06

General Principles and Processes of Isolation of Metals

Metals in their pure form are of great importance. These are utilisated for the synthesis of several compounds, for making articles (as alloys) etc. However, most of metals due to their high reactivity found in the combined form. So, it is necessary to extract metal from the compound.
This chapter deals with the various principles and processes used during the extraction process.

IN THIS CHAPTER ....

Modes of Occurrence of Elements in Nature

Based on their reactivity, elements (metals) generally occur in nature in two forms, i.e.

(i) In native state
(ii) In combined state

Less reactive metals are found in **native state** (free state) in nature, e.g. Ag, Au, Pt etc. Sometimes, Cu is also found in free state. Such metals are not attacked by O_2, H_2O, CO_2 etc.

Reactive metals are found in **combined state** in nature, e.g. of such metals include Na, Ca, Mg, Fe, Cu, Zn, Al etc. Such metals are attacked by O_2, H_2O, CO_2 etc.

Earth crust is a source of many elements. Oxygen is present in the most abundance in the earth crust. Among metals, Al is the most abundant metal of earth crust and Fe comes second. The percentage of different elements in the earth crust is O-49%; Si-26%; Al-7.5%; Fe-4.2%; Ca-3.2%; Na-2.4%; K-2.3%; Mg-.3%; H-1%; other elements-2%.

Besides earth crust, some soluble salts of metals, such as NaCl, $MgCl_2$, KBr, $MgBr_2$, KI etc., are also found in sea water.

Remember In earth crust metals are generally not found as their nitrates because of their high solubility in water.

Minerals, Ores and Matrix

The natural material in the form of which the metal is found in nature is called **mineral** and those minerals from which a metal can be extracted conveniently, economically and in large quantity are called **ores**. Thus, we can say that **all the ores are minerals but all the minerals are not ores**.

Common ores/minerals of some important metals are given as follows

Ores of Some Metals

Metal	Ore/Mineral	Formula
Li	Spodumene	$LiAlSi_2O_6$
	Lepidolite	$(Li, Na, K)_2Al_2(SiO_2)_3F(OH)$
Na	Common salt	NaCl (rock salt)
	Chile salt petre	$NaNO_3$
	Glauberite	$Na_2SO_4 \cdot 10H_2O$ (Glauber's salt)
	Borax	$Na_2B_4O_7 \cdot 10H_2O$
	Trona	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$
	Soda ash	Na_2CO_3
	Feldspar	$NaAlSi_3O_8$
K	Sylvine	KCl
	Nitre	KNO_3 (salt petre)
	Schonite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$
Mg	Magnesite	$MgCO_3$
	Dolomite	$MgCO_3 \cdot CaCO_3$
	Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$
	Epsom salt	$MgSO_4 \cdot 7H_2O$
	Asbestos	$CaMg_3(SiO_3)_4$
	Talc	$Mg_2(Si_2O_5)_2Mg(OH)_2$
Ca	Gypsum	$CaSO_4 \cdot 2H_2O$
	Limestone	$CaCO_3$
	Phosphorite	$Ca_3(PO_4)_2$
	Fluorspar	CaF_2
Al	Bauxite	$Al_2O_3 \cdot 2H_2O$
	Diaspore	$Al_2O_3 \cdot H_2O$
	Corundum	Al_2O_3
	Cryolite	Na_3AlF_6
	Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
	Mica	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$
Sn	Cassiterite	SnO_2 (tin stone)
Pb	Galena	PbS
	Cerussite	$PbCO_3$
	Anglesite	$PbSO_4$
	Lanarkite	$PbO \cdot PbSO_4$
Cu	Chalcopyrite	$CuFeS_2$ (copper pyrites)
	Chalcocite	Cu_2S (copper glance)
	Cuperite	Cu_2O (rubby copper)
	Azurite	$2CuCO_3 \cdot Cu(OH)_2$
	Malachite	$CuCO_3 \cdot Cu(OH)_2$
Ag	Argentite	Ag_2S (silver glance)
	Cerargyrite	AgCl (horn silver)
	Pyrargyrite	$Ag_2S \cdot Sb_2S_3$ (ruby silver)
Fe	Haematite	Fe_2O_3 (red haematite)
	Limonite	$Fe_2O_3 \cdot 3H_2O$ (brown haematite)
	Magnetite (lead stone)	Fe_3O_4 (magnetic oxide of iron)
	Siderite	$FeCO_3$
	Iron pyrite	FeS_2
Hg	Cinnabar	HgS
Zn	Zinc blende	ZnS (black zinc or sphalerite)
	Calamine	$ZnCO_3$
	Zincite	ZnO (red zinc)
	Willemite	Zn_2SiO_4
Mn	Pyrolusite	MnO_2
	Manganite	$Mn_2O_3 \cdot H_2O$
Cr	Chromite	$Cr_2O_3 \cdot FeO$

Metallic ores are often found to contain certain non-metallic rocky substances in them, e.g. sand, clay, quartz, feldspar, silicates, mica, etc. These unwanted impurities are called **gangue** or **matrix.** Thus, the waste material present in an ore is called **gangue.**

Metallurgy

The process of extracting a metal in pure form its ores is known as **metallurgy**. Metallurgical processes can be of following three types i.e. hydrometallurgy, pyrometallurgy and electrometallurgy.

(i) **Hydrometallurgy** The metal present in ore forms soluble salt and comes in solution which is then recovered from the solution either by electrolysis or through precipitation by adding some suitable more electropositive metal in the solution. It is generally applicable for less reactive metals like AgBr or highly reactive metals like Al.

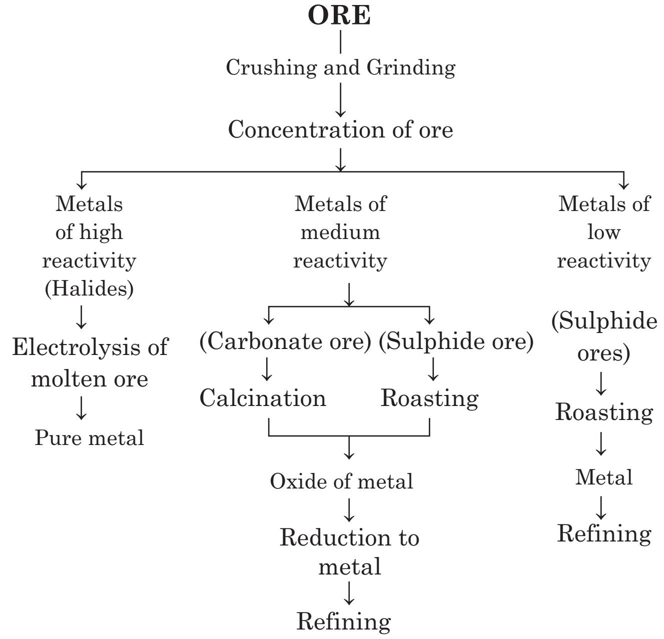
(ii) **Pyrometallurgy** Generally refers to the extraction through heat. Roasting, calcination, smelting etc., processes are included in it. Generally it is applicable for moderately active metals like Cu, Pb, Zn, Fe, etc.

(iii) **Electrometallurgy** Metal is generally extracted with the help of electrolysis. It is applicable for highly reactive metals like Na, K, Al, etc.

Steps Involved in Extraction of Metals

It is not possible to chalk out a universal scheme for the extraction of all metals since the extraction of each metal is an individual problem and the line of treatment depends upon the nature of the ore, impurities and the metal.

The various metallurgical operations used in the extraction of pure metals from their respective ores are given below



Steps involved in the extraction of metals from ores

Crushing and Grinding of the Ore

Generally, ores occur in nature as huge lumps. They are crushed into small pieces in gyratory crushers. The crushed ore is then grinded with the help of rollers or in the stamp mill to powder form.

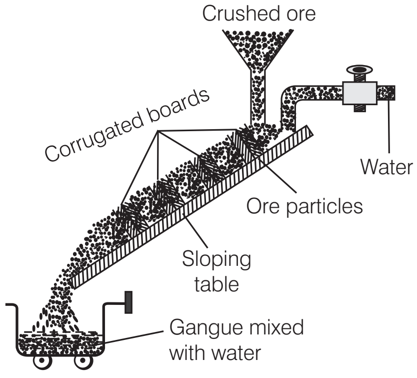
Concentration of the Ore

The process of gangue removal or increase in concentration of ore depends upon the nature of ore and the impurities present in it.

Some of the important methods involved are

1. Gravity Separation or Levigation

Principle The principle of this method is based on the difference in the specific gravity of the metallic ore and the impurity particles.



Concentration of ore by levigation

Process In this method, the ore is powdered and then washed in a running stream of water. The lighter earthy material and gangue are washed away, while the heavy ore particles remain behind. The oxide ores of iron Fe_2O_3 and Fe_3O_4 are concentrated by this method. This method is also called **levigation.**

2. Froth Floatation Process

Principle The principle of this method is based on the difference in the wetting properties of the ore and gangue.

- Ore is preferentially wetted by oil.
- Gangue is preferentially wetted by water.

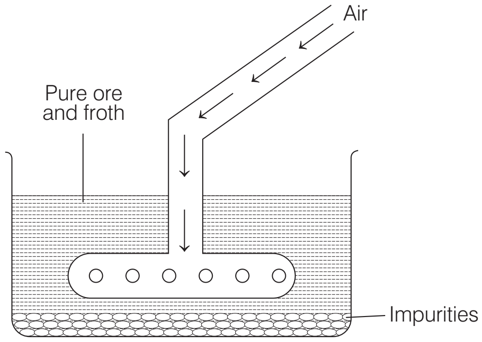
Process In this process, powdered ore is mixed with water containing collectors and froth stabilisers. The mineral particles become wet with oil while the gangue particles by water. A stream of hot compressed air is passed which agitates the mixture and produces froth.

Froth carries mineral particles. The froth is light and is skimmed off. It is then dried for recovery of ore particles.

The details of various chemical substances which help in froth floatation process are given below

(i) **Collector** Chemical substance that enhances non-wettability of mineral particles, e.g. pine oils, fatty acids, xanthates etc.

(ii) **Froth stabilisers** Chemical substance which are used stabilise the froth, e.g. cresols, aniline etc.



Froth floatation process for the concentration of sulphide ores

The sulphide ores of Cu, Ag, Zn, Pb, etc., are concentrated by this process.

It is possible to separate two sulphide ores by adjusting proportion of oil to water or by using **activator** and depressants.

(iii) **Activators** (e.g. $CuSO_4$) **and depressants** (e.g. NaCN, KCN etc.) are the compounds which activate and depress respectively the floating property of one of the components of the ore and thus, help in the separation of different minerals present in the same ore.

The best example of these reagents can be illustrated in the separation of galena PbS, which is usually associated with sphalerite ZnS and pyrites FeS_2.

