

# GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

- Scope** : One qn for JEE (Main)/NEET  
Four equivalent MCQ for JEE (Adv)
- Ref** : JEE (Main)/NEET - Only NCERT text + Exemplar Qns + Exercise  
JEE (Adv). In addition to NCERT text + Exemplar + Exercise
- Inorganic chemistry by Dr. K. Rama Rao, S. Chand
  - Inorganic chemistry by Jaiswal, Balaji Publication
  - Inorganic chemistry by J.D. Lee
  - Any material for practice by famous institutes.

## Video lessons

- 1) IIT PAL - Swayam channel/Ministry of Education, Govt. of India
- 2) Udan - By CBSE

## I. Origin of elements:

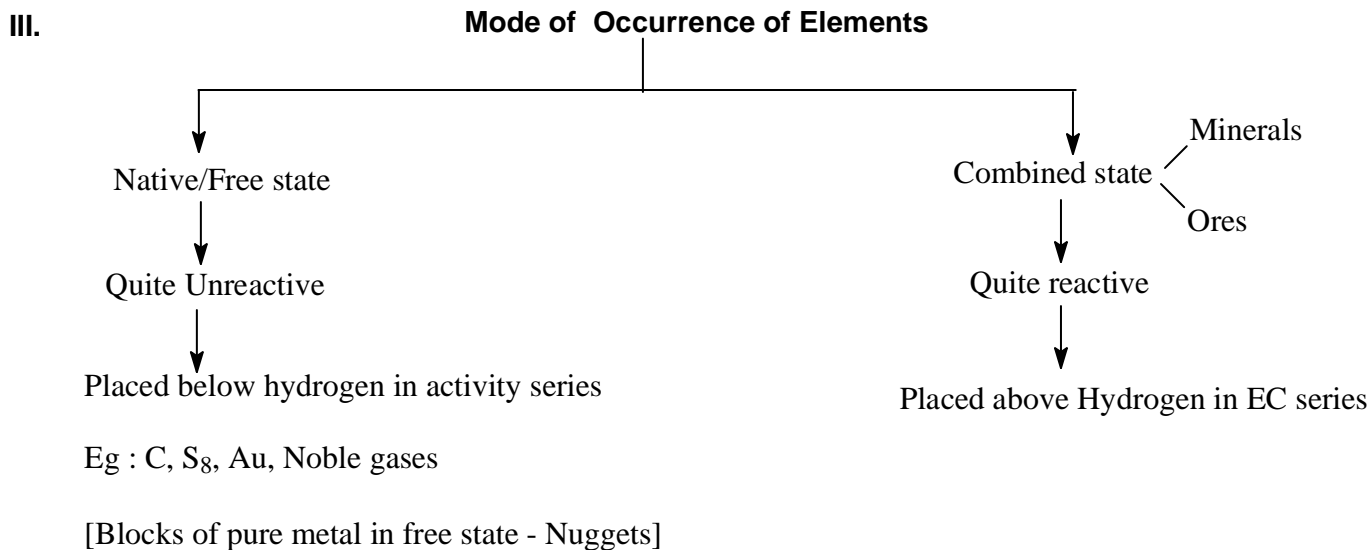
Elements originated as a result of nuclear fusion reactions or other nuclear processes since the beginning of the universe.

## II. Abundance of elements in the Earth's Crust

O > Si > Al > Fe..... C > S > Ba  
49.6% 25.4% 8.3% 5.1% 0.08 0.6 0.04

## Questions (Previous)

1. The most abundant element by wt/which element constitute one half of the earth's crust?
2. The second most abundant element by wt/which constitute one quarter of the earth's crust?
3. 75% of Earth's crust consists of ..... and .....
4. The most abundant metal in the crust.
5. The second most abundant metal in the Earth's crust.
6. The four major elements in the decreasing order of abundance.
7. The least abundant pair of elements in the Earth's Crust.



**Minerals** : Naturally occurring chemical substances in the Earth's Crust obtainable by mining

**Ores** : Minerals from which the metal is extracted most profitably

**Note** : All ores are minerals, but not vice-versa.

#### IV. Classification of Minerals

- 1) Oxides
- 2) Sulphides
- 3) Carbonates
- 4) Silicates
- 5) Sulphates
- 6) Halides
- 7) Phosphates

#### **Questions (Previous)**

1. The least likely to be found as a mineral is nitrate since they are water soluble (or nitrates of hard acids are stable).
2. s-block exist as chlorides, carbonates, silicates mainly  
p and d block - oxides and sulphides  
Exception : Group 3 - phosphates  
Group 8, 9, 10 - native state  
No minerals for  $_{43}\text{Tc}$

**OXIDES**

1. Corundum,  $\text{Al}_2\text{O}_3$   
Exists in two coloured forms  
Gem stones ruby (red) and sapphire (blue)  
Impurity range from Cr in ruby to Cobalt in Sapphire  
Note : Fe/Cr - in ruby  
Co/Ti - in sapphire
2.  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  - Diaspore
3.  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  - Bauxite (Ore)  
New formula :  $\text{AlO}_x(\text{OH})_{3-2x}$ ; where  $0 < x < 1$
4.  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  - Gibbsite
5.  $\text{Fe}_2\text{O}_3$  - Haematite / red iron ore/most abundant ore/ore with maximum silica content/Jeweller's rouge
6.  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  - Limonite/Brown iron ore  
New formula :  $\text{FeO}(\text{OH})n\text{H}_2\text{O}$
7.  $\text{Fe}_3\text{O}_4$  - Magnetite/ore with maximum iron content
8. Cassiterite/Tin stone/ore of tin -  $\text{SnO}_2$
9. Cuprite/ruby copper -  $\text{Cu}_2\text{O}$  - The mineral with +1 oxidation state for the metal
10. Zincite -  $\text{ZnO}$
11. Franklinite -  $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$
12. Pitch blende - Ore of Uranium  $\text{U}_3\text{O}_8$
13. Pyrolusite - Ore of Mn -  $\text{MnO}_2$  [ore used to prepare useful compound :  $\text{KMnO}_4$ ]
14. Chromite - Ore of Cr -  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  or  $\text{FeCr}_2\text{O}_4$  [Used to prepare  $\text{K}_2\text{Cr}_2\text{O}_7$ ]
15. Rutile - Ore of Titanium -  $\text{TiO}_2$
16. Ilmenite - Mineral of Ti -  $\text{FeTiO}_3$

**SULPHIDES**

1. Argentite - Silver glance -  $\text{Ag}_2\text{S}$  ore of silver
2. Chalcosite - Copper glance -  $\text{Cu}_2\text{S}$
3. Chalcopyrites - Copper pyrites -  $\text{CuFeS}_2$  (Old qn. The ore containing both Cu and Fe)
4. Galena -  $\text{PbS}$  - Ore of lead
5. Cinnabar -  $\text{HgS}$  - Ore of Mercury
6. Millerite - Ore of Nickel  $\text{NiS}$
7. Nickel glance -  $\text{NiAsS}$  (Old qn. Composition of nickel glance)
8. Fool's gold - Iron pyrites -  $\text{FeS}_2$
9. Stibnite -  $\text{Sb}_2\text{S}_3$  - Ore of antimony
10. Orpiment -  $\text{As}_2\text{S}_3$  - Ore of Arsenic
11. Pentlandite ( $\text{NiFe}$ )S
12.  $\text{ZnS}$  - Zinc blende - Ore of Zn - Sphalerite/Black Jack

