

## Class 12 Chemistry Chapter 06 General principles and processes of Isolation of Elements

- The study of history of civilization is linked with the uses of metals. The various civilizations are named after metals.
- Our earth's crust has plenty of minerals and ores.
- Minerals are naturally occurring solid inorganic substances. They have characteristic crystalline structure and definite chemical composition. Examples: iron, zinc, chromium, etc.
- Ores are concentrations of minerals in rock, from which metals are extracted. Examples: Cinnabar, ore of mercury (Hg) and cassiterite, ore of tin (Sn).

### Minerals:

The naturally occurring chemical substances in the earth's crust which are obtained by mining are known as minerals.

Metals may or may not be extracted profitably from them.

### Ores:

Those rocky materials which contain sufficient quantity of mineral so that the metal can be extracted profitably or economically are known as ores.

### Gangue:

The earthy or undesirable materials present in ore are known as gangue.

### Metallurgy:

- ☐ The entire step by step scientific and technological process used for isolation of the metal from its ores is known as metallurgy.
- ☐ Chief Ores and Methods of Extraction of Some Common Metals:

### Sodium metal

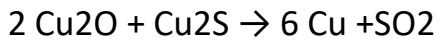
- Occurrence: Rock salt (NaCl), Feldspar ( $\text{Na}_3\text{AlSi}_3\text{O}_8$ )
- Extraction method: Electrolysis of fused NaCl or NaCl/  $\text{CaCl}_2$

c) Inference: Sodium is highly reactive and hence, it reacts with water.

### **Copper metal**

a) Occurrence: Copper pyrites ( $\text{CuFeS}_2$ ), Malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ), Cuprite ( $\text{Cu}_2\text{O}$ ) Copper glance ( $\text{Cu}_2\text{S}$ )

b) Extraction method: Roasting of sulphide partially and reduction.



c) Inference: It is self-reduction in a specially designed converter. Sulphuric acid leaching is also employed.

### **Aluminum metal**

a) Occurrence: Bauxite: ( $\text{AlO}_x (\text{OH})_{3-2x}$  where  $0 < x < 1$ ), Cryolite ( $\text{Na}_3\text{AlF}_6$ ), Kaolinite ( $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$ )

b) Extraction method: Electrolysis of  $\text{Al}_2\text{O}_3$  dissolved in molten cryolite or in  $\text{Na}_3\text{AlCl}_6$

c) Inference: A good source of electricity is needed in the extraction of Al

### **Zinc metal**

a) Occurrence: Zinc blende or Sphalerite ( $\text{ZnS}$ ), Zincite ( $\text{ZnO}$ ), Calamine ( $\text{ZnCO}_3$ )

b) Extraction method: Roasting and then reduction with carbon.

c) Inference: The metal may be purified by fractional distillation.

### Lead metal

a) Occurrence: Galena (PbS)

b) Extraction: Roasting of the sulphide ore and then reduction of the oxide.

c) Inference: Sulphide ore is concentrated by froth floatation process.

**Table: Principal Ores of some metals**

Metal	Ores	Composition
Aluminium	Bauxite Kaolinite	$Al_x(OH)_{3-2x}$ (Here $0 < x < 1$ ) $[Al_2(OH)_4Si_2O_5]$
Iron	Haematite Siderite Iron pyrites	$Fe_2O_3$ $Fe_3O_4$ $FeS_2$
Copper	Copper pyrites Malachite Cuprite Copper glance	$CuFeS_2$ $CuCO_3 \cdot Cu(OH)_2$ $Cu_2O$ $Cu_2S$
Zinc	Zinc blende Calamine Zincite	$ZnS$ $ZnCO_3$ $ZnO$

➤ The extraction of metal from ore involves following steps:

1. Concentration of the ore,
2. Isolation of the metal from its concentrated ore,
3. Purification of the metal.

## 1. Concentration of the ore –

- The removal of unwanted material like clay and sand from the ore is called concentration.
- The ore is grind and crushed in small pieces and then the concentration procedure is done.
- Concentration of ores is done by many procedures, some of them are as follows:

### a. Hydraulic washing-

- It is a type of gravity separation. Ores are of different specific gravities.
- An upward heavy stream of running water washes the powdered ore.
- The lighter gangue particles are run away with stream of water and only the heavier ore particles are left behind.

### b. Magnetic separation-

- There is a difference in the magnetic properties of ore components.
- This method is used only when ore or gangue is attracted to magnetic fields.

