form the oxide of the metal, e.g.,
 
$$\text{FeCO}_3 \text{ (siderite)} \xrightarrow{\Delta} \text{FeO} + \text{CO}_2 ; \text{PbCO}_3 \text{ (cerrussite)} \xrightarrow{\Delta} \text{PbO} + \text{CO}_2$$

$$\text{CaCO}_3 \text{ (calcite ore / lime stone)} \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$$

$$\text{ZnCO}_3 \text{ (calamine)} \xrightarrow{\Delta} \text{ZnO} + \text{CO}_2$$

$$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \text{ (malachite)} \xrightarrow{\Delta} 2\text{CuO} + \text{H}_2\text{O} + \text{CO}_2$$

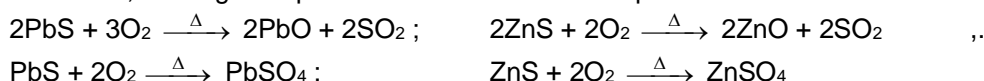
$$\text{MgCO}_3 \cdot \text{CaCO}_3 \text{ (dolomite)} \xrightarrow{\Delta} \text{MgO} + \text{CaO} + 2\text{CO}_2$$



- (b) Water of crystallisation present in the hydrated oxide ore gets lost as moisture, e.g.,  
 $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  (limonite)  $\xrightarrow{\Delta}$   $2\text{Fe}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{g})\uparrow$   
 $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  (bauxite)  $\xrightarrow{\Delta}$   $\text{Al}_2\text{O}_3(\text{s}) + 2\text{H}_2\text{O}(\text{g})\uparrow$
- (c) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

**Roasting.** It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or  $\text{O}_2$  below its melting point. Roasting is an exothermic process once started it does not require additional heating. The process of roasting does the following things :

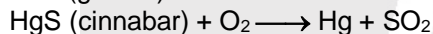
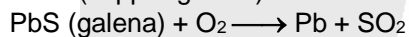
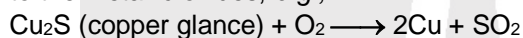
- (a) Roasting at moderate temperature. Some portion of the sulphide ores like galena ( $\text{PbS}$ ), Zinc blende ( $\text{ZnS}$ ) is converted into metallic oxide. If the temperature is fairly low (about  $500^\circ\text{C}$ ) and the concentration of  $\text{SO}_2$  in the gaseous environment is more, sulphate may be produced that are stable, and high temperature is needed to decompose them.



\* Some times roasting may not bring about complete oxidation.

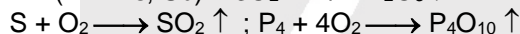
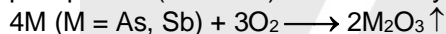


- (b) Roasting at high temperature. The sulphide ores of some of the metals like Cu, Pb, Hg, Sb etc., when heated strongly in the free supply of air or  $\text{O}_2$  are reduced directly to the metal rather than to the metallic oxides, e.g.,



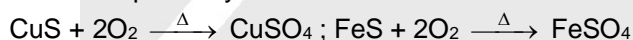
The reduction of the sulphide ore directly into metal by heating it in air or  $\text{O}_2$  is called by various names like self-reduction, auto-reduction, air-reduction etc. The  $\text{SO}_2$  produced is utilised for manufacturing of  $\text{H}_2\text{SO}_4$ .

- (c) It removes easily oxidisable volatile impurities like arsenic (as  $\text{As}_2\text{O}_3$ ) sulphur (as  $\text{SO}_2$ ), phosphorus (as  $\text{P}_4\text{O}_{10}$ ) and antimony (as  $\text{Sb}_2\text{O}_3$ ).



These oxides are volatile and hence escape as gases through the chimney.

- (d) When the concentrated tin stone ore  $\text{SnO}_2$  (ore of Sn) is heated strongly in a free supply of air (roasting), the impurities of  $\text{CuS}$  and  $\text{FeS}$  present in the ore are converted into  $\text{CuSO}_4$  and  $\text{FeSO}_4$  respectively.



Both calcination and roasting are generally carried out in a reverberatory furnace. In case of roasting, the air holes are kept open while they are partially or completely closed during calcination.

## 4. SECTION (B) : THERMODYNAMIC PRINCIPLES OF METALLURGY

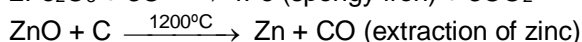
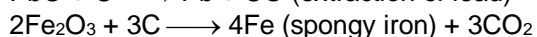
### (ii) Reduction of a metal oxide :

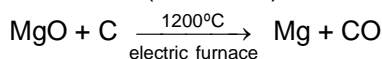
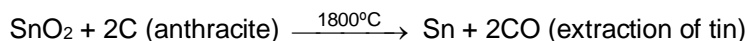
The free metal is obtained by reduction of a compound, using either a chemical reducing agent or electrolysis.

#### 1. Chemical reduction method :

A large number of commercial processes come under this category. Carbon can be used to reduce a number of oxides and other compounds, and because of the low cost and availability of coke this method is widely used. The disadvantages are that a high temperature is needed, which is expensive and necessitates the use of blast furnace.

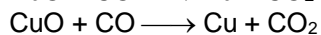
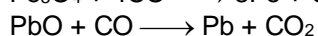
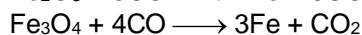
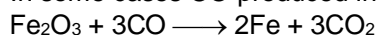
#### (A) Reduction with carbon :





**(B) Reduction with CO :**

In some cases CO produced in the furnace itself is used as a reducing agent.



Carbon or carbon monoxide reduction process is usually carried out in blast furnace. There are some disadvantage of using carbon as reducing agents e.g.,

(a) Some metallic oxides like CaO give metallic carbides instead of metals.

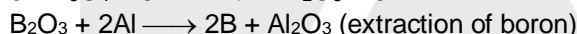
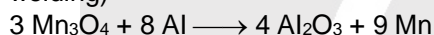
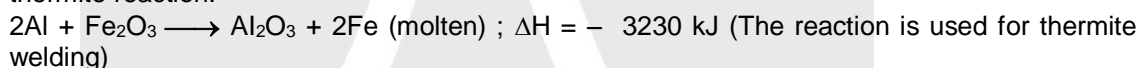


(b) During the cooling of the products, in many cases, reformation of the oxide and carbon may take place.



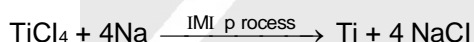
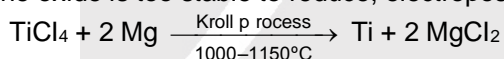
**2. Reduction by other metals :**

If the temperature needed for carbon to reduce an oxide is too high, for economical or practical purposes, reduction by other metals is done. Also, certain metallic oxides cannot be reduced by carbon because the affinity of oxygen for the metal is greater than its affinity for carbon. Such metallic oxides (Cr and Mn) can be reduced by a highly electropositive metal such as aluminium that liberates a large amount of energy (1675 kJ/mol) on oxidation to  $\text{Al}_2\text{O}_3$ . The process is known as Goldschmidt or aluminothermic process and the reaction is known as thermite reaction.



As it is a strongly exothermic reaction, it proceeds with explosive violence and only initial heating is needed.

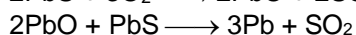
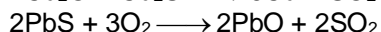
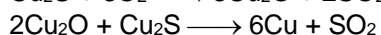
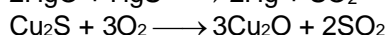
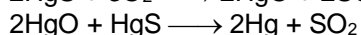
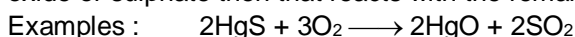
**Magnesium reduction method :** Magnesium is used in similar way to reduce oxides. In certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce halides.



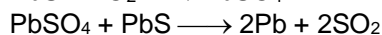
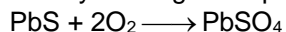
Advantages of using Na and Mg as reducing agents are the higher reducing power of the metals and solubility of their halides in water so that the reduced metals can be washed free from impurities.

**3. Self-reduction method :**

This method is also called auto-reduction method or air reduction method. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb, Sb, etc. are heated in air, a part of these is changed into oxide or sulphate then that reacts with the remaining part of the sulphide ore to give its metal and  $\text{SO}_2$ .



The extraction of Pb by heating its sulphide ore (PbS) in air can also be represented as



**4. Electrolytic reduction :**

It presents the most powerful method of reduction and gives a very pure product. As it is an expensive method compared to chemical methods, it is used either for very reactive metals such as magnesium or



aluminum or for production of samples of high purity. Electrolytic reduction of copper has the additional advantage of allowing the recover of valuable minor contaminants such as silver.

### **THERMODYNAMICS OF EXTRACTION : ELLINGHAM DIAGRAM OF A METAL**

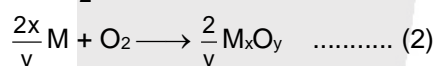
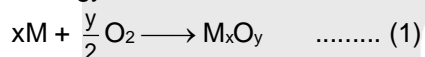
The standard electrode reduction potential of metal provides a very good indicator of the ease or difficulty of extracting the metal from its compounds. However, since most metals of industrial importance are obtained by chemical reduction of their oxide, the free energy changes occurring during these processes are of more fundamental importance. Despite the fact that redox reactions do not always reach equilibrium thermodynamics can at least be used to identify which reactions are feasible. For a spontaneous reaction the change in free energy  $\Delta G$  must be negative,  $\Delta G = \Delta H - T\Delta S$ .

It is sufficient to consider  $\Delta G$  because it is related to the equilibrium constant through,  $\Delta G = -RT \ln K$ .

Here a negative value of  $\Delta G$  corresponds to  $K > 1$  and, therefore, a favourable reaction. Reaction rates are also relevant, but at high temperature reactions are often fast and we can normally assume that any thermodynamically permissible process can occur.

The problem of extracting a metal from its ore is essentially concerned with decomposing the oxide of the metal (apart from simple binary compounds such as metal sulfides and chlorides that occur in nature). Most metal ores consist essentially of a metal oxide in association with one or more nonmetal oxides. Ores like carbonates, sulphides etc., are also converted to oxides, prior to reduction.

The free energy of formation  $\Delta G$  is the standard free energy of the reaction.



$\Delta G$  is the free energy of formation per mole of  $O_2$  consumed.

