# METALLURGY

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# THEORY

## 1. INTRODUCTION

The Compound of a metal found in nature is called a mineral. The minerals from which metal can be economically and conveniently extracted are called ores. An ore is usually contaminated with earthy or undesired materials known as gangue. So all minerals are not ores but all ores are minerals.

### SOME IMPORTANT ORES OF METALS

| Metal | Ores | Composition |
|---|---|---|
| Aluminium | Bauxite | $Al_2O_3.2H_2O$ |
| | Diaspore | $Al_2O_3.H_2O$ |
| | Corundum | $Al_2O_3$ |
| Iron | Haematite | $Fe_2O_3$ |
| | Magnetitie | $Fe_3O_4$ |
| | Siderite | $FeCO_3$ |
| | Iron pyrite | $FeS_2$ |
| | Limonite | $Fe_2O_3.3H_2O$ |
| Copper | Copper pyrite | $CuFeS_2$ |
| | Copper glance | $Cu_2S$ |
| | Cuprite | $Cu_2O$ |
| | Malachite | $CuCO_3.Cu(OH)_2$ |
| | Azurite | $2CuCO_3.Cu(OH)_2$ |
| Zinc | Zinc blende or Sphalerite | ZnS |
| | Calamine | $ZnCO_3$ |
| | Zincite | ZnO |
| Lead | Galena | PbS |
| | Anglesite | $PbSO_4$ |
| | Cerrusite | $PbCO_3$ |
| Magnesium | Carnallite | $KCl.MgCl_2\ 6H_2O\ (K_2MgCl_4.6H_2O)$ |
| | Magnesite | $MgCO_3$ |
| | Dolomite | $MgCO_3\ CaCO_3$ |
| | Epsomsalt (Epsomite) | $MgSO_4\ 7H_2O$ |
| | Langbeinite | $K_2Mg_2(SO_4)_3$ |
| Tin | Cassiterite (Tin Stone) | $SnO_2$ |
| Silver | Silver glance (Argentite) | $Ag_2S$ |
| | Pyrargyrite (Ruby Silver) | $Ag_3SbS_3$ |
| | Chlorargyrite (Horn silver) | AgCl. |
| | Stefinite | $Ag_5SbS_4$ |
| | Proustite | $Ag_3AsS_3$ |

## 2. METALLURGY

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

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

1. Crushing of the ore
2. Dressing or Concentration of the ore
3. Isolation of the crude metal from its ore
4. Purification of refining of the metal

### 2.1 Crushing and Grinding

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

### 2.2 Concentration

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

**2.2.1 Hydraulic washing or Gravity separation :**

It is based on the difference in the densities of the gangue and or particles. In this, the powdered ore is agitated with water or washed with a upward stream of running water, the lighter particles of sand, clay etc are washed away leaving behind heavier ore particles.

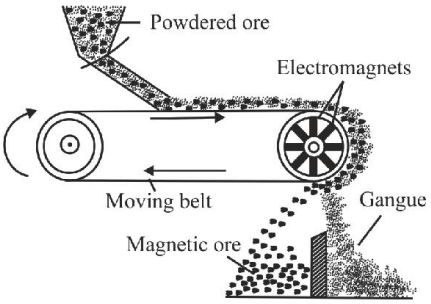
**2.2.2 Electromagnetic separation :**

It is based on differences in magnetic properties of the ore components.

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

**EXAMPLE**

**Chromite ore ($FeO.Cr_2O_3$)** is separated from non-magnetic sillicious impurities and **cassiterite ore ($SnO_2$)** is separated from magnetic **Wolframite ($FeWO_4 + MnWO_4$).**




Electromagnetic separation

**2.2.3 Froth floatation process :**

This method is commonly used for the **concentration of the low grade sulphide** ores like galena, PbS (ore of Pb) ; copper iron pyrites $Cu_2S.Fe_2S_3$ or $CuFeS_2$ (ore of copper); zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wet ability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil. In this process one or more chemical frothing agents are added.

When a mineral contains other minerals as impurities. The addition of these agents activates or depresses the flotation property of other minerals present as impurities and thus helps in separating the impurities. For example galena (PbS) usually contains the minerals namely zinc blende (ZnS) and pyrites ($FeS_2$) as impurities. Flotation is carried out by using potassium ethyl xanthate (used as a collector) along with NaCN and $Na_2CO_3$ (used as depressing agent).

**2.2.4 Leaching of alumina from bauxite :**

The principal ore of aluminium, bauxite, usually contains $SiO_2$, iron oxides and titanium oxide ($TiO_2$) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473-523 K and 35 - 36 bar pressure. This way, $Al_2O_3$ is leached out as sodium aluminate (and also $SiO_2$ as sodium silicate) leaving behind the impurities, iron oxide and titanium oxide.

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

The aluminate in solution is neutralised by passing $CO_2$ gas and hydrated $Al_2O_3$ is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated $Al_2O_3$ which induces the precipitation of $Al(OH)_3$.

$$2Na[Al(OH)_4](aq) + CO_2(g) \longrightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3(aq)$$

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back

$$\text{pure } Al_2O_3 : Al_2O_3.xH_2O(s) \xrightarrow[\text{or } 1200^\circ C]{1470K/\text{calcination}} Al_2O_3(s) + xH_2O(g)$$

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

In the **metallurgy of silver and that of gold,** the respective metal/ore is leached with a dilute solution of NaCN or KCN in the presence of air (or $O_2$) form which the metal is obtained later by displacement with zinc scrap. This is also known as **Mac-Arthur Forest Cyanide** process.

## 2.3 Extraction of crude metal from concentrated ore

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

(i) Conversion to oxide

(ii) Redcution of the oxide to metal.

### 2.3.1 Conversion to oxide :

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

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

(a) The carbonate ore gets decomposed to form the oxide of the metal, e.g.,

$$FeCO_3 \text{ (siderite)} \xrightarrow{\Delta} FeO + CO_2;$$

$$PbCO_3 \text{ (cerrusite))} \xrightarrow{\Delta} PbO + CO_2$$

$$CaCO_3 \text{ (calcite ore/lime stone)} \xrightarrow{\Delta} CaO + CO_2$$

$$ZnCO_3 \text{ (calamine)} \xrightarrow{\Delta} ZnO + CO_2$$

(b) Water of crystallisation present in the hydrated oxide ore gets lost as moisture, e.g.,

$$2Fe2O_3.3H_2O \text{ (limonite)} \xrightarrow{\Delta} 2Fe_2O_3(s) + 3H_2O(g)\uparrow$$

$$Al_2O_3.2H_2O \text{ (bauxite)} \xrightarrow{\Delta} Al_2O_3(s) + 2H_2O(g)\uparrow$$

(c) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

**2.3.1.2 Roasting :**

It is a process of heating the concentratd ore (generally sulphide ore) strongly in the excess of air or $O_2$ below its melting point. Roasting and exothermic process once started it does not require additional heating. Some of the reactions involving sulphide ores are :

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2;$$

$$2ZnS + 2O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$

* Some times roasting may not bring about complete oxidation.

$$2\ CuFeS_2 \text{ (copper pyrite)} + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$$

The reduction of the sulphide ore directly into metal by heating it in air or $O_2$ is called by various names like self-reduction, auto-reduction, air-reduction etc. The $SO_2$ produced is utilised for manufacturing of $H_2SO_4$.

### 2.3.2 Reduction of metal oxide to the metal :

The calcined or roasted ore is then reduced to the metallic state in either of the following ways.

**2.3.2.1 Reduction by carbon (Smelting) :**

**"Reduction of the oxide with carbon at high temperature is known as smelting".**

The oxides of less electropositive metals like Pb, Zn, Fe, Sn, Cu etc. are reduced by strongly heating them with coal or coke, in the blast furnace.

**Slag :** Fusible material during reduction process.

**Slag :** Gangue + substance (for remove gangue)

**Fluxes :** Substance used for removing gangue

**Fluxes acidic :** Borax, $SiO_2$ (remove basic impurity)

**Fluxes basic :** MgO, $MgCO_2$, $CaCO_3$ (remove acidic impurity)

**Smelting :**

**Concentration + gangue + $R_A$ (carbon) + Flux**

↓

**Metal + Slag + gases**

When melting point of compound is too high then Al powder used as reducing agent **Al powder + ore** is called thermite and this process is called **Gold-Schmidt Alumino Thermite** process.

Coke is not used for s-block oxide, $Al_2O_3$ some d-block oxide (due to of metal carbides $CaO + 2C \rightarrow CaC_2 + CO$)

Example of $\left.\begin{matrix} Cr_2O_3 \\ Nn_3O_4 \\ MnO_2 \end{matrix}\right\} \xrightarrow{\text{Coke}} \times$

**Some reaction are :**

(a) $CuO + CO \rightarrow CO_2 + Cu$

(b) $PbO + C \rightarrow Pb + CO$

(c) $Fe_2O_3 + 3C \rightarrow Fe + 3CO$

(d) $ZnO + C \rightarrow Zn + CO$

(e) $ZnO + CO \rightarrow Zn + CO_2$

**(gangue) Acidic impurity + flux $\rightarrow$ slag**

(a) $SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2 \downarrow$

(b) $P_2O_5 + 3CaO \rightarrow Ca_3(PO_4)_2$

**Basic impurity + Flux $\rightarrow$ slag**

(a) $MgCO_3 + SiO_2 \rightarrow MgSiO_3 + CO_3 \downarrow$

(b) $FeO + SiO_2 \rightarrow FeSiO_3$

### 2.3.2.2 Self reduction

Compounds of certain metals are reduced to metal without using additional reducing agent ores of Cu, Pb, Hg etc.

**Their sulphide ores are partially roasted to give some oxide. This oxide is now reduced to the metal by the remaining sulphide ore at elevated temperatures in the absence of air. The process is known as self reduction. or auto reduction**

**Self reduction for Pb :-**

$$\underset{(Galena)}{2PbS} + \underset{(air)}{3O_2} \xrightarrow{Roasting} 2PbO + 2SO_2 \uparrow$$

$$\underset{(unroasted\ ore)}{PbS} + \underset{(roasted\ ore)}{2PbO} \xrightarrow[Absence\ of\ air]{High\ temp.} \underset{(Self\ reduction)}{3Pb} + SO_2 \uparrow$$

$$2\,Cu_2O + Cu_2S \xrightarrow{\Delta} 6\,Cu + SO_2$$

### 2.3.2.3 Metal displacement method

In this method, a water soluble compound is obtained from the ore. The aqueous solution of the compound is reacted with a more electropositive metal which displaces, the metal from the solution.

**EXAMPLE**

**(i) Zairvogel process for silver.**

$$\underset{Argentite}{Ag_2S} + 2O_2 \xrightarrow{85^\circ C} Ag_2SO_4$$

$$Ag_2SO_4(aq) + \underset{(Scrap\ Copper)}{Cu} \rightarrow CuSO_4(aq) + 2Ag(S)$$

**(ii) Seperation of Ag by Complex formation**

Silver and gold are extracted by a method involving complex formation.

**Powdered argentite is reacted with a dilute solution of sodium cyanide in the presence of air. The silver from the ore is dissolved in the cyanide solution forming sodium argentocyanide.**

$$\underset{(Powdered\ argentite)}{Ag_2S} + 4NaCN \xrightarrow{air} 2Na[Ag(CN)_2] + Na_2SO_4$$

Now metallic zinc is added to the complex salt solution which being more electropositive element than silver, displaces it form the solution.

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4](aq) + \underset{Black\ ppt.}{2Ag} \downarrow$$

### 2.3.2.4 Electrolytic reduction

This process is mainly used for the extraction of highly electropositive metals.

Electrolysis is carried out in a large cells and a small amount of **another suitable electrolyte is added** which :

(a) Lowers the melting point of the main electrolyte

(b) Enhances its conductivity

(c) Reduces corrosion troubles

**EXAMPLE**

**Na, K, Mg, Ca, Al, etc.**

**(a) Manufacture of metallic sodium (Down's process)**

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

**On Fusion :** $NaCl \rightleftharpoons \underset{(Ions\ become\ mobile)}{Na^+ + Cl^-}$

**On Electrolysis : At Cathode :** $Na^+ + e^- \rightarrow \underset{(Metallic\ sodiudm)}{Na}$ (reduction)

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

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

The purified $Al_2O_3$ is mixed with $Na_3AlF_6$ (cryolite) or $CaF_2$ (fluorspar) which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful for reduction to the metal. The overall reaction may be taken as :

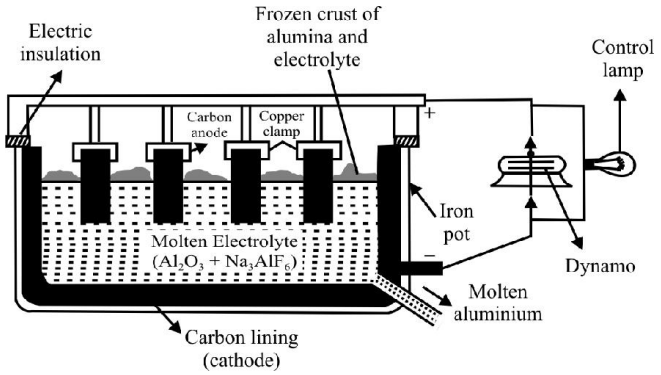
$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and $CO_2$. This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are :

**Cathode :** $Al^{3+}(melt) + 3e^- \longrightarrow Al(l)$

**Anode :** $C(s) + O^{2-}(melt) \longrightarrow CO(g) + 2e^-$

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




## 2.4 Purification or Refining of metals

Metals obtained by reducing processes still contains some objectionable impurities and have to be refined. Refining techniques vary widely from metal to metal and also depend on the use to which a metal has to be put.

### 2.4.1 Liquations process :

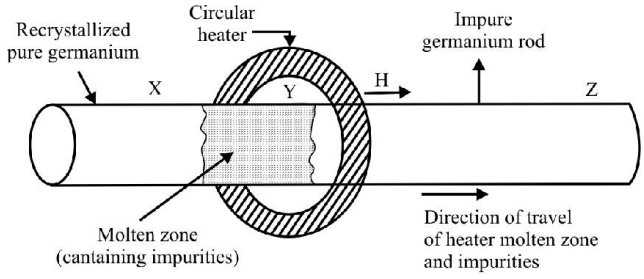
This process is used for the purification of the metal, which itself is readily fusible, but the impurities present in it are not, i.e., the impurities are infusible. In other words, we can say that the melting point of the metal to be purified should be lower than than of each of the impurities associated with the metal. This process is used for the purification of Sn and Zn, and for removing Pb from Zn-Ag alloy, which is obtained at the end of Parke's process and contains Pb as impurity.

### 2.4.2 Distillation process :

This process is used to purify those metals which themselves are volatile and the impurities in them are nonvolatile and vice-versa. Zn, Cd and Hg are purified by this process.

### 2.4.3 Zone refining method (Fractional crystallisation method) :

This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.




**Zone refining of germanium metal**

### 2.4.4 Chromatographic methods :

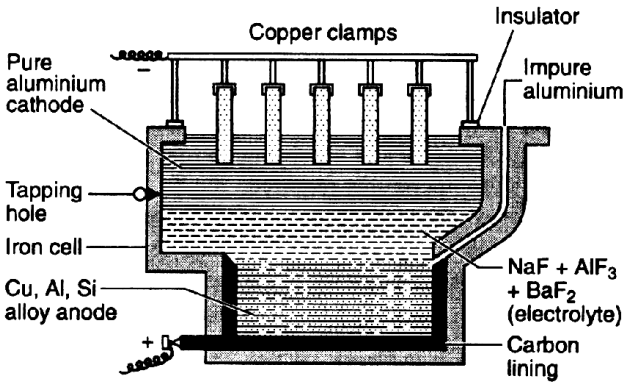
This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent. Different components are adsorbed at different levels on the column. Later the adsorbed components are removed (eluted) by using suitable solvent (eluant).

### 2.4.5 Electrolytic Refining :

Some metals such as Cu, Ni, and Al are refined electrolytically. The **Hoope's process** is a process for the **electrolytic refining of aluminum**. Impure Al forms the anode and pure Al forms the cathode of the Hooper's cell which contains three liquid layers. The bottom layer is molten impure Al, the middle is a fused salt layer containing aluminum fluoride, and the top layer is pure Al. At the anode (bottom layer), Al passes with solution as aluminum ion ($Al^{3+}$), and at the cathode (top layer), these ions are reduced to the pure metal. In operation, molten metal is added to the bottom of the cell and pure aluminum is drawn off the top. Aluminium obtained is 99.98% pure.

**At anode :** $Al \longrightarrow Al^{3+} + 3e^-$

**At cathode :** $Al^{3+} + 3e^- \longrightarrow Al$




### 2.4.6 Vapour Phase Refining :

In this method, the metal is converted into its volatile compound and then collected. It is then heated so that it gets decomposed to give pure metal. So, following two requirements are essential for vapour phase refinning.

(i) The metal should form a volatile compound with an available reagent.

(ii) The volatile compound should be easily decomposable, so that the recovery is easy.

# SOME IMPORTANT COMPOUNDS, MINERALS, MIXTURES & THE FORMULA'S

| | | |
|---|---|---|
| 1. | Epsom salt | $MgSO_4.7H_2O$ |
| 2. | Gypsum salt | $CaSO_4.2H_2O$ |
| 3. | Glauber's salt | $Na_2SO_4.10H_2O$ |
| 4. | Lime water | $Ca(OH)_2$ (slaked lime) |
| 5. | Quick lime | $CaO$ |
| 6. | Washing Soda | $Na_2CO_3.10H_2O$ |
| 7. | Crystal carbonate | $Na_2CO_3.H_2O$ |
| 8. | Soda ash | $Na_2CO_3$ |
| 9. | Baking Soda | $NaHCO_3$ |
| 10. | Turnbull's blue | $Fe_3[Fe(CN)_6]_2$ |
| 11. | Chile salt petre | $NaNO_3$ |
| 12. | Indian salt petre | $KNO_3$ |
| 13. | Brine or Table salt or Rock salt | $NaCl$ |
| 14. | Potash ash or Pearl ash | $K_2CO_3$ |
| 15. | Nitre or Indian salt petre or Chemical refrigerant | $KNO_3$ |
| 16. | Norwegian salt petre | $Ca(NO_3)_2$ |
| 17. | Salt Cake | $K_2SO_4$ |
| 18. | Carnallite | $KCl.MgCl_2.6H_2O$ |
| 19. | Hypo | $Na_2S_2O_3.5H_2O$ |
| 20. | Borax or Tincal | $Na_2B_4O_7.10H_2O$ |
| 21. | Barytes of Heavy spar or Barium meal | $BaSO_4$ |
| 22. | Baryta water | $Ba(OH)_2$ |
| 23. | Magnesia | $MgO$ |
| 24. | Microcosmic salt | $NaNH_4HPO_4.4H_2O$ |
| 25. | Nitrolium | $CaCN_2$ |
| 26. | Hydrolith | $CaH_2$ |
| 27. | Fusion mixture | $Na_2CO_3+K_2CO_3$ |
| 28. | Gun powder | $KNO_3+K_2CO_3$ |
| 29. | Pink salt | $(NH_4)_2SnCl_6$ |
| 30. | Laughing gas | $N_2O$ (nitrous oxide) |
| 31. | Red Lead | $Pb_3O_4$ |
| 32. | Blue vitriol | $CuSO_4.5H_2O$ |
| 33. | Green vitriol | $FeSO_4.7H_2O$ |
| 34. | Chiense white | $ZnO$ |
| 35. | Philospher's wool | $ZnO$ |
| 36. | Potash alum | $K_2SO_4.Al_2(SO_4)_3.24H_2O$ |
| 37. | Chrome alum | $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ |
| 38. | Ferric alum | $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$ |
| 39. | Chrome lemon (or) Yellow chrome | $PbCrO_4$ |
| 40. | Pyrolusite | $MnO_2$ |
| 41. | Rochelle salt | $\begin{matrix}CH(OH)COONa\\ \vert \\ CH(OH)COOK\end{matrix}$ |
| 42. | Sorel's cement | $MgCl_2.5HgO,H_2O$ |
| 43. | Lithopone | $BaSO_4+ZnS$ |
| 44. | Aqua regia | Conc. $HnO_3$ + Conc. $HCl$ (1 : 3) |
| 45. | Ammonium alum | $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$ |
| 46. | Sodium Alum | $Na_2SO_4.Al_2(SO_4)_3.24H_2O$ |
| 47. | Killed salt (or Butter of Zinc) | $ZnCl_2.2H_2O$ |
| 48. | Oxymuriate (or) Butter of Tin | $SnCl_4.5H_2O$ |

# EXTRACTION OF SOME METALS

## MAGNESIUM (Mg)

**Extraction :** It is usually extracted by the electrolysis of fused oxide of fused anhydrous magnesium chloride.

(i) **From magnesite :** The magnesite ore ($MgCO_3$) is calcined into magnesium oxide (magnesia).

$$MgCO_3 \xrightarrow[\text{strongly}]{\text{Heated}} MgO + CO_2$$

Magnesium may be obtained either by electrolysis or by thermal reduction of magnesium oxide. The oxide is dissolved in a mixture of molten fluorides of magnesium, barium and sodium. The electrolysis of molten mixture is done by using carbon rods as anodes which suspend in molten mass and cast iron rods as cathodes at 650°C. On electrolysis magnesium is obtained in molten state.