**CARBONATES**

1.  $\text{CaCO}_3$  - Limestone/Marble/Calcite/Stalegmite/Iceland spar
2.  $\text{FeCO}_3$  - Siderite/Spathic iron ore
3.  $\text{PbCO}_3$  - Cerussite
4.  $\text{BaCO}_3$  - Witherite
5.  $\text{SrCO}_3$  - Strontianite
6.  $\text{ZnCO}_3$  - Calamine/Zinc spar/Smithstone/Smithsonite
7.  $\text{MgCO}_3$  - Magnesite
8.  $\text{CaCO}_3 \cdot \text{MgCO}_3$  - Dolomite : New formula  $\text{MgCa}(\text{CO}_3)_2$
9.  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  - Malachite
10.  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  - Azurite
11.  $\text{MnCO}_3$  - Rhodocrosite
12.  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$  - Trona

**SILICATES**

1. Willimite  $\text{Zn}_2\text{SiO}_4$
2. Zircon -  $\text{ZrSiO}_4$
3. Beryl  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
4. Petalite -  $\text{LiAl}(\text{Si}_2\text{O}_5)_2$
5. Orthoclase/Pot. feldspar -  $\text{KAlSi}_3\text{O}_8$  [Old :  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ]
6. Albite/Sodium feldspar -  $\text{NaAlSi}_3\text{O}_8$  [Old :  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ]
7. Kaolinite/Pure clay -  $\text{Al}_2(\text{OH})_4(\text{Si}_2\text{O}_5)$
8. Mica - general formula :  $\text{XY}_{2-3}\text{Z}_4\text{O}_{10}(\text{OH}, \text{F})_2$   
Where X - Na/K, Y - Al, Mg, Z - Si
9. Lapiz Lazuli /blue coloured zeolite containing sulphur. -  $\text{Na}_8[\text{Al}(\text{SiO}_4)_6]\text{S}_2$

**SULPHATES**

1. Gypsum/Alabaster/selenite  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
2. Anhydrite -  $\text{CaSO}_4$
3. Epsomite -  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
4. Barytes/Heavy spar  $\text{BaSO}_4$
5. Celestine -  $\text{SrSO}_4$
6. Anglesite -  $\text{PbSO}_4$
7. Alunite :  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al}(\text{OH})_3$
8. Lanarkite :  $\text{PbO} \cdot \text{PbSO}_4$
9. Langbeinite :  $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$

**HALIDES**

1.  $\text{CaF}_2$  - Fluorspar
2.  $\text{Na}_3\text{AlF}_6/3\text{NaF} \cdot \text{AlF}_3$  - Cryolite
3. Carnalite  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
4. Sylvine -  $\text{KCl}$
5. Rock salt -  $\text{NaCl}$
6. Horn silver -  $\text{AgCl}$
7. Atacamite -  $\text{Cu}_2\text{Cl}(\text{OH})_3$
8. Matlokite -  $\text{PbCl}_2 \cdot \text{PbO}$
9. Sea water -  $\text{MgCl}_2/\text{MgBr}_2$
10. Caliche -  $\text{NaIO}_3$

**PHOSPHASES**

1. Monozite - 58%  $\text{CePO}_4$
2. Turquoise : Old -  $\text{AlPO}_4 \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; New -  $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$   
Note : Verdigris - Basic copper acetate -  $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{Cu}(\text{OH})_2$

**V. Metallurgy**

The entire scientific and technological processes used for isolation of the metal from its ore is known as metallurgy. It involves three major steps.

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

**Gangue/matrix**

These are the earthly or undesired materials associated with an ore. The most common gangue is silica ( $\text{SiO}_2$ /Acidic)

**Concentration of ores/Dressing/Benefaction/Benefication**

The removal of the gangue by a suitable technique from the ore is called concentration. The method depends on its nature, physical properties of the metal, environmental factors and available facilities.

- A. Hydraulic washing/Levigation/Tabling/Gravity process or separation/Wilfley tabling method

**Principle :** The difference in the density or sp. gravity of the ore and the gangue

Applied to oxides/carbonates

**Method :** An upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind.

**Old question:** Which of the following ore is concentrated by gravity separation?

- B. Magnetic separation (Refer the Diagram in the NCERT)

**Principle :** The ground ore is carried on a conveyer belt which passes over a magnetic roller.

**JEE/NEET old qns**

Cassiterite is concentrated by .....

Cassiterite is the ore of tin ( $\text{SnO}_2$ ). It is contaminated with Wolframite ( $\text{FeWO}_4 + \text{MnWO}_4$ ) which act as gangue. Here the gangue is magnetic and ore non-magnetic

**JEE (Adv)**

Which of the following ore/ores are concentrated by magnetic separation?

Hint : Either the ore or gangue contains a transition metal.

C. Froth floatation method (refer the diagram in the NCERT)

i. This is mainly applied to sulphide ores since they are lighter than the gangue

**NEET/JEE main**

1. Froth floatation process is mainly applied to sulphide ores. Which of the following offers an exception?

Ans : The ore of silver/Argentite/ $\text{Ag}_2\text{S}$  (It is more dense)

**Principle**

ii. Non-wettability of ore particles with water adsorption, Decrease in surface tension at the interface.

**JEE Adv.**

Which of the following is/are the principle associated with froth floatation?

**OR**

Which is not a principle related to the ore concentration process of froth floatation?

iii. Process:

A suspension of the powdered sulphide ore is made with water. To it collectors and froth stabilisers are added. The mineral particles become wet by oils while gangue by water. A rotating paddle agitates the mixture and draws air in it. As a result froth is formed which carries the ore particles which is skimmed off and dried.

iv. Activator - Compounds which activate the required component (attaches to the particles to be floated).  
Eg :  $\text{CuSO}_4$  for the ore of copper

v. Frother/Foaming agent : Pine oil/Eucalyptus oil

vi. Froth stabiliser : Cresol, Aniline (Last for long period or stabilises the froth)

vii. Collectors : Which enhances the non-wettability of the ore particle.

Eg : Fatty acid, Pine oil, Soap, Sodium/potassium ethyl xanthates -  $\text{C}_2\text{H}_5\text{OCS}_2\text{Na}/\text{C}_2\text{H}_5\text{OCS}_2\text{K}$

viii. Depressant : Compounds which depress unwanted components by forming a complex in solution.

Or

It is possible to separate two sulphide ores by adjusting proportion of oil to water by using depressant.

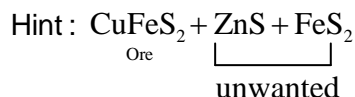
For eg. in case of an ore containing  $\text{ZnS}$  and  $\text{PbS}$

The depressant used is  $\text{NaCN}$ . It selectively prevents  $\text{ZnS}$  from coming to the froth but allows  $\text{PbS}$  to come with the froth.

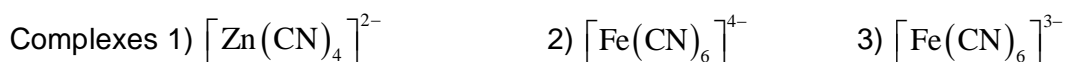
**Note :** The innovative washer woman told her experience of washing the outer garments of minors where the sand and dirt fell to the bottom of the wash tub and the copper bearing compounds caught in the soap sud to the chemist Mrs. Carrie Everson.

**NEET Qn :** The method of ore concentration outlined from washerwoman experience is .....

**JEE (Adv) :** Chalcopyrites is concentrated by froth floatation where NaCN act as depressant. Which of the following complexes are produced in solution?



Fool's gold contain Fe(II) and Fe(III)



#### D. LEACHING (Chemical method)

Selective dissolution of an ore in a suitable solvent to form a complex (Hence chemical method).