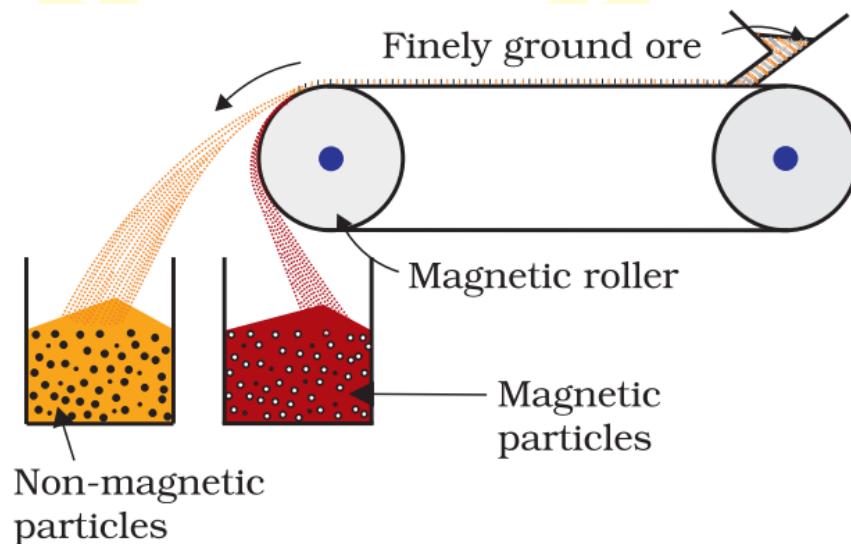


Figure: Magnetic Separation

- Example: ores of iron are attracted towards magnet so non-magnetic impurities can be separated from the iron ore using magnetic separation.

- In this procedure the crushed ore is spread over a conveyer belt which moves in the direction of a magnetic roller.
- Magnetic substance remains attracted towards the belt and falls close to it.

### c. Froth floatation method –

- This method is used to remove the gangue from the sulphide ores. This procedure involves a suspension of the powdered ore is made with water.

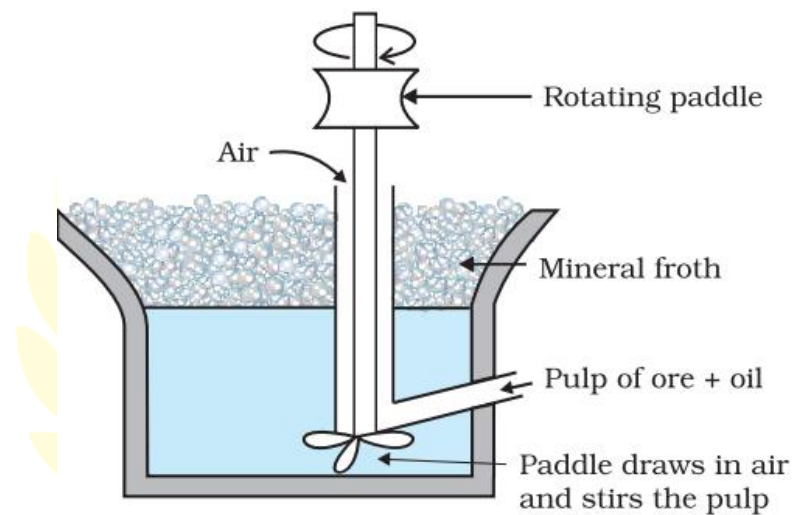


Figure: Froth floatation process

- The collectors and froth stabilisers are added to the suspension. Collectors like fatty acids, xanthates, pine oils, etc. enhance the non-wettability of the mineral particles. Examples of froth stabilisers are cresols, aniline stabilize the froth.
- The mineral particles become wet by the oils while the gangue particles become wet by water.
- A rotating paddle act as agitator to mix well and draws air in it.
- Due to this a froth is formed which carries the mineral particles. The froth is light in weight and is separated. Then it is dried to retrieval the ore particles.
- Two sulphide ores can be separated by adjusting proportion of oil to water or by using the **depressants**. Example: for an ore containing

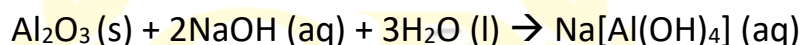
ZnS and PbS; NaCN is used as depressant. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

#### d. Leaching –

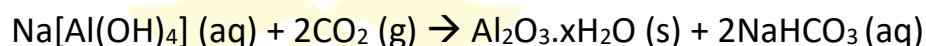
➤ Leaching is used only if the ore is soluble completely in suitable solvent. There are some examples:

##### 1. Leaching of alumina from bauxite:

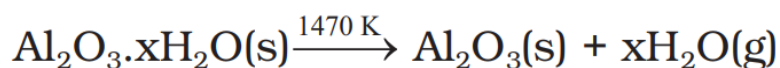
- Bauxite ore contain some impurities of silica, oxide of iron and titanium.
- Concentration is done by heating the grinded ore with sodium hydroxide at 472-523 kelvin temperature and 35 to 36 bar pressure. This procedure is termed as digestion.
- Through digestion  $\text{Al}_2\text{O}_3$  is extracted as  $\text{Na}[\text{Al}(\text{OH})_4]$ . And impurities are left behind.



- $\text{Na}[\text{Al}(\text{OH})_4]$  is neutralized by passing carbon di oxide gas and hydrated  $\text{Al}_2\text{O}_3$  is precipitated. At this stage, small amount of freshly prepared hydrated  $\text{Al}_2\text{O}_3$  is added to the solution to induce the precipitation. This is called seeding.

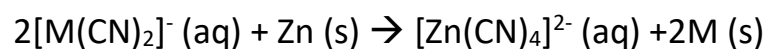
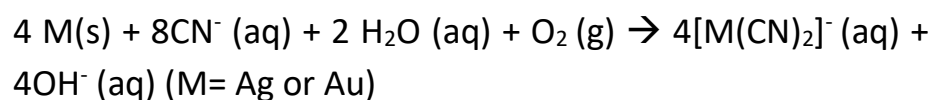


- The hydrated alumina is filtered, dried and heated to give the pure  $\text{Al}_2\text{O}_3$ .