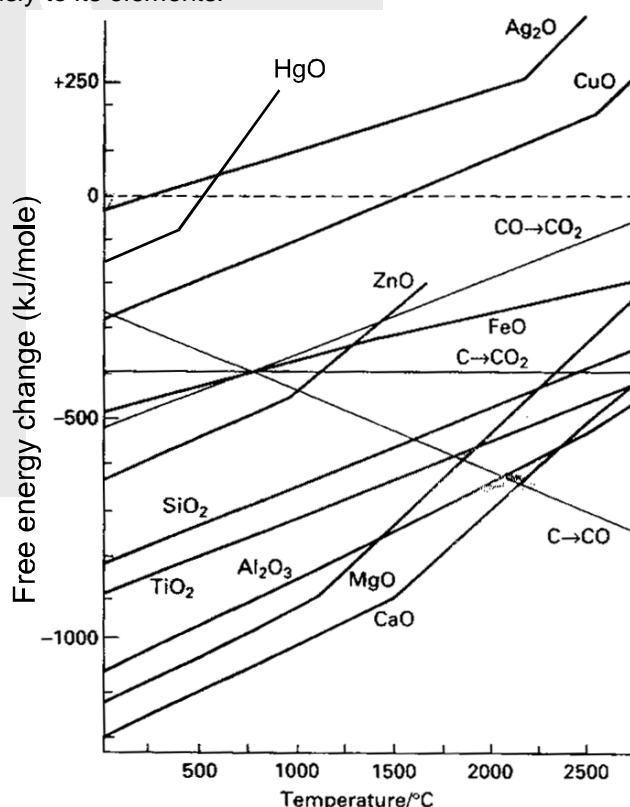
If the standard free energy of formation  $\Delta G$  has a negative sign at a given temperature, then the oxide can be expected to form spontaneously from the metal plus oxygen. If  $\Delta G$  has a positive sign, the oxide will be expected to decompose spontaneously to its elements.

The free energy of formation of an oxide can now be determined, provided we know the entropy of formation.

$$\Delta G = \Delta H - T\Delta S \quad \dots\dots (3)$$

In reaction (2) oxygen is used up in the course of reaction. Gases have a more random structure (less ordered) than liquid or solids. In this reaction the entropy or randomness decreases, and hence  $\Delta S$  is negative (provided that neither the metal nor its oxide  $M_xO_y$  are vaporized). Thus, if the temperature is raised then  $T\Delta S$  becomes more negative. Since  $T\Delta S$  is subtracted in equation (3),  $\Delta G$  then becomes less negative. Thus, the change in free energy decreases with increase in temperature.

The free energy change that occurs when 1 mol of common reactant (in this case  $O_2$ ) is used may be plotted graphically against temperature for a number of reactions of metals to their oxides. This graph is shown in following figure and is called an Ellingham diagram for oxides. Similar diagrams can be produced for 1 mol of S, giving Ellingham diagram for sulphides and similarly for halides using 1 mol of halogen.



This figure shows a number of oxide plots with slopes defined by  $\Delta G / T = -\Delta S$ . It is noted that the entropy change in reaction (2) is roughly the same for all metal oxides provided that the boiling point of neither the metal nor oxide is exceeded. Thus, below the boiling point of metal the slope of all the graphs are roughly the same, since  $T\Delta S$  factor is same whatever be the metal. When the temperature





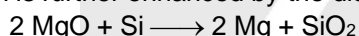
is raised a point will be reached where the graph crossed the  $\Delta G = 0$  line. Below this temperature the free energy of formation of oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of the oxide is positive, and the oxide becomes unstable and should decompose into metal and oxygen. This explains why  $\text{HgO}$ , for instance, decomposes spontaneously into its elements when heated. Theoretically, all oxides can be decomposed to give metal and oxygen if a sufficiently high temperature can be attained. In practice, that are easily attainable and these metals can be extracted by thermal decomposition of their oxides. The diagram predicts that  $\text{MgO}$  and  $\text{ZnO}$  ought to decompose if heated strongly enough, but it does not hold out much hope for obtaining say pure  $\text{Mg}$  by straight forward heating of the oxide to a high temperature where the boiling point of the metal is exceeded. However the slope increases since the reaction is now involving a larger entropy change as the randomness increases in reactants. For example,  $2 \text{Mg}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{MgO}(\text{s})$

Here, three moles of gas phases are converted into solid phase in the reaction. This takes place above  $1120^\circ\text{C}$ , which is the boiling point of  $\text{Mg}$ .

Similarly  $\text{Hg-HgO}$  line changes slope at  $365^\circ\text{C}$ . Several of the plots show abrupt changes in the slopes. These breaks occur at temperature at which the metal undergoes a phase transition. A smaller effect is seen at the melting point. If, however the oxide undergoes a phase change, there will be an increase in the entropy of the oxide, and at such a point the curve becomes less steep. For example in the case of  $\text{Pb}$ , the oxide ( $\text{PbO}$ ) boils while lead is liquid. In these instances the entropy change becomes positive for the reaction and hence the slope  $\Delta G/T$  changes sign, the situation reverting to normal once the boiling point of  $\text{Pb}$  is reached.

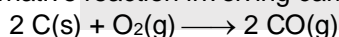
In principle, when the plot of one metal lies below that of another, the first metal is capable of reducing the oxide of the second. A vertical line drawn on the Ellingham plot of the metal oxides at any  $T$  gives the sequence of the stabilities of metal oxides. A metal forming a more stable oxide (higher  $-\Delta G$ ) will be potential reducing agent for a less stable oxide. If the two lines intersect, the free energy change for the reduction will be zero at that temperature and equilibrium results, but a change of temperature will make the reaction proceed provided no kinetic barriers (activation energy) exist. Thus,  $\text{Mg}$  metal will reduce  $\text{CuO}$  and  $\text{FeO}$  but not  $\text{CaO}$ . Also, it is seen that at room temperature ( $27^\circ\text{C}$ ) the order of reducing ability approximates that of standard electrode potential.

Although the  $\text{SiO}_2$  line is above the  $\text{MgO}$  line,  $\text{Si}$  can successfully reduce  $\text{MgO}$  to free metal. Upto  $1100^\circ\text{C}$ , the normal boiling point of  $\text{Mg}$ , the  $\Delta G$  plot for formation of  $\text{SiO}_2$  and  $\text{MgO}$  are parallel. However, above  $1100^\circ\text{C}$  the plot for  $\text{MgO}$  changes slope owing to the increased entropy effect, and above  $1700^\circ\text{C}$  the reaction between  $\text{Si}$  and  $\text{MgO}$  proceeds with decrease in free energy. In practice, the reaction is further enhanced by the distillation of  $\text{Mg}$  metal from the reaction mixture.



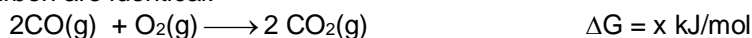
#### Carbon or carbon monoxide as reducing agent.

In figure the plot corresponding to the change  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  is shown by a horizontal line. For this reaction  $\Delta S$  is relatively small because in this case one mole of gaseous product is formed while one mole of gaseous reactant is used up.  $\Delta G$  for this reaction is almost independent of temperature. The plot for  $\text{CO}_2$  is relatively high in the figure, and at low temperature  $\text{C}$  will reduce only a few of metal oxides shown. However, the slopes of the plots for several of the metals are such that they cross the  $\text{CO}_2$  plot; hence theoretically these metals can be reduced by  $\text{C}$  at elevated temperature. An alternative reaction involving carbon and oxygen is the formation of  $\text{CO}$ .

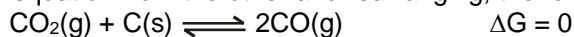


Since two of gaseous product is formed from one mole of gaseous reactant, this process is accompanied by an increase in entropy. Hence, the slope of the corresponding line is negative as shown by the downward sloping line in the figure. If the temperature is high enough,  $\text{C}$  should reduce all the metal oxides, being converted into  $\text{CO}$ . The plot for the reaction of  $\text{CO}$  with oxygen is also shown.

There are three curves for carbon, corresponding to complete oxidation of  $\text{C}$  to  $\text{CO}_2$ , partial oxidation to carbon monoxide, and oxidation of  $\text{CO}$  to carbon dioxide. The three curves pass through a common point at  $710^\circ\text{C}$ . Thus, the free energies of formation of  $\text{CO}_2$  from carbon monoxide and carbon dioxide from carbon are identical.



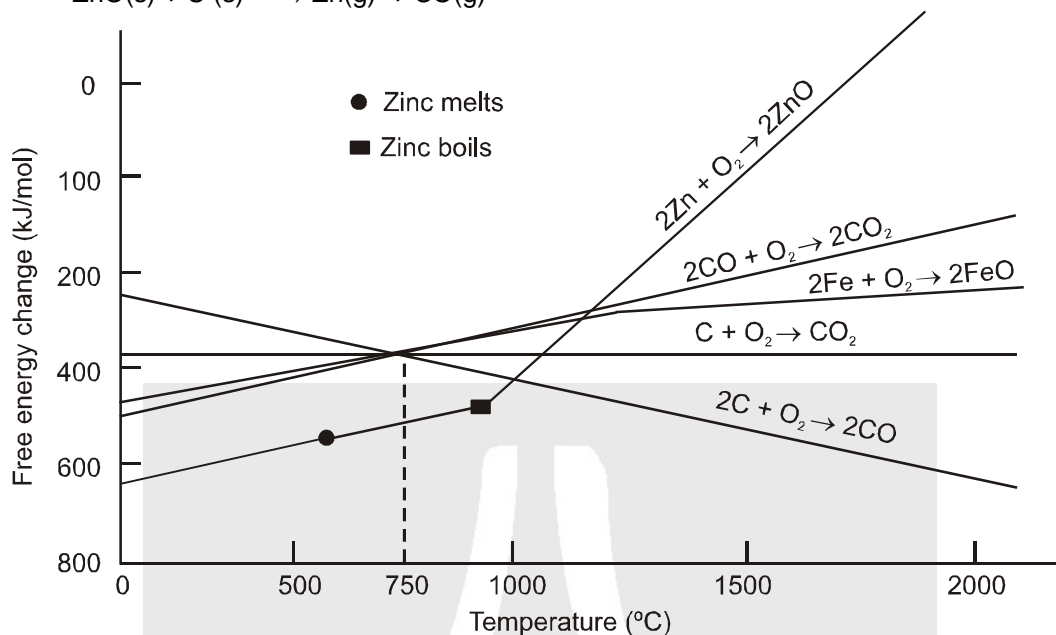
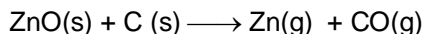
Subtracting one equation from the other and rearranging, the following is obtained :



That is, an equilibrium is set. It is clear below a temperature of  $710^\circ\text{C}$ ,  $\text{CO}$  is a more effective reducing agent than carbon, but above this temperature the reverse is true. All three oxidation curves for the



carbon system lie above that for oxidation of zinc, until a temperature of approximately 1000°C is reached. At this point, carbon is thermodynamically capable of reducing ZnO to Zn. Since this temperature is greater than the boiling point of Zn (907°C), it will be formed as a vapour. The overall equation for reduction is



It is interesting to note that the value of carbon as reducing agent is due to marked increase in disorder that takes place when carbon (an ordered solid) reacts with one mole of oxygen to give two moles of CO. The net effect is an extra mole of gas and hence an increase in disorder (an increase in entropy). It is a fact that in the region of 2000°C, carbon is thermodynamically capable of reducing most metal oxides to metal.