There are three leaching agents in metallurgy

- a) Alkali for bauxide      b) NaCN/KCN for Au or Ag  
 c) con.  $\text{H}_2\text{SO}_4$  (in air/bacteria) for low grade ore of Cu

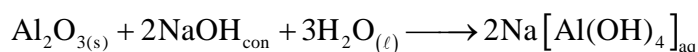
##### a. Leaching of alumina from bauxite

Bauxite is the ore of aluminium which usually contains silica ( $\text{SiO}_2$ ). Iron oxides and  $\text{TiO}_2$  as impurities. When iron oxide is the impurity, it is called red bauxite; the other impurities when present named as white bauxite.

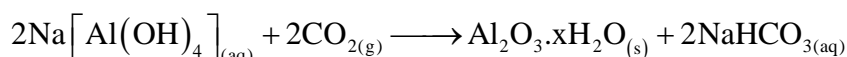
##### 1. Bayer's process - Purification of red bauxite

There are three steps:

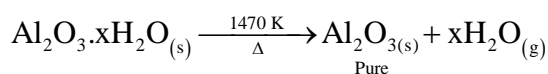
**Step-1 :** Heating the powdered ore with conc. NaOH solution at 473-523 K under 35-36 bar pressure (Digestion process). Impure alumina ( $\text{Al}_2\text{O}_3$ ) is extracted out as sodium aluminate. The impurity silica is dissolved to get soluble sodium silicate. Other gangue (insoluble) left behind.



**Step-2 :**  $\text{CO}_2$  is passed through the solution for neutralisation for the precipitation of hydrated alumina. To induce quick precipitation, a fresh sample of hydrated alumina is added (called seeding).



**Step-3 :** Filter the ppt, dried and heated to get pure  $\text{Al}_2\text{O}_3$ . Sodium silicate remains in solution



**Note :** In the Bayer's process precipitation of  $\text{Al}(\text{OH})_3$  by hydrolysis is not advisable because silicic acid is also precipitated which inturn changes to  $\text{SiO}_2$ .

**Old Qns :**

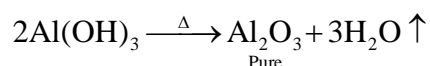
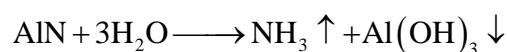
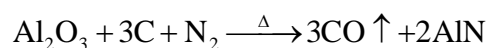
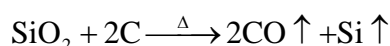
1. White bauxite can be purified by .....
2. Bauxite with silica impurity is purified by .....
3. Bauxite with  $\text{TiO}_2$  impurity is purified by .....
4. JEE ADV

Which of the following are the impurities present in impure bauxite.

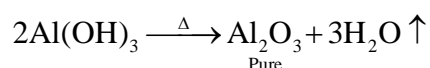
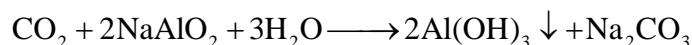
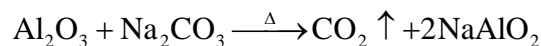
Which of the following is not present in impure bauxite

**Additional Information (For passage qns)**

1. Serpeck's process - Applied when silica is the impurity. The powdered ore is heated to  $1800^\circ\text{C}$  with coke in an atmosphere of  $\text{N}_2$ . Aluminium nitride produced is hydrolysed to get  $\text{Al}(\text{OH})_3$  which is filtered and heated further to get pure  $\text{Al}_2\text{O}_3$ .



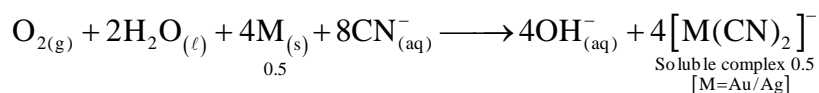
2. Hall's process : Applied when titanium dioxide is the gangue. The powdered impure ore is heated with  $\text{Na}_2\text{CO}_3$  to get soluble sodium aluminate which is further hydrolysed, the ppt is filtered and heated.



JEE (Adv) - Impure bauxite can be purified by ..... (More than one answer type)

**Other example for leaching**

In the metallurgy of silver and gold, the respective metal (native form) is leached with a dilute solution of  $\text{NaCN}$  or  $\text{KCN}$ , in presence of air/ $\text{O}_2$  and moisture.

**Note (Old qn)**

1. Metal is oxidised. Hence leaching is both a complexation and oxidation
2. The presence of  $\text{O}_2/\text{H}_2\text{O}$  is to facilitate oxidation
3. The no. of moles of reactants or products are respectively .....



**E. Electrostatic separation**

This is applicable to a binary mixture where one component is a good conductor and the other non-conductor.

Eg:  $\text{ZnS} + \text{PbS}$  [ZnS – non conductor, PbS – conductor]

**F. Liquation**

This is based on the difference in m.p. of the ore and gangue. It is applied to the ore of antimony. Actually, liquation is a method of purification.

**Old Qn.**

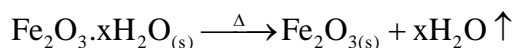
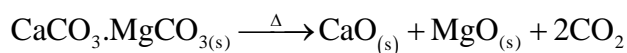
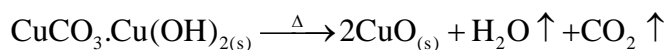
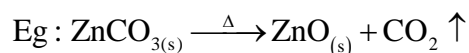
Which of the following is not a method of ore concentration?

**Applied processes [Mainly conversion of concentrated ore to oxide]**

To extract a metal from concentrated ore, it must be converted to a compound suitable for reduction. Usually oxides are easier to reduce. This is accomplished by calcination and roasting.

**1. CALCINATION**

- Heating in absence of air below the m.p. in reverberatory furnace
- To expel  $\text{CO}_2$  or  $\text{H}_2\text{O}$  or both
- Volatile matter escapes leaving the metal oxide
- Leaves the product porous
- Applied to carbonates, hydroxide and hydrated salt



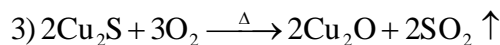
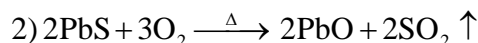
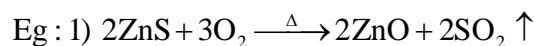
Qn. Which of the following ore is calcined?

**2. ROASTING**

- Strong heating in excess air below the m.p. in reverberatory furnace
- Removal of volatile  $\text{S}_8$  and As impurities as their oxides
- Removes moisture and the oxide produced is porous
- Applied mainly to sulphide ores

**Reason : [Old IIT Qn.]**

- $\Delta_f G^\circ$  of most metallic sulphides are greater than those of  $\text{CS}_2$  and  $\text{H}_2\text{S}$
- Roasting of sulphides to oxide is thermodynamically more advantageous.
- $\text{CS}_2$  is endothermic compound. Neither C nor  $\text{H}_2$  is a suitable red. agent for sulphide ores.



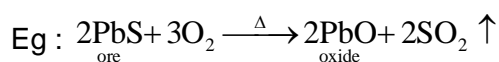
**Qn :** Both calcination and roasting is carried out in ..... furnace.

### **Additional information (JEE Adv)**

There are four types of roasting.

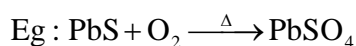
A) Oxidising/Blast roasting

Ore is completely converted to oxide



B) Sulphating roasting

Ore is partially converted to sulphate



**Qn :** Galena is subjected to roasting. Which of the following is not produced?

1) PbO

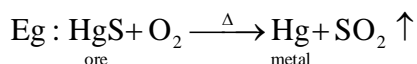
2) SO<sub>2</sub>

3) PbSO<sub>4</sub>

4) Pb

C) Reducing roasting/air reduction

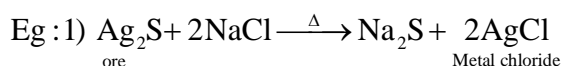
Ore is reduced to the metal



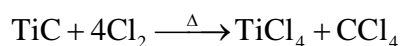
**Qn :** Which metal can be extracted by simple heating in air without the help of a reducing agent?