The thermal reduction of magnesium oxide can be done by using reducing agents like carbon, silicon, aluminium or calcium carbide.

$$MgO + C \rightarrow Mg + CO$$

$$2MgO + Si \rightarrow 2Mg + SiO_2$$

$$3MgO + 2Ai \rightarrow 3Mg\,Al_2O_3$$

$$3MgO + CaC_2 \rightarrow 3Mg + CaO + 2CO$$

The reduction is done at 2000°C in vacuum. The vapours of magnesium are condensed.

(ii) **Electrolysis of anhydrous magnesium chloride : Carnallite** is a hydrated compound. To make it anhydrous, it is first heated in air and then in current of HCl gas.

$$MgCl_2.\,6H_2O \xrightarrow[\text{of HCl gas}]{\text{Heated in presence}} MgCl_2 + 6H_2O$$

Anhydrous magnesium chloride can also be obtained from MgO or sea water. Chlorine is passed over red hot mixture of MgO and carbon

$$MgO + C + Cl_2 \rightarrow MgCl_2 + CO$$

It cannot be dehydrated by heating because the water of **crystallization reacts chemically with magnesium chloride to from magnesium oxychloride and finally magnesium oxide.**

$$\underset{\text{Hexahydrated}}{MgCl_2.6H_2O} \xrightarrow{\text{Heated}} \underset{\text{Dhydrate}}{MgCl_2.2H_2O} \xrightarrow{\text{Heated}} \underset{\text{Oxychloride}}{Mg_2OCl_2}$$

$$Mg_2OCl_2 \xrightarrow{\text{Heated in air}} MgO \xrightarrow{\text{Heated}} Mg$$

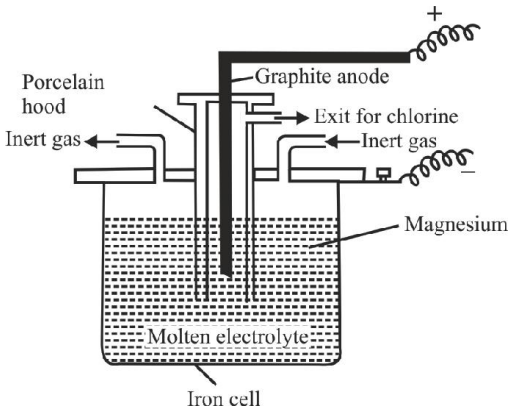
Sea water contains magnesium compounds. It is treated with calcium hydroxide when magnesium hydroxide gets precipitated. It is dissolved in dilute HCl. The solution then concentrated when hydrated magnesium chloride crystallizes out. It is dehydrated as described above.

$$\underset{(MgCl_2 \text{ or } MgSO_4)}{\text{Sea water}} + Ca(OH)_2 \longrightarrow \underset{\text{ppt.}}{Mg(OH)_2}$$

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2.6H_2O$$

$$MgCl_2.6H_2O \xrightarrow[HCl(g)]{\text{Heated}} \underset{\text{Anhydrous}}{MgCl_2} + 6H_2O\uparrow$$

The anhydrous magnesium chloride is fused with NaCl and anhydrous calcium chloride in the ratio of 35% ($MgCl_2$); 50% (NaCl) and 15% ($CaCl_2$). The purpose of addition of NaCl and $CaCl_2$ to anhydrous $MgCl_2$ is to lower the fusion temperature and make the fused mass good conductor of electricity. The mixture is electrolysed at 700°C in presence of an inert gas in electrolytic cell as shown in figure




## ALUMINIUM (Al)

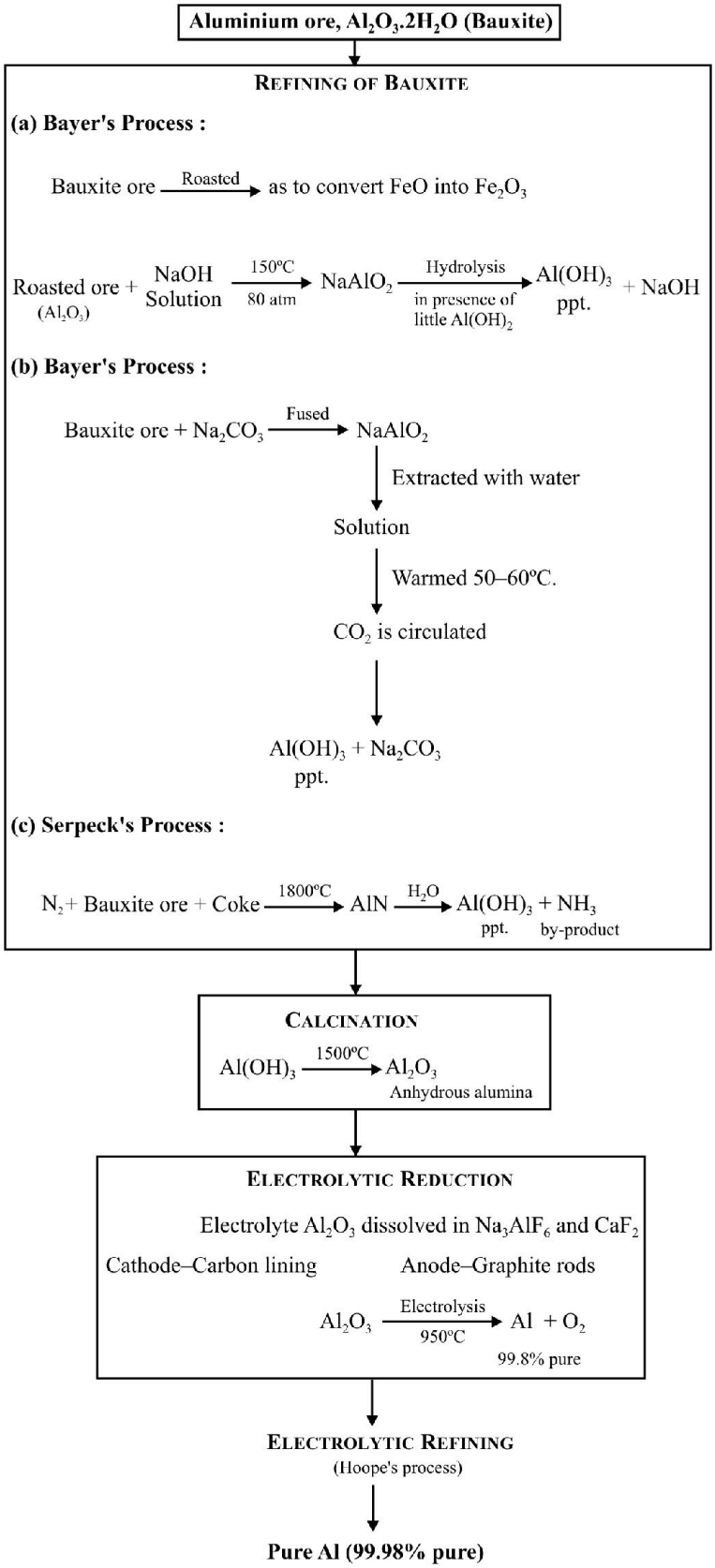
**Extraction :** Aluminium is mainly isolated from bauxite ore which is generally contaminated with ferric oxide and silica. The removal of ferric oxide and silica from bauxite ore is essential before it is subjected to electrolysis. Thus, the extraction of aluminium from bauxite ore involves the following three steps.

(i) Purification of bauxite ore, i.e., removal of ferric oxide and silica.

**(a) Baeyer's process :** This process is mainly applied to bauxite ore containing ferric oxide as chief impurity.

**(b) Hall's process :** This process is mainly applied to bauxite ore containing ferric oxide as a chief impurity.

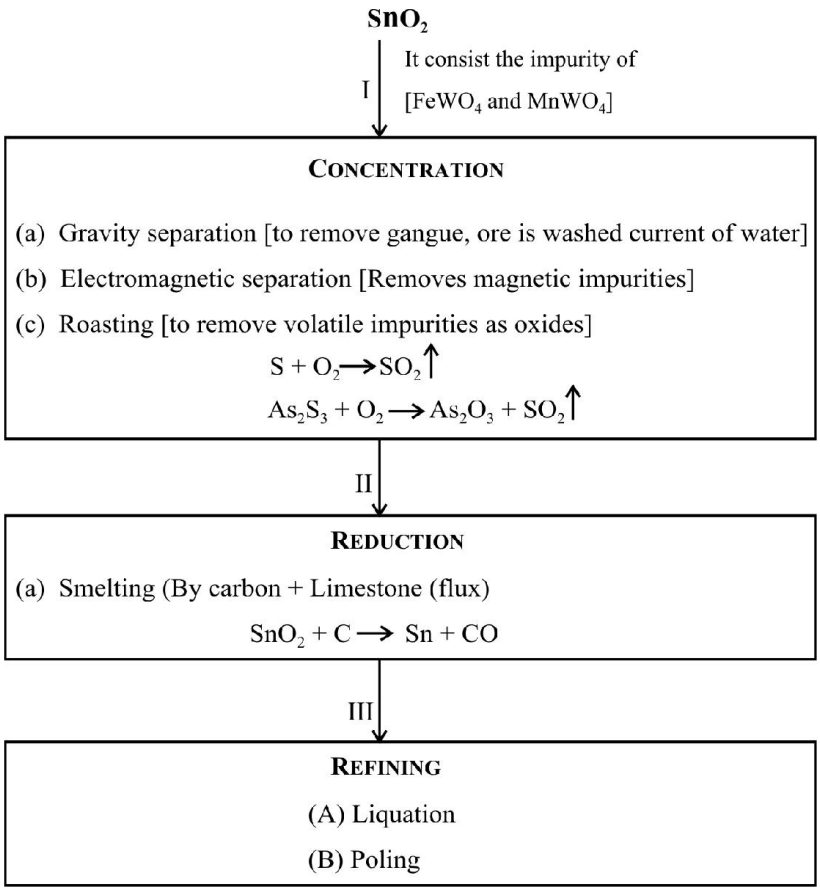
**(c) Serpeck's process :** This process is mainly applied to bauxite ore containing silica as a chief impurity.




FLOW SHEET FOR THE EXTRACTION OF ALUMINIUM

## TIN (Sn)

**Extraction :** Tin is extracted from **cassiterite ore.** The ore is usually associated with siliceous matter, tungestates of iron ($FeWO_4$) and manganese ($MnWO_4$).




## LEAD OR PLUMBUM (Pb)

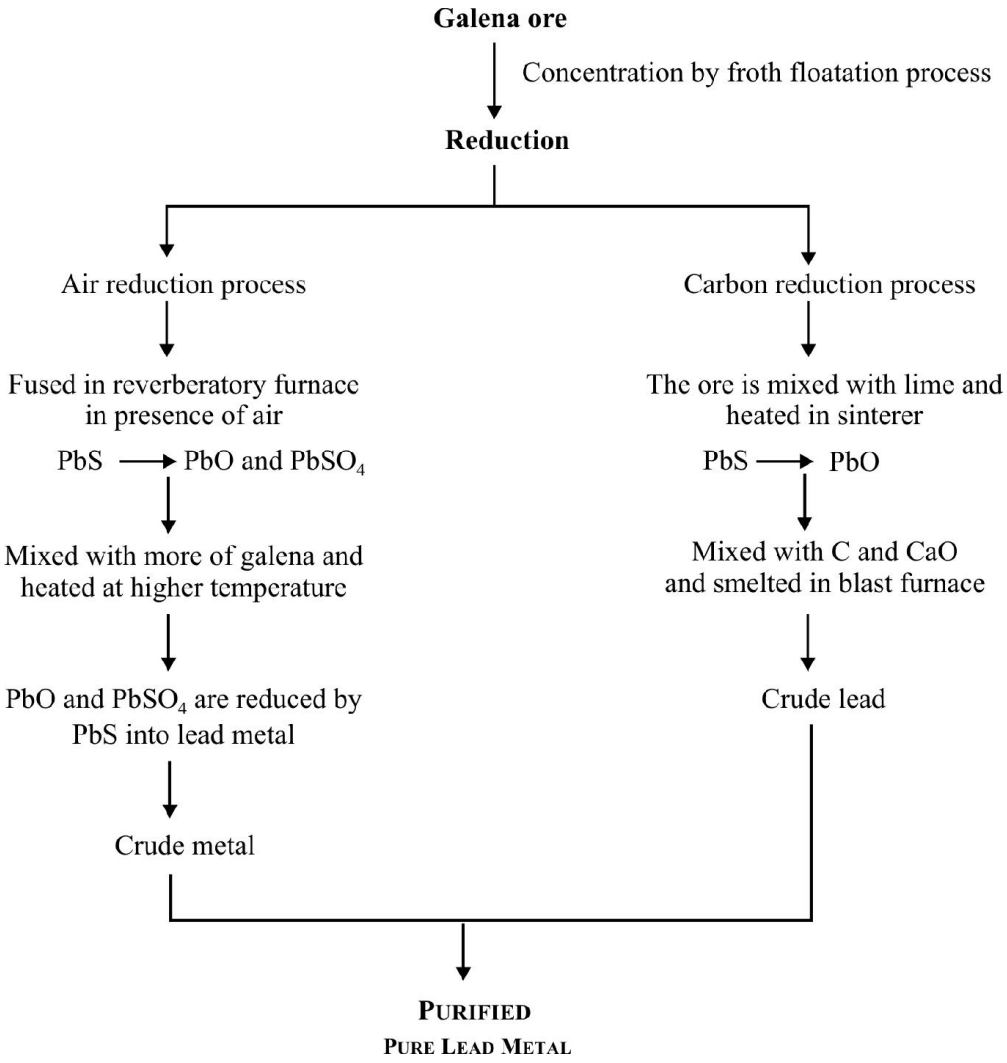
**Extraction :** Lead is mainly extracted, from **galena ore. (PbS)**

The extraction involves the following steps :

(i) Concentration of the ore

(ii) Reduction

(iii) Purification




**Flow Sheet for the Extraction of Lead and Formation of Various Compounds**

# IRON (Fe)

**Extraction :** Iron is extracted from its oxide ores especially from the **magnetite, haematite and limonite** ores. The extraction involve the following steps given in flow sheet :

**IRON ORE**

I ↓

**CONCENTRATION**

Gravity process followed by electromagnetic separation

II ↓

**CALCINATION AND ROASTING**

$$\text{Ore} + \text{air} \xrightarrow{\text{Heat}} \text{moisture},\ CO_2,\ SO_2, As_2O_3 \text{ removed}$$

FeO is Oxidised to ferric oxide

III ↓

**REDUCTION**

Smelting in a blast furnace (ore + coke + limestone). The following reactions occur

$$Fe_2O_3 + 3CO + \xrightarrow{400-700^\circ C} \underset{\text{Spongy iron}}{2Fe} + 3CO_2$$

$$\left[\begin{array}{c} 3Fe_2O_3 + CO \xrightarrow{300-400^\circ C} 2Fe_3O_4 + CO_2 \\ Fe_3O_4 + CO \xrightarrow{500-600^\circ C} 3FeO + CO_2 \\ FeO + CO \xrightarrow{700^\circ C} Fe + CO_2 \end{array}\right]$$

$$CaCO_3 \xrightarrow{1000^\circ C} CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3\,(\text{Slag})$$

Silicates, phosphates and manganates present as impurities in ore, are reduced to Si, P and Mn, respectively

$$P_4O_{10} + 10C \longrightarrow 4P + 10CO$$

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

$$MnO_2 + 2C \longrightarrow Mn + 2CO$$

$$SiO_2 + CO \xrightarrow{1200^\circ C} Si + 2CO$$

$$MnO_2 + 2C \longrightarrow Mn + 2CO$$

$$P_4O_{10} + 10C \longrightarrow 4P + 10CO$$

$$\text{Spongy iron} + \text{C, Mn, Si, etc.} \longrightarrow \text{Impure iron}$$

$$C + O_2 \xrightarrow{1600^\circ C} CO_2$$

$$CO_2 + C \xrightarrow{1500^\circ C} 2CO$$

IV ↓

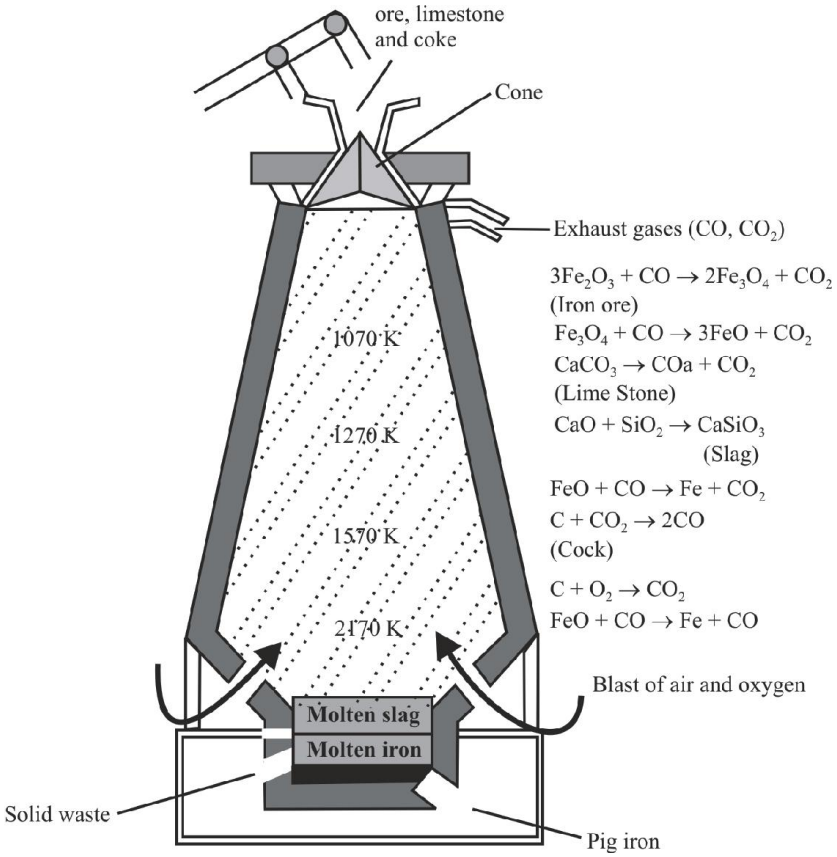
**PIG IRON**

V ↓

**REMELTED AND COOLED : CAST IRON**

(Fe = 93%; C = 5% and impurities of Mn, P, Si, etc. = 2%)

**FLOW SHEET FOR EXTRACTION OF IRON**




When the molten pig iron is cooled at once, the iron is called white cast iron, which contains carbon in the form of cementite, $Fe_3C$ and when the molten pig iron is cooled slowly and slowly, the iron is called as grey cast iron, which contains carbon in the form of graphite.