Example 1. *The idea of froth floatation method came from a person X and this method is related to the process Y of ores. X and Y, respectively, are* ***(JEE Main 2019)***

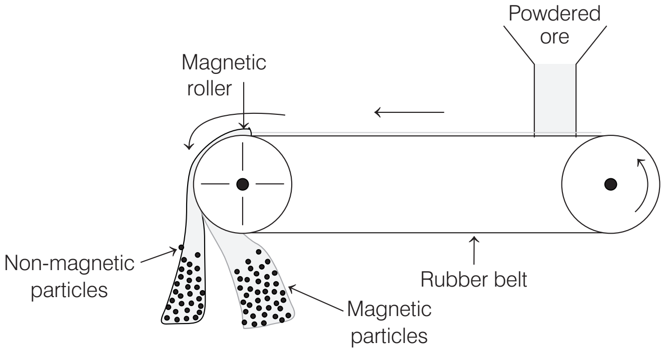
(a) fisher woman and concentration
(b) washer woman and concentration
(c) fisher man and reduction
(d) washer man and reduction

Sol. (*b*) The idea of froth floatation method came from a person 'washer woman' (*X*) and this method is related to the process concentration (*Y*) of ores.

This method is based upon the preferential wetting properties with the frothing agent (collector) and water.

3. Magnetic Separation

Principle The principle of this process is based on the magnetic properties of the ore and the gangue. If the ore or the impurity is magnetic then this process is used to separate the magnetic substance from non-magnetic substance.



An electromagnetic separator, used to concentrate the ore

Process The ore is concentrated by a magnetic separator which consists of a leather belt moving over two rollers. One of the roller is magnetic. The method is useful for separating tungsten ore particles from cassiterite (SnO_2). The process may also be employed for separating other transition metal ores like magnetite (Fe_3O_4), chromite ($FeO \cdot Cr_2O_3$) and pyrolusite (MnO_2) from unwanted gangue.

4. Leaching

Principle Principle of this process is based on the differene in the chemical properties of ore and gangue.

Process It involves the treatment of the ore with a suitable reagent, so as to make it soluble while impurities remain insoluble.

The ore is recovered from the solution by suitable chemical methods. Some important examples of leaching are as follows

(i) In **Bayer's process** pure aluminium oxide is obtained from the bauxite ore by treating the powdered ore with a concentrated solution of NaOH resulting in dissolution of Al_2O_3, leaving the impurities behind as,

$$Al_2O_3(s) + 2OH^-(aq) + 3H_2O \longrightarrow 2Al(OH)_4^-(aq)$$

(ii) Similarly, the **leaching method** is also employed in concentrating Ag and Au ores with the help of their dissolution in NaCN or KCN or Cu with the help of H^+ or Fe scraps. This process is called as **Mac Arthur Forest's cyanide process**.

In case of gold, $O_2(g)$ oxidises free metal to Au^+, which complexes with CN^-.

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

The pure metal is then displaced from the solution by active metal (as Zn).

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

In this reaction, Zn act as reducing agent.

Conversion of Concentrated Ore to Oxide

The concentrated ore, if not an oxide, is converted into oxide because oxides can be reduced easily as compared to sulphides and other such compounds.

The concentrated ore is converted into its oxide by following two ways

1. Roasting

The concentrated ore is heated alone or mixed with some other substance, below its melting point in the presence of air, resulting in oxidation of ore and impurities. This type of specialised heating of concentrated ore is called roasting. Usually the sulphide ores undergo roasting.

In the process of roasting in general, normally the impurities like As and S are oxidised to volatile oxides like SO_2, As_2O_3 etc., and removed.

Some examples of roasting are

(i) In **extraction of iron** as

$$S + O_2 \longrightarrow SO_2\uparrow$$
$$4As + 3O_2 \longrightarrow 2As_2O_3\uparrow$$
$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

Here, sulphur and arsenic impurities are removed as volatile oxides due to roasting, while any ferrous oxide present is converted to ferric oxide.

(ii) Zinc blende (ZnS) is roasted to give ZnO in the extraction of Zn as

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

(iii) On roasting, the copper ore chalcopyrite ($CuFeS_2$), the impurities S and As present in it are removed as volatile SO_2 and $As_2O_3 \cdot CuFeS_2$ is converted into cuprous sulphide and ferrous sulphide as

$$S + O_2 \longrightarrow SO_2\uparrow$$
$$4As + 3O_2 \longrightarrow 2As_2O_3\uparrow$$
$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

Some part of cuprous sulphide and ferrous sulphide is converted into Cu_2O and FeO as

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$$
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

2. Calcination

The hydroxide and carbonate ores after concentration does not undergo roasting, these are subjected to calcination instead.

In the process of calcination, the ore is heated below its melting point in the absence of air or in the limited supply of air. Such a heating results in conversion of these hydroxide and carbonate ores to metal oxides.

During calcination, the ore becomes porous, and volatile impurities are removed.

Some examples of calcination are given below

(i) Aluminium hydroxide is converted to alumina as,

$$2Al(OH)_3 \xrightarrow{1500°C} Al_2O_3 + 3H_2O$$

(ii) Limonite (iron ore) gives anhydrous ferric oxide as,

$$Fe_2O_3 \cdot 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$$

(iii) Siderite (iron ore) gives ferrous oxide as,

$$FeCO_3 \xrightarrow{\Delta} FeO + CO_2$$

(iv) Calamine (zinc ore) gives zinc oxide as,

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$

(v) $NaHCO_3$ gives Na_2CO_3 and $CaCO_3$ gives CaO as,

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

It must be noted that calcination proceeds only with the expulsion of some small molecules like H_2O, CO_2, SO_2, etc., without any other chemical change while during roasting definite chemical changes like oxidation, chlorination etc., takes place.

Calcination and roasting also make the mass porous, so that it can easily be reduced to the metallic state in the next operation.

Calcination and roasting are carried out in various types of furnaces, most important of which is **reverberatory furnace**. The furnaces used in calcination and roasting employ refractory materials which resist high temperature and do not become soft.

Acidic refractories : SiO_2 and $SiO_2 + Al_2O_3$

Basic refractories : CaO and MgO

Neutral refractories : Graphite, chromites, carborundum (SiC).

Refractory material should not combine with the ore or the metal and must be able to protect the furnace from high temperature.

Principles Involved in the Extraction of Metals

Extraction of metal from its ore depends upon thermodynamic as well as electrochemical principles, which are as follows.

1. Electrochemical Principles Involved in Extraction/Reduction of Oxide to Metal

Once the ore has been concentrated, it is reduced to free metal. Selection of the method employed for the extracting metal from its ore depends on the nature of the metal and that of the ore and may be related to the position of the metal in the electrochemical series.

In general, metals with $E° < -1.5$ V yield compounds which are very difficult to reduce. On the other hand, noble metals with $E° > +0.5$ V form easily reducible compounds.

In general, a metal higher up in the electrochemical series should be more difficult to reduce to metallic form. However, this general statement cannot be strictly applied because metals are rarely extracted from aqueous solution. Some of the important method for reduction of roasted/calcined oxide are given below

Smelting

Smelting is a process of extracting metals like Fe, Zn, Sn, Pb, Cr etc.

- The reducing agent usually work on the oxide to extract the metal for, e.g. in the extraction of iron.
- The mixture of oxide with carbon is heated in the presence of air at high temperature and this heating is called **smelting.**

Flux and Slag

Sometime oxide ores contain some infusible earthy impurities even after concentration. The impurities may **be basic** (i.e. metallic oxides like CaO, FeO, MgO etc.) or **acidic** (i.e. non-metallic oxides like SiO_2, P_2O_5, etc.). In order to remove acidic or basic impurities, the concentrated ore is mixed with additional substance, called the **flux.**

The flux combines with acidic or basic impurities present in the oxide ore and forms a fusible mass, called **slag.** Thus, the impurity is removed in the form of fusible slag as

$$\text{Flux} + \text{Impurity} \longrightarrow \text{Fusible slag}$$

Coke or CO reduces oxide ore to free metal, e.g.

$$PbO + C \longrightarrow Pb\text{ (molten lead)} + CO\uparrow$$

$$PbO + CO \xrightarrow[\text{temperature}]{\text{High}} Pb\text{ (molten lead)} + CO_2\uparrow$$

$$Fe_2O_3\text{(haematite)} + 3CO \longrightarrow 2Fe\text{(spongy iron)} + 3CO_2\uparrow$$

$$SnO_2\text{(tinstone)} + 2C \longrightarrow Sn\text{ (molten tin)} + 2CO\uparrow$$

The slag floats over the molten metal and can be removed from upper exit. Smelting is carried out in blast furnaces or reverberatory furnace.

Fluxes are of two types, i.e.

(i) **Acidic fluxes** Basic impurities are mixed with acidic fluxes such as silica (SiO_2) and borax, hence removing them as fusible slag. e.g.

$$SiO_2 + FeO \longrightarrow CaSiO_3$$

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

(ii) **Basic fluxes** Basic fluxes (such as limestone, magnesite, haematite) are added to remove acidic impurities such as silica as fusible slag, e.g.

$$MgCO_3 + SiO_2 \longrightarrow MgSiO_3 + CO_2\uparrow$$
$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2\uparrow$$

Reducing Agent and Process Used in Smelting

Various reducing agent and process used in smelting are as follows

(i) Reduction by Carbon and Carbon Monoxide

In case of tin, the concentrated ore is mixed with one-fifth of its weight of powdered anthracite (carbon) and a little limestone, $CaCO_3$ and heated in a reverberatory furnace at 1200-1300°C.

The ore is reduced to metallic state while silica (impurity) is removed as slag.

$$SnO_2 + 2C \longrightarrow Sn + 2CO\uparrow$$

$$CaCO_3 \xrightarrow[-CO_2]{\Delta} CaO \xrightarrow{SiO_2} \underset{\substack{\text{Calcium silicate}\\ \text{(slag)}}}{CaSiO_3}$$

Carbon (as coal, coke, charcoal, CO etc.,) reduces many metal oxides into respective metals, such as

$$\underset{\text{Cassiterite}}{SnO_2} + 2C \xrightarrow{1473\text{-}1573\text{ K}} Sn + 2CO$$

$$ZnO + CO \xrightarrow{1600\text{ K}} Zn + CO_2$$

$$Fe_2O_3 + CO \xrightarrow{823\text{ K}} 2FeO + CO_2$$

$$FeO + CO \xrightarrow{1123\text{ K}} Fe + CO_2$$

Excess of lime must be avoided because it would otherwise react with tin to form calcium stannate.

The molten metal collects on the bottom of the furnace. It contains 99.5% of metallic tin, called the **black tin.**

Remember

- Some ores are self-fluxing because they contain some gangue (stony matrix accompanying the ore) which is self fusible and thus, no foreign flux is required.
- Blast furnace is used in the reduction of iron oxides while reverberatory furnace is used in the reduction of tin oxide.

(ii) Reduction with Hydrogen

Hydrogen being inflammable is used as a reducing agent in very few cases, e.g.

$$MO_3 + 3H_2 \longrightarrow M + 3H_2O \qquad (M = \text{Mo or W})$$

This method is not widely used, because many metals react with H_2 at elevated temperatures forming hydrides. Also there are chances of explosion of H_2 with O_2.

(iii) Gold schmidt Aluminothermic Process

Chromium and manganese oxides are reduced through aluminothermic reduction processes or Goldschmidt aluminothermic process, e.g.

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

In this process, mixture of the metallic oxide and reducing agent (aluminium powder), commonly known as **thermite** is taken in a steel crucible placed in a bed of sand. A mixture of aluminium powder and barium peroxide (BaO_2) is placed over the charge in the form of a heap and magnesium wire is embedded in it.