##### 2. Other examples:

- In case of Au and Ag, the metal is leached with a dilute solution of sodium or potassium cyanide in presence of air. Air supplies oxygen. The metal is obtained later by replacement reaction.



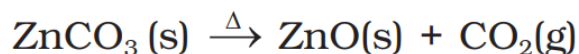
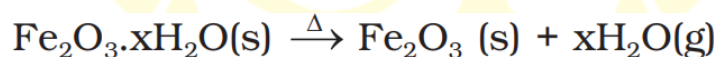
## 2. Isolation of the metal from its concentrated ore

➤ To get metal from concentrated ore, it needs to be converted into a form which is suitable for reduction to metal. Generally, sulphide ores are converted to oxide before reduction because oxides are easy to reduce. Thus isolation of metals from concentrated ore comprises two important steps which are as follows:

1. Conversion to oxide
2. Reduction of oxide into metal

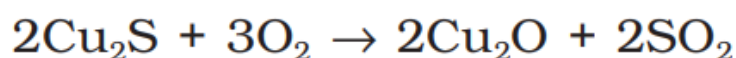
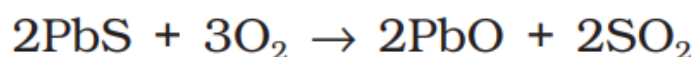
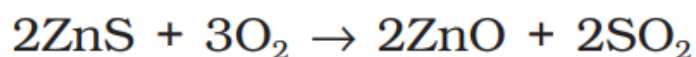
### 1. Conversion to oxide

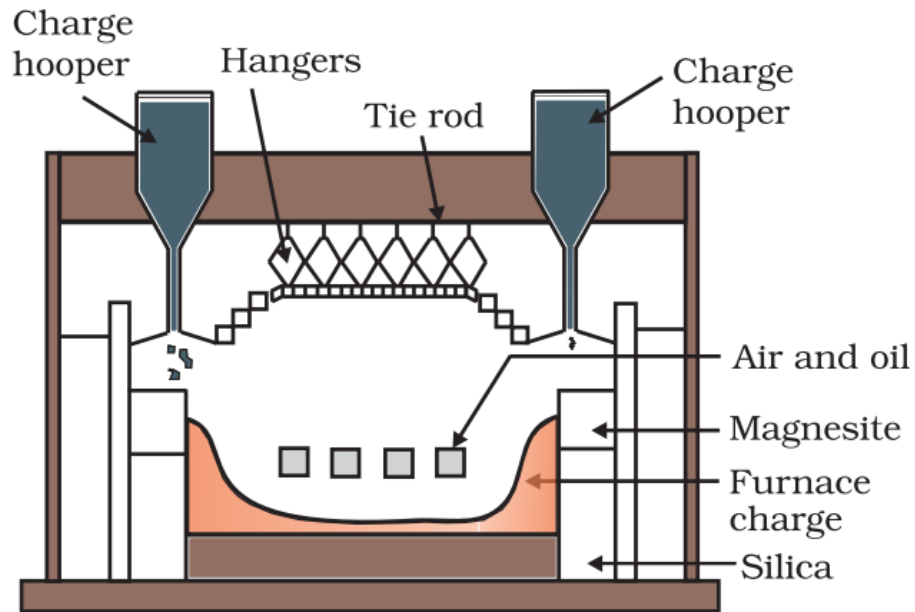
A. Calcination: It involves heating through which the volatile matter is removed which escapes leaving behind the metal oxide as follows:



B. Roasting:

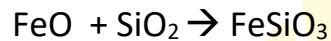
It involves the heating of ore with a regular supply of air in a furnace at a temperature below the melting point of the metal. The reactions involving sulphide ores are as follows:





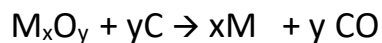
**Figure: Modern reverberatory furnace**

**Reverberatory** furnace is used to heat the sulphide ores of copper are. If the ore contains iron then silica is mixed with it before heating. Slags of FeO as  $\text{FeSiO}_3$  and copper are produced in the form of copper matte which contains  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ . As a by-product sulphur dioxide is produced; which is used in sulphuric acid production.



## 2. Reduction of oxide into metal

- It involves heating of oxide with a reducing agent like Carbon or Carbon mono oxide. The reducing agent i.e. carbon, combines with the oxygen of the metal oxide.



- Heating is required to reduce the metal oxides.

## Thermodynamic principles of metallurgy –



- At a given temperature Gibbs energy change of the reaction should be negative. The change in Gibbs energy,  $\Delta G$  for any process at any specified temperature is as follows:

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

Here  $\Delta H$  = enthalpy change

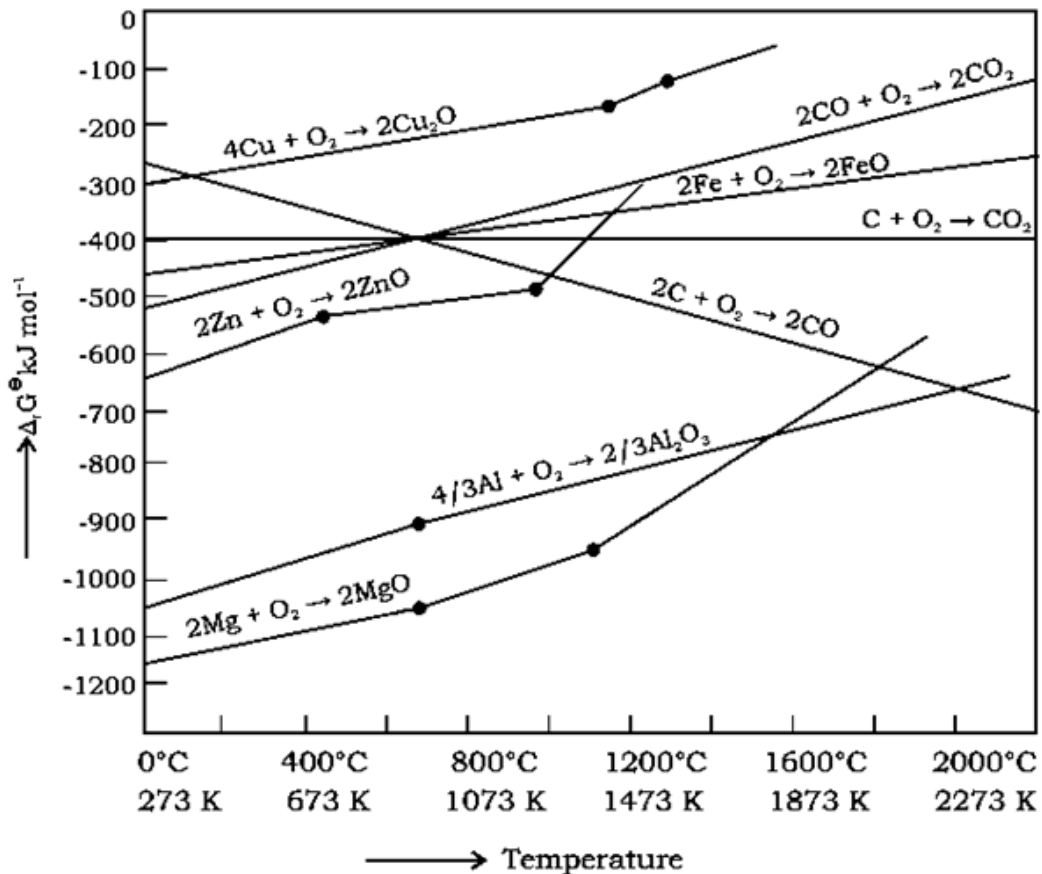
$\Delta S$  = entropy change for the process

- When the value of  $\Delta G$  is -ve in above equation only then the reaction will proceed.  $\Delta G$  can become -ve in the following situations:

1. If  $\Delta S$  is +ve, on increasing the temperature the value of  $T\Delta S$  increases so that  $\Delta H < T\Delta S$ . In this situation  $\Delta G$  will become -ve on increasing temperature.

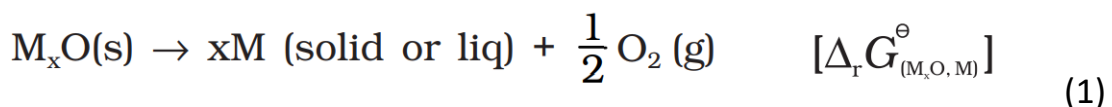
2. Coupling of the two reactions which are reduction and oxidation, results  $\Delta G = -ve$  for overall reaction thus the final reaction becomes feasible. It can be explained well by Gibbs energy ( $\Delta_r G^\ominus$ ) vs T plots for the formation of the oxides. These plots are drawn for free energy changes which occur when one gram mole of  $O_2$  gas is consumed.

- H.J.T. Ellingham the first man who used the graphical representation of Gibbs energy. This provides a wide range of the choices of reducing agents in the reduction of oxides. This is known as Ellingham Diagram. Such diagrams help to predict the feasibility of thermal reduction of an ore.

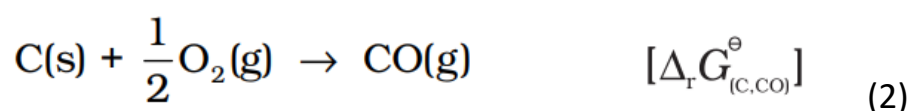


**Figure: Gibbs energy versus T plots for the formation of some oxides per mole of oxygen consumed (Ellingham diagram)**

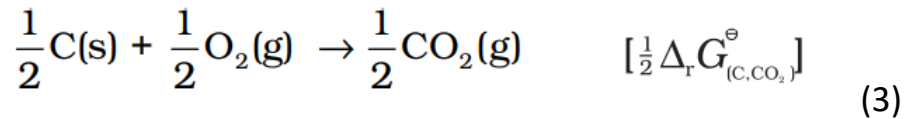
- The oxide of a metal decomposes and the reducing agent captures the oxygen during the reduction. The role of reducing agent is to provide  $\Delta_r G^\ominus = -ve$  and large enough to make the sum of  $\Delta_r G^\ominus$  of the two reactions, that is oxidation of the reducing agent and reduction of the metal oxide -ve.