D) Chloradised roasting

Ore is heated either with a chloride or chlorine to produce volatile metal chloride.



2) TiO<sub>2</sub> ore is converted to Titanium carbide first followed by heating with Cl<sub>2</sub>



### **3. SLAGGING/Slagging operation**

Removal of the gangue by forming molten salt using a suitable flux. There are four common slags in metallurgy.

Gangue + Flux  $\xrightarrow{\Delta}$  molten slag [Floats over the surface, low mp, low density]

Eg : 1)  $\underset{\text{Acidic}}{\text{SiO}_2} + \underset{\text{Basic}}{\text{CaO}} \xrightarrow{\Delta} \text{CaSiO}_{3(\ell)}$  – Extraction of iron in Blast furnace

2)  $\underset{\text{Acidic}}{\text{P}_2\text{O}_5} + 3\underset{\text{Basic}}{\text{CaO}} \xrightarrow{\Delta} \text{Ca}_3(\text{PO}_4)_{2(\ell)}$  – Thomas slag : Extraction of iron (low%)

3)  $\underset{\text{Basic}}{\text{MnO}} + \underset{\text{Acidic}}{\text{SiO}_2} \xrightarrow{\Delta} \text{MnSiO}_{3(\ell)}$  – Manufacture of steel

4)  $\underset{\text{Basic}}{\text{FeO}} + \underset{\text{Acidic}}{\text{SiO}_2} \xrightarrow{\Delta} \text{FeSiO}_{3(\ell)}$  – Extraction of copper

**Qn :** The composition of the slag obtained during the extraction of copper is .....

**Note :** Slags separates more easily from the ore than the gangue. Hence removal of gangue becomes easier (Advantage of slagging)

#### 4. SMELTING

a. Coke combination above m.p. using a convertor (Bessemer/Pierce smith) where CO is a product.

Or

b. It is a process in which metal/metal sulphide is separated in molten condition. Generally the ore is mixed with flux, fuel and red agent. [The mixture is referred to as CHARGE in metallurgy]

Eg : (1)  $\underset{\text{roasted ore}}{\text{ZnO}_{(s)}} + \underset{\text{coke R.agent}}{\text{C}_{(s)}} \xrightarrow{1673\text{K}} \underset{\substack{\text{Impure Molten Zinc} \\ \text{SPELTER} \\ (98\% \text{ Pure})}}{\text{Zn}_{(\ell)}} + \text{CO} \uparrow$

#### IIT Qn (more than one answer)

1. Extractive metallurgy of zinc is achieved by .....

Ans: Smelting/coke reduction/carbon reduction/Belgian process/Retort process or the reduction of the roasted ore with coke or carbon

2. Which of the following is not a smelting process?

Eg :  $\underset{\text{Ore}}{\text{SnO}_2} + \text{C} \xrightarrow{\Delta} \text{CO}_2 \uparrow + \underset{\substack{\text{Impure molten Blacktin} \\ (\text{Sn} + 60-70\% \text{ SnO}_2)}}{\text{Sn}_{(\ell)}}$

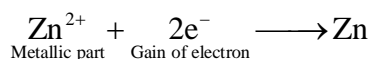
### PRINCIPLES OF ISOLATION OF ELEMENTS

#### I. REDOX concept

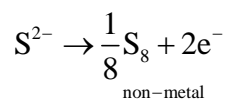
Ore particles consists of two parts - one related to metal and the other with non metal. Eg : ZnS

$\text{Zn}^{2+}$  - Cation - metallic part (in the oxidised state)

$\text{S}^{2-}$  - Anion - non-metallic part (in the reduced state)



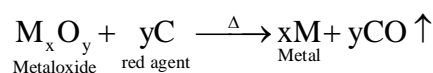
Hence metal is extracted by reduction (gain of electron) or electronation



Non-metal is extracted by oxidation (removal of electron) or Deelectronation.

### Reduction of oxide to the metal (electronation)

Reduction of the metal oxide usually involves heating it with a reducing agent like C, CO or even another metal. The red. agent combines with oxygen of the metal oxide.



Some metal oxides get reduced easily while others are very difficult to be reduced. In any case heating is a must. Hence the general term pyrometallurgy.

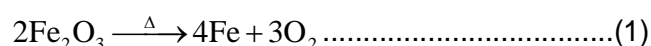
## II. Thermodynamic principles of metallurgy

Metal is extracted by reduction which is a spontaneous process. To understand the variation in temperature required for thermal reduction and to predict which element will suit as red agent for a given metal oxide ( $M_xO_y$ ), Gibbs free energy interpretations are made  $\Delta G = \Delta H - T\Delta S$

**Situation-1** : If  $\Delta S$  is +ve, on increasing the temperature, the value of  $T\Delta S$  increases so that  $\Delta H < T\Delta S$  or  $T\Delta S > \Delta H$

**Situation-2** : If  $\Delta G$  is +ve, reduction is non-spontaneous. In such cases coupling of two reactions (oxidation and reduction) results in -ve value of  $\Delta G$  for overall reaction; then the final reactions becomes feasible. Such coupling is easily understood through  $\Delta G$  Vs  $T$  plots for the formation of oxide.

Eg : Decomposition of  $Fe_2O_3$  is +ve with  $\Delta G (= +1487 \text{ kJ})$



Consider  $2CO + O_2 \longrightarrow 2CO_2 \dots\dots\dots(2); \Delta G = -514.4 \text{ kJ}$

Multiply (2) by (3);  $6CO + 3O_2 \longrightarrow 6CO_2 \dots\dots\dots(3); \Delta G = -1543.2 \text{ kJ}$

Add (3) + (1) ;  $2Fe_2O_3 + 6CO \longrightarrow 4Fe + 6CO_2; \Delta G^0 = -56.2 \text{ kJ} (-ve)$

### Function of red.agent/Role of R.A.

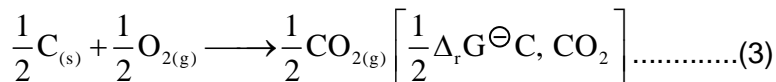
During reduction, the oxide of the metal decomposes and the R.A. takes away the oxygen. The role of R.A. is to provide  $\Delta_r G^\ominus$  of the two reactions, ie oxidation of R.A. and reduction of metal oxide negative.

Consider the general reaction  $M_xO_{(s)} \longrightarrow xM_{(s)/l} + \frac{1}{2}O_{2(g)} [\Delta_r G^\ominus \text{ } M_xO, M] \dots\dots\dots(1)$

If the reduction is carried out by carbon, the oxidation of the R.A. (ie C) will be



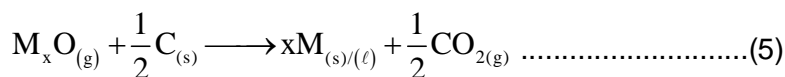
There also may be complete oxidation of carbon to CO<sub>2</sub>



On coupling (combining) equation 1 and equation 2, we get



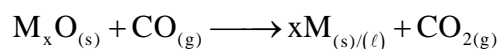
Coupling equation 1 and equation 3, we get



Similarly if CO is a reducing agent,



Coupling (1) with (6)



These reactions describe the actual reduction of the metal oxide M<sub>x</sub>O. Increase in temperature (T) favours -ve value of  $\Delta_r G^\ominus$ . Therefore, the temperature is chosen in such a way that the sum of  $\Delta_r G^\ominus$  in the two combined redox process is -ve.