The charge is covered by a thick layer of carbon followed by a thin layer of feldspar to avoid loss of heat and to protect the mass from oxidation. The magnesium ribbon, which acts as a fuse is lighted. It starts burning and hence, mixture also starts burning.

Since, the reaction is highly exothermic, once it starts, it goes on till all the oxide is converted into metal.

(iv) Reduction by Water Gas

It is applied for nickel oxide.

$$2NiO + CO + H_2 \longrightarrow 2Ni + CO_2 + H_2O$$

(v) Reduction with Other Metals

Na and Mg metals are used in certain cases as reducing agents, e.g.

$$TiO_2 + 2Mg \longrightarrow Ti + 2MgO$$
$$TiO_2 + 4Na \longrightarrow Ti + 2Na_2O$$

2. Auto-reduction or Self Reduction

This process is also known as **self reduction.** This is used when no external reducing agent is required. The sulphide ores of less electropositive metals like Hg, Pb, Cu etc., are heated in air to either convert the complete ore or part of the ore into oxide or sulphate which then reacts with the remaining sulphide ore to give the metal and sulphur dioxide, e.g.

(i) Extraction of Cu from copper glance

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$$

(ii) Extraction of Hg from cinnabar

$$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$$
$$2HgO \xrightarrow{\Delta} 2Hg + O_2$$

(iii) Extraction of Pb from galena

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$2PbO + PbS \longrightarrow 3Pb + SO_2$$

Remember Oxides of metals lying below Hg (and that of Hg) in electrochemical series, i.e. oxides of Ag, Pd, Pt, Au decompose on heating giving metal.

3. Displacement Method

If the temperature needed for carbon to reduce an oxide is too high for economic or practical purpose, the reduction may be affected by another highly electropositive metal. In this process, more electropositive metal displaces less electropositive metal from salt solution.
e.g. Ag and Au are obtained from their complex cyanides (cyanide process) when more reactive Zn metal displaces them as,

$$2M(CN)_2^- + Zn \longrightarrow Zn(CN)_4^{2-} + 2M$$

(where, M = Ag, Au)

4. Electrolytic Method

The oxides of highly electropositive metals of group 1 and 2 cannot be reduced easily with carbon at moderate temperatures. These metals are thus, extracted by the electrolysis of their salts (generally, oxides, hydroxides or chlorides in fused state). The metal is liberated at the cathode. e.g. Sodium is obtained by the electrolysis of fused NaCl or brine.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$Na^+ + e^- \longrightarrow Na \quad \text{(at cathode)}$$

$$Cl^- \longrightarrow Cl + e^- \quad \text{(at anode)}$$

$$Cl + Cl \longrightarrow Cl_2$$

In the case of NaCl (brine solution), Hg electrodes are used so that Na metal after deposition at cathode forms amalgam with Hg.

Metals other than those of *s*-block can also be extracted by electrolysis of fused compounds, e.g. fused Al_2O_3 mixed with Na_3AlF_6 is used for the production of Al.

Remember Electrolysis can be carried out in solvents other than water. F_2 reacts violently with H_2O hence, it is produced by electrolysis of KHF_2 in HF.

Refining of Crude Metal

Metals extracted through any of the methods described above are usually contain some impurities.

Following methods are used to purify the metals

1. Distillation Method

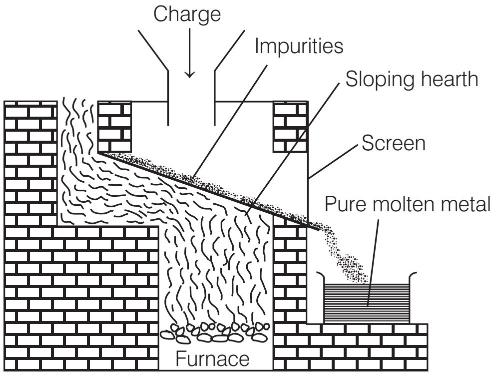
This process is used for those metals which are easily volatile. In this method, the impure metal is heated in a retort and its vapours are separately condensed in a receiver. The non-volatile impurities are left behind in the retort. This is used for the purification of Zn, Cd, Hg, etc.

2. Liquation Method

Low melting metals can be separated by this method. In this method, the impure metal is poured on the sloping hearth of a reverberatory furnance and heated gently to a temperature slightly above the melting point of the metal.

The pure molten metal runs out leaving behind the infusable matter (called dross) on the hearth. This is used for the purification of Bi, Sn, Pb, Hg, etc.

The process of equation is shown below



Liquation method

3. Electrolysis

Many metals such as Cu, Ag, Au, Al, Pb etc., are purified by this method. Here,

Anode ⟶ impure metal

Cathode ⟶ pure metal

Electrolyte ⟶ salt of metal in aqueous solution

On passing electric current, pure metal deposits on cathode. The equivalent mass of anode dissolves in the form of salt and comes in the solution. The impurities either remain dissolved in solution or settled down as anode mud around anode.

The applied voltage here is such that more electropositive metals (impurity) remain as ions in the both whereas, the less electropositive metals (also impurities) remain unionised and fall down as anode mud.

(i) Electrorefining of Cu

Anode Blister copper (98%);

Cathode Pure copper

Electrolyte *Aq*. solution of $CuSO_4$ (15%) + 5% dil. H_2SO_4

(ii) Electrorefining of silver (Moebius process)

Anode Impure silver;
Cathode Pure silver

Electrolyte *Aq*. $AgNO_3$ + 1% dil. HNO_3.

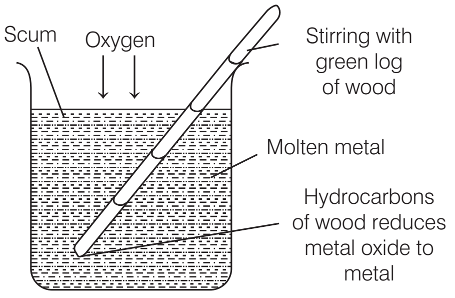
(iii) Electrorefining of lead (Bett's process)

Anode Impure lead;
Cathode Pure lead

Electrolyte A mixture of $PbSiF_6$ and H_2SiF_6.

4. Poling

The impure metal containing its oxides as impurity can be purified by this method. The molten impure metal is stirred with green poles of wood. The green poles of wood release the hydrocarbon gases which reduces the oxide impurities. This method is especially used in the purification of copper (old method).



Refining of metal by poling

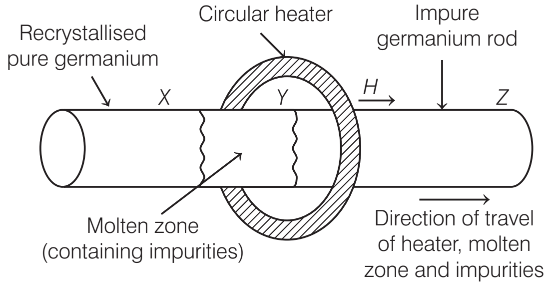
5. Zone-Refining Method

The method is based upon the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal while impurities will be left in remaining part of molten metal.

In this process, the impure metal is taken in the form of rod and a circular heater is fitted around this rod, which is slowly moved along the length of the rod. As the heater moved, the molten impurities also moved along with the heater while the pure metal recrystallises without leaving its position.

Lastly, the end of rod, where the impurities finally get concentrated is cut off, leaving the rod of comparatively more pure metal. The process is repeated a number of times until the desired state of purity is reached.

Uses The method is especially useful for producing the metals especially (semiconductors) of very high purity.



Zone refining of germanium metal

6. Vapour Phase Refining Method

Principle This method is based upon the principle that the impure metal is converted into suitable volatile compound which on being heated, gets decomposed to give pure metal.

Some important methods are as follows

(i) Mond process (also called carbonyl process)

(ii) van-Arkel de-Boer's process (also called iodine refining process)

The **Mond's process** is used for the purification of Ni. It is the most important process for getting 99.9% pure Ni metal from crude Ni. The process was discovered by German chemist, **Ludvig** in 1893.

In the process, the crude Ni is heated in the stream of CO to form volatile nickel carbonyl, Ni(CO)_4. This Ni(CO)_4 when heated higher, it will decompose to give pure metal as

$$\underset{\text{Impure}}{\text{Ni}} + 4\text{CO} \xrightarrow{330\text{-}350\text{ K}} \text{Ni(CO)}_4 \xrightarrow{450\text{ - }470\text{ K}} \underset{\text{Pure}}{\text{Ni}} + 4\text{CO}$$

In the **van-Arkel de-Boer's process,** the impure metal is heated with iodine in a sealed vessel, so that the metal forms volatile metallic iodide and impurities do not react with iodine. The metallic iodide is then decomposed when heated further at higher temperatures.

The metals purified through this way are Zr (zirconium), Ti (titanium), V (vanadium), Th (thorium), etc.

For example, purification of Ti through this method can be done as

$$\underset{\text{(Impure)}}{\text{Ti}} + 2\text{I}_2(g) \xrightarrow{150\text{-}250^\circ\text{C}} \text{TiI}_4(g) \xrightarrow[\text{Tungsten filament}]{1400^\circ\text{C}} \underset{\text{Pure}}{\text{Ti}(s)} + 2\text{I}_2(g)$$

7. Amalgamation Process

This method is used for the extraction of noble metals like Ag, Au etc., from the native ores. The finely powdered ore is brought in contact with Hg, which combines with the particles of the metal present in the ore and form amalgam.

The metal is recovered from the amalgam by subjecting it to distillation, where the Hg distills over, leaving behind the metal.

8. Cupellation

This method is used when impure metal contains impurities of other metals which form volatile oxides, e.g. traces of lead ore removed from silver (as volatile PbO) by this process.

9. Chromatography

This method is used when the elements are available only in minute quantities and the impurities are not very much different in their chemical behaviour from the element to be purified.

Adsorption chromatography is generally used. In this, the impure metal is dissolved in a suitable solvent and the solution is allowed to run slowly into an adsorbent column packed with alumina (Al_2O_3).

The metal and the impurities present are adsorbed at different rates. These are then eluted with suitable eluent (solvent). In this method, weakly adsorbed component is eluted first and the strongly adsorbed component is eluted afterwards.

Thermodynamics

(Principles Involved in Metallurgy)

- The free energy change (ΔG) occurring during the reduction processes help in deciding the suitable method for reduction.
- More the negative value of ΔG, the higher is the reducing power of an element. ΔG can be given as,

$$\Delta G = \Delta H - T\Delta S \qquad \ldots(\text{i})$$

or

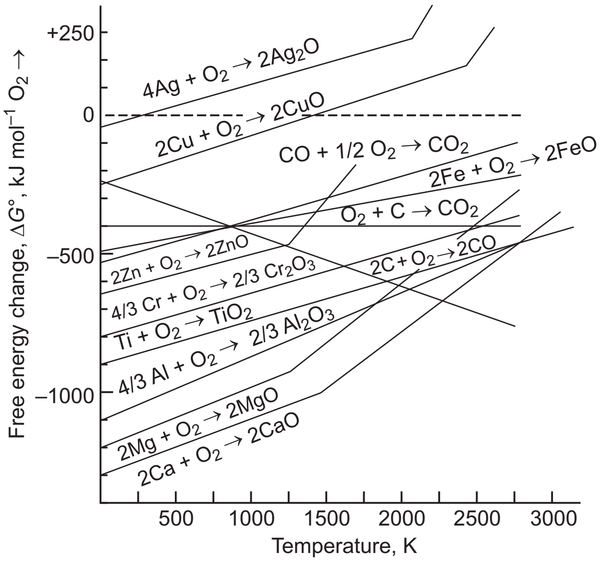
$$\Delta G = -RT \ln K$$

where, ΔH = enthalpy change; ΔG = Gibbs free energy
T = temperature; ΔS = entropy change

For the spontaneous reduction of an oxide, halide or sulphide by an element, the essential condition is that there is a decrease in the free energy of the system (–ve ΔG).