Thus, for most metal oxides, a reducing agent is required and we should consider the overall reaction obtained by subtracting the metal oxidation from one of carbon oxidation as

$$\Delta G_{\text{overall}} = \Delta G_{\text{(C)}} - \Delta G_{\text{(M)}}$$

#### Metals as reducing agents :

Metal oxide reduction is thermodynamically favourable for temperatures at which the line for the metal oxide is above any one of the lines for carbon oxidation, for the  $\Delta G$  for metal oxide reduction by carbon is negative.

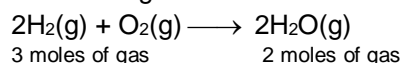
**Note :** The Gibb's energies of formation of most sulphides are greater than that for  $\text{CS}_2$ . In fact,  $\text{CS}_2$  is an endothermic compound. There, the  $\Delta_f G^\ominus$  of  $\text{M}_x\text{S}$  is not compensated. So reduction of  $\text{M}_x\text{S}$  is difficult. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.

Similar principles apply to other types of reduction. For instances if the plot of  $\Delta G_{\text{(M)}}$  from  $\text{M}'$  is now taking the place of C. When  $\Delta G = \Delta G_{\text{(M')}} - \Delta G_{\text{(M)}}$  is negative, the reaction,  $\text{MO} + \text{M}' \longrightarrow \text{M} + \text{M}'\text{O}$  is feasible.

#### Hydrogen as a reducing agent :

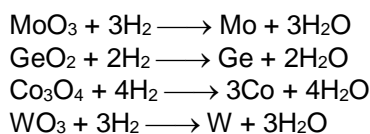
Hydrogen is not very effective reducing agent for obtaining metals from their oxides.

The reason is that  $\Delta S$  is negative for the reaction :



as the products are less disordered. The plot of  $\Delta G$  against T therefore rises with temperature, meaning that not many metal oxide plots are intersected.  $\text{H}_2$  will therefore reduces oxides such as Cu(I) oxide and Cu(II) oxide, but not the oxides of Al, Mg, and Ca. Oxides of iron are reduced only with difficulty. In the case of magnetic iron oxide  $\text{Fe}_3\text{O}_4$  an equilibrium composition is readily established.

In the case of W, Mo, and Co  $\Delta G$  is above that of  $\text{H}_2\text{O}$  so  $\text{H}_2$  can be reduce these oxides.



This method is not widely used because many metals react with  $\text{H}_2$  at elevated temperature forming hydride. There is also a risk of explosion for  $\text{H}_2$  and oxygen in the air.

### Solved Example

**Example 1.** The reaction  $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$  ( $\Delta G^\circ = -421 \text{ kJ}$ ) is thermodynamically feasible as is apparent from the Gibb's energy value. Why does it not take place at room temperature ?

**Solution:** Certain amount of activation energy is essential even for such reactions which are thermodynamically feasible, therefore heating is required.

**Example 2.** Is it true that under certain conditions, Mg can reduce  $\text{Al}_2\text{O}_3$  and Al can reduce MgO? What are those conditions ?

**Solution:** Below  $1350^\circ\text{C}$  Mg can reduce  $\text{Al}_2\text{O}_3$  and above  $1350^\circ\text{C}$ . Al can reduce MgO as evident from the Ellingham diagram.

## 5. SECTION (C) : METALLURGY OF SOME USEFUL METALS

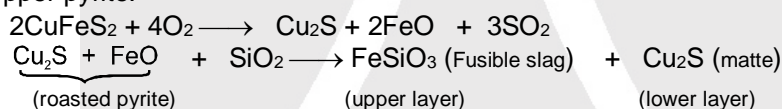
### Smelting :

**Slag formation :** In many extraction processes, an oxide is added deliberately to combine with other impurities and form a stable molten phase immiscible with molten metal called a slag. The process is termed smelting.

The principle of slag formation is essentially the following:

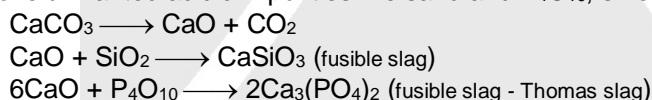
Nonmetal oxide (acidic oxide) + Metal oxide (basic oxide)  $\longrightarrow$  Fusible (easily melted) slag

Removal of unwanted basic and acidic oxides: For example, FeO is the impurity in extraction of Cu from copper pyrite.



Matte also contains a very small amount of iron(II) sulphide.

To remove unwanted acidic impurities like sand and  $\text{P}_4\text{O}_{10}$ , smelting is done in the presence of limestone.



### Properties of a slag :

- Slag is a fusible mass.
- It has low melting point.
- It is lighter than and immiscible with the molten metal. It is due to these impurities that the slag floats as a separate layer on the molten metal and can thus be easily separated from the metal. The layer of the slag on the molten metal prevents the metal from being oxidised.

**Type of flux :** Fluxes are of two types viz., acidic flux and basic flux.

(a) **Acidic flux :** It is an acidic oxide (oxide of a non-metal) like  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$  (from borax). It is used to remove the basic impurity like CaO, FeO, MgO etc. The acidic flux combines with the basic impurity and forms a slag.

(b) **Basic flux :** It is a basic oxide (i.e., oxide of a metal) like CaO (obtained from lime stone,  $\text{CaCO}_3$ ), MgO (from magnesite,  $\text{MgCO}_3$ ), haematite ( $\text{Fe}_2\text{O}_3$ ) etc. It is used to remove the acidic impurity like  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$  etc. The basic flux combines with the acidic impurity and forms a slag.

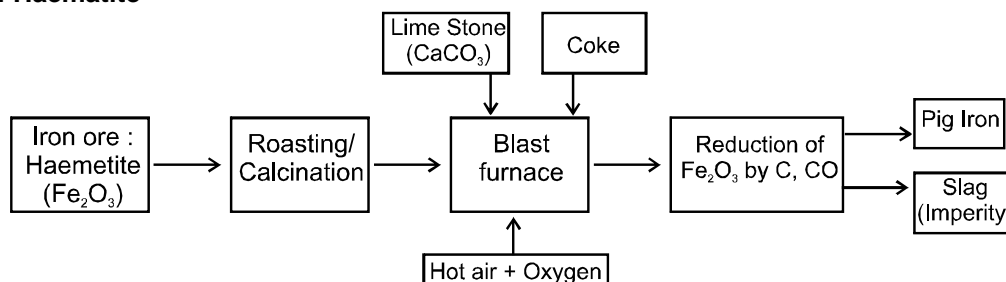
Thus, slag can be defined as a fusible mass, which is obtained when a flux reacts with an infusible acidic or basic impurity present in the oxide ore.



## 5.1. Metallurgy of Some Important Metals

### 1. Extraction of iron (Fe)

Ore: Haemetite

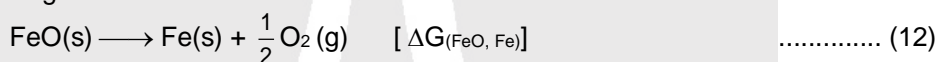


Oxide ores of iron, after concentration through calcination/roasting in reverberatory furnace (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with lime stone and coke and fed into a Blast furnace from its top with the help of a cup and cone arrangement. Here, the oxide is reduced to the metal.

Thermodynamics helps us to understand how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process is :



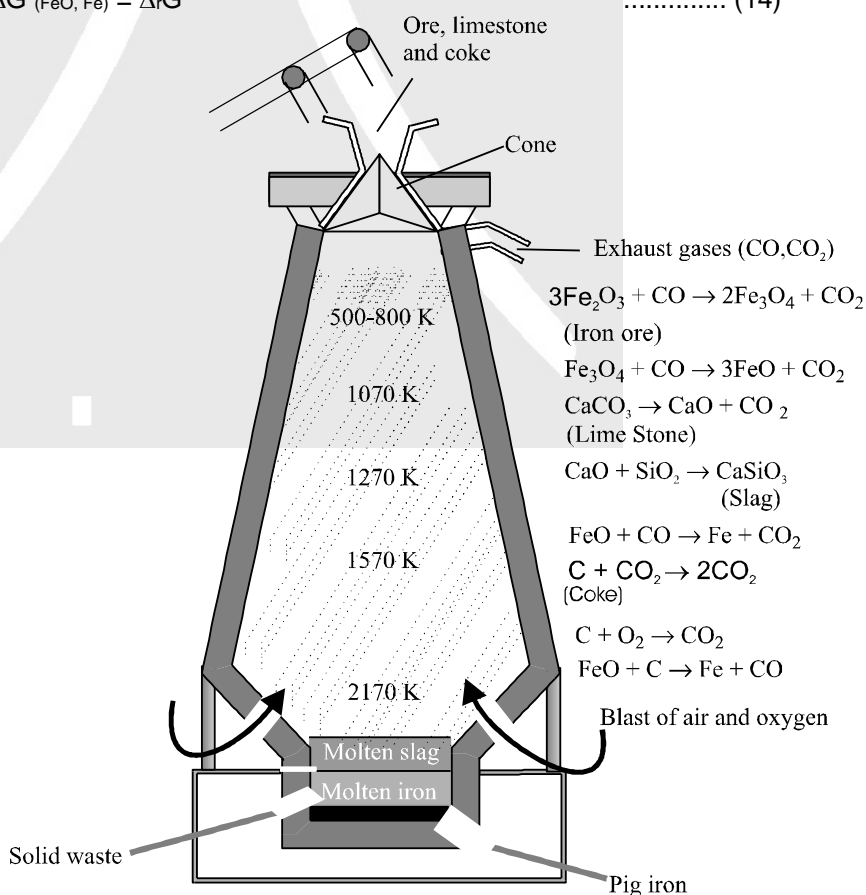
It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO :



When both the reactions take place to yield the equation (10), the net Gibbs energy change becomes:



Naturally, the resultant reaction will take place when the right hand side in equation (14) is negative. In  $\Delta G^\circ$  vs T plot representing reaction (12), the plot goes upward and that representing the change C, CO (C, CO) goes downward. At temperatures above 1073K (approx.), the C, CO line comes below the Fe, FeO line [ $\Delta G_{(\text{C, CO})} < \Delta G_{(\text{Fe, FeO})}$ ]. So in this range, coke will be reducing the FeO and will itself be oxidised to CO. In a similar way the reduction of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  at relatively lower temperatures by CO can be explained on the basis of lower lying points of intersection of their curves with the CO,  $\text{CO}_2$  curve in the given figure.