**1. Cost Iron or Pig Iron :**

This is the least pure form of commercial iron and contains the highest percentage of carbon viz., 2.5 to 4.5% and traces of impurities like S, P, Mn and Si. The average composition of cast iron is : Fe = 93 – 95%, C = 2.5 – 4.5%, Si = 0.6 – 2.8%, P = 0.4 – 1.0%, S = 0.1 – 0.3%, Mn = 0.3 – 1.2%.

**2. Wrought Iron :**

It is the purest form of commercial iron and contains the lowest percentage of carbon viz. 0.12 to 0.25% and 0.3% of impurities like S, P, Si and Mn.

# COPPER (Cu)

**Extraction :** Copper is extracted mainly from **copper pyrites (Cu Fe $S_2$)**. The extraction involve the following steps given in flow sheet.

**COPPER PYRITES**

($CuFeS_2$)

↓

**CRUSHED AND SIEVED**

↓

**CONCENTRATION BY FROTH FLOATATION**

Powdered ore + water + pine oil + air → sulphide ore in the froth

↓

**ROASTING IN REVERBERATORY FURNACE IN PRESENCE OF AIR**

$$S + O_2 \longrightarrow SO_2$$

$$2As + 3O_2 \longrightarrow 2As_2O_3$$

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

↓

Silica + coke → Roasted ore

↓

**SMELTING IN BLAST FURNACE IN PRESENCE OF AIR**

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow FeSiO_3\,(\text{Slag})$$

↓

**BESSEMERISATION IN BESSEMER CONVERTER IN PRESENCE OF AIR**

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow FeSiO_3\,(\text{Slag})$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \xrightarrow[\text{reduction}]{\text{Auto}} 6Cu + SO_2$$

↓

Blister copper (98% Cu + 2% impurities)

**ELECTROLYTIC REFINING**

* Anode–Impure copper plates
* Cathode–Pure copper plates
* Electrolyte–$CuSO_4$ soln. + $H_2SO_4$
* Pure copper deposited at cathode

↓

**PURE COPPER**

(99.6–99.9%)

**FLOW SHEET FOR THE EXTRACTION OF COPPER**

# SILVER (Ag)

Silver is also associated in the form of **$Ag_2S$** in the lead ore, **galena (PbS)**. The lead extracted usually contains silver and called argentiferous lead. Silver is recovered before lead is put into use.

**FLOW SHEET FOR THE EXTRACTION OF SILVER**

**Silver ore**
**(Argentite)**

↓

**CONCENTRATION BY FROTH FLOATATION PROCESS**

Powdered ore + Water + Pine oil + Air

↓

Froth carrying sulphide particles

↓

**CYANIDATION**

Concentrated ore + NaCN solution (0.4 – 0.6%) + Air

$Ag_2S + 4NaCN \rightleftharpoons 2NaAg(CN)_2 + Na_2S$

$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$

↓

**PRECIPITATION OF SILVER WITH ZINC**

$2NaAg(CN)2 + Zn \longrightarrow 2Ag + Na_2Zn(CN)_4$

Black ppt.

Black ppt. of Ag + $KNO_3 \xrightarrow{\text{Fuse}}$ Compact mass (Silver metal)

↓

**ELECTROLYTIC REFINING**

Anode : Impure silver

Cathode : Pure silver plate

Electrolyte : $AgNO_3$ solution + $HNO_3$

Pure silver deposited on the cathode.

Same process is employed for the extraction of gold (Au)

# STEEL

**Composition of Steel :**

Steel is an alloy of iron (as ferrite) containing 0.25 to 2.5% of carbon (as cementite, $Fe_3C$) and traces of S, P, Si and Mn. Thus, we see that the percentage of carbon in steel is intermediate between that in wrought iron and cast iron. S and P are objectionable impurities. The percentage of S and P are usually below 0.05%, depending on the method used for the manufacture of steel. Si is usually between 0.15 to 0.35% and is present as iron silicide, FeSi which is soluble in ferrite. High content of Si gives a fibrous structure to steel. Mn is added to steel during is manufacture to serve as a deoxidiser and to neutralise the harmful effect of sulphur by forming MnS which is inert, while FeS makes steel brittle in hot working.

**Varieties of Steel :**

There are many varieties of steel depending on the amount of carbon present in it.

1. **Mild and quenched steels :**

Mild steel is a variety which contains lower percentage of carbon. It possesses the properties of wrought iorn along with elasticity and hardness of steel. If mild steel is heated to a high temperature (i.e., to bright redness) and then suddenly cooled by plunging in oil or water, it becomes as hard and brittle as glass. This is called quenched steel and process is called quenching or hardening.

2. **Hard Steel :**

This variety contains higher percentage of carbon. It is hard and brittle like glass.

3. **Special Steels or alloy Steels :**

Addition of small amounts of nickel, cobalt, chromium, tungsten, molybdenum, manganese and silicon confer special properties on steel considerably altering its hardness, tenacity, resistance to corrosion and coefficient of expansion. Such products are called special steels or alloy steels and find extensive use in industry.

Some of the alloy steels along with their composition, properties and uses are listed in Table given below :

## Some important alloy steels

| | Name | Percentage composition | Properties | Uses |
|---|---|---|---|---|
| 1. | Stainless | Fe = 73<br>Cr = 18<br>Ni = 8<br>and carbon | Hard and rust-proof | Utensils, cycle and automobile parts, curtlery. |
| 2. | Nickel Steel | Fe = 98 – 96<br>Ni = 2 – 4 | Hard, elastic and rust-proof | Cables, automobile and aeroplane parts, armour plates, gears |
| 3. | Invar | Fe = 64, C = 0.3<br>Ni = 36 | Low expansion on heating | Metre scales, measuring instruments, clock pendulums. |
| 4. | Tungsten steel | Fe = 83 – 72<br>W = 14 – 20<br>Cr = 3 – 8 | Hard, resistant to corrosion | High speed cutting tools, springs |
| **5.** | Silicon steel | Fe = 84<br>Si = 15 | Hard, and resistant to acid | Pumps and pipes for carrying acids. |
| 6. | Manganese steel | Fe = 88 – 85<br>Mn = 12 – 15 | Extremely hard, high m.pt. | Rock crushers, burglar proof safes, rail tracks. |
| **7.** | Perma alloy | Fe = 21<br>Ni = 78<br>and carbon | Strongly magnetised by electric current and demangnetised upon cutting off current. | Electromagnets, cables for oceans. |
| 8. | Alnico | Fe = 63, Ni = 20<br>Al = 12, Co = 5 | Highly magnetic | Permanent magnets. |

4. **Steel containing S and P.** Iron or steel containing excess of S is brittle when hot (hot short) and that containing excess of P is also brittle when cold (cold short).

**Manufacture of steel**

We have already said that the amount of carbon in steel is mid-way between that of cast ron and in wrought iron so that steel can be obtained either by removing a part of carbon from cast iron or by adding some carbon to wrought iron. Thus steel is prepared either from cast iron or from wrought iron. Following methods are used :

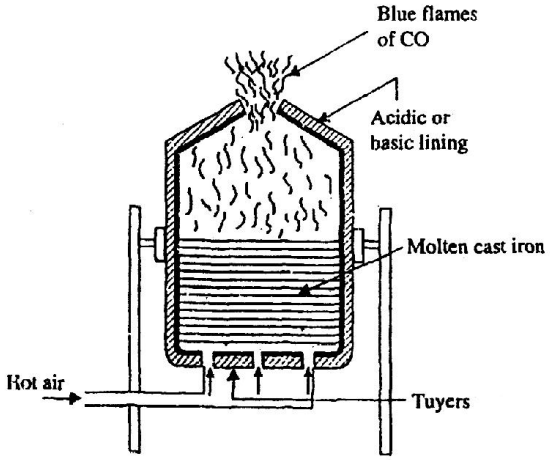
1. **Bessemer's process**

This process was discovered by Sir Henry Bessemer of England in 1856.

**Principle of the process.** This process is based on the fact that the impurities present in cast iron are completely oxidised in presence of hot air blast, i.e., virtually wrought iron is obtained. This is then mixed with known amount of spiegeleisen, an alloy of Fe, Mn and C to obtain steel.

In this process molten cast iron is taken directly from the blast furnace and is put into Bessemer's convertor.

**Construction of Bessemer's convertor.** Bessemer's convertor is a pear-shaped furnace, about 20m high and 10m in diameter. It is made of steel plates and has a number of holes (called tuyers) at its base through which a blast of hot air can be admitter into the convertor. The convertor is rotated on its horizontal central axis fig.




Bessemer's convertor used for the manufacture of steel from cast iron.

Depending on the nature of the impurities present in the cast iron, the convertor is lined on its inside with silica, $SiO_2$ (acidic lining) or lime (CaO)/magnesia (MgO) (basic lining). If the cast iron contains C, S, Si and Mn as impurities silica lining is used and the process is called acid Bessemer's process. On the other hand, it the cast iron contains P as impurity, CaO/MgO lining is used and the process is known as basic Bessemer's process. In actual practice, basic lining is obtained by using a mixture of CaO and MgO mixed with tar to bind them. The materials ($SiO_2$, CaO and MgO) used for lining the convertor act as flux as will be evident from the following discussion.

**Working.** To start with, the convertor is brought into the horizontal position, molten cast iron is put into it and then a blast of hot air or $O_2$ is blown into the convertor through its tuyers. The convertor is then rotated so that its mouth comes in vertically upwards position. The blowing of hot air is continued.

**Reaction taking place in Bessemer's convertor**

(i) In the beginning Si, Mn and P (impurities) get oxidised by $O_2$ to their respective oxides.

$$Si + O_2 \longrightarrow SiO_2$$

$$2Mn + O_2 \longrightarrow 2MnO$$

$$4P + 5O_2 \longrightarrow 2P_2O_5$$

MnO produced as above combines with $SiO_2$ lining (acidic lining) of the Bessemer's convertor to form the slag of $MnSiO_3$ and is thus removed.

MnO (basic impurity) + $SiO_2$ (acidic lining acting as an acidic flux) $\rightarrow$ $MnSiO_3$ (slag)

$P_2O_5$ and $SiO_2$ produced react with CaO lining (basic lining) of the Bessemer's convertor to form the slags of $Ca_3(PO_4)_2$ and $CaSiO_3$ and are thus removed.

$P_2O_5$ (acidic impurity) + 3CaO (basic lining acting as a basic flux) $\rightarrow$ $Ca_3(PO_4)_2$ (slag)

$SiO_2$ (acidic impurity) + CaO (basic lining acting as a basic flux) $\rightarrow$ $CaSiO_3$ (slag)

The mixture of the three slags viz. $MnSiO_3$, $Ca_3(PO_4)_2$ and $CaSiO_3$ is called basic slag which is used as a fertriliser. The present discussion makes it evident that $SiO_2$, CaO and MgO which are used for lining the convertor act as fluxes.

(i) Later on C and S are oxidised to CO ans $SO_2$ respectively by the blast of air. $SO_2$ escapes from the mouth of the convertor and CO burns with a blue flame at the mouth of the Bessmer convertor (Bessemer's condles). When the whole of carbon present in the cast iron has been oxidised to CO, the burning of CO at the mouth of the convertor stops. At this state, the blowing of $O_2$ into the convertor is stopped. Here it should be noted that the formation of slags. After all the impurities

have been removed, the calculated quantity of spiegeleisen alloy (an alloy of iron and manganese having Mn = 20–30%, C = 5%, Fe = remaining quantity) is added to the molten cast iron into the convertor and blast of hot $O_2$ is again allowed to enter into the convertor so that carbon and Mn present in spiegeleisen alloy get mixed with cast iron and steel is obtained which is taken out of the convertor in the molten state. Steel obtained in this way is called manganese steel. Spiegeleisen alloy being added does the following functions :

(a) It acts as a scavenger (i.e., cleaning agent), since Mn present in the alloy removes $O_2$, $N_2$, P and S, if dissolved in the molten steel, in the form of its oxide (MnO), nitride ($Mn_3N_2$), phosphide ($Mn_3P_2$) and sulphide (MnS). If $O_2$ and $N_2$ are not removed, these gases, on cooling, become less soluble and form bubbles (called blow holes) in steel. These bubbles weaken the strength of the steel. Thus Mn prevents the formation of blow holes. Some Al or ferro-silicon may also be added to remove blow holes. Due to the formation of Mns, the harmful effects of sulphur are neutralised.

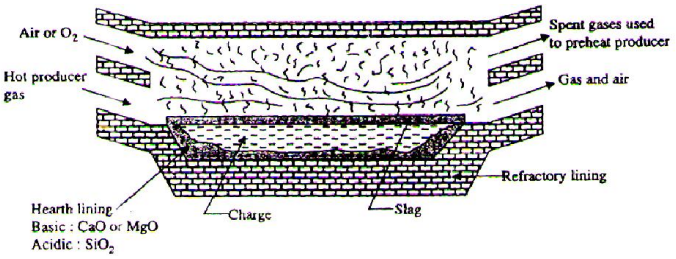
(b) It acts as a de-oxidiser, since Mn present in the alloy reduces oxidisied iron, if present.

(c) The alloy supplies the required quantity of carbon, Mn and Fe to get the steel of the required composition. Note that carbon is an essential constituent of all types of steel. Mn makes the steel hard and increases its tensile strength. If more quantity of Mn (upto 14%) is added in the form of spiegelcisen alloy, manganese steel obtained is very hard, tough for making steel helmets, safes, cross overs etc.

Requisite quantity of other metals like Cr, Ni etc. along with carbon are also added to get the steel of a particular composition.

**2. Open-hearth process of Siemens-Martin process**

This is the modern process and the furnace used in this process is called open-hearth furnace. Since this furnace works on the regenerative principle of heat economy, it is also called regenerative furnace. In this process steel is prepared from cast iron. Open-hearth furnace consists of an open hearth. The hearth is lined with silica or calcined dolomite (CaO.MgO) depending upon the nature of impurities present in pig or cast iron. Silica lining is used if the impurities are manganese, silicon, etc., and calcined dolomite lining is used if much of phosphorus is present. A high temperature of about 1500ºC is generated by burning producer gas which works on regenerative system of heat economy (fig.)




The charge consists of pig or cast iron, scraps, iron are (haematite) and lime. The charge is heated on the hearth of the furnace. The impurities are oxidised by iron ore.

$$3Si + 2Fe_2O_3 \longrightarrow 4Fe + 3SiO_2$$

$$3Mn + Fe2O_3 \longrightarrow 2Fe + 3MnO$$

$$MnO + SiO_2 \longrightarrow MnSiO_3 \text{ (slag)}$$

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

$$12P + 10Fe_2O_3 \longrightarrow 3P_4O_{10} + 20Fe$$

$$6CaO + P4O10 \longrightarrow 2Ca3(PO4)2 \text{ (slag)}$$

$$CaO + SiO_2 \longrightarrow CaSiO_3 \text{ (slag)}$$

$$2Fe_2O_3 + 3S \longrightarrow 3SO_2 + 4Fe$$

Samples of steel are drawn from time to time and tested for carbon content. Finally spiegleisen (an alloy of iron, manganese and carbon) is added to the molten mass and obtain desired steel. The process takes about 8 to 10 hours for completion. The process takes longer time than Bessemer process.

**Advantages of open-hearth process over Bessemer's process.**

Open-hearth process has the following advantages over the Bessemer's process.

(i) The temperature can be controlled as the heating is done externally.

(ii) As it is a slower process, it can be controlled in better way. The composition and quality can be well controlled.

(iii) The loss of iron in this process is only 4% while the loss is about 15% in Bessemer's process.

(iv) In this process scrap iron is re-used.

(v) This yields better quality of steel.

(vi) A considerable economy of the fuel is achieved by using the regenerative system.

**3. Duplex process**

Now-a-days Duplex process is being used for the manufacture of large quantities of steel. This process is a combination of Bessemer's process and open-hearth process. In this process the molten pig iron is first treated in an acid Bessemer's convertor to remove Si, Mn and a part of

C. The molten pig iron is then transferred to open-hearth furnace with a basic lining to remove P and remaining C and is finished off as usual. Tata Iron and Steel Works as using Duplex process for the manufacture of steel.

**4. Electric process**

In this process steel is prepared in arc furnace (also called Heroult's furnace). This is a crucible-shaped furnace and consists of steel shell which is lined inside with magnesite of dolomite and is covered with heat resisting bricks. The furnace is provided with movable and water jacketed graphite electrodes coming in from the roof or from the sides (fig.). Each electrode can be raised or lowered independently by a rack or pinion arrangement. The electrodes are held vertically and the charge which consists of Bessemer's steel, iron ore haematite and calculated quantity of lime is run into the arc furnace and the current is switched on the produce electric arc between the electrodes. This electric arc produces a temperature of 3000–3500ºC.

**Reactions :** Reactions taking place in this process are :

(a) Oxidation and formation of slag. At the temperature of the electric arc, the charge melts and vigorous reaction starts. In this reaction Si, Mn, C and P are oxidised to $SiO_2$, MnO, CO and $P_4O_{10}$ respectively and $CaCO_3$ gets decomposed.

$$3Si + \underset{\text{(Iron ore)}}{2Fe_2O_3} \longrightarrow 4Fe + 3SiO_2$$

$$3Mn + Fe_2O_3 \longrightarrow 2Fe + 3MnO$$

$$C + O_2 \longrightarrow CO_2$$

$$CO_2 + C \longrightarrow 2CO$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

The oxides viz. $SiO_2$, MnO, Co and $P_4O_{10}$ are removed as slags.

$$SiO2 + CaO \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

$$MnO + SiO_2 \longrightarrow \underset{\text{Slag}}{MnSiO_3}$$

$$Fe_2O_3 + CO \longrightarrow CO_2 + 2FeO$$

$$FeO + SiO2 \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

$$P_4O_{10} + 6CaO \longrightarrow \underset{\text{Slag}}{2Ca_3(PO_4)_2}$$

This slag being lighter floats over the metallic portion. As soon as the oxidation and formation of slag is complete, the furnace is carefully tilted and the slag is pured out of it.

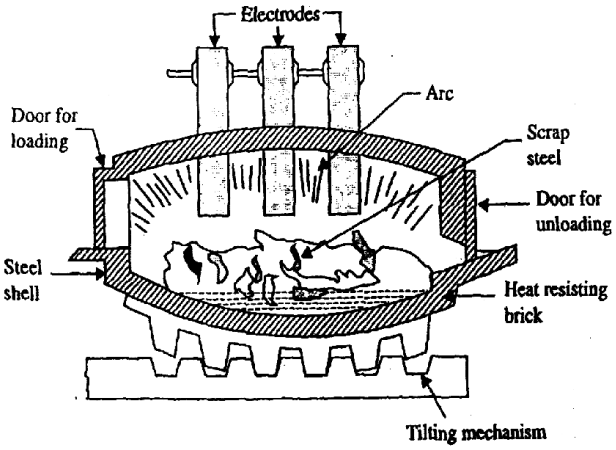
(b) Deoxidation and desulphurization. After the slag is poured out of the furnace, a charge consisting of lime, sand, fluorspar and some coke and ferro-silicon is added to the furnace. Any FeO present in the steel is removed as Fe by reducing it with the added coke.

$$FeO + C \longrightarrow Fe + CO \text{ (Removal of FeO)}$$

Sulphur present as FeS is removed as CaS by treating it with CaO

$$FeS + CaO \longrightarrow FeO + CaS \text{ (Removal of S)}$$

FeO thus produced is at once reduced to Fe as before while CaS goes into the slag. When desulphurization (i.e., removal of sulphur) is complete, the steel is poured out into moulds.