The graphical representatino of Gibbs free energy was first used by H.J.T. Ellingham. This provides a sound basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham diagram. [Refer the diagram Page 157 - NCERT]

- a. It normally consists of plots of  $\Delta_r G^\ominus$  Vs T for the formation of oxides of common metals and reducing agents. Eg:  $2xM_{(s)} + O_{2(g)} \longrightarrow 2M_xO_{(s)}$

In this reaction gas is consumed, hence molecular randomness decreases which leads to negative value of  $\Delta S$ . As a result  $T\Delta S$  becomes positive and  $\Delta_r G^\ominus$  shifts to higher side despite rise in Temperature. The result is +ve slope [Formation of CO has negative slope  $2C + O_2 \longrightarrow 2CO$  is with decrease in the no.of moles. Hence the  $\Delta G$  is -ve or  $\Delta S$  positive].

- b. Each plot is a straight line with slope upwards except in phase changes  $s \rightarrow \ell$  or  $\ell \rightarrow g$ . Eg: Zn - ZnO line, the m.p. is indicated by an abrupt change in the curve.

- c. When Temperature is rised, a point is reached in the curve where it crosses  $\Delta_r G^\ominus = 0$  line. Below this temperature,  $\Delta G$  is negative for the formation of oxide, So  $M_xO$  is stable. Above this point free energy is +ve. The oxide  $M_xO$  will decompose
- d. Similar diagrams are constructed for sulphides, halides etc
- e.  $C + O_2 \longrightarrow CO_2$ , volume of  $O_2$  used = volume of  $CO_2$  produced. Hence  $\Delta G$  has no change with temperature. Hence the (C,  $CO_2$ ) line is parallel to x-axis/
- f. A metal can reduce oxides of other metals which lie above it in Ellingham Diagram [ $\Delta G$  -ve by an amount equal to the difference between two graphs at that temperature]  
 Eg: According to the diagram, it is easily to reduce  $Cu_2O$  directly to the metal by heating with coke.  $Cu_2O$  line is at the top: Lines of C, CO and  $CO_2$  are at lower position.

### LIMITATIONS

1. It doesn't say about the kinetics of the reduction process
2. The interpretation of  $\Delta G^\ominus$  is based on eq. constant K

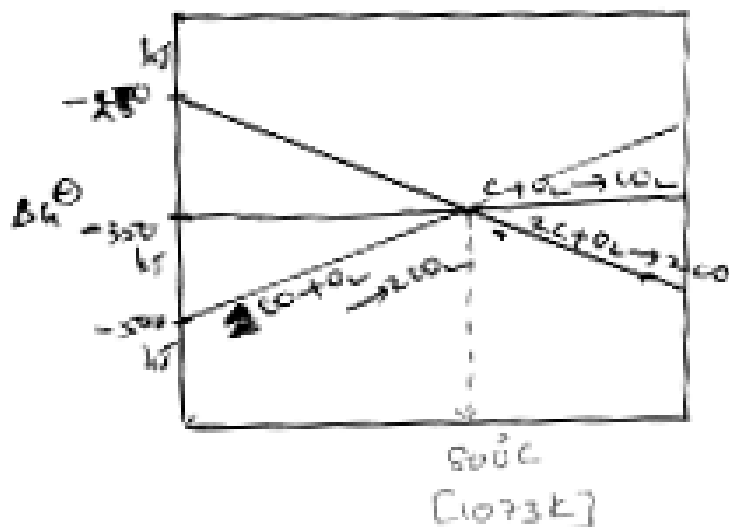
$$\Delta G^\ominus = -RT \ln K. \text{ (K has +ve value)}$$

Thus it is pressured that  $M_xO + A_{red} \rightleftharpoons xM + AO_{ox}$  or the reactants and products are at equilibrium. But this is not true always.

### NOTE:

1. Heating favours the negative value of free energy. Therefore the temperature is chosen such that the sum of  $\Delta G^\ominus$  of redox process is negative. This is indicated by the point of intersection of the two curves or if two red agents are possible, select the intersection point in the diagram  $[\Delta G^\ominus = \text{Zero}]$  and arrive at the conclusion.  
 Eg : Al and Mg [Refer the text diagram]. The intersection point A corresponds to  $1350^\circ\text{C}$ . Below this temperature, Mg can reduce  $Al_2O_3$  and above  $1350^\circ\text{C}$ , Al can reduce MgO
2. CO is a better red agent at 673 K
3. When coke is a red agent, temperature should be high ( $>1073$  K)

4.



Consider the curves  $(C, CO_2)$ ,  $(C, CO)$  and  $(CO, CO_2)$ . The three curves pass through a point at  $800^\circ\text{C}$  ( $1073\text{ K}$ ). At this temperature  $\Delta_r G^\ominus$  are identical.

### Extraction of metals - (Brief outline)

#### Type-I - Pyrometallurgy

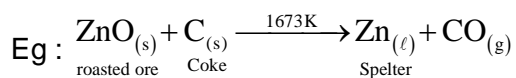
The common red agents are C, CO,  $H_2$ , water gas, Aluminium powder, Mg and Na.

A. R.A. - Carbon/coke

Name - Carbon reduction/coke reduction/smelting

T.D. - High temperature ( $>1073\text{ K}$ )

Metals extracted : Zn, Fe, Sn, Pb, Cu,  $P_4$ , Si .....



B. R.A. - CO

Name - CO reduction

T.D - Low temperature of  $673\text{ K}$

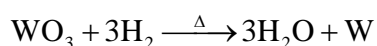
Eg : Extraction of iron in blast furnace

C. R.A. -  $H_2$

Name - Hydrogen reduction

T.D. - Proper heating

Metals extracted - W, Rb, B

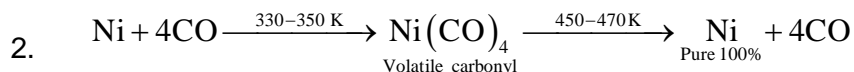
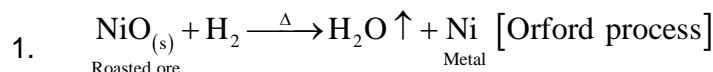


D. R.A. - Water gas/syn gas ( $\text{CO} + \text{H}_2$ )

Name - Water gas reduction

T.D. - Proper Heating

Metal extracted - Nickel



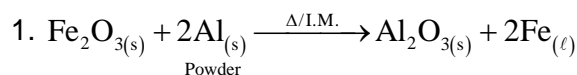
This step is called Mond's process or vapour phase refining

## E. R.A. - Aluminium powder

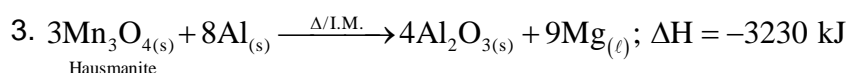
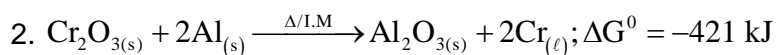
Name - Aluminothermite process/Thermi/Metallothermi/Goldschmidt's process

T.D. - Heating with ignition mixture ( $\text{BaO}_2 + \text{Mg}$  powder)

Metals extracted – Group : 6	Group : 7	Group : 8
Cr	Mn	Fe
Mo		
W		

**Examples:**

Reaction is highly exothermic, metal is obtained in liquid. Hence the use for welding/cracks of ship.