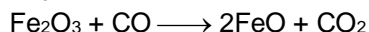
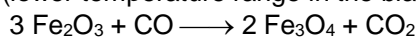




In the Blast furnace, reduction of iron oxides takes place in different temperature ranges. Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto about 2200K in the lower portion itself. The burning of coke therefore supplies most of the heat required in the process. The CO and heat moves to upper part of the furnace. In upper part, the temperature is lower and the iron oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ) coming from the top are reduced in steps to FeO.

**Reactions involved :** The reactions proceed in several stages at different temperatures. Since the air passes through in a few seconds, the individual reactions does not reach equilibrium.

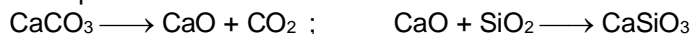
At 500 – 800 K (lower temperature range in the blast furnace)



At 900 – 1500 K (higher temperature range in the blast furnace):

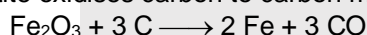


Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.



The iron obtained from blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn). This is known as pig iron and cast into variety of shapes. Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

**Further Reductions :** Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide:



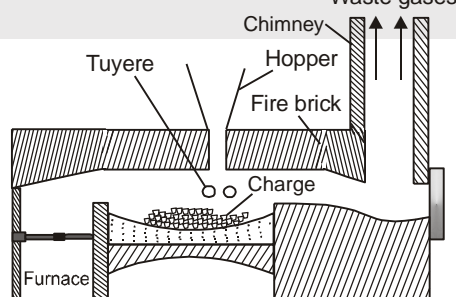
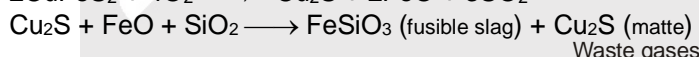
Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag. The metal is removed and freed from the slag by passing through rollers.

## 2. Extraction of copper :

(a) **From cuprous oxide [Copper(I) oxide] :** In the graph of  $\Delta_r G^0$  vs T for formation of oxides the  $\text{Cu}_2\text{O}$  line is almost at the top. So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C,  $\text{CO}_2$  are at much lower positions in the graph particularly after 500-600K). However most of the ores are sulphide and some may also contain iron. The sulphide ores are roasted/smelted to give oxides :  $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$

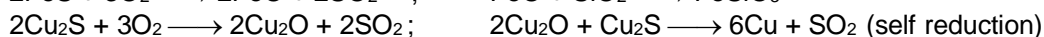
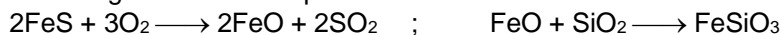
The oxide can then be easily reduced to metallic copper using coke:  $\text{Cu}_2\text{O} + \text{C} \longrightarrow 2\text{Cu} + \text{CO}$

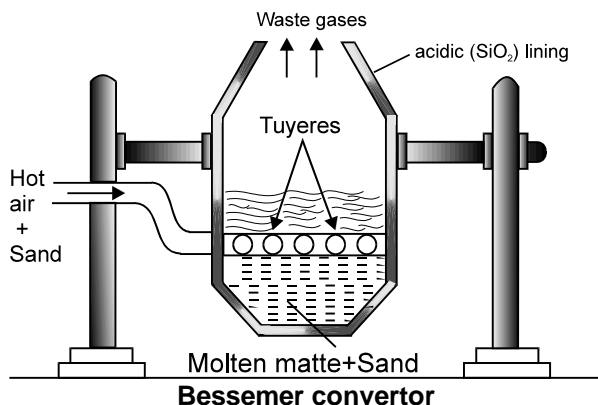
(b) **From copper glance / copper pyrite (self reduction) :** In actual process the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags off' as iron silicate and copper is produced in the form of copper matte. This contains mostly  $\text{Cu}_2\text{S}$  and some FeS.



**Reverberatory furnace**

Copper matte is then charged into silica lined converter (Bessemer converter). Some silica is also added and hot air blast is blown to convert the remaining  $\text{FeS}_2$ , FeO and  $\text{Cu}_2\text{S}/\text{Cu}_2\text{O}$  to the metallic copper. Following reactions take place:



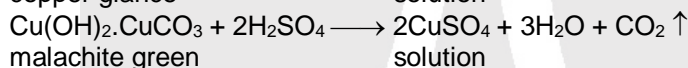
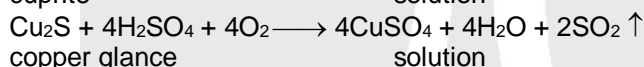
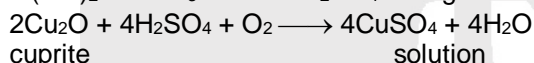


**Bessemer convertor**

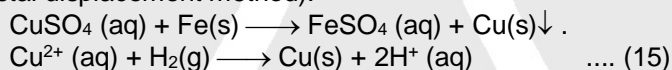
The solidified copper obtained has blistered appearance due to the evolution of  $\text{SO}_2$  and so it is called blister copper.

**(c) From low grade ores and scraps :**

Leaching of cuprite ( $\text{Cu}_2\text{O}$ ) or copper glance ( $\text{Cu}_2\text{S}$ ) with dil.  $\text{H}_2\text{SO}_4$  in presence of air, gives a solution of  $\text{CuSO}_4$  and the impurities present in the ores remain undissolved in the acid. Leaching of malachite green,  $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$  with dil.  $\text{H}_2\text{SO}_4$  also gives a solution of  $\text{CuSO}_4$ .



Copper metal can be recovered from  $\text{CuSO}_4$  solution (obtained as above) either by electrolysis (cathode is of Cu-metal and anode is of lead) Cu-metal is collected at cathode or by treating it with scrap iron which, being more reactive than Cu, displaces Cu from  $\text{CuSO}_4$  solution and Cu gets precipitated (Metal displacement method).



**3. Extraction of lead :**

**Ore: PbS (Lead sulphide)**

There are two methods of extracting the element :

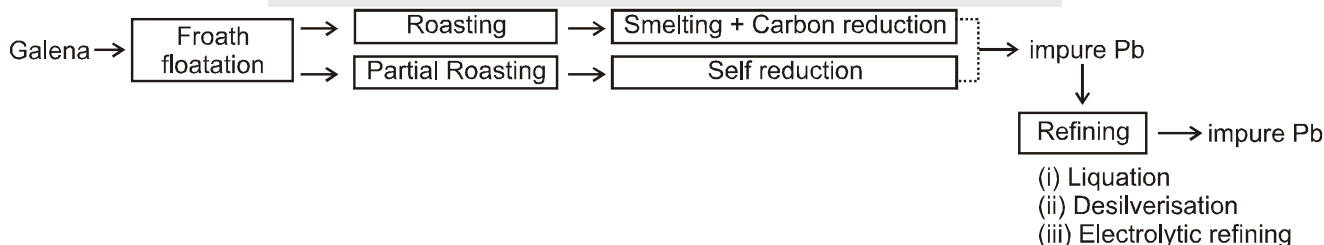
- (i) Roast in air to give  $\text{PbO}$ , and then reduce with coke or CO in a blast furnace.



- (ii) PbS is partially oxidized by heating and blowing air through it. After some time the air is turned off and heating is continued. The mixture undergoes self reduction as given below.



**Chart3:**



**Solved Example**

**Example 1.** Auto reduction process is used in extraction of :

- (A) Cu (B) Hg (C) Al (D) Fe

**Solution:** (A) and (B) :  $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \longrightarrow 6\text{Cu} + \text{SO}_2$  ;  $\text{HgS} + 2\text{HgO} \longrightarrow 3\text{Hg} + \text{SO}_2$



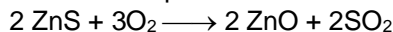
**Example 2.** Why the sulphide ore is roasted to convert it in to the oxide before reduction?

**Solution:**  $\Delta_r G^\ominus$  of most sulphide ore are greater than those of  $CS_2$  and  $H_2S$ . Hence neither carbon nor hydrogen is a suitable reducing agent for the metal sulphides. Moreover, the roasting of a sulphide to the oxide is quite advantageous thermodynamically because  $\Delta_r G^\ominus$  of oxides are much lower than those of  $SO_2$ .

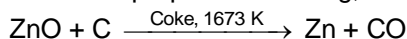
#### 4. Extraction of zinc :

**Ore: ZnS (Zinc blende)**

The ore is roasted in presence of excess of air at temperature 1200 K.

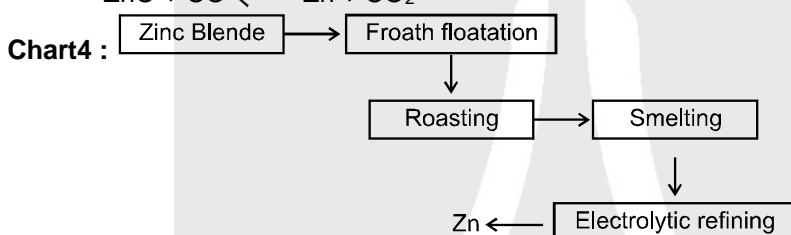
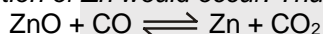


The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.



The metal is distilled off and collected by rapid chilling.

**Note :** *ZnO may be reduced by carbon monoxide at 1473 K (i.e. 1200°C) in smelter. The reaction is reversible, and the high temperature is required to move the equilibrium to the right. At this temperature the Zn is gaseous. If the gaseous mixture of Zn and  $CO_2$  was simply removed from the furnace and cooled, then reoxidation of Zn would occur. Thus the zinc powder obtained would contain large amounts of ZnO.*



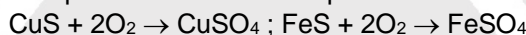
#### 5. Extraction of tin from cassiterite ( $SnO_2$ ) : It involves following steps.