Arc furnace (Heroult's furnace) for the manufacture of steel.

This method is also used for the manufacture of alloy steels, tool steels, stainless steels and special quality steels.

**5. L.D. process :**

This process has recently been developed in Lintz and Dusenverfahren in Austria and is in use at the Rourkela steel plant. The main advantages of the process are :

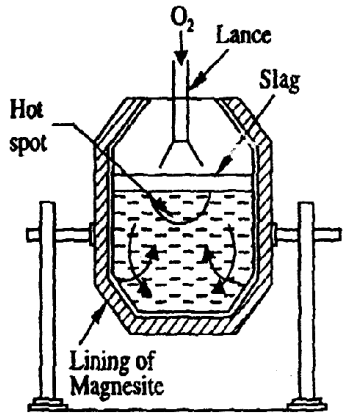
(i) Less capital expenditure and more productivty.

(ii) It takes only 45 minutes to treat one lot.

(iii) Even scrap iron can be used.

(iv) Less operating cost and better quality of steel.

The process is carried out in a convertor lined with magnesite which differs from the Bessemer convertor in not having the perforated base but a solid bottom. Pure $O_2$ is blown from the top through a copper lance (fig.)




Converter for L.D. process.

**Properties of steel**

1. **Mechanical properties.** Steel combines the useful properties of cast iron and wrought iron, being both hard and elastic and provided the proportion of carbon is not high, it can be forged and welded.

2. **Action of Heat : Heat treatment of steel.** A characteristic behaviour or steel which distinguishes it from other commercial forms of iron is that its hardness and elasticity can be varied by proper heat treatment of steel. For example :

(a) **Anealing.** When hard steel is heated to bright redness and then allowed to cool slowly, hardness of steel is considerably decreased and it gets softened. This process is called anealing.

**(b) Quenching or hardening.** When mild steel is heated to a high temperature (i.e., to bright redness) and then suddenly cooled by plunging it in oil or water, it becomes as hard and brittle as glass. This process is called quenching or hardening and the steel obtained by this method is called quenched steel.

**(c) Tempering.** The quenched steel can be made to lose its brittleness by heating it to varying temperatures for varying periods. The process. The process is called tempering and is empolyed for bringing the steel into a suitable state of hardness and elasticity. The temperature is generally judged from the colour of a thin film of oxide which is formed on the surface and varies from yellow (200–230°C) to brown (225–270°C) to blue (300°C) as the temperature rises. Steel for cutting blades and tools is made yellow but that required for springs, saws, etc., is tampered blue.

3. **Surface treatement of steel.** The surface treatement of the steel is done by the following process :

**(a) Case hardening.** The process of producing a thin coating of hardened steel on the surface of the mild steel is called case hardening. This is done by heating the mild steel with charcoal and then plunging into oil. This produces a thin coating of hardened steel on the surface. Such a steel becomes resistant to wear and tear.

**(b) Nitriding.** The process of producing a hard coating of iron nitride on the surface of steel is called nitriding. Steel is heated in the atmosphere of dry ammonia at 500–600°C for about 3 to 4 days when a hard coating of iron nitride is produced on the surface.

**Comparison between cast iron, wrought iron and steel**

| Property | Cast iron | Wrought iron | Steel |
|---|---|---|---|
| Chemical composition | Iron 93–95%,<br>Carbon 2.5–5%<br>Impurities about 2% | Iron 99.5–99.8%,<br>Carbon 0.1–0.25%<br>Impurities about 0.3% | Iron 99.5–98.0%,<br>Carbon 0.25 to 2.0% |

## SOME SPECIAL PROCESSES FOR SILVER

**Mexican Amalgamation Process**

Mercury and magistral (burnt pyrites-sulphates and oxides of copper and iron) are added to the powdered mineral containing $H_2O$ and NaCl. The mixture is kept for several days. Silver is formed in the amalgam form. On washing, drying and subsequent distillation, silver is obtained.

$$CuSO_4 + 2NaCl \longrightarrow CuCl_2 + Na2SO_4$$

$$CuCl2 + Ag_2S \longrightarrow Cu_2Cl_2 + 2AgCl + S$$

$$Cu_2Cl_2 + Ag_2S \longrightarrow Cu_2S + 2AgCl$$

$$2AgCl + 2Hg \longrightarrow Hg_2Cl_2 + 2Ag$$

$$Ag + Hg \longrightarrow Ag(Hg) \xrightarrow{\text{distill}} Ag\downarrow + Hg\uparrow$$

**Desilverisation of Lead :** When lead-silver alloy is poor in silver (such as argentiferrous lead of galena), desilverisation of lead is affected by **Parke's process.** It depends upon the fact that :

(i) when zinc is added to a melted alloy of silver and lead, zinc takes away silver from the alloy and iteself forms an alloy with silver and not with lead

(ii) alloy of zinc and silver melts at a higher temperature than lead

(iii) the alloy of silver and zinc is lighter than lead and forms two separate layers

(iv) on distillation of silver and zinc, zinc separates

**Pattinson's Process**

It depends upon the fact that the alloy of lead and silver containing less than 1.8 percent of silver, melts at a low temperature than pure lead. If this type of alloy is melted, and the melted alloy is allowed to cool, lead first separates and repeating the process, one becomes richer in silver. Further recovery is done by cupellation process.

**Lead Process**

This process depends upon the fact that when ores of silver are smelted down with lead, and alloy of lead and silver is formed; from this alloy lead is removed by oxidation.

$$\text{ores of silver} \xrightarrow[\text{lead}]{\text{smelted with}} (Pb - Ag)\text{ alloy} \xrightarrow{\text{cupellation}} \text{silver}$$

* (Pb–Ag) alloy rich in silver : Cupellation process is used

* (Pb–Ag) alloy poor in silver : Parke's or Pattinson's process is used

## 3. THERMODYNAMIC PRINCIPLES OF METALLURGY

The basic concepts of thermodynamics are quite helpful in selecting which element will be the most suitable reducing agent for a particular oxide during a metallurgical operation. It can also predict the optimum temperature at which the reduction can occur smoothly.

For any reaction or process, Gibb's Helmholtz free energy change ($\Delta G$) is given by the equation,

$$\Delta G = \Delta H - T\Delta S \quad \ldots\ldots (i)$$

where $\Delta H$ is the enthalpy change and $\Delta S$ is the entropy change and T is the absolute temperature at which the reaction is carried out. For the feasibility of any reaction at any temperature the value of $\Delta G$ must be negative at the temperature. The free energy change is also related to the equilibrium constant 'K' of the reaction at temperature T by the following equation,

$$\Delta G = -RT \ln K \ldots\ldots (ii)$$

A negative $\Delta G$ implies a + ve K in the equation. This can happen only if the reaction proceeds towards the products. The following conclusions can be drawn :

**(i) Greater the negative value of free energy change ($\Delta G$), more spontaneous is the reaction.**

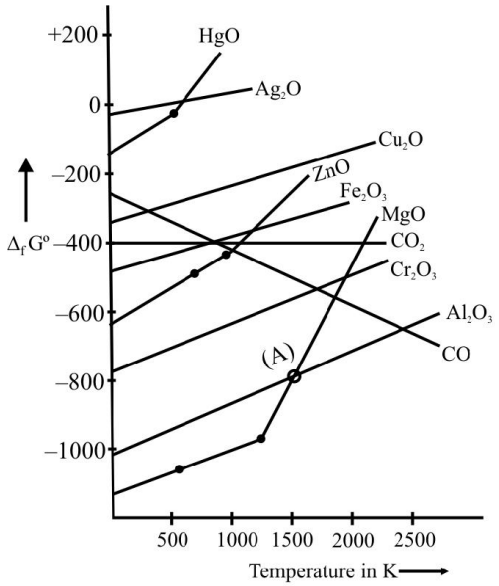
| $\Delta G$ | $T\Delta S$ | Favourable conditions |
|---|---|---|
| – ve | + ve | Any temperature |
| – ve | – ve | $\Delta H > T\Delta S$ (Temp. should be low) |
| + ve | + ve | $T\Delta S > \Delta H$ (Temp. should be high) |

(ii) If two reactions are put together in a system and the net $\Delta G$ of both the reactions is –ve, the overall reaction will occur, i.e., a reaction with $\Delta G$ positive can be made to occur if it is coupled with another reaction having a large negative $\Delta G$ so that the net $\Delta G$ of both the reactions is negative.

Such coupling reactions can be easily understood through **Ellingham diagram.**

**Ellingham diagram :** Ellingham diagram consists of graphs which represent the variation of standard free energy with temperature of the formation of oxides of various elements, i.e., of $\Delta_f G^\circ$ vs T. Similar plots can also

be plotted for sulphides and halides. These were first plotted by H.J.T. Ellingham. These diagrams help us in predicting the feasibility of thermal reduction of an ore.




**Elligham diagrams for oxides of some elements**

Consider the formation of a metal oxide ($M_xO$).

$$2xM(s) + O_2(g) \rightarrow 2M_xO(s)$$

In this reaction, there is decrease in the value of $\Delta S^\circ$ as $M_xO$ is solid and $O_2$ is a gas, i.e., $\Delta S$ is negative. Thus, if temperature is increased, $T\Delta S^\circ$ becomes more negative.

As in the equation

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

$T\Delta S^\circ$ is subtracted, therefore, $\Delta G^\circ$ becomes less negative, i.e., $\Delta G^\circ$ is likely to increase with rise in temperature and this trend is confirmed from the curves.

(i) The slope of the curves of the formation of metal oxides is +ve because $\Delta G^\circ$ becomes less negative or increases with the rise in temperature.

(ii) Each curve is a straight line except when some change takes place in phase (s $\rightarrow$ *l* or *l* $\rightarrow$ g). The temperature at which such a change occurs is indicated by an increase in the slope on the +ve side. For example, in the Zn–ZnO curve, the melting of zinc is indicated by an abrupt increase in the +ve slope at temperature 692 K.

(iii) In the case of less reactive metals like silver and mercury, $\Delta G^\circ$ becomes positive at high temperatures. It indicates that both silver oxide ($Ag_2O$) and mercury oxide (HgO) are unstable and decompose at high temperature.

$$2Ag_2O \xrightarrow{\text{Heat}} 4Ag + O_2$$

$$2HgO \xrightarrow{\text{Heat}} 2Hg + O_2$$

(iv) In the curve of CO, $\Delta G^\circ$ decreases as $\Delta S^\circ$ increases. This is indicated by the downward trend.

(v) Any metal oxide with lower value of $\Delta G^\circ$ is more stable than a metal oxide with higher $\Delta G^\circ$. This implies that the metal oxide placed higher in the diagram can be reduced by the metal involved in the formation of the oxide placed lower in the diagram. For example, $Cr_2O_3$ can be reduced by Al metal but $Al_2O_3$ cannot be reduced by Cr.

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$

Thus, the relative tendency of the various metals to act as reducing agents is :

$$Ca > Mg > Al > Cr > Zn > Fe > Ni$$

## 3.1 Reducing Nature of Carbon

Carbon in the form of coke, charcoal or carbon monoxide is used as a reducing agent in pyrometalurgical operations. Such a reduction process used in the extraction of a metal is termed **smelting.**

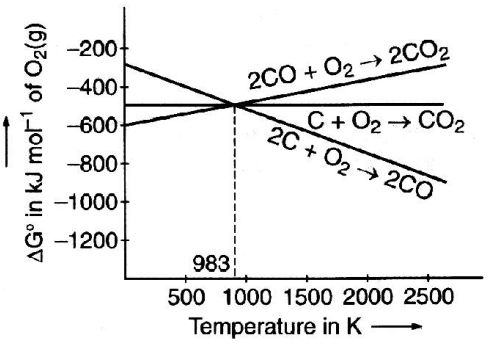
When carbon is to act as a reducing agent, the following three reactions are possible :

$C(s) + O_2(g) \rightarrow CO_2(g)$ ..... (i)

$2C(s) + O_2(g) \rightarrow 2CO(g)$ ..... (ii)

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ ..... (iii)

In the first reaction (formation of $CO_2$) there is hardly any change in entropy, i.e., $\Delta S^\circ \approx 0$ and therefore, $\Delta G^\circ$ remains nearly the same with rise in temperature, i.e., $\Delta G^\circ$ is independent of temperature.




**Ellingham diagram for the reducing nature of carbon**

In the second reaction (formation of CO), there is increase in entropy ($\Delta S^\circ$ is positive) and therefore, $\Delta G^\circ$ becomes more negative with increase in temperature.

However, in third reaction, there is decrease in entropy ($\Delta S^\circ$ is negative) and therefore, $\Delta G^\circ$ becomes less negative with increase in temperature.

The above observations can be seen in Fig. The three curves have been found to intersect at 983 K. It implies that above this temperature, the reaction (ii) is most suitable. It means that carbon can reduce any metal oxide at very high temperatures and is then itself oxidised to CO. However, the reduction with carbon at high temperatures is not preferred in all cases due to the following reasons :

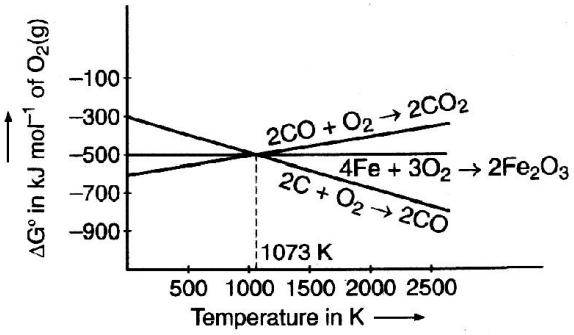
(a) It involves high cost.

(b) Some metals react with carbon at high temperatures and form carbides.

(c) There are many practical difficulties in the maintenance of high temperature.

**(A) Theory of reduction of Haematite**

In the Ellingham diagram, there are three curves which illustrate the formation of ferric oxide from Iron, formation of CO from carbon and formation of $CO_2$ from CO. The curves cross each other at 1073 K.




**Ellingham diagram for the reduction of haematite**

Above 1073 K, $\Delta G^\circ$ for the formation of $Fe_2O_3$ is less negative than $\Delta G^\circ$ for the formation of carbon monoxide from carbon. Thus, above 1073 K, carbon (coke) can reduce $Fe_2O_3$, i.e., $\Delta rG^\circ$ for the reaction,

$$Fe_2O_3\,(s)\,3C(s) \xrightarrow{>1073\,K} 2Fe(s) + 3CO(g)$$

is negative.

Below 1073 K, $\Delta G^\circ$ for formation of CO from carbon is less negative than $\Delta G^\circ$ for the formation of $Fe_2O_3$. $\Delta_r G^\circ$ for the reduction of $Fe_2O_3$ with carbon will be positive and hence, reduction is not possible. However, it is observed from the diagram that $\Delta G^\circ$ of formation of $CO_2$ from CO is more negative than $\Delta G^\circ$ of formation of $Fe_2O_3$. This means that $Fe_2O_3$ can be reduced by CO below 1073 K, i.e., $\Delta_r G^\circ$ for the reaction,

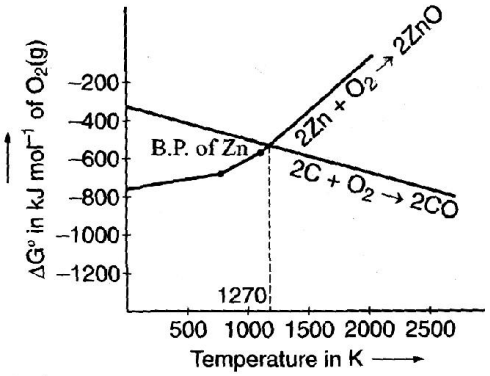
$$Fe_2O_3\,(s) + 3CO(g) \xrightarrow{>1073\,K} 2Fe(s) + 3CO_2(g)$$

is negative.

Thus, in the blast furnace, reduction of $Fe_2O_3$ occurs in different temperature ranges either below 1073 K by carbon monoxide or above 1073 K by carbon (coke).

**(B) Theory of reduction of ZnO**

Ellingham diagram reveals that the curves involving the formation of ZnO and carbon monoxide cross each other at about 1270 K.




**Ellingham diagram for formation of ZnO and CO**

There is sudden increase in the value of $\Delta G^\circ$ for the formation of ZnO above 1180 K. This is due to the fact that zinc begins to boil at this temperature. Above 1270 K, $\Delta_r G^\circ$ of the following equation,

$$ZnO(s) + C(s) \xrightarrow{>1270\,K} Zn(g) + CO(g)$$

is considerable negative and thus, reduction of ZnO with coke occurs easily.

# SOLVED EXAMPLES

**Example - 1**

**In blast furnace, iron oxide is reduced by-**

**(a) Silica** **(b) CO**

**(c) C** **(d) lime stone**

**Ans. (b)**

**Example - 2**

**Refining of Iron is done by-**

**(a) Electrolytic method** **(b) Zone refining**

**(c) Poling**

**(d) Selective oxidation (oxidation process)**

**Ans. (d)**

**Example - 3**

**Exothermic reactions taking place in ..... zone**

**(a) Central zone** **(b) Combustion zone**

**(c) Fusion zone** **(d) Reduction zone**

**Ans. (b)**

**Example - 4**

**Purple of cassius is –**

**(a) Pure gold**

**(b) Solid solution of gold**

**(c) Gold (I) hydroxide** **(d) Gold (III) chloride**

**Sol. (b)**

It is obtained by treating gold (III) chloride solution with $SnCl_2$

$$2AuCl_3 + SnCl_2 \rightarrow 2Au + 3\ SnCl_4$$

$SnCl_4$ so formed hydrolyses as follows

$$SnCl_4 + 4H_2O \rightarrow \underset{\text{stannic acid}}{Sn(OH)_4} + 4HCl$$

The colloidal precipitate of stannic acid absorbs colloidal particles of gold. This has beautiful purple colour and is known as purple of cassius. It is used for colouring glass (ruby red) and pottery.

**Example - 5**

**Percentage of gold in 20 Carat gold-**

**(a) 80%** **(b) 83.33%**

**(c) 86.66%** **(d) 96%**

**Sol. (c)**

20 karat gold means it consists of 20 parts gold out of 24 parts and four parts of copper.

$$\% \text{ of gold} = \frac{20}{24} \times 100 = 83.33\%$$

**Example - 6**

**Product obtained after Bessemerisation is called as ..... because .....**

**(a) Concentrated copper ; copper percentage is high**

**(b) Copper matte ; of its appearance**

**(c) Blister copper : of its appearance**

**(d) Ultra pure** copper ; 100 percent copper

**Ans. (c)**

**Example - 7**

**Copper matte consists of :-**

**(a) Copper oxide and ferrous sulphide**

**(b) Copper sulphide and ferrous oxide**

**(c) Copper sulphide and ferrous sulphide**

**(d) Copper oxide and ferrous oxide.**

**Ans. (c)**

**Example - 8**

**High purity copper is obtained by-**

**(a) Zone refining**

**(b) Poling**

**(c) Electrolytic refining** **(d) Cupelling**

**Sol. (c)**

After electrolytic refining. Purity of copper is 99.99% which is enough for electrical applications.

**Example - 9**

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

Metal sulphide $\xrightarrow{(A)}$ Concentrated ore $\xrightarrow{(B)}$ Matte $\xrightarrow{(C)}$ Impure metal $\xrightarrow{(D)}$ Pure metal. Identity the steps (A), (B), (C) and (D).

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

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

In roasting; $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$.

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$.

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$.

$FeO + SiO_2 \rightarrow FeSiO_3$

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

(D) Electro-refining. Pure metal is obtained at cathode.