In Eq. (i), if ΔG is –ve then K should be +ve.

For the reduction of a metal oxide with a reducing agent, the plot of ΔG° against temperature is studied, which is called **Ellingham diagram.**



Combined Ellingham diagram for metals and carbon

For a general reaction,

$$2xM(s) + O_2(g) \longrightarrow MxO(s)$$

In this reaction, O_2 is gas and MxO is a solid. That means on increasing temperature ΔS become negative due to which $T\Delta S$ becomes more negative.

In eq. (i), $T\Delta S$ is subtracted hence ΔG becomes less and less negative. That is the reason of the line in ΔG *vs* T plot have positive slopes for most of the reactions involving the formation of metal oxides.

Characteristics of Ellingham Diagram

- All the plots slope upwards since ΔG° becomes more positive when temperature increases, i.e. stability of oxides decreases.
- Due to change in phase, some lines are not straight. The temperature at which such change occurs is indicated by an increase in the slope on the positive side.
- Ag_2O and HgO are unstable and decompose at high temperature that's why they have positive ΔG at high temperature.
- In the plot of CO, ΔG decreases as ΔS increases, this is indicated by downward trend.
- Any metal oxide with lower value of ΔG is more stable as compared to metal oxide with higher value of ΔG.

  Hence, a metal will reduce the oxide of other metals which lie above it in Ellingham diagram, i.e.t he metals for which the free energy of formation (ΔG_f°) of their oxides is more negative can reduce those metal oxides which has less negative ΔG_f°.
- The decreasing order of the negative values of ΔG_f° of metal oxides is
  Ca > Mg (below 1773 K) > Al > Ti > Cr > C > Fe > Ni > Hg > Ag

  Thus, Al reduces FeO, CrO and NiO in thermite reduction but it will not reduce MgO at temperature below 1773 K.

  Mg can reduce Al_2O_3 below 162 K but above 1023 K, Al can reduce MgO.
- CO is more effective reducing agent below 1073 K and above 1073 K, coke is more effective reducing agent, e.g. CO reduces Fe_2O_3 below 1073 K but above it, coke reduces Fe_2O_3. Coke reduces ZnO above 1270 K.

Application

It is interesting to think of the reduction of ZnO with C as involving a competition between Zn and C for O atoms.

We consider following values at 1100°C for the oxidation of Zn and C.

(i) $2Zn + O_2 \longrightarrow 2ZnO; \Delta G^\circ = -360 \text{ kJ}$

(ii) $2C + O_2 \longrightarrow 2CO; \Delta G^\circ = -460 \text{ kJ}$

(i) and (ii) gives,

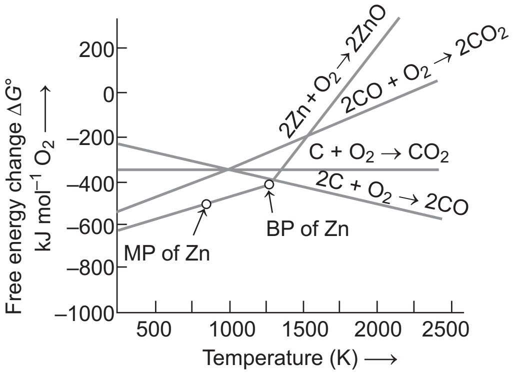
$2Zn + 2CO \longrightarrow 2ZnO + 2C; \ \Delta G^\circ = +100 \text{ kJ}$

(iii) $Zn + CO \longrightarrow ZnO + C; \ \Delta G^\circ = +50 \text{ kJ mol}^{-1}$

(iv) $ZnO + C \longrightarrow Zn + CO; \ \Delta G^\circ = -50 \text{ kJ mol}^{-1}$

For reaction (iii), in which Zn reduces CO, ΔG° is positive indicating that this reduction is non-spontaneous (in forward direction) but for the reaction (iv) with negative value of ΔG° in which C reduces ZnO is spontaneous (in forward direction).

The application of this diagram is pyrometallurgy can be illustrated by the extraction of iron, copper and zinc from their respective oxides.



Ellingham diagram for carbon, carbon monoxide and zinc systems

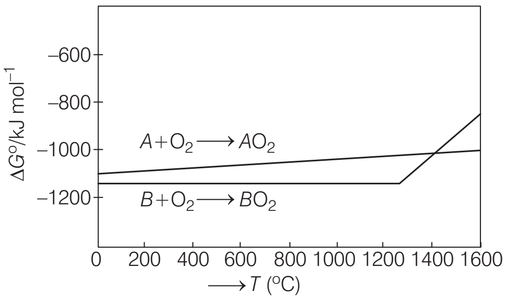
> Why must we carry out the reduction of ZnO with C at 1100°C? From an energy stand point it would certainly be more economical to carry it out at a lower temperature. Ellingham diagram is useful tool to help answer such questions. The lines ($2C + O_2 \longrightarrow 2CO$) and ($2Zn + O_2 \longrightarrow 2ZnO$) cross at about 950°C.
>
> At about this temperature, Zn and C have equal affinities for O atoms. $\Delta G°$ for reaction (iv) is zero. Above this temperature $\Delta G°$ is negative, and below this temperature $\Delta G°$ is positive. To make reaction (iv) go essentially to completion we need a temperature somewhat in excess of 950°C.

Limitations of Ellingham Diagram

Limitations of this diagram are as follows

- It does not tell whether reduction reaction is slow or fast, i.e. kinetics of a reaction.
- For equation, $\Delta = RT \ln K$, the interpretation of value of ΔG is based on the equilibrium constant K. That means, it is assumed that reactants and products are in equilibrium. But this assumptions is not always true for every case.

Example 2. *According to the following diagram, A reduces BO_2 when the temperature is* ***(JEE Main 2020)***



(a) > 1200°C but < 1400°C

(b) > 1400°C

(c) < 1200°C

(d) < 1400°C

Sol. (*b*) A metal with more negative value of $\Delta G°$ of oxide formation reduces oxide of another metal which has less negative value of $\Delta G°$.

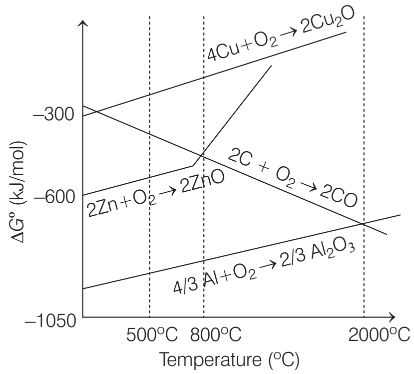
Value of $\Delta G°$ of oxide formation plotted against temperature (as given in question) is called Ellingham's diagram.

From the graph given, $\Delta G°$ of BO_2 formation is more negative than AO_2 upto 1400°C.

$\therefore$ B can reduce AO_2 at these conditions. But above 1400°C, AO_2 formation has more negative $\Delta G°$ than BO_2.

$\therefore$ A can reduce BO_2.

Example 3. *The correct statement regarding the given Ellingham diagram is*



(JEE Main 2019)

(a) At 800°C, Cu can be used for the extraction of Zn from ZnO

(b) At 1400°C, Al can be used for the extraction of Zn from ZnO

(c) At 500°C, coke can be used for the extraction of Zn from ZnO

(d) Coke cannot be used for the extraction of Cu from Cu_2O

Sol. (*b*) From the Ellingham diagram, we can say that any oxide with lower value of $\Delta G°$ is more stable than a oxide with higher value of $\Delta G°$.

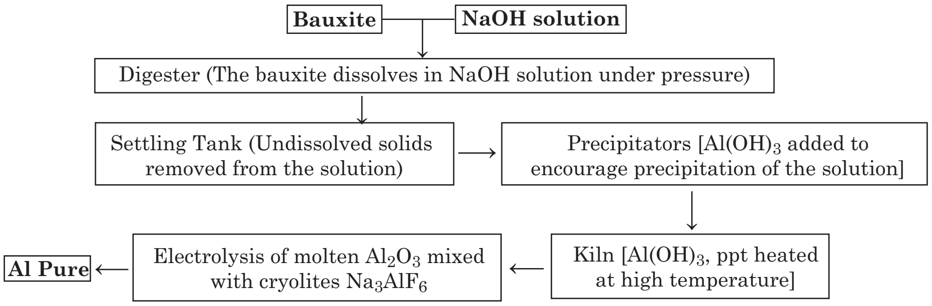
We can also predict that the oxide placed higher in the diagram can be reduced by the element involved in the formation of its oxide placed lower at that temperature in the diagram. It is happening in case of ZnO for its reduction by Al at 1400°C.

Extraction Schemes of Some Metals

The extraction schemes of some important metals are described below

Aluminium

Its chief ore is bauxite ($Al_2O_3 \cdot 2H_2O$). The outline of its extraction from its ore is shown below



Cryolite improves the electrical conductivity of the cell as Al_2O_3 is poor conductor. This also serves as an added impurity and lower the melting point of the mixture to about 950°C. Al of 99.6 to 99.8% purity is obtained. Probable net reactions are

Oxidation at anode $\quad C + 2O^{2-} \longrightarrow CO_2 + 4e^-] \times 3$

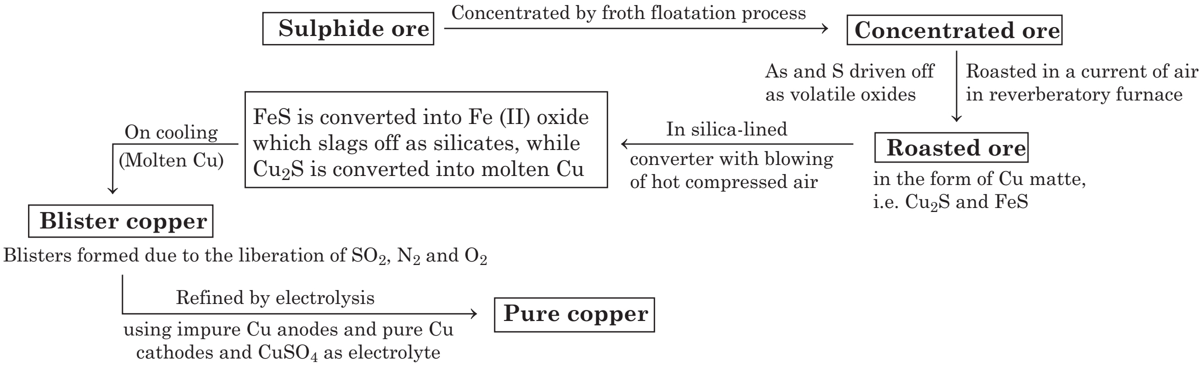
Reduction at cathode $\quad Al^{3+} + 3e^- \longrightarrow Al] \times 4$

Further, $\quad 3C + 4Al^{3+} + 6O^{2-} \longrightarrow 4Al + 3CO_2$

Note For further detailed study of extraction of aluminium see chapter *p*-block element.