(A) **Purification :**

(i) **Crushing and concentration :** The ore is crushed and washed with a stream of running water to remove the lighter earthy and silicious impurities.

(ii) **Electromagnetic separation :** The concentrated ore is subjected to the electromagnetic separation to remove magnetic impurity of Wolframite.

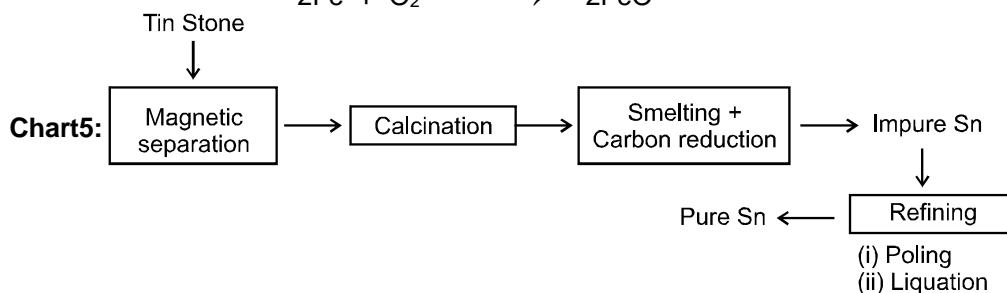
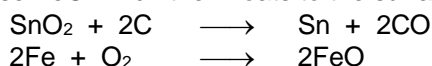
(iii) **Roasting:** The ore is then heated in presence of air, when volatile impurities (S as  $SO_2$ , As as  $As_2O_3$  and Sb as  $Sb_2O_3$ ) are removed. The impurities of pyrites of copper and iron are converted into their respective oxides and sulphates



(iv) **Leaching :** Sulphates of copper and iron are dissolved in water.

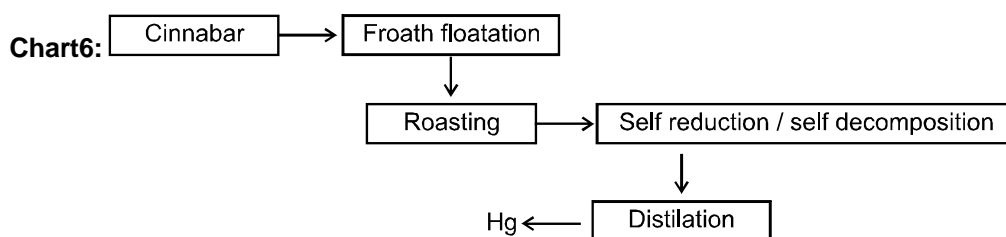
(v) **Washing :** The ore is washed with running water to remove the finer iron oxide produced in roasting. The ore thus obtained contains 60–70%  $SnO_2$  and is called as black tin.

(B) **Smelting :**  $SnO_2$  is reduced to metal using carbon at 1200–1300°C in an electric furnace. The product often contains traces of Fe, which is removed by blowing air through the molten mixture to oxidise FeO which then floats to the surface.





### Extraction of Mercury



## 6. SECTION (D) : ELECTROCHEMICAL PRINCIPLES OF METALLURGY

### Medium :

- In aqueous solution :** Electrolysis can be carried out conveniently and cheaply in aqueous solution that the products do not react with water. Copper and zinc are obtained by electrolysis of aqueous solution of their sulphates.
- In other solvents :** Electrolysis can be carried out in solvents other than water. Fluorine reacts violently with water and it is produced by electrolysis of  $\text{KHF}_2$  dissolved in anhydrous HF.
- In fused melts :** Elements that react with water are often extracted from fused melts of their ionic salts. Aluminum is obtained by electrolysis of a fused mixture of  $\text{Al}_2\text{O}_3$  and cryolite  $\text{Na}_3[\text{AlF}_6]$ . Both sodium and chlorine are obtained from the electrolysis of fused NaCl. In this case upto two-third by weight of  $\text{CaCl}_2$  is added as an impurity to lower the melting point from 803 to 505°C.

**Electrochemical principles of metallurgy :** Electrolytic reduction can be regarded as a technique for driving a reduction by coupling it through electrodes and external circuit to a reactive or a physical process with a more negative  $\Delta G$ . The free energy available from the external source can be assessed from the potential it produces across the electrodes using the thermodynamic relation :

$$\Delta G = -nFE \quad \dots\dots\dots(i)$$

where  $n$  is the number of electrons transferred,  $F$  is Faraday's constant ( $F = 96.5 \text{ kJ/mol}$ ) and  $E^0$  is electrode potential of the redox coupled formed in the system.

Hence, the total Gibb's energy of the coupled internal and external process is

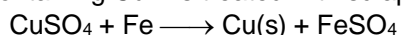
$$\Delta G + \Delta G (\text{external}) = \Delta G - nFE_{\text{ext}}$$

If the potential difference of the external source exceeds,  $E_{\text{ext}} = -\frac{\Delta G}{nF}$

The reduction is thermodynamically feasible; thus, the overall process occurs with a decrease in free energy. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two  $E^0$  values corresponds to a positive  $E^0$  and consequently negative  $\Delta G^0$  in equation (i), then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g.,  $\text{Cu}^{2+} (\text{aq}) + \text{Fe}(\text{s}) \longrightarrow \text{Cu}(\text{s}) + \text{Fe}^{2+}(\text{aq})$

In simple electrolysis, the  $\text{M}^{n+}$  ions are discharged at negative electrodes (cathodes) and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added for making the molten mass more conducting.

**Hydrometallurgy :** The processing of ores and minerals as well as metals and their compounds at relatively low, often ambient temperatures employing aqueous solution is known as hydrometallurgy. Occasionally, organic reagents are also used. This method of extraction is generally used for low grade ores. Copper is extracted by hydrometallurgy from low grade ore it is leached out using acid and bacteria. The solution containing  $\text{Cu}^{2+}$  is treated with scrap iron or  $\text{H}_2$ .



A hydrometallurgical process for the extraction of metals from ores, concentrates, or secondary materials essentially contains three basic steps-dissolution of the valuable metal in the aqueous solution (leaching) purification of leach solution and subsequent recovery of metal from the purified solutions either by electrolysis or by adding some electropositive metal to it.

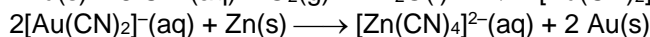
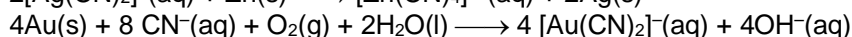
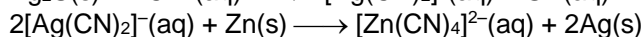
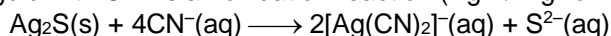
**Some of the metals obtained by hydrometallurgy are as follows :**

**(A) Extraction of Ag and Au :** Metals like Au and Ag can be precipitated for their salt solution by electropositive metals for example, Zn.





Metallic Ag is dissolved from its ore in dilute NaCN solution, and the solute so obtained is treated with scrap Zn when Ag is precipitated. Air is blown into the solution oxidize Na<sub>2</sub>S. Leaching the metals like silver, gold with CN<sup>-</sup> is an oxidation reaction (Ag → Ag<sup>+</sup> or Au → Au<sup>+</sup>)



Here Zn acts as reducing agent.

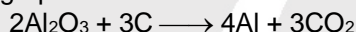
**(B) Extraction of Aluminium :** It involves the following processes

**(a) Purification of bauxite :**

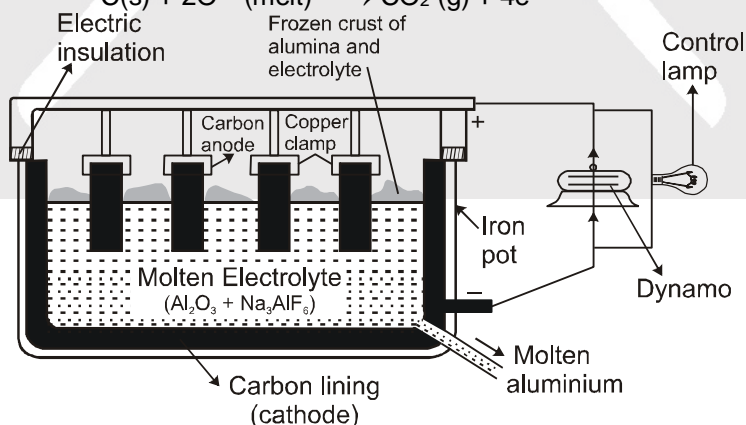
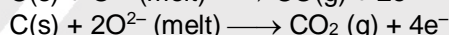
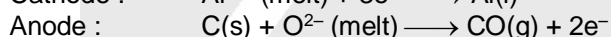
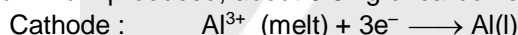
<b>(i) Bayer's Method</b>	<b>(ii) Hall's Method</b>	<b>(iii) Serpeck's Method</b>
(used for red bauxite containing Fe <sub>2</sub> O <sub>3</sub> and silicates as impurities) $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \xrightarrow[8 \text{ atm}]{190^\circ\text{C}} 2\text{NaAlO}_2(\text{soluble}) + 3\text{H}_2\text{O}$ Fe <sub>2</sub> O <sub>3</sub> (insoluble) separated as red mud by filtration solution is diluted with water and seeded with freshly prepared Al(OH) <sub>3</sub> . It induces the precipitation of Al(OH) <sub>3</sub> . Al(OH) <sub>3</sub> is filtered leaving behind silicates in solution. $\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NaOH} + \text{Al}(\text{OH})_3 \downarrow$ $2\text{Al}(\text{OH})_3 \xrightarrow{1473 \text{ K } \Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$	(used for red bauxite containing Fe <sub>2</sub> O <sub>3</sub> and silicates as impurities) $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \xrightarrow{\text{Fuse}} 2\text{NaAlO}_2(\text{soluble}) + \text{CO}_2 + 2\text{H}_2\text{O}$ $2\text{NaAlO}_2 + 3\text{H}_2\text{O} + \text{CO}_2 \xrightarrow{60^\circ\text{C}} 2\text{Al}(\text{OH})_3 \downarrow + \text{Na}_2\text{CO}_3$ $2\text{Al}(\text{OH})_3 \xrightarrow{1473 \text{ K } \Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$	(used for white bauxite containing silica as impurities) $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 3\text{C} + \text{N}_2 \xrightarrow[\text{Electric furnace}]{1800^\circ\text{C}} 2\text{AlN} + 3\text{CO} + 2\text{H}_2\text{O}$ $2\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 \downarrow + \text{NH}_3$ $\text{SiO}_2 + 2\text{CO} \rightarrow 2\text{CO}_2 + \text{Si}$ Silicone volatilises at this temp. $2\text{Al}(\text{OH})_3 \xrightarrow{1473 \text{ K } \Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$

**(b) Electrolytic reduction (Hall-Heroult process) :**

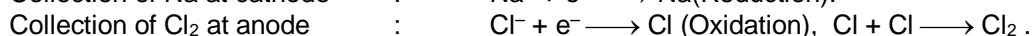
The purified Al<sub>2</sub>O<sub>3</sub> is mixed with Na<sub>3</sub>AlF<sub>6</sub> (cryolite) or CaF<sub>2</sub> (fluorspar) which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal. The overall reaction may be taken as :



The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO<sub>2</sub>. This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are :



**Extraction of Na:** The fused mixture of NaCl and CaCl<sub>2</sub> is taken in Down's cell which consists of circular iron cathode and carbon anode. On passing the electric current the following reactions take place :



Na can also be obtained by electrolysing molten NaOH in Castner's cell.