$M^{n+} + n\,e^- \rightarrow M$

**Example - 10**

**Write chemical equations for metallurgical processes to represent :**

**(i) roasting of galena (PbS) in limited supply of air at moderate temperature.**

**(ii) reduction of $Cu_2O$ using coke as a reducing agent.**

**(iii) deposition of pure silver from an aqueous solution of $Ag^+$.**

**Sol.** (i) $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$ ;

$PbS + 2O_2 \rightarrow PbSO_4$

(ii) $Cu_2O + C \rightarrow 2Cu + CO$

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

**Example - 11**

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

| **Column - I** | **Column - II** |
|---|---|
| **(A) Pb** | **(p) Bessemerisation** |
| **(B) Cu** | **(q) Roasting** |
| **(C) Zn** | **(r) Carbon or carbon monoxide reduction** |
| **(D) Fe (pig iron)** | **(s) Self-reduction method** |

**Sol.** A : q, s ; B : q, s; C : q, r; D : r

(A) $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$ (Roasting)

$PbS + PbO_2 \xrightarrow{\Delta} 2Pb + SO_2$ (Self-reduction method)

$PbO + C \longrightarrow Pb + CO$

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

$Cu_2S + 2Cu_2O \xrightarrow{\Delta} 6Cu + SO_2$

(Self-reduction takes place in Bessemer converter)

$Cu_2O + C \xrightarrow{\Delta} Zn + CO$

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

$ZnO + C \xrightarrow{\Delta} Zn + CO$ (Carbon reduction)

(D) Haematite ore is calcined.

$3Fe_2O_3 + CO \xrightarrow{\Delta} 2Fe_3O_4 + CO_2$

$Fe_3O_4 + CO \xrightarrow{\Delta} 3FeO + CO_2$

$FeO + CO \xrightarrow{\Delta} Fe + CO_2$

**Example - 12**

**Write the overall reaction taking place in the process used for the electrolysis of Alumina by Hall-Heroult process.**

**Sol.** The reaction taking place in process used for the electrolysis of Alumina by Hall-Heroult process is

$$\underset{(Alumina)}{2Al_2O_3} + \underset{(Carbon)}{3C} \longrightarrow \underset{(Aluminium)}{4Al} + 3CO_2$$

**Example - 13**

**(a) Extraction of Au by leaching with NaCN involves both oxidation and reduction. Justify by giving equations for the reactions involved.**

**(b) Why is the froth flotation method selected for the concentration of sulphide ores ?**

**Sol.** (a) Oxidation of Au

$$4Au(s) + 8\,CN^-(aq) + 2H_2O + O_2(g) \rightarrow 4[Au(CN)_2]^- + 4OH^-$$

Reduction of $Au^+$ to Au

$$2[Au(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Au$$

(b) Because sulphide ores are preferentially wetted by oil and impurities by water.

**Example - 14**

**Write a non-exothermic reaction taking place in the blast furnace during extraction of iron.**

**Sol.** $\underset{\text{Calcium Carbonate}}{CaCO_3} \xrightarrow{\text{heat}} \underset{\text{Calcium oxide}}{CaO} + CO_2$

**Example - 15**

**What is a flux ? What is the role of flux in the metallurgy of Iron and Copper ?**

**Sol.** **Flux :** Flux is a substance that combines with gangue to form slag. The gangue may be present in roasted or the calcined ore.

$$FeO + SiO_2 \rightarrow \underset{\text{(Slag)}}{Fe\,SiO_3}$$

In the blast furnace, CaO (flux) removes silica presentation in the ore

$$CaO + SiO_2 \rightarrow \underset{\text{(Slag)}}{Ca\,SiO_3}$$

**Example - 16**

**Why can't aluminium be reduced by carbon ?**

**Sol.** Aluminium is a strong reducing agent than carbon. Hence aluminium (Al) cannot be reduced by carbon.

**Example - 17**

**(a) What is the role of depressant in froth floatation process ?**

**(b) Out of C and CO which is a better reducing agent for FeO**

**(i) In the lower part of blast furnace**

**(Higher temperature)**

**(ii) In the upper part of blast furnace**

**(Lower temperature)**

**Sol.** (a) Depressant is used in the froth floatation process for preventing the specific sulphide are from forming froth in a mixture of sulphides.

(b) C is better reducing agent of higher temperature.

CO is better reducing agent at lower temperature.

**Example - 18**

**What are chief ores of Zinc ? Write chemical reactions taking place in the extraction of zinc from zinc blende.**

**Sol.** The chief ores of zinc are :

(i) Zinc blende, ZnS

(ii) Calamine, $ZnCO_3$

(iii) Zincite, ZnO

**Extraction of zinc :** The zinc from zinc blende is extracted by roasting followed by reduction with coke.

**(a) Roasting :** The concentrated ore is heated with oxygen at 900°C in reverberatory furnace to convert zinc sulphide to zinc oxide.

$$\underset{\text{(Zinc blende)}}{2\,ZnS} + 3O_2 \rightarrow \underset{\text{(Zinc oxide)}}{2\,ZnO} + 2SO_2$$

**(b) Reduction :** The reduction of zinc oxide is done using coke.

$$ZnO + C \xrightarrow{673\ K} Zn + CO$$

The metal is distilled off and collected by rapid chilling.

**Example - 19**

**Outline the principles of refining of metals by the following methods :**

**(i) Zone refining**

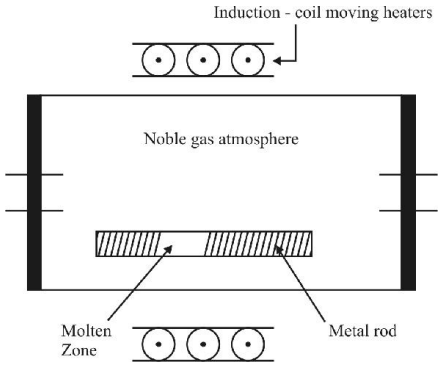
**(ii) Electrolytic refining**

**(iii) Distillation**

**Sol.** **(i) Zone refining :** This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal.

A circular mobile heater is fixed at one end of the rod of the impure metal. The molten zone moves along with the heater which is moved forward. As the heater moves forward, the

pure metal crystalises out of melt and the impurities pass on into the adjacent molten zone. This process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated.




This method is very useful for producing semiconductor and other metals of very high purity like germanium, silicon, boron etc.

**(ii) Electrolytic refining :** In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as Cathode. They are put in a suitable electrolyte both containing soluble salt of the same metal. The more basic metal remains in the solution and the less basic ones go to the anode mud. The reactions are

**Anode :** $M \rightarrow M^{n+} + ne^-$

**Cathode :** $M^{n+} + ne^- \rightarrow M$

Copper and zinc are refined by this method.

**(iii) Distillation :** In this method, the impure metal is evaporated to obtain the pure metal as distillate. This method is very useful for low boiling metals like zinc and mercury.

**Example - 20**

**Explain the vapour phase refining method for extraction of metal. Give example.**

**Sol. Vapour phase refining :** In this method, the metal is converted into its volatile compound and collected elsewhere. It is then 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 easily decomposable, so that recovery is easy.

**Example - 21**

**Name the principal ore of aluminium and describe how aluminium metal is extracted from this ore.**

**Sol. Extraction of Aluminium :**

Principal (main) ore of aluminium = Bauxite ($Al_2O_3.H_2O$)

**Other ores :**

(i) cryolite - $Na_3AlF_6$

(ii) Orthoclase - $KAlSi_3O_8$

Aluminium metal is extracted from bauxite in two stage process.

(i) pure alumina ($Al_2O_3$) is obtained from bauxite.

(ii) Electrolysis of $Al_2O_3$ in molten cryolite : $Na_3AlF_6$ to obtained aluminium metal.

**Stage-1 : (Leaching) :** The bauxite ore contains the impurities like silica ($SiO_2$), ironoxide and titanium (IV) oxide.

The ore is treated with sodium hydroxide solution. Aluminium oxide and silica dissolve to form sodium aluminate and sodium silicate respectively. Iron oxide and $TiO_2$ is filtered off.

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$$

Or

$$Al_2O_3\,(s) + 2NaOH\,(aq) + 3H_2O\,(\ell) \rightarrow 2Na[Al(OH)_4]\,(aq)$$

The filtrate sodium aluminate and sodium silicate is diluted with aluminium hydroxide which precipitates the aluminium hydroxide leaving behind sodium silicate in solution.

$$Na[Al(OH)_4] \xrightarrow{H_2O} Al(OH)_3 + NaOH$$

Or

$$Na[Al(OH)_4]\,(aq) \xrightarrow{H_2O} Al(OH)_3\,(s) + NaOH\,(aq)$$

The aluminium hydroxide is filtered, dried and calcined (heated) at 1473 K to get pure alumina. This process is known as Hall-Heroult process.

$$\underset{\text{aluminium hydroxide}}{2Al(OH)_3} \longrightarrow \underset{\text{pure alumina}}{Al_2O_3} + 3H_2O$$

**Stage-II :** The alumina is dissolved in molten cryolite $Na_3[AlF_6]$ and then electrolysed in a large steel tank lined with graphite which acts as Cathode. The anodes are made of carbon (graphite) on passing current, molten aluminium is produced at Cathode and oxygen gas is evolved at the anode reacts with carbon anode producing CO and $CO_2$. The molten aluminium is drawn from the bottom of the tank.

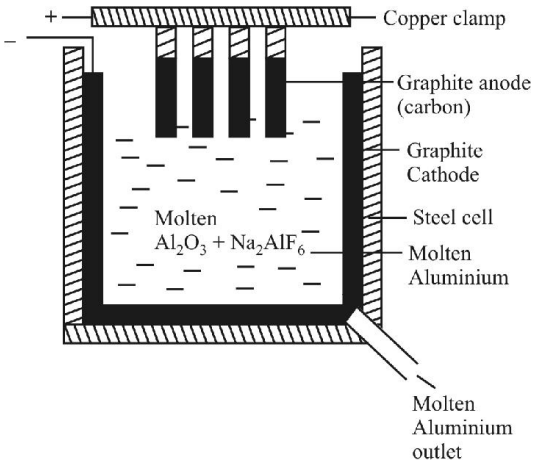
The overall reactions may be written as

**Cathode :** $2Al^{3+}\,(melt) + 6e^- \rightarrow 2Al\,(\ell)$

**Anode :** $C(s) + O^{2-}\,(melt) \rightarrow CO\,(g) + 2e^-$

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

The anodes burn away. Therefore, they must be replaced from time to time.

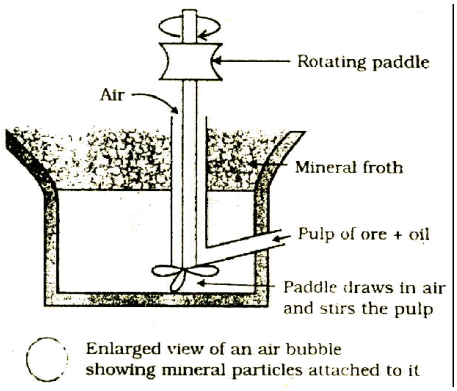



**Electrolytic reduction of alumina**

**Example - 22**

**Explain the Froth Floatation Method.**

**Sol. Froth Floatation Method :**




The method has been in use for removing gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. To it, collectors and froth stabilisers are added. Collectors (e.g., pine oils, fatty acids, xanthates, etc.) enhance non-wettability of the mineral particles and froth stabilisers (e.g., Cresols, aniline) stabilise the froth.

The mineral particles become wet by oils while the gangue particles by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles.

**Example - 23**

**Explain the magnetic separation process.**

**Sol. Magnetic separation process :** This process is based on differences in magnetic properties of the ore components. If either the ore or the gangue (one of these two) is capable of being attracted by a magnetic field, then such separations are carried out (e.g., in case of iron ores). The ground ore is carried on a conveyer belt which passes over a magnetic roller.

**Example - 24**

**Give the names of two chief ores of aluminium.**

**Sol.** (i) Bauxite : $Al_2O_3.H_2O$

(ii) Cryolite : $Na_3AlF_6$

**Example - 25**

**Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.**

**Sol. Extraction of iron :** In the **Blast furnace**, reduction of iron oxides takes place in different temperature. Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto 2200 K in the lower portion itself. The burning of coke supplies most of the heat required in this process. The CO (Carbon monoxide) and heat moves to upper part of the furnace. The temperature is lower in upper part.

The reduction of $Fe_2O_3$ takes place at about 500-800 K

$$\underset{\text{(Iron ore)}}{3Fe_2O_3} + CO \rightarrow 2Fe_3O_4 + CO_2$$

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

At 900-1500 K, the carbon-dioxide reacts with coke to give CO which combine FeO to give Iron.

$$C + CO_2 \rightarrow 2\,CO$$

$$FeO + CO \rightarrow Fe + CO_2$$

Limestone is decomposed to CaO which removes silicate impurity of the ore as slag

$$\underset{\text{(Limestone)}}{CaCO_3} \rightarrow CaO + CO_2$$

$$CaO + SiO_2 \rightarrow \underset{\text{Slag}}{CaSiO_3}$$

The slag is in molten state and separated out from iron.

**Example - 26**

**(a) Write the names of two ores of copper.**

**(b) Which method is commonly used to extract copper.**

**Sol.** (a) Main ores of copper are :

(i) Copper pyrites - $CuFeS_2$

(ii) Copper glance - $Cu_2S$

(iii) Malachite - $CuCO_3Cu(OH)_2$

(b) Commonly used method to extract the copper metal from its ore is roasting of sulphide partially and reduction.

**Example - 27**

**(a) Write the names of any two principal ore of zinc.**

**(b) What are its uses.**

**Sol.** (a) The principal ore of zinc

(i) Zinc blende - ZnS

(ii) Calamine - $ZnCO_3$

(iii) Zincite - ZnO

**(b)** **Uses :** (i) Zinc is used for galvanising iron.

(ii) Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

**Example - 28**

**Write chemical reactions taking place in the extraction of copper from sulphide ores.**

**Sol.** **Extraction of copper from cuprous oxide :** The sulphide ores are roasted to give oxides

$$2\,Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

The oxide can be reduced to metallic copper using coke

$$Cu_2O + C \rightarrow 2\,Cu + CO$$

**Example - 29**

**(a) What are main ores of iron.**

**(b) What is Pig Iron and Cast Iron.**

**(c) Give the uses of cast iron.**

**Sol.** **(a) Main ores of Iron :**

(i) Haematite - $Fe_2O_3$

(ii) Magnetite - $Fe_3O_4$

(b) The iron obtained from Blast furnace contains about 4% carbon and many impurities in smaller amount is known as **Pig Iron**.

**Cast Iron** is made by melting pig iron with scrap iron and coke using hot air blast. It is extremely hard and brittle.

**(c)** **Uses :** (i) Cast Iron is used for casting stoves, railway sleepers, gutter pipes and toys etc.

(ii) It is used in the manufacture of wrought iron and steel.

**Example - 30**

**What is the chief ore of iron ? Write chemical reactions taking place in the extraction of iron from its ore.**

**Sol.** Chief ore of iron is **haematite** $Fe_2O_3$. Iron is obtained by the reduction of its ore, haematite $Fe_2O_3$ in a blast furnace. The iron ore is mixed with coke and limestone to form a mixture. This mixture is known as **Charge**. The charge is then introduced into the blast furnace from the top. A blast of hot air is blown in through the base of furnace.

The following reactions take place in the blast furnace :

(i) The coke combines with oxygen to form carbon dioxide

$$C(s) + O_2(g) \rightarrow CO_2(g) + \text{Heat}$$

(ii) Due to the intense heat in the furnace, limestone $(CaCO_3)$ decomposes to form calcium oxide and carbon dioxide.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

(iii) The carbondioxide reacts with more coke to form carbon monoxide

$$CO_2(g) + C(s) \rightarrow 2\,CO(g)$$

(iv) Iron (III) oxide present in the ore is then reduced by carbon monoxide to form liquid iron. The molten iron is collects at the bottom of the furnace

$$Fe_2O_3(s) + 3\,CO(g) \rightarrow 2Fe(\ell) + 3\,CO_2(g)$$

Liquid Iron metal

(v) Calcium oxide formed in reaction (ii) reacts with silicondioxide present in the ore to form molten calcium silicate known as **slag**

$$CaO(s) + SiO_2(s) \rightarrow Ca\,SiO_3(\ell)$$

**Example - 31**

**(a) Name the principal ore of aluminium.**

**(b) Describe the leaching of aluminium ore.**

**Sol.** (a) The principal ore of aluminium is bauxite, $Al_2O_3.\,x\,H_2O$

(b) **Leaching of alumina from bauxite :** Bauxite, usually contains, $SiO_2$, iron oxides and titanium oxide $(TiO_2)$ as impurities. Concentration is carried out by the digesting the powdered ore with concentrated solution of NaOH at 473 – 523 K and 35 – 36 bar pressure. The $Al_2O_3$ is leached out as sodium aluminate.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(\ell) \rightarrow \underset{\text{Sodium aluminate}}{2Na[Al(OH)_4](aq)}$$

The sodium aluminate is solution is neutralised by passing $CO_2$ gas and hydrated $Al_2O_3$ is precipitated.

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

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give pure $Al_2O_3$

$$\underset{\text{hydrated alumina}}{Al_2O_3.xH_2O\,(s)} \xrightarrow{1470\ K} \underset{\text{pure alumina}}{Al_2O_3\,(s)} + x\,H_2O\,(g)$$

**Example - 32**

**Describe the role of the following :**

**(i) Depressant in Froth floatation process**

**(ii) Silica in the extraction of copper from copper pyrites ore**

**(iii) Cryolite in the metallurgy of aluminium**

**Sol.** (i) In Froth floatation process, the role of the depressant is to prevent one type of sulphide ore particles from forming the froth with air bubble.

(ii) During roasting, copper pyrites are converted into a mixture of FeO and $Cu_2O$

$$\underset{\text{Copper pyrites}}{2CuFeS_2 + O_2} \xrightarrow{heat} Cu_2S + 2FeS + SO_2$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

To remove FeO (basic), an acidic flux silica is added during smelting. FeO then combines with $SiO_2$ to form ferrous silicate ($FeSiO_3$) slag which floats over molten matte.

(iii) The role of cryolite is

(a) to make alumina a good conductor of electricity.

(b) to lowers the fusion (melting point) temperature of the bath from 2323K to about 140 K.

**Example - 33**

**Why is the froth flotation method selected for the concentration of Sulphide ores ?**

**Sol.** Froth flotation method selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

**Example - 34**

**Give reasons for the following :**

**(i) Alumina is dissolved in cryolite for electrolysis instead of being electrolysed directly.**

**(ii) Zinc oxide can be reduced to the metal by heating with carbon but not $Cr_2O_3$.**

**(iii) Extraction of copper directly from sulphide ores is less favourable than that from its oxide ore through reduction.**

**Sol.** (i) Cryolite lowers the melting point of the mixture and improves the electrical conductivity of the cell.

(ii) Since carbon is better reducing agent for reduction of zinc oxide (ZnO).

(iii) It is quite easy to reduce oxide are ($Cu_2O$) directly to metal by heating with coke. However, most of the ores of copper are sulphide ores. These sulphide ores are roasted/smelted to obtain oxide ores.

**Example - 35**

**Describe the role of the following :**

**(i) NaCN in the extraction of silver from a silver ore**

**(ii) Iodine in the refining of titanium**

**(iii) Cryolite in the metallurgy of aluminium**

**Sol.** (i) Role of NaCN in the extraction of silver is to do the leaching of silver ore in the presence of air from which the silver is obtained later by replacement

$$4\,Ag(s) + 8CN^-(aq) + 2\,H_2O\,(aq) + O_2\,(g) \rightarrow 4\,[Ag(CN)_2]^-(aq) + 4\,OH^-(aq)$$

$$2\,[Ag(CN)_2]^-(aq) + Zn\,(s) \rightarrow 2\,Ag\,(s) + [Zn(CN)_4]^{2-}(aq)$$

(ii) Iodine is heated with Titanium to form a volatile compound which on further heating decompose to give pure titanium

$$T_i\,(impure) + 2I_2 \rightarrow T_iI_4 \rightarrow T_i\,(Pure) + 2I_2$$

(iii) Cryolite lowers the melting point of the mixture and improves the electrical conductivity of the cell.