**Previous Qns.**

1. The red agent in Goldschmidt's process is .....

2. The ignition mixture used is .....

3. The mixture used in thermite process is .....

Ans : Al powder + Ig. mixture

4. The word thermite means .....

Ans : 3 : 1 ratio of reactants

ie 3parts oxide + one part Alum powder

5. It doesn't takesplace at room temperature because.....

Ans : No equil. between the solid product and reactant



6. The process requires heating because .....

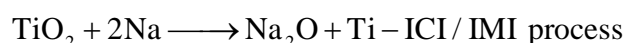
Ans : To overcome the minimum energy of activation

F. R - A - Na or Mg

Name - Kroll's process/ICI process

T.D. - Heating with Argon

Metal extracted - Titanium



### TYPE-II - ELECTROMETALLURGY

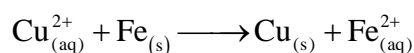
- Electrons act as red agent
- Applied to highly reactive or electropositive metals. Eg: group 1, group 2 and Al.
- Method : Electrolysis/electrolytic reduction of moltenhalides with suitable additives to decrease the m.p./temp of the melt and to increase the conductivity.

### Electrochemical principle

In the reduction of molten metal salt, electrolysis is done.  $\Delta G^0 = -nFE_{\text{cell}}^0$

$\Delta G^0$  is negative with positive values of  $E_{\text{cell}}^0$ . More reactive metals have large -ve value of  $E^\ominus$ .

Hence, reduction is difficult. If the difference of two  $E^\ominus$  values corresponds to positive  $E^0$ , then the less reactive metal will come out of the solution and the more reactive metal will go into solution. Eg.



In simple electrolysis, the  $M^{n+}$  ions are discharged at cathode and get deposited.

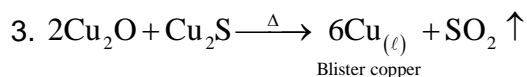
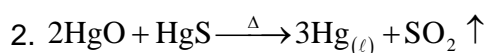
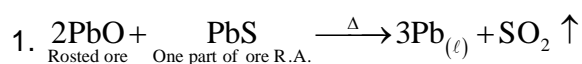
### Precautions :

- Suitable material is used as electrode considering the reactivity of the metal produced.
- Sometimes flux/compounds are added to make it more conducting.

### TYPE-III SELF REDUCTION/AUTO REDUCTION

- Applied to Cu, Pb and Hg
- Definition : The oxide produced during roasting combines with one part of the ore which act as red agent to get the molten metal.
- Precaution : Partial roasting is carried out to retain one part of the ore to act as red agent.

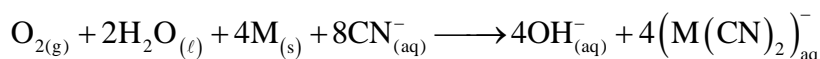
### Examples



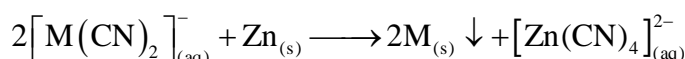
**TYPE-IV - HYDROMETALLURGY**

- Other terms : Wet process/Cyanide process/Mac.Arthur Forest process/Displacement method/reduciton of precipitation
- Applied mainly to Au/Ag (=M)

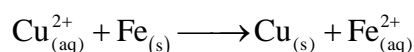
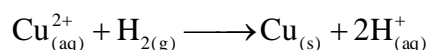
**Step-1 :** Leaching with NaCN/KCN



**Step-2 :** Adding a reactive metal like zinc to the complex. The reactive metal added act as R-agent.

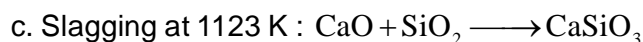
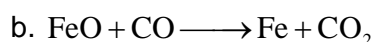
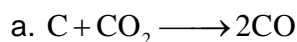


**Note :** Cu can also be extracted by hydrometallurgy from low grade ore. It is leached out using con.  $\text{H}_2\text{SO}_4$  in presence of air or bacteria. The solution containing  $\text{Cu}^{2+}_{(aq)}$  is treated with scrap iron or  $\text{H}_2$ . [Zn is not used since it is costlier than iron]

**APPLICATIONS**

1. Extraction of iron from its oxides - Blastfurnace [Refer the diagram]
- A. Oxides ores of iron [ $\text{Fe}_2\text{O}_3$  &  $\text{Fe}_3\text{O}_4$ ] after concentration are subjected to calcination/roasting [To remove  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$  .....]. The ore is then mixed with lime stone (flux) and coke (fuel) and fed into the Blast Furnace from the top.
- B. Inside of the furnace is made thick by the refractory material of fire clay bricks.
- C. Process : Hot air is passed from the bottom of the furnace and coke is burnt to give a temperature  $\approx 2200$  K in the lower portion itself. The burning of coke supplied most of the heat required in the process. The CO and heat moves to the upper part of the furnace where the temperature is lower and iron oxides are reduced in steps.
- D. Different zones and the involved reactions
  1. Initial zone-lowest temperature zone - 500 K - Moisture is removed from the charge (Charge  $\Rightarrow$  one particles + flux + fuel) Charge ratio  $\Rightarrow 8 : 4 : 1$ .
  2. Low temperature zone/reduction zone - 500 K - 800 K
    - i. Decomposition of limestone  $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$
    - ii.  $3\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$
    - iii.  $\text{Fe}_3\text{O}_4 + 4\text{CO} \longrightarrow 3\text{Fe} + 4\text{CO}_2$
    - iv.  $\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow 2\text{FeO} + \text{CO}_2$

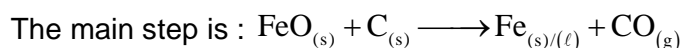
3. Higher temperature zone/combustion zone : 900 K – 1500 K



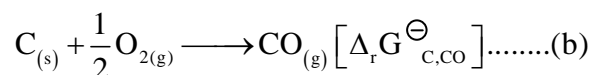
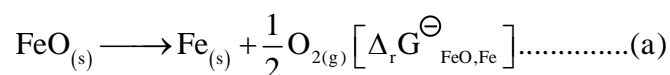
4. Highest temperature zone/melting zone [1500 K - 2170 K] :  $FeO + C \rightarrow Fe + CO$

E. Thermodynamics of iron oxide reduction

Thermodynamics helps us to understand how coke reduces the oxide and why the furnace is chosen.



This reaction include two coupled reactions. In one the reduction of FeO and in other the oxidation of C to CO.



The net Gibbs F.E. change is

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

The reaction takes place with a negative value for  $\Delta_r G^\ominus$

In the Ellingham Diagram,  $Fe \rightarrow FeO$  line goes upward (a) and  $C \rightarrow CO$  line (b) goes downward. They cross each other at about 1073 K (800°C). At temperature above 1073 K, the (C, CO) line is below (Fe, FeO) line. So above 1073 K, in the range of 900K - 1500 K, coke will reduce FeO.