**Solved Example**

**Example 3.** Common impurities present in Bauxite are :

- (A) CuO                      (B) ZnO                      (C) Fe<sub>2</sub>O<sub>3</sub>                      (D) SiO<sub>2</sub>

**Solution:** (C) Red Bauxite contains Fe<sub>2</sub>O<sub>3</sub> as impurity. (D) white Bauxite contains SiO<sub>2</sub> as impurity. Therefore, (C) and (D) are correct options.

**Example 4.** Which metals are generally extracted by the electrolytic reduction and why ?

**Solution:** Sodium, aluminium, magnesium etc. are extracted by the electrolytic reduction of their fused salts because being more reactive and electropositive elements they themselves acts as strong reducing agents. Hence they can not be extracted by any of the chemical methods.

**6. Extraction of Magnesium :**

(i) **From Carnallite :** The ore is dehydrated in a current of hydrogen chloride and the mixture of fused chlorides is electrolysed.

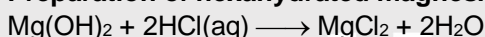
(ii) **From Sea water (Dow's process) :**

Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

(a) **Precipitation of magnesium as magnesium hydroxide by slaked lime :**

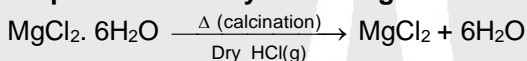


(b) **Preparation of hexahydrated magnesium chloride :**



The solution on concentration and crystallisation gives the crystals of MgCl<sub>2</sub>·6H<sub>2</sub>O

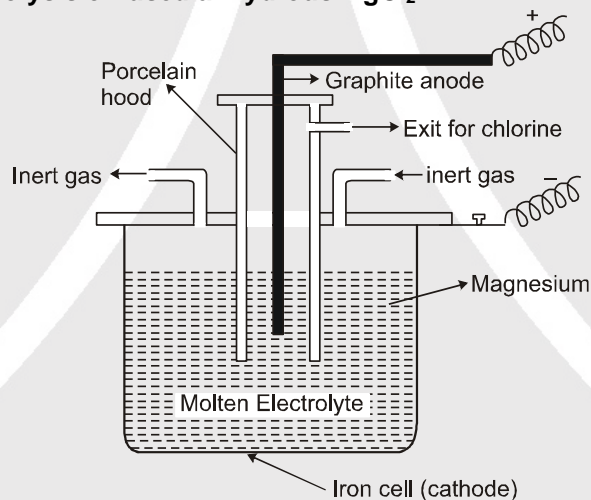
(c) **Preparation of anhydrous magnesium chloride :**



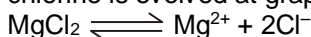
It is not made anhydrous by simple heating because it gets hydrolysed



(d) **Electrolysis of fused anhydrous MgCl<sub>2</sub> :**



Magnesium chloride obtained by any of the above methods is fused and mixed with sodium chloride and calcium chloride in the temperature range of 973–1023 K. The molten mixture is electrolysed. Magnesium is liberated at the cathode (iron pot) and chlorine is evolved at graphite anode.



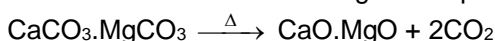
**At cathode :**  $\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg(99\% pure)} ;$

**At anode :**  $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$

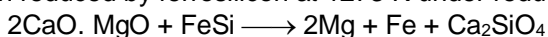
☞ A stream of coal gas is passed through the pot to prevent oxidation of magnesium metal. The magnesium obtained in liquid state is purified by distillation under reduced pressure. (1 mm of Hg at 873 K).

(iii) **From dolomite :**

The concentrated ore is calcined at higher temperature



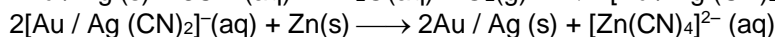
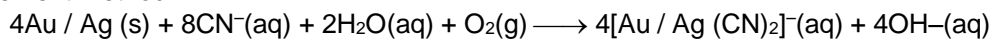
It is then reduced by ferrosilicon at 1273 K under reduced pressure.



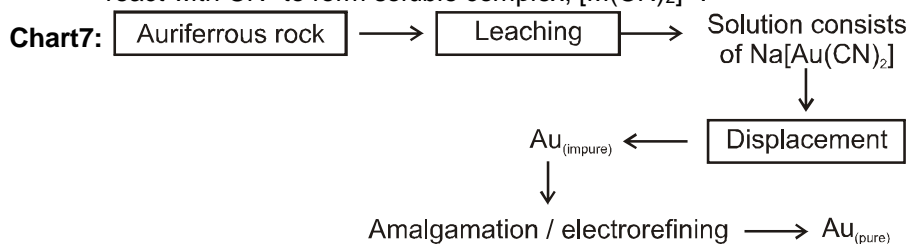


### 7. Extraction of gold and silver (MacArthur-Forrest cyanide process) :

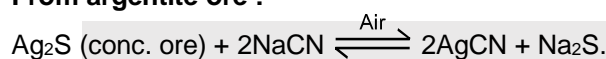
(a) **From native ores** : Extraction of gold and silver involves leaching the metal with  $\text{CN}^-$ . This is also an oxidation reaction ( $\text{Ag} \rightarrow \text{Ag}^+$  or  $\text{Au} \rightarrow \text{Au}^+$ ). The metal is later recovered by displacement method.



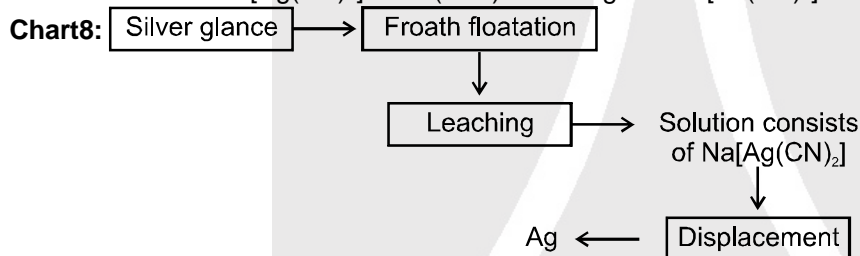
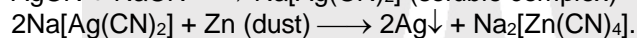
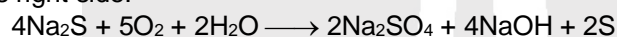
**Note** : The leaching is carried out in presence of air or oxygen to oxidise metal, M (Ag / Au) to  $\text{M}^+$  which then react with  $\text{CN}^-$  to form soluble complex,  $[\text{M(CN)}_2]^-$ .



(b) **From argentite ore** :



$\text{Ag}_2\text{S}$  and  $\text{AgCN}$  are in equilibrium so  $\text{Na}_2\text{S}$  is oxidised by air in to  $\text{Na}_2\text{SO}_4$ . Hence equilibrium shifts towards right side.



## 7. SECTION (E) : PURIFICATION OR REFINING OF IMPURE METALS

(D) **Purification or Refining of metals** :

Metals obtained by reduction processes still contain some objectionable impurities and have to be refined. Refining techniques vary widely from metal to metal and also depend on the use to which a metal has to be put. Sometimes during refining some substances may have to be added to impart some desirable characteristic to the metal. In some cases a metal is refined to recover some valuable by-products, for example, Ag, Au, Pt etc., may be present as impurities. 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 present in it are not, i.e., the impurities are infusible. In other words, we can say that the melting point of the metal to be purified should be lower than that of each of the impurities associated with the metal. This process is used for the purification of Sn and Zn, and for removing Pb from Zn-Ag alloy, which is obtained at the end of Parke's process and contains Pb as impurity.

**Examples :**

**Purification of impure tin metal :** The impure tin metal contains Cu, Fe, W etc. as impurities. This metal is placed on the sloping heat of a reverberatory furnace and gently heated. When the temperature of the furnace reaches the melting point of tin metal, this metal, on account of its lower melting point melts earlier than the impurities and hence flows down the inclined hearth and the solid infusible (non-fusible) impurities (called dross) are left behind on the hearth. The pure tin metal is collected in a cast iron vessel in the molten state. The metal obtained in this manner is called **pig tin**.

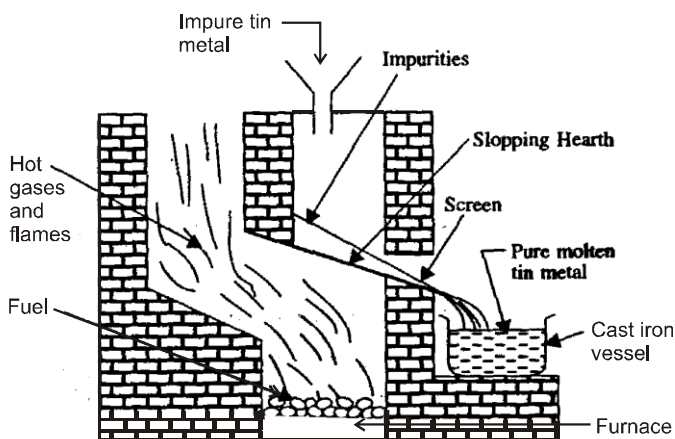


Fig. Purification of tin metal by liquation process.

**Purification of crude zinc :** The crude zinc or the spelter is melted on the sloping hearth of a reverberatory furnace. Molten zinc flows down while the non-fusible impurities are left on the hearth.

(iii) **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.