Copper

It does not occur abundantly in nature. Its chief ore are **copper pyrites** ($CuFeS_2$), **malachite** [$CuCO_3 \cdot Cu(OH)_2$], **cuperite** (Cu_2O), **copper glance** (Cu_2S). The outline of its extraction from its ore looks like



Low grade copper can be extracted by hydrometallurgical process (wet process) as

***Step* I** Leaching with H_2SO_4 converts salts into sulphates

$$CuCO_3 + H_2SO_4 \xrightarrow{\Delta} CuSO_4 + H_2O + CO_2$$

$$Cu(OH)_2 + H_2SO_4 \xrightarrow{\Delta} CuSO_4 + 2H_2O$$

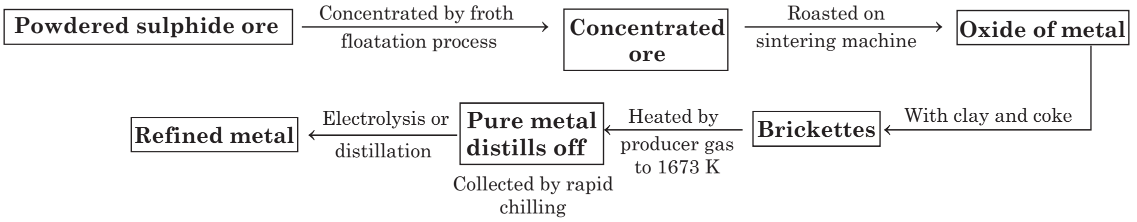
$$CuFeS_2 + 2H_2SO_4 \xrightarrow{\Delta} CuSO_4 + FeSO_4 + 2H_2S$$

***Step* II** **Electrochemical Displacement** Fe is above Cu in electrochemical series hence, if Fe scrap is added to $CuSO_4$ solution, Cu is displaced

$$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu\downarrow$$

Zinc

Its chief ore is **zinc blende** (ZnS) and other ores are **calamine** ($ZnCO_3$), **zincite** (ZnO), **willemite** (Zn_2SiO_4) etc. The outline of its extraction looks like

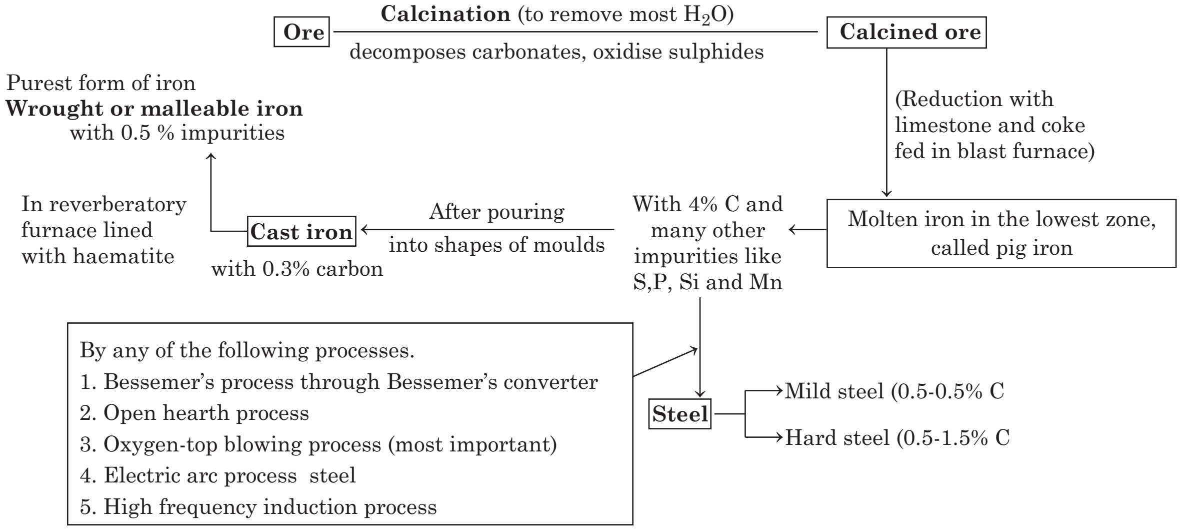


Roasting

- $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$
- $ZnS + 2O_2 \longrightarrow ZnSO_4$
- $2ZnSO_4 \longrightarrow 2ZnO + 2SO_2 + O_2$
- When the ore is calamine, it shall decompose into oxide with evolution of CO_2 [calcination process is used. For roastion, a reverberatory furnace may be used].

Iron

Iron is the second most abundant metal after Al in the earth's crust. Its most important ores are **haematite** (Fe_2O_3), **magnetite** (Fe_3O_4), **siderite** ($FeCO_3$) and **iron pyrites** (FeS_2). The outline of its extraction from its ore looks like



Reactions Occurring in Blast Furnace

The various zones and the reactions occurring in blast furnace are as follows

(i) **Reduction zone** (uppermost part of the furnace) In this zone temperature is about 500-800K and metal oxide is reduced to metal.

$$3Fe_2O_3 + CO \xrightarrow{573\text{-}673\text{ K}} 2Fe_3O_4 + CO_2 \uparrow$$

$$Fe_3O_4 + 4CO \xrightarrow{773\text{-}883\text{ K}} 3Fe + 4CO_2 \uparrow$$

$$Fe_2O_3 + CO \xrightarrow{773\text{-}873\text{ K}} 2FeO + CO_2 \uparrow$$

(ii) **Combustion zone** (middle part of furnace) At 900-1500 K coke burns to form CO_2.

$$C + O_2 \longrightarrow CO_2 + 97 \text{ kcal}$$

CO_2 rise upward and reduces to carbon monoxide

$$CO_2 + C \longrightarrow 2CO(g)$$

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

Iron formed is called spongy iron.

$$CaCO_3 \longrightarrow CaO + CO_2$$

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

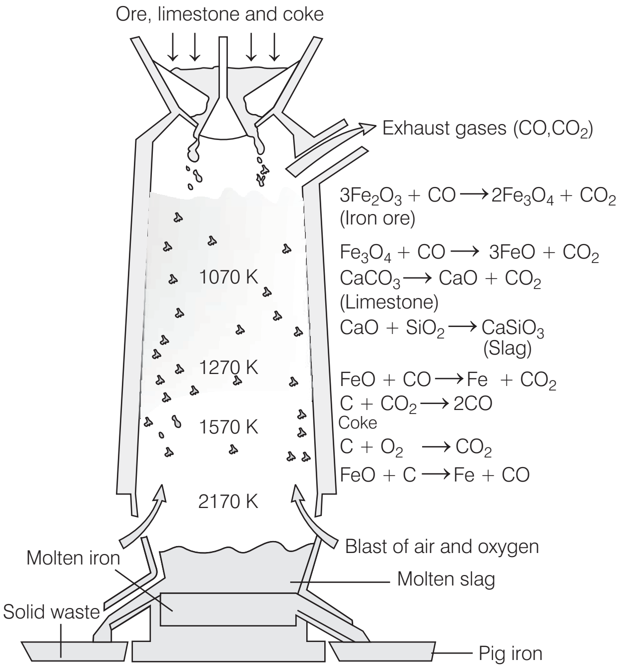
CaO formed help in slag formation of slag therefore, sometimes this zone is also called slag formation zone.

(iii) **Melting zone** (lower part of furnace, 1500-2100 K) Spongy iron melts at 1600 K and collects at the bottom of the hearth. The slag being lighter, floats over the molten zone. The molten iron is called pig iron.

$$FeO + C \longrightarrow Fe + CO$$

Iron obtained from a blast furnace is called **pig iron**. It contains about 95% Fe, 4% C and varying quantities of other impurities. **Cast iron** can be obtained by pouring pig iron directly into molds of the desired shape.

Cast iron is very hard and brittle and can be used where it will not be subjected to mechanical or thermal shock.



Reduction process of iron once in blast furnace

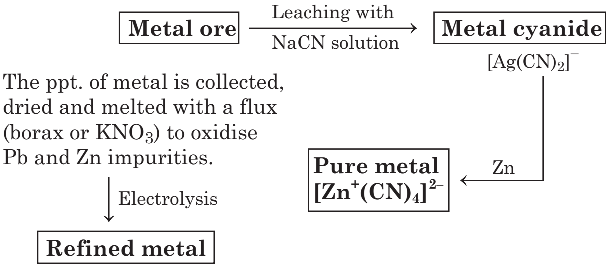
Remember Heating the steel to appropriate temperature for a short time and then cooling it rapidly in order to give it the desired mechanical properties is called **tempering**. In this way, the ratio of carbon present as graphite and as cementite can be varied within rather wider limits.

Extraction of Gold and Silver

The extraction of gold and silver involves leaching the metal with CN^-, which is also an oxidation reaction. The metal is later recovered by the displacement method using more electropositive zinc metal.

Silver

It occurs as argentite or silver glance (Ag_2S), pyrargyrite or ruby silver (Ag_3SbS_3), proustite (Ag_3AsS_3) and horn silver (AgCl). The outline of its extraction looks like.



Desilverisation of Lead

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

- When zinc is added to a melted alloy of silver and lead, zinc takes away silver from the alloy and itself forms an alloy with silver and not with lead.
- Alloy of zinc and silver melts at a higher temperature than lead.
- The alloy of silver and zinc is lighter than lead and forms two separate layers.
- On distillation of silver and zinc alloy, zinc separates.

Pattinson's Process

It depends upon the fact that the alloy of lead and silver containing less than 1.8 per cent of silver, melts at a lower 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.

Gold

- It is usually found in native state.
- It important ore are calaverite, sylvanite, krennerite etc.
- Leaching process is intended to concentrate the gold metal.

Mercury

It is found as 1×10^{-5}% of earth crust and its most important ore is cinnabar (HgS).

$$\boxed{\text{Ore}} \xrightarrow[\text{above 773 K}]{\text{Roasted in air}} \boxed{\begin{array}{l}\text{Hg vapours distills}\\ \text{over and condensed}\end{array}}$$

or

$$\boxed{\begin{array}{c}\text{Richer ore}\\ +\\ \text{Quick lime}\end{array}} \xrightarrow[\text{(in iron retorts)}]{\text{Distillation}} \boxed{\text{Metal}}$$

It can be purified by dropping slowly through dil. HNO_3. The metallic impurities displace Hg from nitrate and go into the solution. Further purification is carried out by distillation under reduced pressure.