Case at 1400°C/1673 K [Refer diagram page 161]

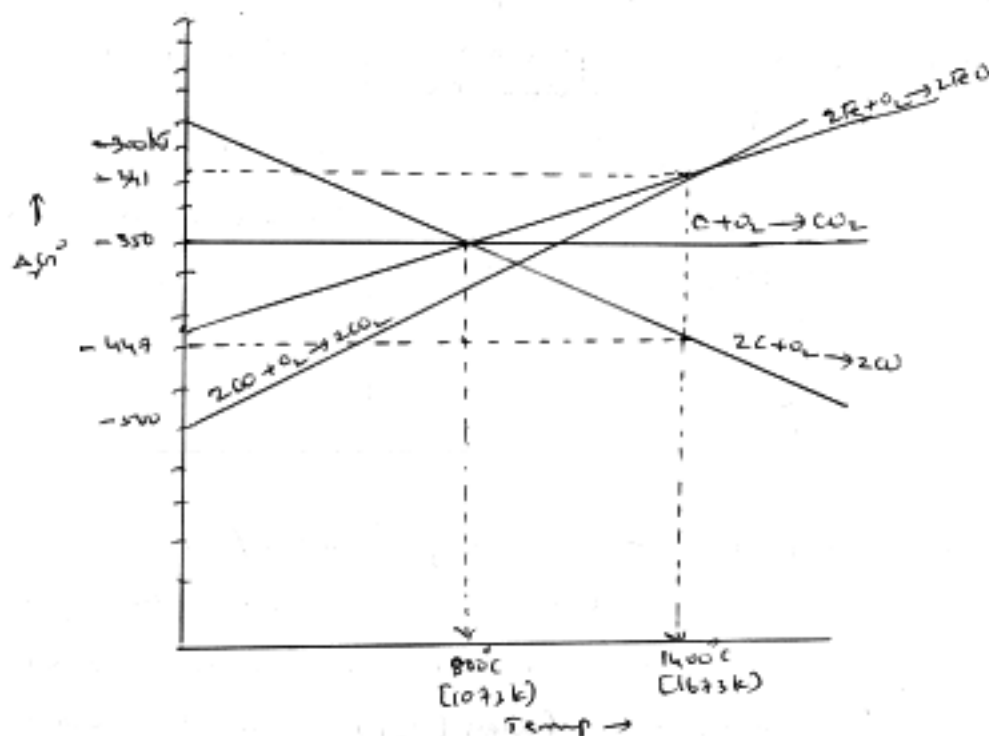
**Iron oxide reduction at 1400°C/1673 K [NCERT Page Diagram P.161]**

At about 1673 K [1400°C],  $\Delta_r G^\ominus$  value for the reaction

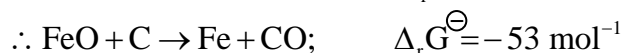
$2FeO \rightarrow 2Fe + O_2$  is +341 kJmol<sup>-1</sup> because it is the reverse of  $Fe \rightarrow FeO$  change and for the reaction

$2C + O_2 \rightarrow 2CO$ ,  $\Delta_r G^\ominus$  is -447 kJmol<sup>-1</sup>. If we calculate  $\Delta_r G^\ominus$  for the overall reaction.

$FeO + C \rightarrow Fe + CO$ , the value will be -53 kJ mol<sup>-1</sup>. Hence reaction is feasible.



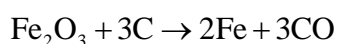
### Around 1400°C



### NOTE:

1. In a similar way, the reduction of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  by CO at relatively lower temperature can be explained on the basis of lower lying points of intersection of their curves with CO,  $\text{CO}_2$  curve
2. The iron obtained from Blast furnace contains 4% carbon and 2% Si, P, S and Mn. This is known as pig iron.
3. Cast iron is made by melting pig iron with scrap iron and coke using hot air blast. It contains 3% carbon and is extremely hard and brittle.
4. Further reductions:

Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron by heating with Haematite in a reverberatory furnace. Haematite oxidises carbon to CO [Puddling Process]



Limestone is added as flux. Sulphur, Si, P etc are oxidised and passed into slag (Thomas slag)

### Additional information

Pig iron	Cast iron	Wrought iron
Most impure form 4%C + 2%Mn, Si, P, S	Contains 3% C (C as graphite)	Contains 0.5% of impurity/purest form
Preparation - Blast furnace	Melting pig iron with scrap iron and coke, followed by cooling.	Puddling/Pudding process
mp 1273 K	mp 1473 K white cast iron - Fe <sub>3</sub> C Grey cast iron - C <sub>gr</sub>	mp 1673 K Fibrous, resistant to corrosion

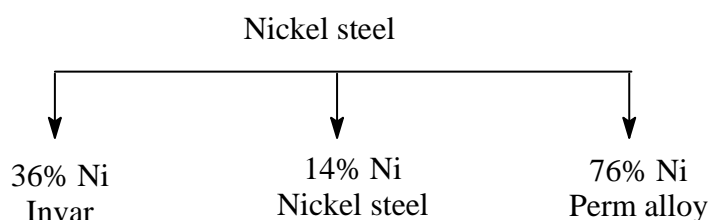
- Steel is a ferrous alloy ie iron containing 0.1 - 1.5%C mild steel (0.1 - 0.5%C), hard steel (0.6 - 1.5%C), nowadays bulk of pig iron is converted to steel. Bessmer and open - Hearth process are outdated. Modern methods involve basic oxygen process (BOP), electric Arc process, oxygen top blowing process and high frequency induction process.
- There are six heat treatment of steel
  - Quenching
  - Tempering
  - Annealing
  - Case hardening
  - sherardising
  - Nitriding
- Alloy steels:
 

Stainless steel - 18% Cr

Tungsten steel - 5% W

Manganese steel - 13% Mn

Chrome steel - 1.1% Cr



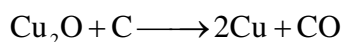
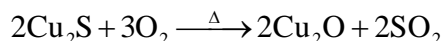
**Old IIT qn :** Conversion of Haematite to steel involves .....

### Extraction of copper from cuprous oxide [Copper (I) oxide]

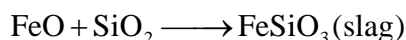
#### Method-1 : Coke reduction

In the Ellingham diagram, the Cu<sub>2</sub>O line is almost at the top. So it is quite easy to reduce the oxide of copper directly to the metal by heating with coke. The lines (C, CO) and (C, CO<sub>2</sub>) are at much lower positions in the graph at 500–600 K.

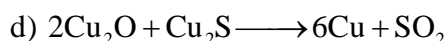
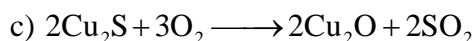
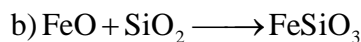
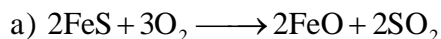
The sulphide ore is roasted/smelted first followed by reduction with coke.



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. Copper is produced in the form of coppermatte which contains  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ .



Copper matte is then charged into silica lined convertor. Some more silica is added followed by the passage of hot air blast to convert  $\text{FeS}$ ,  $\text{FeO}$  and  $\text{Cu}_2\text{S}/\text{Cu}_2\text{O}$  to metallic copper. Following reactions takesplace



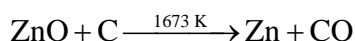
Copper obtained has blistrous appearance due to  $\text{SO}_2$  adsorption . (Hence the name blister copper)

The above reactions are also possible in Bessemer convertor

### **Method-2 : Autoreduction/self reduction**

#### **Extraction of zinc from zinc oxide**

The reduction of  $\text{ZnO}$  is done with coke. The temperature is higher than that of  $\text{Cu}$ . For the purpose of heating, the oxide is made into bricketts with coke and clay. The metal is distilled off and collected by rapid chilling.



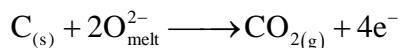
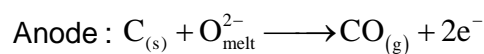
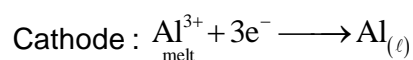
Note : Excess  $\text{ZnO}$  adhered is removed by shock cooling by contact with shower of molten lead.

#### **Extraction of Aluminium [HALL - HEROULT Process]**

In the met allurgy of  $\text{Al}$ , purified  $\text{Al}_2\text{O}_3$  is mixed with cryolite  $\text{CaF}_2/\text{AlF}_3$  which lowers the mp of the mixture and bring conductivity. The fused matrix is electrolysed. Steel vessel with C-lining act as cathode and graphite anode is used (to be removed occassionally since it burns).