(iv) **Zone refining method (Fractional crystallisation method) :**

This process is used when metals are required in very high purity, for specific application. 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.

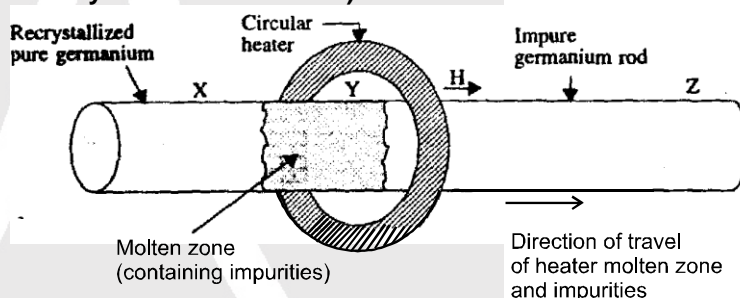


Fig. Zone refining of germanium metal

Germanium metal, which is used in semiconductor devices, is refined (purified) by the zone refining method. The impure germanium metal to be refined is taken in the form of a rod. A circular heater H is fitted around this rod and this heater is slowly moved along the length of the rod. When the heater is at the extreme left end of the impure germanium rod, it melts a narrow zone (narrow region) of the germanium rod at that place. Now, when the heater moves a little to the right side, then the molten metal at the previous position cools down and crystallizes to give pure metal at region X of the rod. The impurities, which were initially present in region X of germanium rod, now pass on to the region Y in the adjacent molten zone. Now, as the heater is shifted more and more to the right side on the germanium rod, the impurities also keep on shifting to the right side in to the newer and newer molten zones. Ultimately, the impurities reach the extreme right end Z of the germanium rod. This end Z of the germanium rod containing all the impurities is then discarded. The remaining rod is now of highly pure germanium metal. In addition to germanium, silicon and gallium used as semiconductors are also refined by the zone refining method.

(v) **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. Different components are adsorbed at different levels on the column. Later the adsorbed components are removed (eluted) by using suitable solvent (eluant). Depending upon the physical state of the moving medium and the adsorbent material and also on the process of passage of the moving medium, the chromatographic method is given the name. In one such method the column of  $Al_2O_3$  is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form. This is an example of column chromatography. This is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the



element to be purified. There are several chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc. Procedures followed in column chromatography have been depicted in the following figures.

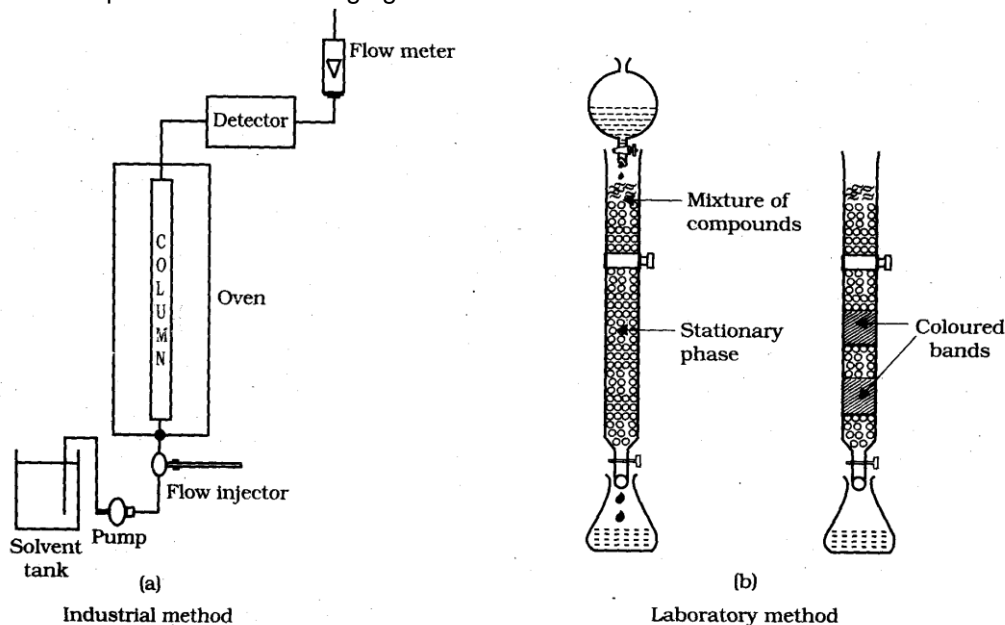


Fig. Schematic diagrams showing column chromatography

## 7.1. Chemical methods :

These methods include the following methods :

### (I) OXIDATIVE REFINING :

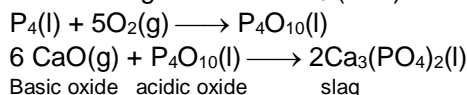
The method is used when the impurities present in the metal have a greater affinity for oxygen and are more readily oxidized than the metal. Then these oxides may be removed as follows :

- These oxide may form a scum on the surface of the metal. This scum can easily be removed by skimming.
- If the oxides are volatile, they escape from the mouth of the furnace.
- The oxides may form a slag with the lining on the inside surface of the furnace and may thus be removed. In the formation of the slag, the lining acts as a flux.

This method is usually employed for refining metals like **Pb, Ag, Cu, Fe**, etc. In this method the molten impure metal is subjected to oxidation by various ways.

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

The **iron** obtained from a blast furnace is a brittle material called cast iron or pig iron. It contains about 4% elemental C and smaller amounts of other impurities such as elemental Si, P, S and Mn that are formed from their compounds in the reducing atmosphere of the furnace. The most important of several methods for purifying the iron and converting it to steel is the basic oxygen process or oxidative refining. 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  $Ca_3(PO_4)_2$ .

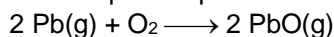


Mn also passes into the slag because its oxide is basic and reacts with  $SiO_2$  yielding molten manganese silicate.

This process produces steel that contains about 1% carbon but only very small amount of P and S. Usually the composition of liquid steel is monitored by chemical analysis and the amount of oxygen and impure iron used are adjusted to achieve the desired concentration of carbon and other impurities.

(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.

(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.

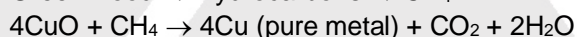
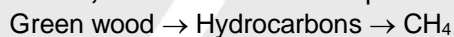
(i) **Parting with sulfuric acid or nitric acid:** Gold is not attacked by these acids while Cu and Ag dissolve. If, however, the Au content in an impure sample is more than 30%, the Cu and Ag are also not attacked by the acid of any strength. Hence, before the acid treatment, the impure sample is melted 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  $\text{H}_2\text{SO}_4$  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  $\text{Cl}_2$ :** Sometimes chlorine is used for the purification of Au. The impure sample of Au is fused with borax and  $\text{Cl}_2$  gas is forced through it. The base metals are converted into chlorides that pass out as fumes at this high temperature, and AgCl 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**.

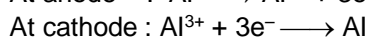
(i) **Purification of impure copper :** Impure copper is remelted in a reverberatory furnace lined with  $\text{SiO}_2$  and a blast of  $\text{O}_2$  is blown into the furnace.  $\text{O}_2$  oxidises S, Sb and As to their respective oxides which, being, volatile, get volatilised and are thus removed. Fe is oxidised to FeO which forms a slag of  $\text{FeSiO}_3$  with  $\text{SiO}_2$  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 ( $\text{CH}_4$ ). Methane thus obtained reduces CuO to free Cu-metal**, which is about 99.5% pure and is called tough pitch copper.



(ii) **Purification of impure tin :** Impure tin metal contains the impurities of Cu, Fe, W and  $\text{SnO}_2$ . The impurity of  $\text{SnO}_2$  is due to the incomplete reduction of tin stone ore ( $\text{SnO}_2$ ) 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  $\text{CH}_4$ . Methane thus obtained reduces  $\text{SnO}_2$  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.

(IV) **ELECTROLYTIC REFINING :**

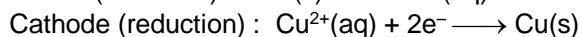
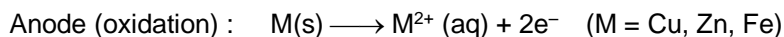
Some metals such as **Cu, Ni, and Al** are refined electrolytically. The Hooper process is a process for the electrolytic refining of aluminum. Impure Al forms the anode and pure Al forms the cathode of the Hooper's cell which contains three liquid layers. The bottom layer is molten impure Al, the middle 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 ( $\text{Al}^{3+}$ ), 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.





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 and pure copper as the cathode. The electrolyte is an aqueous solution of  $\text{CuSO}_4$ . 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,  $\text{Cu}^{2+}$  ions get reduced to pure copper metal, but the less easily reduced metal ions ( $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$  and so forth) remain in the solution.

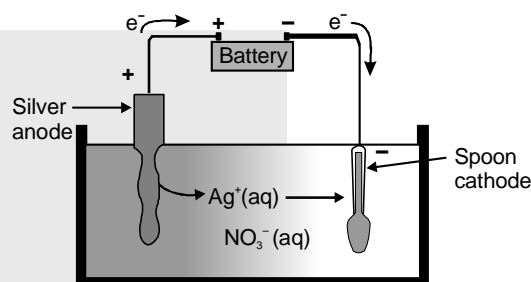


Thus, the net cell reaction simply involves transfer of Cu metal from the impure anode to the pure cathode, Cu obtained by this process is 99.95% pure.

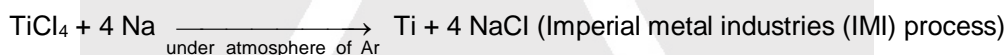
### Solved Example

**Example 1.** Sketch an electrolytic cell suitable for electroplating a silver spoon. Describe the electrode and the electrolyte. Label the anode and cathode, and indicate the direction of electron and ion flow. Write balanced equations for the anode and cathode half reaction.

**Solution:** Anode :  $\text{Ag(s)} \longrightarrow \text{Ag}^+(\text{aq}) + \text{e}^-$   
 Cathode :  $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag(s)}$   
 The overall reaction is transfer of Ag metal from silver anode to the silver spoon.



### (V) KROLL'S PROCESS :



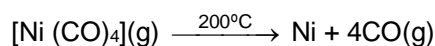
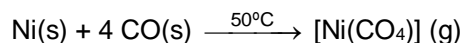
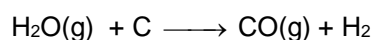
NaCl is leached with  $\text{H}_2\text{O}$ . Ti is in the form of small granules. These can be fabricated into metal parts using "powder forming" techniques and sintering in an inert atmosphere. Zr is also produced by Kroll's process.