**Example - 36**

**What is meant by the term, 'Chromatography' ? What criterion is followed for the selection of the stationary phase in chromatography ?**

**Sol.** **Chromatography :** It is a technique for the separation and purification based on the differences in the absorbing tendencies of the metal and its impurities on a suitable adsorbent. It is based on the principle that different components of a mixture are differently adsorbed on an adsorbent.

The stationary phase acts as adsorbent and may have the following characteristics :

(i) It should have high and selective adsorption power.

(ii) It should be finely divided to offer greater surface area for adsorption.

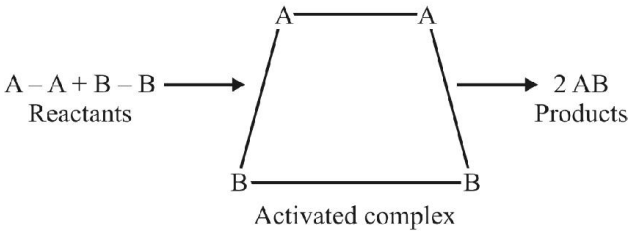
(iii) It should not react chemically either with the sample components.

(iv) It should be pure.

**Example - 37**

**State the role of activated complex in a reaction and state its relation with activation energy.**

**Sol.** **Activated complex :** In order that the reactants may change into products, they have to cross an energy barrier. When the reactant molecules absorb energy, their bonds are loosened and new bonds start forming between them. This highly unstable transition state between reactants and products is called activated complex. If immediately dissociates to form the stable products.




Activation energy = Energy of activated complex – Average energy of reactants

**Example - 38**

**Describe the principle behind each of the following processes**

**(i) Vapour phase refining of a metal.**

**(ii) Recovery of silver after silver ore was leached with NaCN.**

**Sol.** (i) In this method crude metal is freed from impurities by first converting it into a suitable volatile compound by heating it with a specific reagent at a lower temperature and then decomposing the volatile compound at some higher temperature to give the pure metal. Thus, the two requirements are :

- the metal should from a volatile compound with a suitable reagent.

- the volatile compound should be easily decomposable so that the recovery is easy.

(ii) Role of NaCN in the extraction of silver is to do the Leaching of silver ore in the presence of air from which the silver is obtained Later by replacement

$$4Ag(s) + 8\,CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[Ag(CN)_2]^-(aq) + 4\,OH^-(aq)$$

$$2[Ag(CN)_2]^-(aq) + Zn^-(s) \rightarrow 2Ag(s) + [Zn(CN_4)]^{2-}(aq)$$

**Example - 39**

**Explain the role of each of the following in the extraction of metals from their ores :**

**(i) CO in the extraction of nickel.**

**(ii) Zinc in the extraction of silver.**

**(iii) Silica in the extraction of copper.**

**Sol.** **(i) CO in the extraction of nickel :** The $Cu_2O$ line is almost at the top. So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C, $CO_2$ are at much lower positions in the particularly after 500-600 K). However most of the ores are sulphide and some may also contains iron. The sulphide ores are smelted to give oxides.

$$2\,Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

The oxides can then be easily reduced to metallic copper using coke.

$$Cu_2O + C \rightarrow 2Cu + CO$$

**(ii)** **Zinc in the extraction of silver :** The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.

$$ZnO + C \xrightarrow{\text{Coke, } 673\,K} Zn + CO$$

The metal is distilled off and collected by rapid chilling.

(iii) The ore is heated in a reverberatory furnance after mixing with silica. In the furnance, iron oxide slags of as iron silicate and copper is produced in the form of copper matte. This contains $Cu_2S$ and FeS.

$$FeO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

Copper matte is then charged into silica lined convertor. Some silica is also added and hot air blast is blow to convert the remaining $FeS_2$, FeO and $Cu_2S/Cu_2O$ to metallic copper. Following reactions take place :

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO2_2$$

$$FeO + SiO_2 \rightarrow FeSiO_3$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

The solidified copper obtained has blistered appearance due to the evolution of $SO_2$ and so it is called blister copper.

**Example - 40**

**Differentiate between a mineral and an ore.**

**Sol.** **Minerals :** Which are naturally occuring chemical substances in the earth's crust obtainable by mining.

**Ores :** Only a few are viable to be used as sources of that metal. Such minerals are known as ores.

**Example - 41**

**What type of ores can be concentrated by magnetic separation method ?**

**Sol.** These are four types :

1. Hydraulic washing
2. Magnetic separation
3. Froth floatation method
4. Leaching

**Example - 42**

**State the principles of the following methods of refining crude metals**

**(i) Zone refining**

**(ii) Liquation method**

**(iii) Chromatographic method**

**Sol.** **(i) Zone refining :** This method is used for metals which are required in very high purity. For example, extremely pure silicon, germanium, boron, gallium and indium are refined by this method. This method is based in the principle that the impurities are more soluble in the melt than in the solid state of the metal.

**(ii)** **Liquation :** This method is used refining the metals having low-melting points, such as tin, lead, bismuth, etc. In this method, the impure metal is placed on the sloping hearth of the reverberatory furnance and is gently heated in an inert atmosphere of carbon monoxide. The metal melts and flows down leaving the non-fusible impurities (called dross) on the hearth. The pure metal is collected at the bottom of the sloping hearth in a receiver.

**(iii)** **Chromatographic method :** This is a modern method of separation or purification based on the differences in the adsorbing capacities of the metal and its impurities on a suitable adsorbent. This technique of chromatography is based on the principle that different components of a mixture are differently absorbed on an adsorbent. The mixture is put in a liquid or gaseous medium (called moving phase) which is moved through a porous medium (adsorbent called stationary phase).

**Example - 43**

**How can you obtain pure alumina from a bauxite ore associated with silica ? Write the reactions involved in this process.**

**Sol.** "Al" is extracted from bauxite $Al_2O_3.2H_2O$.

(i) concentration of bauxite is done by leaching Process.

(ii) Electrolytic reduction is that the purified bauxite ore mixed with cryolite or $CaF_2$ which lowers its melting point and increases electrical conductivity. Molten mixture is electrolysed using number of graphite rods as anode and carbon lining as cathode.

The graphite anode is useful for reduction of metal oxide to metal.

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

$$Al_2O_3 \xrightarrow{\text{electrolysis}} 2Al^{3+} + 3O^{2-}$$

**At cathode :** $Al^{3+}(\text{melt}) + 3e^- \rightarrow Al(\ell)$

**At anode :** $O^{2-} - 2e^- \rightarrow O$

$$O + O \rightarrow O_2$$

$$C + O_2 \rightarrow CO_2$$

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

**At anode :** $Al \rightarrow Al^{3+} + 3e^-$
(impure)

**At cathode :** $Al^{3+} + 3e^- \rightarrow Al$ (pure)

**Example - 44**

**Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction ?**

**Sol.** The standard Gibbs energy of formation of $Cu_2S$ is more negative than that of $CS_2$ and $H_2S$. Therefore, neither carbon nor hydrogen can reduce $Cu_2S$ to Cu metal. In contrast, $\Delta G^\circ$ of $Cu_2S$ is less negative than that of CO, and hence carbon can easily reduce $Cu_2O$ to Cu.

**Example - 45**

**Out of C and CO, which is a better reducing agent at 673 K ?**

**Sol.** From Ellingham diagram (refer to), it is clear that below 673 K, both C and CO can be used as reducing agent but since CO can be more easily oxidized to $CO_2$ than C to $CO_2$; therefore below 673 K, CO is more stable and hence its oxidation to $CO_2$ is less rapid than that of C to $CO_2$. Therefore, above 673 K, C is a better reducing agent than CO.

**Example - 46**

**How is "cast iron" different from "pig iron" ?**

**Sol.** Pig iron contains 4% carbon and impurities such as P, S, Si, Mn in small amounts, while cast iron is obtained by melting pig iron. It has lesser carbon content (3%) and is more hard and brittle than pig iron.

**Example - 47**

**Why copper matte is put in silica-lined converter ?**

**Sol.** Copper matte is put in silica-lined converter to remove the remaining FeO and FeS present in the matte as slag ($FeSiO_3$).

**Example - 48**

**Why is zinc not extracted from zinc oxide through reduction using CO ?**

**Sol.** Zinc is not extracted from zinc oxide through reduction using CO because the standard Gibbs energy of formation of ZnO from Zn is lower than that of $CO_2$ from CO. So, thermodynamically it is not favorable.

**Example - 49**

**Which metals are generally extracted by the electrolytic processes ? What position these metals generally occupy in the periodic table ?**

**Sol.** Metals such as Al, Mg, that is, which are highly electropositive elements and which lie above in the reactivity series are extracted by electrolytic process. Most of them belong to s-block elements and some metals like Al, belong to p-block elements of the periodic table.

**Example - 50**

**What is meant by the term "chromatography" ?**

**Sol.** Chromatography is used for the separation of mixtures. It is one of the methods used for the refining of the impure metal. The criterion for the selection phase is that the stationary phase should be such that the impurities are more strongly adsorbed or more soluble in the stationary phase than the element to be purified.

**Example - 51**

**Describe the principle involved in each of the following processes of metallurgy :**

**(a) Froth floatation method**

**(b) Electrolytic refining of metals**

**(c) Zone refining of metals**

**Sol.** **(a) Froth floatation method :** The mineral particles become wet by oils, whereas the gangue particles by water.

**(b)** **Electrolytic refining :** Crude metal is made as anode and pure metal as cathode. When current is passed through electrolyte of same metal ions, then pure metal gets deposited at cathode and impurities settle at the bottom of anode.

**(c)** **Zone refining :** The impurities are more soluble in the melt than in the solid state of the metal.

# EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

**1.** Which of the following statements is correct?
(a) All ores are minerals.
(b) All minerals are ores.
(c) A mineral cannot be an ore.
(d) An ore is always obtained in a pure form.

**2.** The impurities present in a mineral are called
(a) gangue (b) flux
(c) froth (d) nuggets

**3.** Concentration of ores is not done by the
(a) gravity separation process
(b) electromagnetic separation process
(c) froth-floatation process
(d) roasting process

**4.** Sulphide ores are generally concentrated by the
(a) gravity separation process
(b) calcination process
(c) froth-floatation process
(d) carbon-reduction process

**5.** In the froth-floatation process, the ore particles float because
(a) they are light
(b) their surface is not easily wetted by water
(c) they bear electrostatic charge
(d) they are insoluble

**6.** Which of the following is a sulphide ore?
(a) Argentite (b) Cuprite
(c) Azurite (d) Cerussite

**7.** Which of the following is a fluoride ore?
(a) Cryolite (b) Carnallite
(c) Feldspar (d) Ilmenite

**8.** The ore of calcium which contains phosphorus is
(a) gypsum (b) talc
(c) fluorapatite (d) asbestos

**9.** Of the following metals, the one which cannot be obtained by the electrolysis of the aqueous solution of its salt is
(a) Ag (b) Mg
(c) Cu (d) Hg

**10.** The electrometallurgical process (electrolysis of fused salts) is employed to extract
(a) lead (b) silver
(c) sodium (d) copper

**11.** In the aluminothermic process, aluminium acts as
(a) an oxidizing agent (b) a reducing agent
(c) a flux (d) a solder

**12.** In the froth-floatation process, the sulphide ores are concentrated by mixing the ore with
(a) water, pine oil and sodium ethyl xanthate
(b) water, wax and benzene
(c) water, benzene and sodium ethyl xanthate
(d) water, matrix and air

**13.** Calcination of ores involves heating the ore below its fusion temperature
(a) in presence of air
(b) in an atmosphere of nitrogen
(c) in absence of air
(d) in presence of superheated steam

**14.** Roasting or ores is done
(a) in absence of air
(b) in presence of a limited supply of air
(c) in presence of superheated steam
(d) in presence of an excess of oxygen

**15.** Which of the following changes takes place during roasting?
(a) Oxidation-reduction
(b) only oxidation
(c) Neither oxidation nor reduction
(d) Expulsion of metals

**16.** By which of the following processes is an oxide ore reduced to the free metal?
(a) Leaching (b) Smelting
(c) Roasting (d) Calcination

**17.** Which one of the following is not a basic flux?
(a) $CaCO_3$ (b) $SiO_2$
(c) CaO (d) MgO

**18.** Which of the following metals cannot be extracted by the carbon reduction process?

(a) Zn (b) Fe

(c) Al (d) Sn

**19.** Which one of the following reactions represents a calcination reaction?

(a) $HgS + O_2 \rightarrow Hg + SO_2$

(b) $Ag_2S + NaCl \rightarrow AgCl + Na_2S$

(c) $CuCO_3\,Cu(OH)_2 \rightarrow CuO + CO_2 + H_2O$

(d) $Al_2O_3 + NaOH \rightarrow NaAlO_2 + H_2O$

**20.** In extractive metallurgy of zinc, partial fusion of ZnO with coke is called

(a) smelting (b) calcination

(c) roasting (d) sintering

**21.** Cassiterite is an ore of

(a) manganese (b) tin

(c) silicon (d) zinc

**22.** The mineral carnallite contains

(a) Ca and Na (b) Ca and Mg

(c) Mg and K (d) Al and K

**23.** In electrorefining of metals, the anode is made of

(a) the impure metal concerned

(b) the pure metal concerned

(c) graphite

(d) silica

**24.** Impure nickel is purified by

(a) the distillation process (b) the Mond process

(c) liquation

(d) the zone-refining process

**25.** Among the following, the most abundant metal in the earth's crust is

(a) Fe (b) Al

(c) Cu (d) Na

**26.** Certain metals can be obtained in the ultrapure state by heating with iodine and then decomposing the metal iodide at a much higher temperature. This method is known as

(a) the van Arkel porocess (b) the Mond process

(c) the liquation process (d) the zone-refining process

**27.** Which of the following metals is refined by the van Arkel process?

(a) Au (b) Cu

(c) Ni (d) Ti

**28.** In the extraction of iron, $Fe_2O_3$ is reduced by

(a) carbon dioxide

(b) aluminium

(c) carbon and carbon monoxide

(d) electrolytic reduction

**29.** Which of the following reactions represents the self-reduction process?

(a) $\begin{cases} HgS + O_2 \rightarrow HgO + SO_2 \\ HgO + HgS \rightarrow Hg + SO_2 \end{cases}$

(b) $\begin{cases} Cu_2S + O_2 \rightarrow Cu_2O + SO_2 \\ Cu_2S + Cu_2O \rightarrow Cu + SO_2 \end{cases}$

(c) $\begin{cases} PbS + O_2 \rightarrow PbO + SO_2 \\ PbO + PbS \rightarrow Pb + SO_2 \end{cases}$

(d) All of these

**30.** Which of the following represents the thermite reaction?

(a) $Mn_3O_4 + Al \rightarrow Mn + Al_2O_3$

(b) $MgCO_3 + SiO_2 \rightarrow MgSiO_3 + CO_2$

(c) $Cu_2S + Cu_2O \rightarrow Cu + SO_2$

(d) $Fe_2O_3 + CO \rightarrow Fe + CO_2$

**31.** Which of the following ligands is used to form the complex from which silver is extracted?

(a) NaCNS (b) $NH_3$

(c) NaCN (d) NaCNO

**32.** Among the following, the maximum amount of carbon is present in

(a) pig iron (b) steel

(c) wrought iron (d) Invar

**33.** The metal which is extracted by electrolytic reduction is

(a) Sn (b) Pb

(c) Zn (d) Ca

**34.** The liquation process is used for the purification of

(a) Sn (b) Al

(c) Zn (d) Hg

**35.** The distillation process (under reduced pressure) is used for the purification of

(a) Pb (b) Hg

(c) Sn (d) Cs

**36.** During the electrolytic production of aluminium, the carbon anodes are replaced from time to time because

(a) the carbon anodes get decayed

(b) the carbon prevents atmospheric oxygen from coming in contact with aluminium

(c) oxygen liberated at the carbon anodes reacts with anodes to form $CO_2$

(d) carbon converts $Al_2O_3$ to Al

**37.** Electrolytic reduction of alumina to aluminium by the Hall-Heroult process is carried out

(a) in the presence of NaCl

(b) in the presence of fluorite

(c) in the presence of cryolite which forms a melt at lower temperature and increases the electrical conductivity

(d) in the presence of cryolite which forms a melt at higher temperature and increases the electrical conductivity

**38.** The main function of roasting is

(a) to remove the volatile impurities

(b) to oxidize the metal

(c) to reduce the metal oxide

(d) to make a slag

**39.** The van Arkel method for purification of metals involves the conversion of the metal into a

(a) volatile stable compund

(b) volatile unstable compound

(c) nonvolatile stable compound

(d) metal carbonyl

**40.** Which method of purification is represented by the following equation?

$$Ti + 2I_2 \xrightarrow{773K} TiI_4 \xrightarrow{1675K} Ti + 2I_2$$

(a) Cupellation (b) Poling

(c) Van Arkel method (d) Zone-refining process

**41.** Which of the following minerals contains calcium as well as magnesium?

(a) Tridymite (b) Aragonite

(c) Dolomite (d) Carnallite

**42.** Which of the following mixtures is called matter?

(a) $CuO + Cu_2S$ (b) $PbS + PbSO_4$

(c) $Cu_2S + FeO$ (d) $Cu_2S + FeS$

**43.** Blister copper is obtained in

(a) Bessemer converter (b) blast furnace

(c) muffle furnace (d) reverberatory furance

**44.** Copper and lead are mainly extracted by

(a) electrolysis

(b) the carbon reduction process

(c) the self-reduction process

(d) the thermite process

**45.** A flux is often added to remove impurites from an ore in a blast furnace. In the reaction

$$CaO + SiO_2 \rightarrow CaSiO_3$$

the slag and the flux are

(a) $CaSiO_3$ and $SiO_2$ (b) $CaSiO_3$ and CaO

(c) CaO and $SiO_2$ (d) $SiO_2$ and $CaSiO_3$

**46.** The cyanide process is used for the extraction of

(a) Cu (b) Ag

(c) Zn (d) Al

**47.** Wolframite ($FeWO_4$), present as an impurity in cassiterite ($SnO_2$), can be removed by the process of

(a) froth floatation

(b) gravity separation

(c) electromagnetic separation

(d) zone refining

**48.** The zone-refining process for purification of metals is based on

(a) the difference in volatilities of the metal and the impurities

(b) the difference in fusibilities of the metal and the impurities

(c) the difference in solubilities of the impurities in the molten and solid states of the metal

(d) the difference in the oxidizabilities of the metal and the impurities

# EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTION

**1.** Of the following metals the one which cannot be obtained by electrolysis of the aqueous solution of its self : **(1990)**

(a) Ag (b) Mg

(c) Cu (d) Al

**2.** Cryotite is the ore of : **(1991)**

(a) Al (b) Cu

(c) Ag (d) Fe

**3.** Carbonate of which of the following metal does not liberate carbon dioxide on heating: **(1992)**

(a) Li (b) Mg

(c) Na (d) Ca

**4.** Calcium is obtained by : **(1995)**

(a) Roasting of lime stone

(b) Electrolysis of calcium chloride in $H_2O$

(c) Electrolysis of molten anhydrous calcium chloride

(d) Reduction of calcium chloride with carbon

**5.** Fused cryolite is used in the elctrolytic extraction of aluminium : **(1997)**

(a) To decomposes alumina

(b) To oxidise alumina

(c) To protect anode

(d) To protect cathode

**6.** Which of the following metals is obtained by elctrolytic reduction process : **(1998)**

(a) Fe (b) Cu

(c) Ag (d) Al

**7.** Aluminium is not present in which of the following mineral ? **(1999)**

(a) Cryolite (b) Felsper

(c) Fluosper (d) Mica

**8.** Among the following statements, the incorrect one is : **(2000)**

(a) Calamine and siderite are carbonates

(b) Argentite and cuprite are oxides

(c) Zinc blende and pyrites are sulphides

(d) Malachite and azurite are ores of copper

**9.** Which of the following properties of pure metal makes them more useful than alloys : **(2002)**

(a) They are more harder than alloys

(b) They have high density

(c) Can be extracted very easily

(d) Conduct heat and electricity very easily

**10.** Aluminium is extracted by the electrolysis of **(2002)**

(a) alumina (b) bauxite

(c) molten cryolite

(d) alumina mixed with molten cryolite

**11.** Which one is the ore of iron : **(2003)**

(a) Cuprite (b) Magnetitie

(c) Bauxite (d) None of these

**12.** The solubilities of carbonates decrease down the magnesium group due to a decrease in **(2003)**

(a) entropy of solution formation

(b) lattice energies of solids

(c) hydration energies of cations

(d) inter-ionic attraction

**13.** One mole of magnesium nitride on the reaction with an excess of water gives **(2004)**

(a) one mole of ammonia

(b) two moles of nitric acid

(c) two moles of ammonia

(d) one mole of nitric acid

**14.** Which one of the following ores is best concentrated by froth-flotation method ? **(2004)**

(a) Magnetite (b) Malachite

(c) Galena (d) Cassiterite

**15.** During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are **(2005)**

(a) Fe and Ni (b) Ag and Au

(c) Pb and Zn (d) Sn and Ag

**16.** Several blocks of magnesium are fixed to the bottom of a ship to **(2006)**

(a) prevent puncturing by under-sea rocks

(b) keep away the sharks

(c) make the ship lighter

(d) prevent action of water and salt

**17.** Cyanide process is used for the extraction of **(2006)**

(a) barium (b) silver

(c) boron (d) zinc

**18.** Refining of impure copper with zinc impurity is to be done by electrolysis using electrodes as **(2007)**

| | **Cathode** | **Anode** |
|---|---|---|
| (a) | pure copper | pure zinc |
| (b) | pure zinc | pure copper |
| (c) | pure copper | impure copper |
| (d) | pure zinc | impure zinc |

**19.** Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly **(2008)**

(a) Metal sulphides are thermodynamically more stable than $CS_2$

(b) $CO_2$ is thermodynamically more stable than $CS_2$

(c) Metal sulphides are less stable than the corresponding oxides.