The overall reaction is  $2\text{Al}_2\text{O}_3 + 3\text{C} \longrightarrow 4\text{Al} + 3\text{CO}_2$

The  $\text{O}_2$  liberated at the anode reacts with graphite producing  $\text{CO}_2$  and  $\text{CO}$ . For each kg of  $\text{Al}$  produced, about 0.5 kg of graphite anode is burnt away.



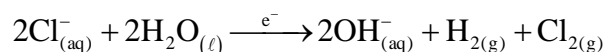
### Precautions

1. Excess coke powder is spread over the electrolyte
2. Bauxite (2.8%) +  $\text{Na}_3\text{AlF}_6$  (80 - 95%) +  $\text{CaF}_2/\text{AlF}_3$  (5 - 7%)
3. 99.98% pure aluminium is produced at the cathode

### Extraction of non-metal by oxidation

A very common example of extraction based on oxidation is the extraction of chlorine from Brine.

Method : Electrolytic oxidation of aq. dilute chloride solution (Brine).



$\Delta G^0$  for the reaction is +422 kJ

Apply the relation  $\Delta G^{\ominus} = -nFE_{\text{cell}}^0$ , we get  $E_{\text{cell}}^0 = -2.2 \text{ V}$

Naturally it requires an external emf greater than 2.2 V. But the electrolytic requires excess potential to overcome some hindering reactions.

### Refining/Purification

A metal extracted by any method is usually contaminated. For obtaining metals of high purity, several techniques are used.

#### **1. Cupellation**

An example of oxidation refining. This method is used when silver containing lead as impurity (Argentiferous lead). The impure metal is melted in crucibles made of bone ash over which a current of air is blown, lead is oxidised to litharge ( $\text{PbO}$ ).

**Note :** Silver can also be purified by Parke's process (to the molten form adding Zn) and Pattinson's process (Molten silver is cooled).

#### **2. Poling/Furnace refining**

If the metals contain their own oxides as impurities, poling is applicable. Principle is the reduction of unstable oxides. Method involves stirring the molten metal with poles of green wood. Eg : Refining of copper and tin

**Old qn :** During the refining process of poling w.r.t impure copper and tin the oxides removed are respectively .....

**3. Liquation**

This is based on low mp or one component is easily fusible. In this method a low melting metal like tin can be made to flow on a sloping surface where it is separated from higher melting impurities.

Other Eg : is the removal of Zn from lead

Note : Used for concentration of Sb ores

**4. Distillation**

This is very useful for low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

**5. Chromatography**

Column chromatography is useful for the purification of elements available in minute quantities (low abundant metals) as lanthanoids, Ba etc. The principle is adsorption using  $\text{Al}_2\text{O}_3$  (alumina)

**6. Zone refining**

This will provide 100% pure / ultra pure metals.

Semiconductors like Ge, Si, B, Ga, In etc are refined by this method.

Principle - Fractional crystallisation/the impurities are more soluble in the melt than in the solid form of the metal.

**Method**

A mobile heater surrounding the rod of impure metal is fixed at its one end. The molten zone moves along with the heater moving forward. As the heater moves forward, the pure metal crystallises and the impurities pass on to the adjacent new molten zone created by movement of heater. The process is repeated several times and the heater is moved in the same direction again and again. Impurities get concentrated at one end which is cut off.

**Note :**

$$1. \text{ Purity} \propto \frac{1}{\text{Radius of metal rod}}$$

2. Best method for an element in which gangue has chemical properties close to that of metal.

**7. Vapour phase refining (100% pure metal)**

In this method, the metal is converted to its volatile compound which is collected and decomposed to get pure metal.

**Requirements**

a) The metal form a volatile compound with available reagent.

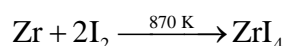
b) Volatile compound is easily decomposable

**Example**

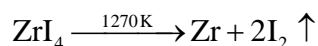
1. Mond's process for refining of nickel
2. Van Arkel method/Deover process/filament method

This method is highly useful for removing all the oxygen and nitrogen present in the form of impurity in group 4 metals like Ti and Zr. The crude metal is heated in an evacuated vessel with iodine. The covalent volatile metal iodide volatalises.





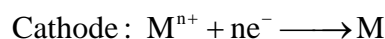
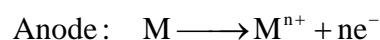
The metal iodide is decomposed on a W-filament, electrically heated to 1800 K. The pure metal deposits on the filament.



## 8. Electrolytic refining

This is the most common technique

**Method :** Impure metal is made anode and pure metal as cathode. They are put in a suitable electrolytic path containing soluble salt of the same metal. The more basic metal remains in solution and less basic gives to a anode mud. The process is explained by electrode potential, over potentials and Gibbs energy.



Eg : 1) Copper is refined by this method. Anodes are of impure copper and pure Cu - strips are taken as cathode. The electrolyte is acidified  $\text{CuSO}_4$  solution. Pure Cu is deposited at the cathode. All the impurities are deposited as anode mud which contain Sb, Se, Te, Ag, Au and Pt.

2) Zinc may also be refined

**Note :** Electrolytic refining of the following metals are named after the scientists.

A) Electro refining of Ag - Moebius process : Electrolyte used -  $\text{AgNO}_3 + \text{dil. HNO}_3$

B) Electro refining of Pb - Bett's proces : Electrolyte :  $\text{PbSiF}_6 + \text{H}_2\text{SiF}_6$

C) Electro refining of Al - Hoope's process : Electrolyte :  $\text{Na}_3\text{AlF}_6$ ;  $\text{BaF}_2$

Three fused layers: 1) Bottom anode layer - Alloy of Al, Cu, Si

2) Middle layer - Cryolite +  $\text{BaF}_2$

3) Top cathode layer - Pure Al

## Uses of Al, Cu, Zn, Fe

### A. Aluminium

1. Al foil - wrappers for chocolates
2. Al - dust - paints, lacquers
3. Al powder - R.A. on metallurgy
4. Al wire - Electricity conductors
5. Light alloys of Al - like magnalium - Air craft parts

### B. Copper

1. Electrical industry
2. Water and steam pipes
3. Alloys - like Brass, bronze, coinage alloys with nickel

**C. Zinc**

1. Galvanising iron
2. Battery
3. Zn-dust - R.Agent
4. Alloys : Brass (60% Cu + 40% Zn)  
German silver (Cu : 25-30% + Zn 25-30% + Ni 40-50%)

**D Iron**

- a. Cast iron - stove, railway sleepers, toys etc
- b. Wrought iron - Anchors, bolts, chain, agricultural implements
- c. Alloy steels -  
    Chrome steel - Cutting tools  
    Nickel steel - pendulum, measuring tapes  
    Stainless steel - utensils

**INDIAN TRADITION IN METALLURGY**

1. Seven metals of antiquity - Au, Cu, Ag, Pb, Sn, Fe, Hg
2. Rich tradition of metallurgy skills - Source Asl : excavation and literary evidences
  - a) Eg : Copper
  - b) Au/Ag alloy - electrum/ornaments
  - c) Alluvial placer gold - Rigveda, Palitext, Arthasastra (Kautilya)
  - d) Fe - wrought iron
  - e) Indian steel - Wootz steel (1-1.9% C)
  - f) Iron pillar  $0.15\%C + 0.05\%Si + 0.05\%Mn$   
Wrought Fe  $99.72\%C + 0.25\%P + 0.005\%Ni + 0.03\%Cu$
  - g) Iron blocks
  - h) Zn - Distillation
  - i) Hg - Sanskrit text