Practice Exercise

ROUND I Topically Divided Problems

Occurrence of Metals

1. Metal occur in the native form because of their
(a) high electronegativity (b) high reactivity
(c) low reactivity (d) low density

2. Which of the following metal is sometimes found native in nature?
(a) Mg (b) Cu
(c) Al (d) Fe

3. A number of elements are available in earth's crust but most abundant elements are
(a) Al and Fe (b) Al and Cu
(c) Fe and Cu (d) Cu and Ag

4. Formula of magnetite is
(a) Fe_3O_4 (b) Fe_2O_3
(c) FeS_2 (d) $FeCO_3$

5. Which is not a mineral of aluminium?
(a) Corundum (b) Anhydrite
(c) Diaspore (d) Bauxite

6. An important ore of iron is
(a) pyrites (b) malachite
(c) haematite (d) siderite

7. Which of the following is a carbonate ore?
(a) Pyrolusite (b) Diaspore
(c) Cassiterite (d) Malachite

8. Metal which can be extracted from all the three dolomite, magnesite and carnallite is
(a) Na (b) K
(c) Mg (d) Ca

9. One of the following metals forms a volatile compound and this property is taken advantage for its extraction. This metal is
(a) cobalt (b) iron
(c) tungsten (d) nickel

10. The ore that contains the metal in the form of fluoride is *(JEE Main 2019)*
(a) magnetite (b) sphalerite
(c) malachite (d) cryolite

11. The one that is not a carbonate ore is *(JEE Main 2019)*
(a) siderite (b) calamine
(c) malachite (d) bauxite

12. The ore that contains both iron and copper is *(JEE Main 2019)*
(a) malachite (b) azurite
(c) dolomite (d) copper pyrites

Steps Involved in the Extraction of Metals

13. All ores are minerals, while all minerals are not ores because
(a) minerals are complex compounds
(b) the minerals are obtained from mines
(c) the metal cannot be extracted economically from all the minerals
(d) All of the above are correct

14. In metallurgy, flux is a substance used to convert
(a) soluble impurities to insoluble impurities
(b) infusible impurities to fusible material
(c) fusible impurities to infusible impurities
(d) mineral into silicate

15. The alloy used in the construction of aircrafts is *(JEE Main 2019)*
(a) Mg-Zn (b) Mg-Mn
(c) Mg-Sn (d) Mg-Al

16. What should be the considerations during the extraction of metals by electrochemical method? *(NCERT Exemplar)*
(a) Reactivity of metal obtained
(b) Selectivity of metal obtained
(c) Suitability of electrodes
(d) Both (a) and (c)

17. The method of concentrating the ore which makes use of the difference in density between ore and impurities is called
(a) leaching
(b) liquation
(c) levigation
(d) magnetic separation

18. Froth floatation process for the concentration of the ores is an illustration of the practical application of

(a) adsorption (b) sedimentation
(c) coagulation (d) absorption

19. How do we separate two sulphide ores by froth floatation method ?

(a) By adding pine oil
(b) By adding sodium cyanide
(c) By adding foaming agent
(d) By passing air

20. Copper pyrites is concentrated by

(a) gravity method (b) froth floatation process
(c) electromagnetic method (d) All of these

21. Which one of the following ores is best concentrated by froth-floatation method ? *(AIEEE 2004)*

(a) Magnetite (b) Cassiterite
(c) Galena (d) Malachite

22. The ore that can be concentrated by magnetic separation method is

(a) magnetite (b) haematite
(c) siderite (d) All of these

23. An ore of tin containing $FeCrO_4$ is concentrated by

(a) electrostatic method (b) gravity separation
(c) magnetic separation (d) froth floatation

24. Which of the following reduction reaction cannot be carried out with coke ? *(JEE Main 2021)*

(a) $Al_2O_3 \longrightarrow Al$
(b) $ZnO \longrightarrow Zn$
(c) $Fe_2O_3 \longrightarrow Fe$
(d) $Cu_2O \longrightarrow Cu$

25. Which of the following statements is correct about the role of substances added in the froth floatation process ? *(NCERT Exemplar)*

(a) Collectors enhance the non-wettability of the mineral particles
(b) Collectors enhance the wettability of gangue particles
(c) By using depressants in the process two sulphide ores can be separated
(d) Both (a) and (b)

26. Cyanide process is used for the extraction of

(a) barium (b) silver
(c) boron (d) zinc

27. The reaction $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$ in the metallurgical process of zinc is called

(a) roasting (b) smelting
(c) cupellation (d) calcination

28. The processes of calcination and roasting in metallurgical industries, respectively, can lead to

(a) global warming and acid rain *(JEE Main 2020)*
(b) global warming and photochemical smog
(c) photochemical smog and ozone layer depletion
(d) photochemical smog and global warming

29. Which of the following reactions occur during calcination ? *(NCERT Exemplar)*

(a) $CaCO_3 \longrightarrow CaO + CO_2$
(b) $2FeS_2 + \frac{11}{2} O_2 \longrightarrow Fe_2O_3 + 4SO_2$
(c) $Al_2O_3 \cdot xH_2O \longrightarrow Al_2O_3 + xH_2O$
(d) Both (a) and (c)

30. The reaction that does not define calcination is *(JEE Main 2019)*

(a) $Fe_2O_3 \cdot xH_2O \xrightarrow{\Delta} Fe_2O_3 + xH_2O$
(b) $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$
(c) $CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + 2CO_2$
(d) $2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$

31. The pair that does not require calcination is

(a) ZnO and MgO *(JEE Main 2019)*
(b) ZnO and $Fe_2O_3 \cdot xH_2O$
(c) $ZnCO_3$ and CaO
(d) Fe_2O_3 and $CaCO_3 \cdot MgCO_3$

32. Thermite is a mixture of

(a) Fe powder and Al_2O_3 (b) Al powder and Fe_2O_3
(c) Cu powder and Fe_2O_3 (d) Zn powder and Cr_2O_3

33. Which of the following reactions is an example of auto-reduction? *(NCERT Exemplar)*

(a) $Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$
(b) $Cu_2O + C \longrightarrow 2Cu + CO$
(c) $Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$
(d) $Cu_2O + \frac{1}{2} Cu_2S \longrightarrow 3Cu + \frac{1}{2} SO_2$

34. Extraction of gold and silver involves leaching the metal with CN^- ion. The metal is recovered by … . *(NCERT Exemplar)*

(a) displacement of metal by some other metal from the complex ion
(b) roasting of metal complex
(c) calcination followed by roasting
(d) thermal decomposition of metal complex

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

(a) Fe and Ni (b) Ag and Au
(c) Pb and Zn (d) Se and Ag

36. The electrolytes usually used in the electroplating of gold and silver, respectively, are *(JEE Main 2019)*

(a) $[Au(OH)_4]^-$ and $[Ag(OH)_2]^-$
(b) $[Au(NH_3)_2]^+$ and $[Ag(CN)_2]^-$
(c) $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$
(d) $[Au(CN)_2]^-$ and $[AgCl_2]^-$

37. The element that can be refined by distillation is *(JEE Main 2020)*

(a) nickel (b) zinc
(c) tin (d) gallium

38. The refining method used when the metal and the impurities have low and high melting temperatures, respectively, is *(JEE Main 2020)*

(a) distillation (b) zone refining
(c) liquation (d) vapour phase refining

39. Boron and silicon of very high purity can be obtained through *(JEE Main 2020)*

(a) liquation
(b) zone refining
(c) vapour phase refining
(d) electrolytic refining

40. Which method is used to refine Zr and Ti ? *(NCERT Exemplar)*

(a) Mond's process (b) Cyanide process
(c) van Arkel method (d) Lavigation

41. With respect to an ore, Ellingham diagram helps to predict the feasibility of its *(JEE Main 2019)*

(a) electrolysis
(b) zone refining
(c) vapour phase refining
(d) thermal reduction

42. Aluminium is extracted by the electrolysis of

(a) alumina *(AIEEE 2002)*
(b) bauxite
(c) molten cryolite
(d) alumina mixed with molten cryolite

43. In the Hall-Heroult process, aluminium is formed at the cathode. The cathode is made out of *(JEE Main 2019)*

(a) platinum (b) carbon
(c) pure aluminium (d) copper

44. What is the role of graphite rod in the electrometallurgy of aluminium? *(NCERT)*

(a) It acts as anode
(b) It acts as cathode
(c) It acts as oxidising agent
(d) Both (a) and (c)

45. Brine is electrolysed by using inert electrodes. The reaction at anode is *(NCERT Exemplar)*

(a) $Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-;$ $E^{\ominus}_{\text{cell}} = 1.36\text{ V}$
(b) $2H_2O(l) \longrightarrow O_2(g) + 4H^+ + 4e^-;$ $E^{\ominus}_{\text{cell}} = 1.23\text{ V}$
(c) $Na^+(aq) + e^- \longrightarrow Na(s);$ $E^{\ominus}_{\text{cell}} = 2.71\text{ V}$
(d) $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g);$ $E^{\ominus}_{\text{cell}} = 0.00\text{ V}$

46. In the metallurgy of aluminium …… .

(a) Al^{3+} is oxidised to $Al(s)$. *(NCERT Exemplar)*
(b) graphite anode is oxidised to carbon monoxide and carbon dioxide.
(c) oxidation state of oxygen changes in the reaction at anode.
(d) oxidation state of oxygen changes in the overall reaction involved in the process.

47. Hall-Heroult's process is given by *(JEE Main 2019)*

(a) $ZnO + C \xrightarrow{\text{Coke, 1673 K}} Zn + CO$
(b) $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$
(c) $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$
(d) $Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$

48. Electrolytic reduction of alumina to aluminium by 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 with lower melting point
(d) in the presence of cryolite which forms a melt with high melting point

49. In the extraction of copper from its sulphide ore, the metal is formed by the reduction of Cu_2O with *(NCERT Exemplar)*

(a) FeS (b) CO (c) Cu_2S (d) SO_2

50. The slag obtained during the extraction of copper from copper pyrites is composed of

(a) Cu_2S (b) SiO_2 (c) $CuSiO_3$ (d) $FeSiO_3$

51. When copper ore is mixed with silica in a reverberatory furnace, copper matte is produced. The copper matte contains …… . *(NCERT Exemplar)*

(a) sulphides of copper (III) and iron (II)
(b) sulphides of copper (II) and iron (III)
(c) sulphides of copper (I) and iron (II)
(d) sulphides of copper (I) and iron (III)

52. Why copper matte is put in silica lined converted?

(a) To oxidise it
(b) To reduce it
(c) To convert its impurities into fusible mass
(d) To convert its impurities into infusible mass

53. In order to refine blister copper, it is melted in a furnace and is stirred with green logs of wood. The purpose is

(a) to expel the dissolved gases in blister copper
(b) to bring the impurities to surface and oxidise them
(c) to increase the carbon content of copper
(d) to reduce the metallic oxide impurities with hydrocarbon gases liberated from the wood

54. Refining of impure copper with zinc impurity is to be done by electrolysis using electrodes as *(AIEEE 2002)*

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

55. In the metallurgy of iron, when $CaCO_3$ is added to blast furnace, calcium ion appears as

(a) slag (b) gangue
(c) CaO (d) metallic Ca

56. The purest form of commercial iron is *(JEE Main 2020)*

(a) cast iron
(b) scrap iron and pig iron
(c) wrought iron
(d) pig iron

57. Which of the following options are correct? *(NCERT Exemplar)*

(a) Cast iron is obtained by remelting pig iron with scrap iron and coke using hot air blast
(b) In extraction of silver, silver is extracted as cationic complex
(c) Nickel is purified by zone refining
(d) Zr and Ti are purified by Mond's method

58. Cast iron is used for the manufacture of *(JEE Main 2020)*

(a) wrought iron and pig iron
(b) pig iron, scarp iron and steel
(c) wrought iron, pig iron and steel
(d) wrought iron and steel

ROUND II Mixed Bag

1. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of

(a) nitrogen (b) oxygen
(c) carbon dioxide (d) argon

2. Among the following groups of oxides, the group containing oxides that cannot be reduced by carbon to give the respective metals is