(d) $CO_2$ is more volatile than $CS_2$

**20.** In forth floatation process for the purification of ores, the particles of ore float because: **(2010)**

(a) Their surface is not easily wetted by water

(b) They are light

(c) They are insoluble

(d) They bear electrostatic charge

**21.** In the context of the Hall - Heroult process for the extraction of Al, which of the following statements is false ? **(2015)**

(a) $Al^{3+}$ is reduced at the cathode to form Al

(b) $Na_3AlF_6$ serves as the electrolyte

(c) CO and $CO_2$ are produced in this process

(d) $Al_2O_3$ is mixed with $CaF_2$ which lowers the melting point of the mixture and brings conductivity

**22.** Which one of the following ores is best concentrated by froth floatation method ? **(2016)**

(a) Siderite (b) Galena

(c) Malachite (d) Magnetite

## JEE MAINS ONLINE QUESTION

**1.** Which one of the following ores is known as Malachite ? **Online 2014 SET (4)**

(a) $Cu_2S$ (b) $CuFeS_2$

(c) $Cu_2O$ (d) $Cu(OH)_2.CuCO_3$

**2.** Calamine is an ore of : **Online 2015 SET (1)**

(a) Zinc (b) Aluminium

(c) Iron (d) Cooper

**3.** Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false.

(i) Every mineral is an ore but every ore is not a mineral.

(ii) Slag is product formed during extraction of metal by combination of flux and impurities.

(iii) Highly pure metals can be obtained by zone refining.

(iv) Carnallite is an ore of magnesium and sodium.

**Online 2016 SET (1)**

(a) TTTF (b) FTTF

(c) FTTT (d) TFTF

**4.** Extraction of copper by smelting uses silica as an additive to remove : **Online 2016 SET (2)**

(a) $Cu_2S$ (b) FeO

(c) FeS (d) $Cu_2O$

**5.** The transition metal ions responsible for color in ruby and emerald are, respectively : **Online 2016 SET (2)**

(a) $Cr^{3+}$ and $Co^{3+}$ (b) $Co^{3+}$ and $Cr^{3+}$

(c) $Co^{3+}$ and $Co^{3+}$ (d) $Cr^{3+}$ and $Cr^{3+}$

**6.** In the leaching method, bauxite ore is digested with a concentrated solution of NaOH that produces 'X'. When $CO_2$ gas is passed through the aqueous solution of 'X', a hydrated compound 'Y' is precipitated. 'X' and 'Y' respectively are : **Online 2018 SET (2)**

(a) $NaAlO_2$ and $Al_2(CO_3)_3$Å"x $H_2O$

(b) $Al(OH)_3$ and $Al_2O_3$Å"x $H_2O$

(c) $Na[Al(OH)_4]$ and $Al_2O_3$Å"x $H_2O$

(d) $Na[Al(OH)_4]$ and $Al_2(CO_3)_3$Å"x $H_2O$

**7.** In the extraction of copper from its sulphide ore, metal is finally obtained by the oxidation of cuprous sulphide with : **Online 2018 SET (3)**

(a) $Fe_2O_3$ (b) $Cu_2O$

(c) $SO_2$ (d) CO

# EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. All questions marked **"S"** are single choice questions
2. All questions marked **"M"** are multiple choice questions
3. All questions marked **"C"** are comprehension based questions
4. All questions marked **"A"** are assertion–reason type questions

   **(A)** If both assertion and reason are correct and reason is the correct explanation of assertion.

   **(B)** If both assertion and reason are true but reason is not the correct explanation of assertion.

   **(C)** If assertion is true but reason is false.

   **(D)** If reason is true but assertion is false.
5. All questions marked **"X"** are matrix–match type questions
6. All questions marked **"I"** are integer type questions

**1. (S)** Which of the following pair of ores cannot be converted into corresponding metals by pyrometallurgy?

(a) $Ag_2S$, ZnS (b) $Cu_2S$, HgS

(c) $MnO_2$, $SnO_2$ (d) None of these

**2. (S)** Which of the following minerals does not contain iron?

(a) Magnetite (b) Magnesite

(c) Haematite (d) Limonite

**3. (S)** The two most abundant metals in the earth crust are:

(a) Al, Zn (b) Ag, Au

(c) Fe, Cu (d) Fe, Al

**4. (S)** The metal which mainly occurs as oxide ore in nature is:

(a) Silver (b) Lead

(c) Aluminium (d) Copper

**5. (S)** Chemical leaching is useful in the concentration of:

(a) Copper pyrite (b) Bauxite

(c) Cassiterite (d) Cinnabar

**6. (S)** Which of the following reaction forms the basis of Goldschmidt alumino-thermite process?

(a) $2Al + N_2 \rightarrow 2AlN$ (b) $2Al + 3Cl_2 \rightarrow 2AlCl_3$

(c) $2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$

(d) $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$

**7. (S)** Copper is extracted from sulphide ore using the method:

(a) carbon reduction

(b) carbon monoxide reduction

(c) auto reduction

(d) none of these

**8. (S)** Silver can be separated from lead by:

(a) fractional crystallisation

(b) amalgamation

(c) cupellation

(d) addition of zinc (Parke's method)

9. **(S)** Which of the following pair is incorrectly matched?

(a) van Arkel method — Zirconium

(b) Kroll's process — Titanium

(c) Froth Floatation — Cerussite

(d) Distillation — Zinc

**10. (S)** Formation of metallic copper from the sulphide ore in the commercial metallurgical process involves.

(a) $Cu_2S+\frac{3}{2}O_2 \rightarrow Cu_2O+SO_2;\ Cu_2O+C \rightarrow 2Cu+CO$

(b) $Cu_2S+\frac{3}{2}O_2 \rightarrow Cu_2O+SO_2;\ 2Cu_2O+Cu_2S \rightarrow 6Cu+SO_2$

(c) $Cu_2S+2O_2 \rightarrow CuSO_4;\ CuSO_4+Cu_2S \rightarrow 3Cu+2SO_2$

(d) $Cu_2S+\frac{3}{2}O_2 \rightarrow Cu_2O+SO_2;\ Cu_2O+CO \rightarrow 2Cu+CO_2$

**11. (S)** Blister copper is refined by stirring molten impure metal with green logs of wood because such a wood liberates hydrocarbon gases (like $CH_4$). This Process X is called ..... and the metal contains impurities of Y is .....

(a) X = cupellation, Y = $CuO_2$

(b) X = polling, Y = $Cu_2O$

(c) X = polling, Y = CuO

(d) X = cupellation, Y = CuO

**12. (S)** The anode mud in the electrolytic refining of silver contains:

(a) Zn, Cu, Ag, Au (b) Zn, Ag, Au

(c) Cu, Ag, Au (d) Au only

**13. (S)** Boron can be obtained by various methods but not by:

(a) thermal decomposition of $B_2H_6$

(b) pyrolysis of $BI_3$ (van Arkel)

(c) reducing $BCl_3$ with $H_2$

(d) electrolysis of fused $BCl_3$

**14. (S)** Select correct statement:

(a) The decomposition of an oxide into oxygen and metal vapour entropy increases

(b) Decomposition of an oxide is an endothermic change

(c) To make $\Delta G^0$ negative, temperature should be high enough so that $T\,\Delta S^0 > \Delta H^0$

(d) All are correct statement:

**15. (S)** Consider the following metallurgical processes:

(I) Heating impure metal with CO and distilling the resulting volatile carbonyl (b.p. $43^0$C) and finally decomposition at $150^0$-$200^0$C to get the pure metal

(II) Heating the sulphide ore in air until a part is converted to oxide and then further heating in the absence of air to let the oxide react with unchanged metal sulphide

(III) Electrolysis of the molten electrolyte containing approximately equal amounts of the metal chloride and NaCl to obtained the metal

The processes used for obtaining magnesium nickel and copper are respectively:

(a) I, II and III (b) II, III and I

(c) III, I and II (d) II, I and III

**16. (M)** Which of the following metal (s) is/are commercially extracted by self reduction method from their corresponding ore?

(a) Cu (b) Fe

(c) Pb (d) Hg

**17. (M)** Which of the following process makes the ore porous?

(a) Roasting (b) Calcination

(c) Reduction (d) Distillateion

**18. (M)** Which of the following ores is/are oxide ore (s)?

(a) Tinstone (b) Bauxite

(c) Cryolite (d) Carnallite

**19. (M)** Roasting of copper pyrites is done:

(a) to remove moisture (b) to oxidise free sulphur

(c) to decompose pyrite into $Cu_2S$ and FeS

(d) to remove volatile organic impurities

**20. (M)** Which of the following is a correct statement?

(a) Calamine is the ore of zinc

(b) Pyrolusite is the ore of manganese

(c) Cassiterite is the ore of tin

(d) Calcite is the ore of calcium

**21. (M)** Which of the following pair consists of ore of the same metal?

(a) Bauxite, Limonite (b) Haematite, Siderite

(c) Cinnabar, Cassiterite (d) Galena, Cerrusite

**22. (M)** The process (es) by which lighter earthy particles are freed from the heavier particles using water is/are:

(a) Gravity separation (b) Levigation

(c) Hydraulic washing (d) Leaching

**23. (M)** Roasting is carried out to:

(a) Convert sulphide to oxide and sulphate

(b) remove water of hydration

(c) melt the ore

(d) remove arsenic and sulphur impurities

**24. (M)** The chemical treatment of the ore for concentration is done in the case of:

(a) aluminium (b) silver

(c) copper (d) gold

**25. (M)** Froth floatation:

(a) is a physical method of separating mineral from the gangue

(b) is a method to concentrate the ore depending on the difference in wetability of gangue and the ore

(c) is used for the sulphide ores

(d) is a method in which impurities sink to the bottom

**26. (M)** Which of the following reaction (s) occur during calcination?

(a) $CaCO_3 \rightarrow CaO + CO_2$

(b) $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

(c) $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

(d) $CuS + CuSO_4 \rightarrow 2Cu + 2SO_2$

**27. (M)** Amphoteric nature of aluminium is employed in which of the following process for extraction of aluminium?

(a) Baeyer's process (b) Hall's process

(c) Serpek's process (d) Dow's process

**28. (M)** Which of the following is true for calcination of a metal ore?

(a) It makes the ore more porous

(b) The ore is heated to a temperature when fusion just begins

(c) Hydrated salts lose their water of crystallisation

(d) Impurities of S, As and Sb are removed in the form of their volatile oxides

**29. (M)** The difference (s) between roasting and calcination is are:

(a) roasting is highly endothermic while calcination is not

(b) partial fusion occurs in calcination but not in roasting

(c) calcination is performed in limited amount of air but roasting employs excess air

(d) combustion reaction occur in roasting but not in calcination

**30. (M)** The extraction of metals from oxide ores involve:

(a) Reduction with carbon

(b) Reduction with aluminium

(c) Electrolyte reduction

(d) Reduction with CO

**31. (M)** Metals which can be extracted by smelting process are:

(a) Pb (b) Fe

(c) Zn (d) Al

**32. (M)** In the extraction of aluminium metal, one of the process is summarised as follows:

$$\underset{\substack{\text{(bauxite)}\\ \text{Impure}}}{Al_2O_3.3H_2O} \xrightarrow[\text{concentrated 'A'}]{\text{hot}} \underset{\text{(aqueous soln.)}}{\text{Product 'B'}} \xrightarrow[\text{to change pH}]{\text{bubble gas 'C'}} \underset{Al_2O_3.3H_2O}{\text{Pure}}$$

$$\text{Aluminium at 'E'} \xleftarrow[\text{with carbon electrodes}]{\text{electrolyse molten material}} \left|\begin{array}{l}\text{mix with 'D'}\\ \text{melt at } 1000^0\text{C}\end{array}\right.$$

Which of the following entries correctly summarises reagents, electrodes & products of the process?

| | I | II | III | IV | V |
|---|---|---|---|---|---|
| (a) | NaOH | $Al^{3+}$ | HF | $Na_3AlF_6$ | Cathode |
| (b) | NaOH | $NaAlO_2$ | $CO_2$ | NaF | Anode |
| (c) | $H_2SO_4$ | $Al_2(SO_4)_3$ | $NH_3$ | $Na_3AlF_6$ | Cathode |
| (d) | NaOH | $NaAlO_2$ | $CO_2$ | $Na_3AlF_6$ | Cathode |

**33. (M)** The smelting of iron in a blast furnace involves the following processes:

(a) combustion (b) reduction

(c) slag formation (d) sublimation

**34. (M)** Which one of the following metals can be extracted by aluminothermic process?

(a) Manganese (b) Iron

(c) Chromium (d) Magnesium

**35. (M)** For which of the following metal, the carbon reduction cannot be used?

(a) Lead (b) Manganese

(c) Tungsten (d) Iron

**36. (M)** The advantage (s) of using carbon to reduce a number of oxides and other compounds are:

(a) easy availability of coke

(b) low cost of carbon

(c) tendency of carbon to show catenation

(d) presence of carbon lowers the melting point of the oxides

**37. (M)** The disadvantage of carbon reduction method are:

(a) high temperature needed which is expensive and requires the use of a blast furnace

(b) many metals combine with carbon forming carbides

(c) carbon combines with oxygen to form poisonous CO

(d) carbon cannot be used with highly electropositive metals

**38. (M)** Which of the following metals are extracted from its ore by using self-reduction method?

(a) Copper (b) Mercury

(c) Lead (d) Silver

**39. (M)** The function of adding cryolite in the electrolytic reduction of alumina by Hall-Heroult process is to :

(a) dissolve alumina

(b) lower the melting point of alumina

(c) lower the fuel bill

(d) increase the electrical conductivity of alumina

**40. (M)** Which of the following reduction reactions are actually employed in commercial extraction of metals?

(a) $Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$

(b) $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$

(c) $2Na\,[Au\,(CN)_2] + Zn \rightarrow Na_2\,[Zn\,(CN)_4] + 2Au$

(d) $Cu_2S + Pb \rightarrow Cu + PbS\downarrow$

**41. (M)** The chief reaction(s) occurring in blast furnace during extraction of iron from haematite is/are:

(a) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

(b) $FeO + SiO_2 \rightarrow FeSiO_3$

(c) $Fe_2O_3 + C \rightarrow 2Fe + 3CO$

(d) $CaO + SiO_2 \rightarrow CaSiO_3$

**42. (M)** Which of the following are true for electrolytic extraction of aluminium?

(a) Cathode material contains graphite

(b) Anode material contains graphite

(c) Cathode reacts away forming $CO_2$

(d) Anode reacts away forming $CO_2$

**43. (M)** Highly electropositive metals can not be extracted by carbon reduction process because these:

(a) Metals combine with carbon to form carbides

(b) Metals do not react with carbon

(c) Metal oxides are not reduced by carbon

(d) Loss of metal is more by vaporisation

**44. (M)** Which of the following reaction in the blast furnace is/are endothermic?

(a) $C(s) + O_2(g) \rightleftharpoons CO_2(g)$

(b) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

(c) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(d) $Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(l) + 3CO_2(g)$

**45. (M)** Pick up the correct statement (s)

(a) All minerals are ores

(b) All minerals cannot be an ore

(c) All ores are minerals

(d) The minerals from which metals can be extracted profitably are called ores

**46. (X)**

| Column-I | Columan-II |
|---|---|
| (A) Ca | (p) Found as its native state |
| (B) Zn | (q) Found as its sulphide |
| (C) Cr | (r) Found as its carbonate |
| (D) Ag | (s) Found as its oxide |

**47. (X)**

| Column-I | Columan-II |
|---|---|
| (A) Poling | (p) Titanium |
| (B) Cupellation | (q) Copper |
| (C) Electro-refining | (r) Silver |
| (D) van Arkel method | (s) Tin |

**48. (X)**

| Column-I | Columan-II |
|---|---|
| (A) Metal which occur in the native state in nature is | (p) Hg |
| (B) The oxides of metal that can be commercially reduced by Alumino-thermic reduction process is | (q) Ti |
| (C) Van Arkel method is used for preparing ultrapure metal of | (r) Cr |
| (D) Auto reduction process is employed for the sulphide ore of | (s) Ag |

**49. (X)**

| Column-I | Columan-II |
|---|---|
| (A) Mond's process | (p) $Cr_2O_3 + 2Al \xrightarrow{\Delta} 2Cr + Al_2O_3$ |
| (B) van Arkel process | (q) $TiCl_4 + 2Mg \xrightarrow{\Delta} Ti + 2MgCl_2$ |
| (C) Thermite process | (r) $Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO$ |
| (D) Kroll's process | (s) $ZrI_4 \xrightarrow{\Delta} Zr + 2I_2$ |