### (VI) VAPOR PHASE REFINING :

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

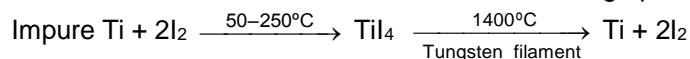
**Nickel** is extracted from sulfide ore by roasting followed by reduction with carbon, but the process is complicated by the fact that nickel is found in association with other metals. The refining is rather unusual, for nickel forms a complex with carbon monoxide tetracarbonylnickel (O)  $[\text{Ni}(\text{CO})_4]$ . This substance is molecular in structure and readily volatilized (boiling point  $43^\circ\text{C}$ ). It is made by heating nickel powder to  $50^\circ\text{C}$ , in a stream of CO and then decomposed at  $200^\circ\text{C}$ . Any impurity in the nickel sample remains in the solid state and the gas is heated to  $230^\circ\text{C}$ , when it decomposes, giving pure metal and CO, which is recycled.  $\text{Ni}(\text{CO})_4$  is gaseous and may be produced by warming nickel with CO at  $50^\circ\text{C}$ .

The sequence of reaction is



(ii) **Van Arkel–De Boer process :**

Small amounts of very pure metals (**Ti, Zr, or Bi**) can be produced by this method. This process is based on the fact that iodides are the least stable of the halides. The impure element is heated with iodine, producing a volatile iodide,  $TiI_4$ ,  $ZrI_4$  or  $BiI_3$ . These are decomposed by passing the gas over an electrically heated filament of tungsten or tantalum that is white hot. The element is deposited on the filament and the iodine is recycled. As more metal is deposited on the filament, it conducts electricity better. Thus, more electric current must be passed to keep it white hot. Thus the filament grows fatter and eventually the metal is recovered. The tungsten core is distilled out of the center and a small amount of high purity metal is obtained.



The method is very expensive and is employed for the preparation of very pure metal for specific use.

(VII) **PARKE'S PROCESS :**

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

In Parke's 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 Parke's 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 haematite ( $Fe_2O_3$ ) lining of the furnace.





## 8. MISCELLANEOUS SOLVED PROBLEMS (MSPS)

**Problem 1.** At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why?

**Solution:** Since zinc lies above iron in electrochemical series, it is more reactive than iron. As a result, if zinc scraps are used the reduction will be faster. However, zinc is a costlier metal than iron. Therefore, it will be advisable and advantageous to use iron scraps.

**Problem 2.** A metal is extracted from its sulphide ore and the process of extraction involves the following steps.

Metal sulphide  $\xrightarrow{(A)}$  Concentrated ore  $\xrightarrow{(B)}$  Matte  $\xrightarrow{(C)}$  Impure metal  $\xrightarrow{(D)}$  Pure metal

Identify the steps (A), (B), (C) and (D).

**Solution:** (A) Froth floatation process. Sulphide ores are concentrated by froth-floatation process.

(B) Roasting. Metal sulphides are roasted to convert into metal oxide and to remove impurities.

In roasting ;  $2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2$ .

$2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2$ .

$2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$ .

$\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$

(C) Bessemerisation/self reduction. Reduction of metal oxide by its sulphide takes place in Bessemer converter.

In Bessemerisation ;  $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$  (self - reduction)

(D) Electro-refining. Pure metal is obtained at cathode ;  $\text{M}^{n+} + n\text{e}^- \longrightarrow \text{m}$

**Problem 3.** Write chemical equations for metallurgical processes to represent :

(i) roasting of galena ( $\text{PbS}$ ) in limited supply of air at moderate temperature.

(ii) reduction of  $\text{Cu}_2\text{O}$  using coke as a reducing agent.

(iii) deposition of pure silver from an aqueous solution of  $\text{Ag}^+$ .

**Solution:** (i)  $2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$ ;  $\text{PbS} + 2\text{O}_2 \longrightarrow \text{PbSO}_4$

(ii)  $\text{Cu}_2\text{O} + \text{C} \longrightarrow 2\text{Cu} + \text{CO}$

(iii)  $\text{Ag}^+ + \text{e}^- \xrightarrow{\text{Electrolysis}} \text{Ag}\downarrow$  (at cathode)

**Problem 4.** Using data given below, predict whether the reduction of  $\text{MgO}$  with  $\text{C}$  is spontaneous or not at  $1500^\circ\text{C}$ .

$2\text{C} + \text{O}_2 \longrightarrow 2\text{CO}$   $\Delta G^\circ \approx -530\text{ kJ}$

$2\text{MgO} \longrightarrow 2\text{Mg} + \text{O}_2$   $\Delta G^\circ \approx +730\text{ kJ}$

**Solution:** The positive value of  $\Delta G^\circ$  indicates that the reduction of  $\text{MgO}$  with  $\text{C}$  does not occur to a significant extent at  $1500^\circ\text{C}$ .

$2\text{C} + \text{O}_2 \longrightarrow 2\text{CO}$   $\Delta G^\circ \approx -530\text{ kJ}$

$2\text{MgO} \longrightarrow 2\text{Mg} + \text{O}_2$   $\Delta G^\circ \approx +730\text{ kJ}$

$2\text{MgO} + 2\text{C} \longrightarrow 2\text{Mg} + 2\text{CO}$

or  $\text{MgO} + \text{C} \longrightarrow \text{Mg} + \text{CO}$

$\Delta G^\circ$  positive value.

**Problem 5.** Sea water  $\xrightarrow{(A)}$   $\text{Mg}(\text{OH})_2$   $\xrightarrow{(B)}$   $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$   $\xrightarrow{(C)}$   $\text{MgCl}_2$   $\xrightarrow{(D)}$   $\text{Mg} + \text{Cl}_2\uparrow$

Identify the reagents and processes (A) to (D) and give the name of this process.

**Solution:**  $\text{MgCl}_2$  (from sea water) +  $\text{Ca}(\text{OH})_2$  (A)  $\rightarrow \text{Mg}(\text{OH})_2\downarrow + \text{CaCl}_2$  ;

$\text{Mg}(\text{OH})_2 + 2\text{HCl}$  (B)  $\rightarrow \text{MgCl}_2$  (aq.) +  $2\text{H}_2\text{O}$

Crystallisation of  $\text{MgCl}_2$ (aq) yields  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow[\Delta \text{ Dry HCl}]{\text{Calcination (C)}} \text{MgCl}_2 + 6\text{H}_2\text{O}$

$\text{MgCl}_2(l) \xrightarrow{\text{Electrolysis(D)}} \text{Mg}^{2+} + 2\text{Cl}^-$

$\downarrow + 2\text{e}^-$   $\downarrow \text{Cl}_2$

$\text{Mg}$   $\text{Cl}_2$

(cathode) (anode)

Name of the process is Dow's process.



**Problem 6.** Convert magnesite into anhydrous  $MgCl_2$ .

**Solution:**  $MgCO_3 \xrightarrow{\Delta} MgO + CO_2$  ;  $MgO + C + Cl_2 \longrightarrow MgCl_2 + CO$

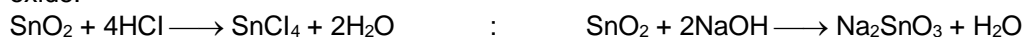
**Problem 7.** Which is not the correct process-mineral matching in metallurgical extraction.

(A) Leaching : silver (B) Zone refining : lead.  
(C) Liquefaction : tin (D) Van Arkel : Zr

**Solution:** Lead is purified by Electro-refining. Zone refining is used for the purification of Si and Ge. Therefore, (B) option is correct.

**Problem 8.** Tin stone, an oxide of tin is amphoteric in nature. Explain.

**Solution:** Tin stone is cassiterite i.e.  $SnO_2$ .  $SnO_2$  dissolves in acid and alkali both, hence amphoteric oxide.



**Problem 9.** Select the incorrect statement.

(A) In the Bayer's  $Al_2O_3$  goes in to solution as soluble  $[Al(OH)_4]^-$  while other basic oxides as  $TiO_2$  and  $Fe_2O_3$  remain insoluble  
(B) Extraction of zinc from zinc blende is achieved by roasting followed by reduction with carbon.  
(C) The methods chiefly used for the extraction of lead and tin are respectively carbon reduction and electrolytic reduction.  
(D) Extractive metallurgy of magnesium involves fused salt electrolysis.

**Solution:** Lead  $\rightarrow$  self reduction;  $2PbO + PbS \longrightarrow 3Pb + SO_2$

Tin  $\rightarrow$  carbon reduction,  $SnO_2 + 2C \longrightarrow Sn + 2CO$

Therefore, (C) option is correct.

**Problem 10.** Which of the following is not an ore of iron ?

(A) limonite (B) cassiterite (C) magnetite (D) none of these

**Solution:**  $SnO_2$ , cassiterite is an ore of tin.

Therefore, (B) option is correct.

**Problem 11.** In the extraction of copper from sulphide ore the metal is formed by reduction of  $Cu_2O$  with :

(A)  $FeS$  (B)  $CO$  (C)  $Cu_2S$  (D)  $SO_2$

**Solution:**  $2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$  Therefore, (C) option is correct.

**Problem 12.** Which of the following is a carbonate ore ?

(A) pyrolusite (B) malachite (C) diaspore (D) cassiterite

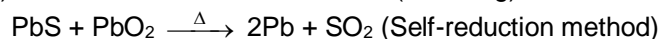
**Solution:**  $CuCO_3 \cdot Cu(OH)_2 \rightleftharpoons$  Malachite. Therefore, (B) option is correct.

**Problem 13.** Column-I and column-II contains four entries each. Entries of column-I are to be matched with some entries of column-II. Each entry of column-I may have the matching with one or more than one entries of column-II.

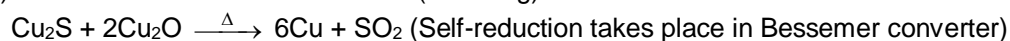
	Column-I		Column-II
(A)	Pb	(p)	Bessemerisation
(B)	Cu	(q)	Roasting
(C)	Zn	(r)	Pyrometallurgy
(D)	Fe (pig iron)	(s)	Self-reduction method

**Ans.** (A) q, r, s; (B) p, q, r, s; (C) q, r; (D) r;

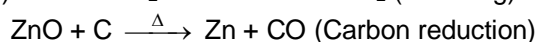
**Solution:** (A)  $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$  (Roasting)



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



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



(D) Haematite ore is calcined.