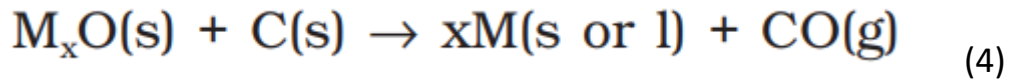
- If reduction is carried out by carbon the oxidation of the reducing agent will be there:



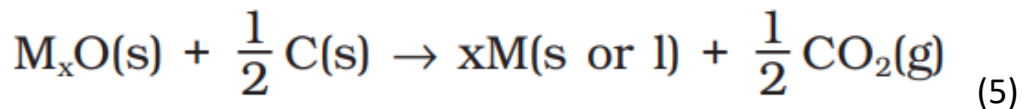
- There may also be complete oxidation of carbon to carbon di oxide.



- On combining first and second reaction:



- On combining reaction first and third equation:



- The reactions (2) and (5) tell about the actual reduction of the metal oxide. The  $\Delta_r G^\ominus$  values for these reactions can be obtained by the corresponding  $\Delta_f G^\ominus$  values of oxides.

## Applications

### 1. Extraction of iron from its oxides:

- When concentration is done, the mixture of oxide ores of iron ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ) is put through the roasting or calcination to remove water. Calcination helps to decompose the carbonates and to oxidise the sulphides.

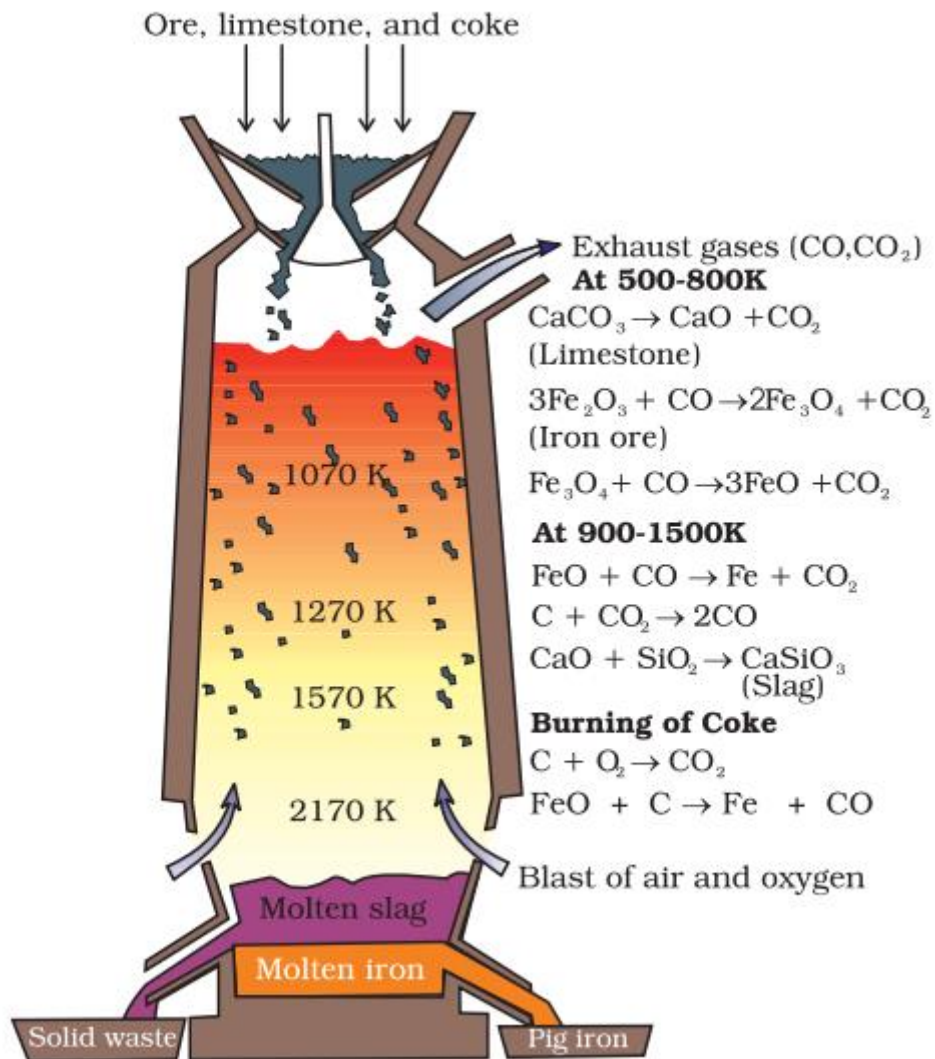
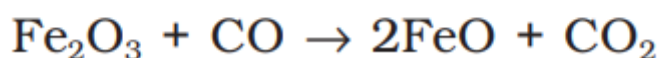
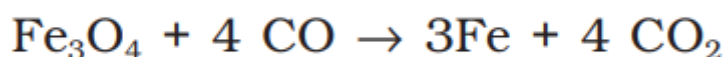
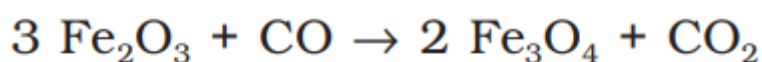
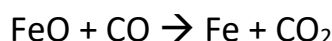
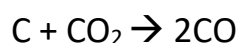


Figure: Blast furnace

- After that these are mixed with coke and limestone then it is fed into a blast furnace from the top side, in which the oxide is reduced to the metal. Reduction of iron oxides takes place in blast furnace, at different temperature ranges.
- A blast of hot air is blown from the bottom of the furnace by burning coke in the lower portion to give temperature up to about 2200K.
- The burning of coke supplies the heat required in the process. The CO and heat move to the 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 to FeO. These reactions are as follows:



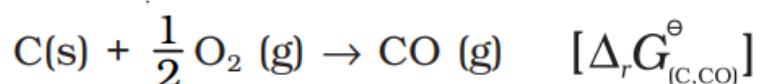
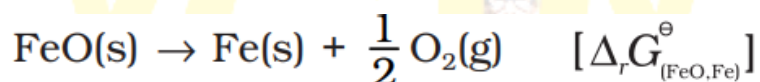
- Limestone is decomposed to CaO which removes silicate impurity of the ore in form of slag. The slag is in molten state and separates out from iron.
- At 900-1500 K:



- One of the main reduction steps is as follows:



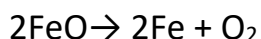
- In above reaction two simpler reactions have combined. In one the reduction of FeO is takes place and in the other one carbon is oxidised to carbon mono oxide:



- The net Gibbs energy change is as follows:

$$\Delta_r G_{(\text{C}, \text{CO})}^\ominus + \Delta_r G_{(\text{FeO}, \text{Fe})}^\ominus = \Delta_r G^\ominus$$

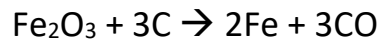
- At about 1673K  $\Delta_r G^\ominus$  value for the following reaction is +341 kJmol<sup>-1</sup>:



- As it is reverse of  $\text{Fe} \rightarrow \text{FeO}$  change and for the reaction  $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$   $\Delta_r G^\ominus$  is - 447 kJ mol<sup>-1</sup>.
- The iron obtained from this furnace contains approximately 4% of carbon and many impurities like Si, S, P, Mn, etc. in slight amount. This is known as pig iron. It can be moulded in various shapes.
- Cast iron is made by melting pig iron with scrap iron and coke via hot air blast. It has low carbon content and it is extremely hard and brittle.

### Further reduction-

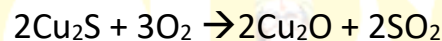
- Malleable iron or wrought iron is the purest form of iron and it is prepared from cast iron by oxidising the impurities in a reverberatory furnace lined with the haematite. The haematite oxidises carbon to carbon monoxide:



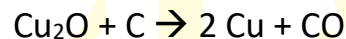
- Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and discarded into the slag. The metal is removed and slag is removed by passing through rollers.

## 2. Extraction of copper from cuprous oxide

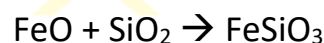
- In the graph of  $\Delta_r G^\circ$  versus T for the formation of, the  $\text{Cu}_2\text{O}$  line is at the top. The oxides ores of copper are easy to reduce directly to the metal by heating with coke.
- The ores of sulphides contain iron. The sulphide ores are smelted to give oxides in following reaction:



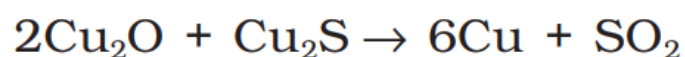
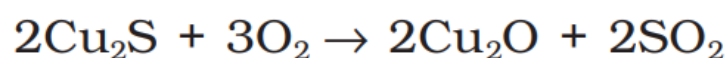
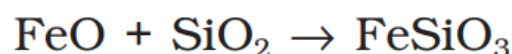
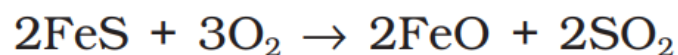
- The oxide reduced to metallic copper by using coke:



- Actually, ore is heated in a reverberatory furnace after mixing with silica. In furnace the iron oxide 'slags off' as iron silicate is formed and copper is formed as copper matte. This contains  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ .

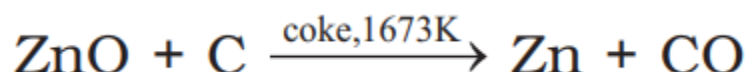


- Copper matte is charged into silica lined convertor and silica is added and hot air blast is blown to convert the remaining  $\text{FeO}$ ,  $\text{FeS}$  and  $\text{Cu}_2\text{S}$  to metallic copper. The solid copper acquired has bubbled or blistered appearance due to the evolution of  $\text{SO}_2$ ; so it is known as blister copper. These are the chemical reactions:



### 3. Extraction of zinc from zinc oxide –

- The reduction of ZnO is done by using coke. The temperature is higher than the copper extraction.
- For high temperature the oxide is made into briquettes with coke and clay. The metal is purified and collected by rapid chilling.



### Electrochemical principles of metallurgy

- Metal oxides are reduced by electrolysis or by adding some reducing element.
- In the reduction of a molten metal salt, electrolysis is done. This method is based on electrochemical principle, which is as follows:

$$\Delta G^\ominus = - nE^\ominus F$$

Here n = number of electrons

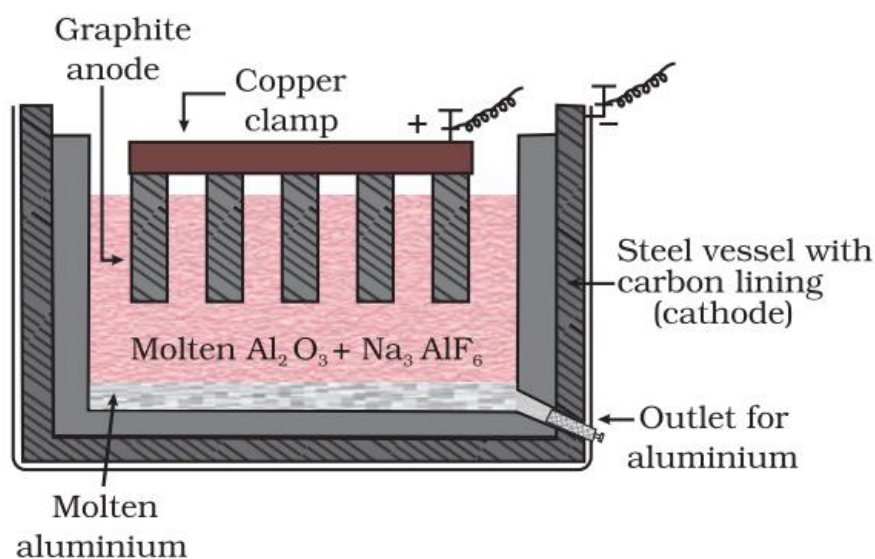
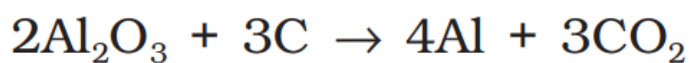
$E^\ominus$  = electrode potential of the redox couple formed in the system

- If the difference of two  $E^\ominus$  values corresponds to a positive  $E^\ominus$  and consequently negative  $\Delta G^\ominus$  in above equation.
- The less reactive metal will come out of the solution and the more reactive metal will go into the solution. For example –  
$$\text{Cu}^{2+} (\text{aq}) + \text{Fe} (\text{s}) \rightarrow \text{Cu} (\text{s}) + \text{Fe}^{2+} (\text{aq})$$
- In simple electrolysis, the  $M^{n+}$  ions are discharged at -ive electrodes means cathode and deposited on it.
- Suitable materials are used as electrodes.
- A flux is added to increase the conductance of the molten mass.

### Aluminium

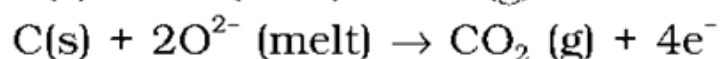
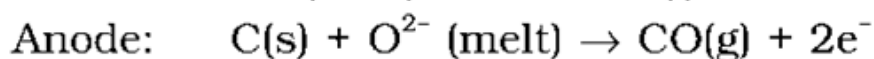
- In the metallurgy of Al; the purified  $\text{Al}_2\text{O}_3$  is mixed with  $\text{Na}_3\text{AlF}_6$  or  $\text{CaF}_2$ . It helps to lowers the melting point of the mixture and brings conductivity to it.

- The fused matrix is electrolysed. Steel vessel with lining of carbon acts as cathode and graphite act as anode. The overall reaction is as follows:



**Figure: Electrolytic cell for the extraction of aluminium**

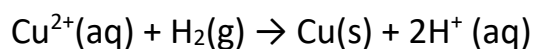
- This procedure of electrolysis is called Hall-Heroult process. Thus electrolysis of the molten mass is carried out in an electrolytic cell using the carbon electrodes.
- The  $\text{O}_2$  liberated at the anode reacts with the carbon of anode and produce carbon mono oxide and carbon di oxide. Thus approximately 0.5 kg of carbon anode is burnt away to produce one kg of aluminium. The electrolytic reactions are as follows:



## Copper from Low Grade Ores and Scraps



- Copper (Cu) is extracted from low grade ores by hydrometallurgy. It is leached out by using acid or bacteria. The solution containing  $\text{Cu}^{2+}$  is treated with scrap iron or  $\text{H}_2$ .

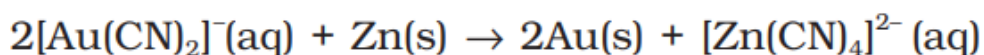
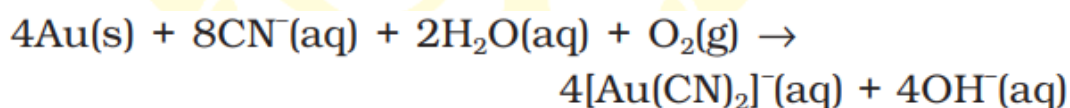


### Oxidation reduction

- An example of extraction based on oxidation is the extraction of chlorine from brine. Reaction is as follows:



- The  $\Delta G^\ominus$  for this reaction is + 422 kJ. When it is converted to  $E^\ominus$  by using the equation  $\Delta G^\ominus = -nE^\ominus F$ , we get  $E^\ominus = -2.2 \text{ V}$ .
- It requires an external emf > 2.2 V.  $\text{Cl}_2$  and  $\text{H}_2$  are obtained by electrolysis and aqueous NaOH as by-products.
- The extraction of gold(Au) and silver(Ag) involves leaching the metal with cyanides ( $\text{CN}^-$ ). This is also an oxidation reaction ( $\text{Ag} \rightarrow \text{Ag}^+$  or  $\text{Au} \rightarrow \text{Au}^+$ ).
- The metal is later recovered by replacement reaction. The reaction is as follows:



In above reaction Zn acts as reducing agent.