**50. (A)** **Assertion :** Ores are generally converted into oxides, prior to reduction.

**Reason :** Metal oxides can be easily reduced.

(a) A (b) B

(c) C (d) D

**51. (A)** **Assertion :** In the extraction of Ag, complex Na [Ag $(CN)_2$] is reacted with Zn.

**Reason :** Zn is d-block transition metal.

(a) A (b) B

(c) C (d) D

**52. (A)** **Assertion :** Thermite mixture $Fe_2O_3$ + Al (powder) is used in the welding.

**Reason :** Al is a good reductant.

(a) A (b) B

(c) C (d) D

**53. (A)** **Assertion :** In froth floatation process sodium ethyl xanthate is used as collector.

**Reason :** Sulphide ores are water soluble.

(a) A (b) B

(c) C (d) D

**54. (A)** **Assertion :** Cryolite is used in electrolytic extraction of Al from alumina.

**Reason :** It dissolves alumina.

(a) A (b) B

(c) C (d) D

**55. (A)** **Assertion :** $CuFeS_2$ is concentrated by froth floatation method.

**Reason :** $CuFeS_2$ is main ore of copper.

(a) A (b) B

(c) C (d) D

**56. (A)** **Assertion :** In the electrolytic reduction of $Al_2O_3$, cryolite is used.

**Reason :** Cryolite is an ore of aluminium.

(a) A (b) B

(c) C (d) D

**57. (A)** **Assertion :** Wrought iron is more malleable and ductile than steel.

**Reason :** It contains slightly less percentage of carbon.

(a) A (b) B

(c) C (d) D

**58. (A)** **Assertion :** Lead, tin and bismuth are purified by liquation method.

**Reason :** Lead, tin and bismuth have low m.p. as compared to impurities.

(a) A (b) B

(c) C (d) D

**59. (A)** **Assertion :** $Al_2O_3$ is converted into Al by reduction with carbon at high temp.

**Reason :** Carbon has greater affinity for oxygen than aluminium.

(a) A (b) B

(c) C (d) D

**60. (A)** **Assertion :** All the ores are mineral.

**Reason :** Ores contains metals in combined state

(a) A (b) B

(c) C (d) D

# EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTION

## Objective Questions (Only One correct option)

**1.** Iron is rendered passive by treatment with concentrated **(1982)**

(a) $H_2SO_4$ (b) $H_3PO_4$

(c) HCl (d) $HNO_3$

**2.** In metallurgy of iron, when lime stone is added to the blast furnace, the calcium ion ends up in **(1982)**

(a) slag (b) gangue

(c) metallic calcium (d) calcium carbonate

**3.** Type of bonds present in $CuSO_4.5H_2O$ are only **(1983)**

(a) electrovalent and covalent

(b) electrovalent and coordinate covalent

(c) electrovalent, covalent and coordinate covalent

(d) covalent and coordinate covalent

**4.** In the alumino-thermite process, aluminium acts as **(1983)**

(a) an oxidizing agent (b) a flux

(c) a reducing agent (d) a solder

**5.** Hydrogen gas will not reduce **(1985)**

(a) heated cupric oxide

(b) heated ferric oxide

(c) heated stannic oxide

(d) heated aluminium oxide

**6.** The major role of fluorspar ($CaF_2$) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite ($Na_3AlF_6$) is **(1993)**

(a) as a catalyst

(b) to make the fused mixture very conducting

(c) to increase the temperature of the melt

(d) to decrease the rate of oxidation of carbon at the anode

**7.** In the commercial electrochemical process for aluminium extraction, the electrolyte used as **(1999)**

(a) $Al(OH)_3$ in NaOH solution

(b) an aqueous solution of $Al_2(SO_4)_3$

(c) a molten mixture of $Al_2O_3$ and $Na_3AlF_6$

(d) a molten mixture of AlO (OH) and Al $(OH)_3$

**8.** The chemical process in the production of steel from haematite ore involve **(2000)**

(a) reduction (b) oxidation

(c) reduction followed by oxidation

(d) oxidation followed by reduction

**9.** Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out **(2000)**

(a) in the presence of NaCl

(b) in the presence of fluorite

(c) in the presence of cryolite which forms a melt with lower melting temperature

(d) in the presence of cryolite which forms a melt with higher melting temperature

**10.** The chemical composition of 'slag' formed during the smelting process in the extraction of copper is **(2001)**

(a) $Cu_2O + FeS$ (b) $FeSiO_3$

(c) $CuFeS_2$ (d) $Cu_2S + FeO$

**11.** Which of the following processes is used in extractive metallurgy of magnesium ? **(2002)**

(a) Fused salt electrolysis (b) Self reduction

(c) Aqueous solution electrolysis

(d) Thermite reduction

**12.** Anhydrous ferric chloride is prepared by **(2002)**

(a) Heating hydrated ferric chloride at a high temperature in a stream of air

(b) Heating metallic iron in a stream of dry chlorine gas

(c) Reaction of ferric oxide with hydrochloric acid

(d) Reaction of metallic iron with hydrochloric acid

**13.** In the process of extraction of gold, **(2003)**

$$\text{Roasted gold ore} + CN^- + H_2O \xrightarrow{O_2} [X] + HO$$

$$[X] + Zn \longrightarrow [Y] + Au$$

Identify the complexes [X] and [Y]

(a) $X = [Au(CN)_2]^-$, $Y = Zn(CN)_4]^{2-}$

(b) $X = [Au(CN)_4]^{3-}$, $Y = [Zn(CN)_4]^{2-}$

(c) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_6]^{4-}$

(d) $X = [Au(CN)_4]^-$, $Y = [Zn(CN)_4]^{2-}$

**14.** The methods chiefly used for the extraction of lead and tin from their ores are respectively **(2004)**

(a) self reduction and carbon reduction

(b) self reduction and electrolytic reduction

(c) carbon reduction and self reduction

(d) cyanide process and carbon reduction

**15.** Which ore contains both iron and copper ? **(2005)**

(a) Cuprite (b) Chalcocite

(c) Chalcopyrite (d) Malachite

**16.** Extraction for zinc from zinc blende is achieved by **(2007)**

(a) electrolytic reduction

(b) roasting followed by reduction with carbon

(c) roasting followed by reduction with another metal

(d) roasting followed by self-reduction

**17.** Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of **(2008)**

(a) nitrogen (b) oxygen

(c) carbon dioxide (d) argon

## Objective Questions (One or more than one correct option)

**18.** In the electrolysis of alumina, cryolite is added to **(1986)**

(a) lower the melting point of alumina

(b) increase the electrical conductivity

(c) minimise the anode effect

(d) remove impurities from alumina

**19.** Of the following, the metals that cannot be obtained by electrolysis of the aqueous solution of their salts are **(1990)**

(a) Ag (b) Mg

(c) Cu (d) Al

**20.** Addition of high proportions of manganese makes steel useful in making rails **(1998)**

(a) gives hardness to steel

(b) helps the formation of oxides of iron

(c) can remove oxygen and sulphur

(d) can show highest oxidation state of + 7

**21.** Upon heating with $Cu_2S$, the reagent(s) that give copper metal is/are **(2014)**

(a) $CuFeS_2$ (b) CuO

(c) $Cu_2O$ (d) $CuSO_4$

**22.** Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is (are) **(2015)**

(a) Impure Cu strip is used as cathode

(b) Acidified aqueous $CuSO_4$ is used as electrolyte

(c) Pure Cu deposits at cathode

(d) Impurities settle as anode-mud

**23.** Extraction of copper from copper pyrite ($CuFeS_2$) involves **(2016)**

(a) crushing followed by concentration of the ore by froth-flotation

(b) removal of iron as slag

(c) self-reduction step to produce 'blister copper' following evolution of $SO_2$

(d) refining of 'blister copper' by carbon reduction.

## Assertion and Reason

A) If both ASSERTION and REASON are true and reason is the correct explanation of the assertion.

(B) If both ASSERTION and REASON are true but reason is not the correct explanation of the assertion.

(C) If ASSERTION is true but REASON is false.

(D) If ASSERTION is false but REASON is true.

**24.** **Assertion :** $Al(OH)_3$ is amphoteric in nature.

**Reason :** Al—O and O—H bonds can be broken with equal ease $Al(OH)_3$. **(1998)**

(a) A (b) B

(c) C (d) D

## Match the Columns

**25.** Match the following metals listed in column I with extraction processes listed in column II. **(1979)**

| | **Column I** | **Column II** |
|---|---|---|
| (A) | Silver | (p) Fused salt electrolysis |
| (B) | Calcium | (q) Carbon reduction |
| (C) | Zinc | (r) Carbon monoxide reduction |
| (D) | Iron | (s) Amalgamation |
| (E) | Copper | (t) Self reduction |

**26.** Match the following choosing one item from column X and the appropriate item from column Y. **(1983)**

| | **Column X** | **Column Y** |
|---|---|---|
| (A) | Al | (p) Calamine |
| (B) | Cu | (q) Cryolite |
| (C) | Mg | (r) Malachite |
| (D) | Zn | (s) Carnalite |

**27.** Each entry in column X is in some way related to the entries in columns Y and Z. Match the appropriate entries. **(1988)**

| **Column X** | **Column Y** | **Column Z** |
|---|---|---|
| (A) Invar | (p) Co, Ni | (m) Cutlery |
| (B) Nichrome | (q) Fe, Ni | (n) Heating element |
| (C) Stainless steel | (r) Fe, Cr, Ni | (o) Watch spring |

**28.** Match the extraction processes listed in column I with metals listed in column II. **(2006)**

| | **Column I** | **Column II** |
|---|---|---|
| (A) | Self reduction | (p) Lead |
| (B) | Carbon reduction | (q) Silver |
| (C) | Complex formation and displacement by metal | (r) Copper |
| (D) | Decomposition of iodide | (s) Boron |

**29.** Match the conversions in column I with the type(s) of reaction(s) given in column II. **(2008)**

| | **Column I** | **Column II** |
|---|---|---|
| (A) | $PbS \longrightarrow PbO$ | (p) Roasting |
| (B) | $CaCO_3 \longrightarrow CaO$ | (q) Calcination |
| (C) | $ZnS \longrightarrow Zn$ | (r) Carbon reduction |
| (D) | $Cu_2S \longrightarrow Cu$ | (s) Self reduction |

**30.** Match each of the reactions given in column I with the corresponding product(s) given in column II. **(2009)**

| | **Column I** | **Column II** |
|---|---|---|
| (A) | Cu + dil. $HNO_3$ | (p) NO |
| (B) | Cu + conc. $HNO_3$ | (q) $NO_2$ |
| (C) | Zn + dil. $HNO_3$ | (r) $N_2O$ |
| (D) | Zn + conc. $HNO_3$ | (s) $Cu(NO_3)_2$ |
| | | (t) $Zn(NO_3)_2$ |

## Fill in the Blanks

**31.** AgCl dissolve in excess of KCN solution to give ..... complex compound. **(1980)**

**32.** In the basic Bessemer process for the manufacture of steel, the lining of the converter is made up of ..... The slag formed consists of ..... **(1980)**

**33.** In the thermite process ..... is used as a reducing agent. **(1980)**

**34.** Cassiterite is an ore of ..... **(1980)**

**35.** Galvanization of iron denote coating with ..... **(1983)**

**36.** Silver chloride is sparingly soluble in water because its lattice energy greater than ..... energy. **(1987)**

**37.** In the extractive metallurgy of zinc, partial fusion of ZnO with coke is called ..... and reduction of the ore to the molten metal is called ..... (smelting, calcining, roasting, sintering). **(1988)**

**38.** Silver jewellery items tarnish slowly in the air due to their reaction with ..... **(1997)**

## True/False

**39.** Silver fluoride is fairly soluble in water. **(1982)**

**40.** Dilute HCl oxidises metallic Fe to $Fe^{2+}$. **(1983)**

**41.** Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water. **(1984)**

**42.** $Cu^{+}$ disproportionate to $Cu^{2+}$ and elemental copper in solution. **(1991)**

## Subjective Questions

**43.** Write balanced equation involved in the preparation of tin metal from cassiterite. **(1979)**

**44.** Write the chemical equations involved in the extraction of lead from galena by self reduction process. **(1979)**

**45.** State the conditions under which the preparation of alumina from aluminium is carried out. Give the necessary equations which need not be balanced. **(1983)**

**46.** Give reason for the following in one or two sentences :

"Silver bromide is used in photography." **(1983)**

**47.** Each of the following statement is true, only under some specific conditions. Write the condition for each subquestion in not more than two sentences.

(i) Metals can be recovered from their ores by chemical methods.

(ii) High purity metals can be obtained by zone refining method. **(1984)**

**48.** Write balanced chemical equation for the following

"Gold is dissolved in aqua regia." **(1987)**

**49.** Answer the following questions briefly

(i) What is the actual reducing agent of haematite in blast furnace ?

(ii) Give the equation for the recovery of lead from galena by air reduction.

(iii) Why is sodium chloride added during electrolysis of fused anhydrous magnesium chloride ?

(iv) Zinc, not copper is used for the recovery of metallic silver from complex $[Ag(CN)_2]^-$, explain.

(v) Why is chalcocite roasted and not calcinated during recovery of copper ? **(1987)**

**50.** Give balanced equations for the extraction of "Silver from silver glance by cyanide process." **(1988)**

**51.** Write balanced equation for the extraction of "Copper from copper pyrites by self reduction." **(1990)**

**52.** Complete and balance the following reaction :

Copper reacts with $HNO_3$ to give NO and $NO_2$ in the molar ratio of 2 : 1

$Cu + HNO_3 \longrightarrow ..... + NO + NO_2 + .....$ **(1992)**

**53.** Give briefly the isolation of magnesium from sea water by the Dow's process.

Give equations for the steps involved. **(1993)**

**54.** Complete the following reaction :

$Sn + 2KOH + 4H_2O \longrightarrow ..... + .....$ **(1994)**

**55.** Give reasons for the following

"Although aluminium is above hydrogen in the electro-chemical series, it is stable in air and water." **(1994)**

**56.** Write a balanced equation for the reaction of argentite with KCN and name the products in the solution. **(1996)**

**57.** Give balance equation for the reaction of aluminium with aqueous sodium hyroxide. **(1997)**

**58.** When the ore haematite is burnt in air with coke around 2000ºC along with lime, the process not only produces steel but also produces a silicate slag, that is useful in making building materials such as cement. Discuss the same and show through balanced chemical equations. **(1998)**

**59.** Work out the following using chemical equations.

(i) In moist air, copper corrodes to produce a green layer on the surface. **(1998)**

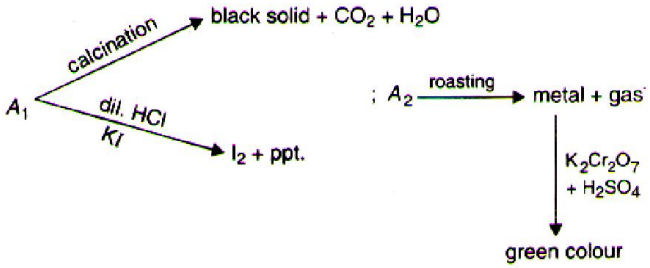
**60.** Write the chemical reactions involved in the extraction of silver from argentite. **(2000)**

**61.** Write the balanced chemical equation for developing photographic films. **(2000)**

**62.** Write the balanced chemical reactions involved in the extraction of lead from galena. Mention oxidation state of lead in litharge. **(2003)**

**63.** Which of the two, anhydrous or hydrated $AlCl_3$ is more soluble in diethyl ether ? Justify using the concepts of bonding in not more than 2 or 3 sentences. **(2003)**

**64.** $A_1$ and $A_2$ are two ores of metal M. $A_1$ on calcination gives black precipitate, $CO_2$ and water.




Identify $A_1$ and $A_2$. **(2004)**

**65.** Write balanced chemical equation for developing a black and white photographic film. Also give reason, why the solution of sodium thiosulphate on acidification turns milky white and give balance equation of this reaction. **(2005)**

**66.** Give the number of water molecule (s) directly bonded to the metal centre in $CuSO_4.5H_2O$. **(2009)**

**67.** Give the coordination number of Al in the crystalline state of $AlCl_3$. **(2009)**

# ANSWER KEY

## EXERCISE - 1 : (Basic Objective Questions)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** (a) | **2.** (a) | **3.** (d) | **4.** (c) | **5.** (b) | **6.** (a) | **7.** (a) | **8.** (c) |
| **9.** (b) | **10.** (c) | **11.** (b) | **12.** (a) | **13.** (c) | **14.** (d) | **15.** (a) | **16.** (b) |
| **17.** (b) | **18.** (c) | **19.** (c) | **20.** (d) | **21.** (b) | **22.** (c) | **23.** (a) | **24.** (b) |
| **25.** (b) | **26.** (a) | **27.** (d) | **28.** (c) | **29.** (d) | **30.** (a) | **31.** (c) | **32.** (a) |
| **33.** (d) | **34.** (a) | **35.** (b) | **36.** (c) | **37.** (c) | **38.** (a) | **39.** (a) | **40.** (c) |
| **41.** (c) | **42.** (d) | **43.** (a) | **44.** (c) | **45.** (a) | **46.** (b) | **47.** (c) | **48.** (c) |

## EXERCISE - 2 : (Previous year JEE Mains Questions)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** (b) | **2.** (a) | **3.** (c) | **4.** (c) | **5.** (a) | **6.** (d) | **7.** (c) | **8.** (b) |
| **9.** (d) | **10.** (d) | **11.** (b) | **12.** (c) | **13.** (c) | **14.** (c) | **15.** (b) | **16.** (d) |
| **17.** (b) | **18.** (c) | **19.** (c) | **20.** (a) | **21.** (b) | **22.** (b) | | |

### JEE Mains Online

| | | | | | | |
|---|---|---|---|---|---|---|
| **1.** (d) | **2.** (a) | **3.** (b) | **4.** (b) | **5.** (d) | **6.** (c) | **7.** (b) |

## EXERCISE - 3 : (Advanced Objective Questions)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** (a) | **2.** (b) | **3.** (d) | **4.** (c) | **5.** (b) | **6.** (d) | **7.** (c) | **8.** (d) |
| **9.** (c) | **10.** (b) | **11.** (b) | **12.** (d) | **13.** (d) | **14.** (d) | **15.** (c) | **16.** (acd) |
| **17.** (ab) | **18.** (ab) | **19.** (abcd) | **20.** (abcd) | **21.** (bd) | **22.** (abc) | **23.** (abd) | **24.** (abd) |
| **25.** (abcd) | **26.** (ac) | **27.** (ab) | **28.** (ac) | **29.** (cd) | **30.** (abcd) | **31.** (abc) | **32.** (d) |
| **33.** (abc) | **34.** (abc) | **35.** (bc) | **36.** (ab) | **37.** (ab) | **38.** (abc) | **39.** (abcd) | **40.** (bc) |
| **41.** (ad) | **42.** (abd) | **43.** (ad) | **44.** (bc) | **45.** (bcd) | **46.** A — r; B — q, r, s ; C — s; D — p, q) | | |
| **47.** (A — q, s; B — r; C — q, r, s; D — p) | | | **48.** (A — s; B — r; C — q; D — p) | | | | |
| **49.** (A — r; B — s; C — p; D — q) | | | **50.** (c) | **51.** (c) | **52.** (b) | **53.** (c) | **54.** (a) |
| **55.** (b) | **56.** (b) | **57.** (a) | **58.** (a) | **59.** (c) | **60.** (c) | | |

## EXERCISE - 4 : (Previous year JEE ADVANCED Questions)

**1.** (d) **2.** (a) **3.** (c) **4.** (c) **5.** (d) **6.** (b) **7.** (c) **8.** (a)

**9.** (c) **10.** (b) **11.** (a) **12.** (b) **13.** (a) **14.** (a) **15.** (c) **16.** (b)

**17.** (b) **18.** (a, b) **19.** (b, d) **20.** (a, c) **21.** (b,c) **22.** (b,c,d) **23.** (a,b,c,d)

**24.** (a) **25.** A – s; B – p; C – q; D – q, r; E – t

**26.** A – q; B – r; C – s; D – p **27.** A – q, o; B – p, n; C – r, m

**28.** A – p, r; B – p; C – q; D – s **29.** A – p; B – q; C – r, s; D – p, s

**30.** A – p, s; B – q, s; C – r, t; D – q, t **31.** $K[Ag(CN)_2]$ **32.** Lime, calcium phosphate **33.** Al

**34.** Sn **35.** Zn **36.** Hydration **37.** Sintering, smelting **38.** $H_2S$ **39.** (T) **40.** (T)

**41.** (T) **42.** (T)

***Dream on !!***