(a) Cu_2O, K_2O (b) PbO, Fe_3O_4
(c) Fe_2O_3, ZnO (d) CaO, K_2O

3. When a metal is to be extracted from its ore, if the gangue associated with the ore is silica, then

(a) a basic flux is needed
(b) an acidic flux is needed
(c) both basic and acidic flux are needed
(d) neither of them is needed

4. Pb and Sn are extracted from their chief ore by

(a) electrolysis and self reduction
(b) self reduction and electrolysis
(c) carbon reduction and self reduction
(d) self reduction and carbon reduction

5. 'Lapis-Lazuli' is a blue coloured precious stone. It is mineral of the class

(a) sodium alumino silicate
(b) basic copper carbonate
(c) zinc cobalt
(d) Prussian blue

6. Which of the following statement is incorrect ?

(a) Silver glance mainly contains silver sulphide
(b) Zinc blende mainly contains zinc chloride
(c) Gold is found in native state
(d) Copper pyrites also contains Fe_2S_3

7. Among the following statements, the incorrect one is

(a) calamine and siderite are carbonates
(b) malachite and azurite are ores of copper
(c) argentite and cuprite are oxides
(d) zinc blende and pyrites are sulphides

8. Bauxite ore is made up of $Al_2O_3 + SiO_2 + TiO_2 + Fe_2O_3$. This ore is treated with conc. NaOH solution at 500 K and 35 bar pressure for few hours and filtered, when hot. In the filtrate, the species present are

(a) $NaAl(OH)_4$ only
(b) $Na_2Ti(OH)_6$ only
(c) $NaAl(OH)_4$ and Na_2SiO_3 both
(d) Na_2SiO_3 only

9. Which statement is incorrect ?

(a) Galena is an ore of Pb
(b) Electrostatic separation is used for lead sulphide
(c) Ore is heated strongly, above its melting point in roasting
(d) Silica acts as acidic flux

10. Which of the following statements are correct?

(a) A depressant prevents certain type of particles to come to the froth

(b) Copper matte contains Cu_2S and ZnS

(c) Zinc can not be extracted by self-reduction

(d) Both (a) and (c)

11. The incorrect statement is *(JEE Main 2020)*

(a) bronze is an alloy of copper and tin.

(b) cast iron is used to manufacture wrought iron.

(c) german silver is an alloy of zinc, copper and nickel.

(d) brass is an alloy of copper and nickel.

12. Among the reactions (A) - (D), the reaction that does/do not occur in the blast furnace during the extraction of iron is/are

(A) $CaO + SiO_2 \longrightarrow CaSiO_3$

(B) $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$

(C) $FeO + SiO_2 \longrightarrow FeSiO_3$

(D) $FeO \longrightarrow Fe + \frac{1}{2} O_2$

(JEE Main 2020)

(a) (C) and (D) (b) Only (A)

(c) (A) and (D) (d) Only (D)

13. The correct statement is *(JEE Main 2019)*

(a) zone refining process is used for the refining of titanium.

(b) zincite is a carbonate ore.

(c) sodium cyanide cannot be used in the metallurgy of silver.

(d) aniline is a froth stabiliser.

14. The correct statement is *(JEE Main 2019)*

(a) leaching of bauxite using concentrated NaOH solution gives sodium aluminate and sodium silicate.

(b) the hall-heroult process is used for the production of aluminium and iron.

(c) pig iron is obtained from cast iron.

(d) the blistered appearance of copper during the metallurgical process is due to the evolution of CO_2.

15. Which series of reactions correctly represent chemical relations related to iron and its compound ? *(JEE Main 2014)*

(a) $Fe \xrightarrow{\text{Dil. } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4,\, O_2} Fe_2(SO_4)_3 \xrightarrow{\text{Heat}} Fe$

(b) $Fe \xrightarrow{O_2,\text{ heat}} FeO \xrightarrow{\text{Dil. } H_2SO_4} FeSO_4 \xrightarrow{\text{Heat}} Fe$

(c) $Fe \xrightarrow{Cl_2,\text{ heat}} FeCl_3 \xrightarrow{\text{Heat, air}} FeCl_2 \xrightarrow{\text{Zn}} Fe$

(d) $Fe \xrightarrow{O_2,\text{ heat}} Fe_3O_4 \xrightarrow{\text{CO, }600°C} FeO \xrightarrow{\text{CO, }700°C} Fe$

16. 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 *(AIEEE 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

17. Which statement is correct?

(a) Slags are carefully choosen to combine with the slag present in the ore to produce easily fusible gangue to carry away the impurities

(b) Gangues are carefully choosen to combine with the slag present in the ore to produce easily fusible flux to carry away the impurities

(c) Gangues are carefully choosen to combine with flux present in the ore to produce easily fusible slag to carry away the impurities

(d) Fluxes are carefully choosen to combine with the gangue present in the ore to produce easily fusible slag to carry away the impurities

18. Among statements (A)-(D), the correct ones are

A. Limestone is decomposed to CaO during the extraction of iron from its oxides.

B. In the extraction of silver, silver is extracted as an anionic complex.

C. Nickel is purified by Mond's process.

D. Zr and Ti are purified by van-Arkel method.

(JEE Main 2020)

(a) (A), (B), (C) and (D)

(b) (A), (C) and (D) only

(c) (C) and (D) only

(d) (B), (C) and (D) only

19. An Ellingham diagram provides information about *(JEE Main 2020)*

(a) the kinetics of the reduction process.

(b) the pressure dependence of the standard electrode potentials of reduction reactions involved in the extraction of metals.

(c) the temperature dependence of the standard Gibbs energies of formation of some metal oxides.

(d) the conditions of pH and potential under which a species is thermodynamically stable.

20. Of the following reduction processes

I. $PbO + C \longrightarrow Pb$ II. $ZnO + C \longrightarrow Zn$

III. $Fe_2O_3 + C \longrightarrow FeO$

IV. $Ca_3(PO_4)_2 + C \longrightarrow P$

Correct processes are

(a) I, II (b) I, II, IV

(c) II, III (d) All of these

21. In which of the following isolations no reducing agent is required ?
(a) Iron from haematite
(b) Aluminium from bauxite
(c) Zinc from zinc blende
(d) Mercury from cinnabar

22. Match Column I with Column II and select the correct answer using the codes given below the list.

	Column I		Column II
A.	Ti	1.	Bauxite
B.	Si	2.	Cerussite
C.	Al	3.	van-Arkel method
D.	Pb	4.	Zone refining

Codes

	A	B	C	D		A	B	C	D
(a)	2	1	3	4	(b)	2	3	1	4
(c)	3	1	2	4	(d)	3	4	1	2

23. Match items of Column I with the items of Column II and assign the correct codes.

	Column I		Column II
A.	Cyanide process	1.	Ultrapure Ge
B.	Froth-floatation process	2.	Dressing of ZnS
C.	Electrolytic reduction	3.	Extraction of Al
D.	Zone refining	4.	Extraction of Au
		5.	Purification of Ni

Codes

	A	B	C	D		A	B	C	D
(a)	4	2	3	1	(b)	2	3	1	5
(c)	1	2	3	4	(d)	3	4	5	1

24. Match Column I and Column II *(JEE Main 2021)*

	Column I		Column II
A.	Hematite	1.	$Al_2O_3 \cdot xH_2O$
B.	Bauxite	2.	Fe_2O_3
C.	Magnetic	3.	$CuCO_3$, $Cu(OH)_2$
D.	Malachite	4.	Fe_3O_4

Choose the correct answer from the options given below.

Codes

	A	B	C	D		A	B	C	D
(a)	2	3	1	4	(b)	4	1	2	3
(c)	1	3	2	4	(d)	2	1	4	3

25. Match the ores (Column I) with the metals (Column II). *(JEE Main 2019)*

	Column I (Ores)		**Column II** (Metals)
A.	Siderite	1.	Zinc
B.	Kaolinite	2.	Copper
C.	Malachite	3.	Iron
D.	Calamine	4.	Aluminium

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	3	4	1	2
(c)	2	3	4	1	(d)	3	4	2	1

Numeric Value Questions

26. Rutile has the formula TiO_x and magnetic has Fe_3O_{2x}. Here, the value of x is ?

27. See following calcination reaction

(A) $CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + xCO_2$

(B) $CuCO_3 \cdot Cu(OH)_2 \xrightarrow{\Delta} yCuO + H_2O + xCO_2$

The value of $x \times y$ will be …… .

28. Amongst the following elements, how many occurs in the earth's crust in the native state?

Au, Pt, Hg, Zn and Fe.

29. Find the number of metals from given metals which can be commercially purified by zone refining methods

Si, Ge, Ga, Al, Ti and Zr.

30. Find the number of acidic flux from the given compounds

$CaCO_3$, $Na_2B_4O_7$, $MgSiO_3$, $FeSiO_3$ and P_2O_5

31. How many of the following metals can be refined by vapour phase refining?

Zn, Zr, Hg, Cd, Ni, Ti, Co, Pt and Fe

Answers

Round I

1. (c)	*2.* (b)	*3.* (a)	*4.* (a)	*5.* (b)	*6.* (c)	*7.* (d)	*8.* (c)	*9.* (d)	*10.* (d)
11. (d)	*12.* (d)	*13.* (c)	*14.* (b)	*15.* (d)	*16.* (d)	*17.* (c)	*18.* (a)	*19.* (b)	*20.* (b)
21. (c)	*22.* (d)	*23.* (c)	*24.* (a)	*25.* (d)	*26.* (b)	*27.* (a)	*28.* (a)	*29.* (d)	*30.* (d)
31. (a)	*32.* (b)	*33.* (d)	*34.* (a)	*35.* (b)	*36.* (c)	*37.* (b)	*38.* (c)	*39.* (b)	*40.* (c)
41. (d)	*42.* (d)	*43.* (b)	*44.* (a)	*45.* (a)	*46.* (b)	*47.* (c)	*48.* (c)	*49.* (c)	*50.* (d)
51. (c)	*52.* (c)	*53.* (d)	*54.* (c)	*55.* (a)	*56.* (c)	*57.* (a)	*58.* (d)		

Round II

1. (b)	*2.* (d)	*3.* (a)	*4.* (d)	*5.* (a)	*6.* (b)	*7.* (c)	*8.* (c)	*9.* (c)	*10.* (c)
11. (d)	*12.* (a)	*13.* (d)	*14.* (a)	*15.* (d)	*16.* (c)	*17.* (d)	*18.* (a)	*19.* (c)	*20.* (b)
21. (d)	*22.* (d)	*23.* (a)	*24.* (d)	*25.* (d)	*26.* (2)	*27.* (2)	*28.* (2)	*29.* (3)	*30.* (2)
31. (3)									

Solutions

Round I

1. Less reactive metals are found in native state (free state).

2. Copper is found in native as well as in combined state.

5. Bauxite ($Al_2O_3 \cdot 2H_2O$)

Corundum (Al_2O_3)
Diaspore ($Al_2O_3 \cdot H_2O$)

7. Pyrolusite — MnO_2

Malachite — $CuCO_3 \cdot Cu(OH)_2$
Diaspore — $Al_2O_3 \cdot H_2O$
Cassiterite — SnO_2

8. Dolomite $MgCO_3 \cdot CaCO_3$

Magnesite $MgCO_3$
Carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$

9. Mond's process for refining of Ni is an example of vapour phase refining.

10. Cryolite ore (Na_3AlF_6, sodium hexafluoroaluminate) contain fluorine while other given options such as malachite ($Cu_2(CO)_3(OH)_2$), sphalerite (Zn, Fe, S) and bauxite (Al_2O_3) does not contain fluorine.