### Refining

- Metals of high purity can be obtained by several techniques; some of them are as follows: distillation liquation, zone refining, electrolysis, vapour phase refining, chromatographic methods, etc.

#### 1. Distillation

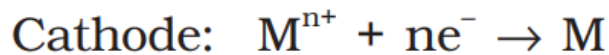
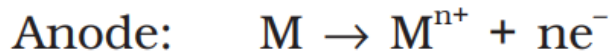
- This is used for metals with low boiling point like Zn and Hg.
- The pure metal is obtained by evaporation of impure metal.

#### 2. Liquation

- In this method metals with low melting for example Sn can be made to flow on a sloping surface. Through this is separated from higher melting impurities.

### 3. Electrolytic refining

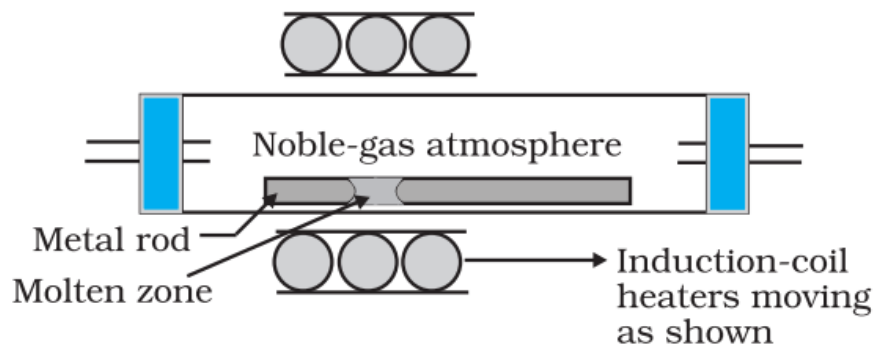
- A strip of the same metal in pure form is used as cathode and the impure metal is act as anode.
- Both electrodes are dipped in suitable electrolytic bath containing soluble salt of same metal.
- The metal which is more basic remains in the solution and the less basic metal go to the anode mud. The reactions are:



- Impurities from the blister copper deposit as anode mud which contains Sb, Se, Te, Ag, Au and Pt; recovery of these elements can encounter the cost of refining.

### 4. Zone refining

- The solubility of impurities is higher in the melt as compare to the solid state of the metal.
- The rod of impure metal is surrounded by a mobile heater. The molten zone moves along with the heater.
- The pure metal crystallises out of the melt left behind as the heater move forward. The impurities pass on into the adjacent new molten zone which is created by movement of heaters.



**Figure: Zone refining process**

- The process is repeated many times and the heater is moved in the same direction continuously.
- Impurities get concentrated at one end. This end is cut off. This method is very useful for producing semiconductor and highly pure metals e.g., Ge, Si, B, Ga and In.

## 5. Vapour phase refining

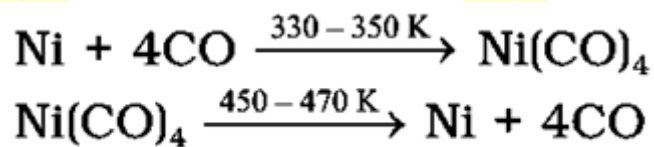
- This method comprises the conversion of metal into its volatile compound which is collected and decomposed to give pure metal.

There are two requirements:

- (i) The metal should form a volatile compound with an available reagent,
- (ii) The volatile compound should be decomposable for easy recovery.

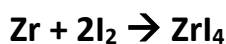
- Following examples will illustrate this technique. [Mond Process for Refining Nickel:](#)

- In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex named as nickel tetracarbonyl; which is decomposed at high temperature to get pure metal.



[Van Arkel Method for Refining Zirconium or Titanium:](#) - This method is used to remove all the oxygen and nitrogen present in the form of impurity in metals like Zirconium and Titanium.

- In an evacuated vessel the crude metal is heated with iodine. The metal iodide is more covalent, volatilises. The metal iodide is decomposed on a tungsten filament which is electrically heated to 1800K temperature. The pure metal deposits on the filament.



## 6. Chromatographic methods

- Column chromatography is used for purification of the elements which are available in small quantities and the impurities are almost same in chemical properties from the element to be purified.

[Uses of Aluminium, copper, zinc and iron](#)

- Aluminium foils are used as wrappers for food materials. The fine dust of the metal is used in paints and varnishes.
- Aluminium is highly reactive; it is also used in the extraction of Cr and Mn from their oxides. Wires of Al are used as electricity conductors.
- Alloys containing aluminium, being light are very useful.
- Copper is used for making wires used in electrical industry and for water and steam pipes.
- It is also used in several alloys that are rather tougher than the metal itself, like brass, bronze and coinage alloy.
- Zinc is used for galvanising iron. It is constituent of many alloys, e.g., brass, (Cu and Zn) and German silver (Cu, Zn, Ni).
- Cast iron is very important form of iron; it is used for gutter pipes, casting stoves, railway sleepers, toys, etc.
- It is used in the manufacture of wrought iron and steel. Wrought iron is used in making of bolts, chains anchors, wires, and agricultural apparatuses. Alloy steel is obtained when other metals are added to it.
- Chrome steel is used for cutting tools and crushing machines, and stainless steel is used for cycles, automobiles, utensils, pens, etc.
- Nickel steel is used for making cables, automobiles and aeroplane parts, pendulum, measuring tapes.