11. Bauxite is not a carbonate ore. Its chemical formula is Al_2O_3 or $AlO_x(OH)_{3-2x}$, where $0 < x < 1$.

12. The formulae of the given ores are as follows

Malachite: $CuCO_3 \cdot Cu(OH)_2$
Copper pyrites : $CuFeS_2$
Dolomite : $CaMg(CO_3)_2$
Azurite : $Cu_3(CO)_3(OH)_2$

13. Metals cannot be extracted economically from all the minerals that is why all minerals are not ores.

14. Flux is mixed with concentrated ore which is not soluble in molten metal. It converts the infusible impurities to fusible material.

15. Among the alloys given, Mg – Al (Magnalium ; Mg = 5%, Al =95%) is being light, tough and strong, hence it is used in aircrafts.

16. (a) Reactivity of metal produced.

(c) Suitability of electrodes.

Above two considerations are taken into account during extraction of metals by electrochemical method.

17. Levigation (gravity separation) is based on the difference in the specific gravities of the gangue particles and the ore particles.

18. The adsorption phenomenon is involved in the froth floatation process.

19. Two sulphide ores can be separated by adjusting the proportion of oil and water or by using depressants, e.g. If an ore contains ZnS and PbS both, a depressant NaCN is added during froth floatation. It forms a complex with ZnS and prevents it from coming into froth. PbS comes into the froth and thus, separated.

22. Magnetic ores (iron ores) are generally separated by this method. Magnetite (Fe_3O_4), haematite (Fe_2O_3), siderite ($FeCO_3$) are such ores.

23. Electromagnetic separation is used when either the ore or the impurities associated with it, are magnetic in nature.

24. Reduction of $Al_2O_3 \longrightarrow Al$ is carried out by electrolytic reduction of its fused salts.

ZnO, Fe_2O_3 and Cu_2O can be reduce by carbon.

25. In the froth floatation process collector enhance the non-wettability of the mineral particles. In this process, depressant helps in separating two different sulphide ores.

26. Cyanide process or Mac Arthur-Forest cyanide process

$$2Ag_2S + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na\,[Ag(CN)_2] + 4NaOH + 2S$$

Soluble silver complex is filtered and treated with zinc dust and silver gets precipitated.

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

28. Due to industrial process, CO_2 release from calcination and SO_2 release from roasting respectively which is responsible for global warming and acid rain.

Calcination It involves heating where the volatile matter escapes leaving behind the metal oxide. In this process, the ore is heated below its melting point in the absence of air or in the limited supply of air.

e.g. $$CaCO_3\,(s) \xrightarrow{\Delta} CaO\,(s) + \underset{\substack{\text{(Carbon dioxide)}\\ \text{Responsible for}\\ \text{global warming}}}{CO_2\uparrow}$$

Roasting In this process the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal.

e.g. $$2ZnS + 3O_2 \longrightarrow 2ZnO + \underset{\substack{\text{(Sulphur dioxide)}\\ \text{Responsible for}\\ \text{acid rain}}}{2SO_2\uparrow}$$

29. Calcination involves heating of the ore below its melting point in the absence of air or in limited supply. Oxygen containing ores like oxide, hydroxides and carbonates are calcined. Thus, the following reactions occurs during calcination.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$Al_2O_3 \cdot xH_2O \xrightarrow{\Delta} Al_2O_3 + xH_2O$$

30. In calcination, a hydrated carbonate or bicarbonate ore or a hydrated ore is heated at lower temperature (compared to roasting) in absence of air to give its oxide as in options (a), (b) and (c). Here, volatile non-metallic oxides like H_2O, CO_2, are also produced. Roasting is valid mainly for sulphide ores like option (d), where SO_2 gets liberated. In this reaction, calcination cannot be used.

31. Among the given options, the options having either carbonates (e.g. $ZnCO_3$ and $CaCO_3 \cdot MgCO_3$) or hydrated oxide (e.g. $Fe_2O_3 \cdot xH_2O$), require calcination while pair of option (a), i.e. ZnO and MgO does not require calcination.

32. Thermite is a mixture of Al and Fe_2O_3 in 1 : 3 ratio.

33. Auto-reduction is also known as self-reduction. This is used when no external reducing agent is required. The sulphide ores of less electropositive metal like Hg, Pb, Cu etc., are heated in air to convert a part of the ore into oxide or sulphide which then reacts with the remaining sulphide ore to give the metal and sulphur dioxide. e.g.

$$Cu_2O + \frac{1}{2}\,Cu_2S \longrightarrow 3Cu + \frac{1}{2}\,SO_2$$

34. Extraction of gold and silver involves leaching the metals with CN^- ion. The metal is recovered by displacement of metal by some other metals from the complex ion.

35. During electrolysis, noble metals (inert metals) like Ag, Au and Pt are not affected and separate as anode mud from the impure anode.

36. Electroplating is a process of coating one metal or metal object with a very thin layer of another metal typically applying a direct electric current.

Electrolytes used in the electroplating of gold and silver are given in the table below

	Process	Article to be plated out acts as cathode	Pure metal block acts an anode by which electroplating will be done	Electrolyte (aqueous solution)
(a)	Gold plating	Article	Ai(S)	$Na[\overset{I}{Au}(CN)_2]$ (Sodium auro-cyanide)
(b)	Silver plating	Article	Ag(S)	$Na[\overset{I}{Ag}(CN)_2]$ (Sodium argento cyanide)

37. Zinc is refined by distillation.

It is used for purification of low boiling point or volatile metals, such as mercury (Hg), zinc (Zn), cadmium (Cd) etc. In this method, pure metal is heated and its vapours are separately condensed in a receiver, while the pure metal distils out, impurities (non-volatile) are left behind.

38. Liquation is used when melting points of metal and impurity are quite different.

Metal melts at a lower temperature and flows down a slope while the impurity stays as solid.

39. In zone refining, the impure metal rod is electrically heated till life metal in the heated zone melts. There metal is collected at one end of the rod. Repeating the metal with the product obtained each time highly pure metal is obtained. This method is very useful for producing semiconductor and other metals with high purity. e.g. Germanium, silicon, boron, gallium and indium etc.

40. Zr and Ti are refined by van Arkel method. It involves two steps

(a) **Formation of iodide**; e.g. zirconium

$$Zr + 2I_2 \longrightarrow ZrI_4$$

(b) **Decomposition of iodide**

$$ZrI_4 \xrightarrow{1800\text{ K}} \underset{\text{Pure}}{Zr} + 2I_2$$

41. With respect to an ore, Ellingham diagram helps to predict the feasibility of its thermal reduction. It is a graph representation of Gibbs energy change *versus* absolute temperature.

Generally, the diagram consists of plots of $\Delta G°$ *versus* T for the formation of oxides of elements

$$2xM(s) + O_2(g) \longrightarrow \underset{\substack{\text{Thermal reduction}\\ \text{product}}}{2M_xO(s)}$$

42. Aluminium is extracted by electrolysis of a fused mixture of alumina (2-8%), synthetic cryolite Na_3AlF_6 (80-85%), AlF_3 and fluorspar. This makes alumina good conductor and lowers the fusion temperature also.

43. In the Hall-Heroult's process, aluminium in formed at the cathode. The cathode is made out of carbon.

The cell runs continuously and at intervals molten aluminium is drained from the bottom of the cell and more bauxite is added. The electrolytic reactions are as follows:

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

At anode $C(s) + O^{2-}(\text{melt}) \longrightarrow CO(g) + 2e^-$

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

44. Graphite rods act as anode during the electrolytic reduction of alumina (Hall-Heroult process).

At anode, O_2 gas is produced which reacts with the carbon of anode (rods) to produce CO_2 gas, so these graphite rods are consumed slowly and need to be replaced from time to time.

$$Al_2O_3 \rightleftharpoons 2Al^{3+} + 3O^{2-}$$

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

At anode $3O^{2-} \longrightarrow 3[O] + 6e^-] \times 2$

or $C(s) + O_2(g) \longrightarrow CO_2(g)$

45. Brine is electrolysed by using inert electrodes. And at anode the reaction is

$$Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-; \quad E^{\ominus}_{\text{cell}} = 1.36\text{ V}$$

As anode is always the site of oxidation.

46. In the metallurgy of aluminium (Al) graphite anode is oxidised to carbon monoxide (CO) and carbon dioxide (CO_2).

47. Hall-Heroult's process is an electro-reduction process by which pure alumina (Al_2O_3) is reduced to crude Al.

In this process, electrolysis of a fused mixture of Al_2O_3, $Na_3[AlF_6]$ (cryolite) and CaF_2 (fluorspar) is carried out at carbon cathode and graphite anode.

The overall reaction is represented as

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

49. In the extraction of copper (Cu) from its sulphide ore, the metal is formed by the reduction of Cu_2O with Cu_2S (cuprous sulphide).

50. The slag obtained during the extraction of copper from copper pyrites is of $FeSiO_3$. It is carried out in smelting.

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

51. Copper matte is produced when copper ore is mixed with silica in reverberatory furnace. The copper matte contains sulphide of copper (I) and iron (II).

52. In copper matte iron sulphide, FeS is present as impurity which in the presence of oxygen converts into iron oxide, a basic impurity. Silica (SiO_2) is an acidic flux.

Copper matte mainly contains Cu_2S and FeS. For removing the gangue FeS, silica present in the lining of the Bessemer's converter acts as a flux and forms slag (iron silicate) on reaction with FeO.

$$\underset{\text{Gangue}}{2FeS} + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$\underset{\text{Gangue}}{FeO} + \underset{\text{Flux}}{SiO_2} \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

54. In the metallurgy of iron, when $CaCO_3$ is added to blast furnace, it removes impurities from ore and forms slag.

$$CaCO_3 \longrightarrow CaO + CO_2 \quad (1070\text{-}1170\text{ K})$$

$$CaO + SiO_2 \longrightarrow CaSiO_3 \quad (1470\text{ K})$$

$$3CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2$$

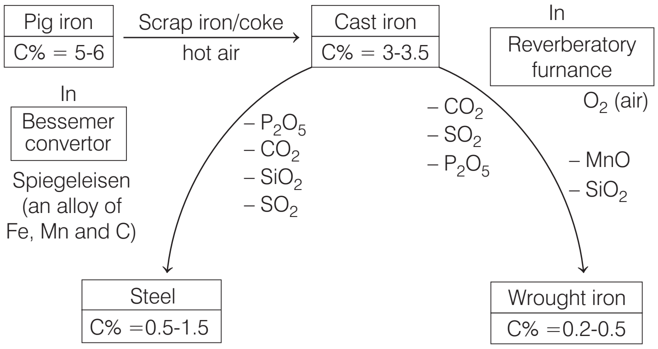
56. Wrought iron is the purest form of commercial iron.

57. Zr (zirconium), Ti (titanium), V (vanadium), Th (thorium) etc., are purified by van-Arkel method.

Cast iron is obtained by remelting pig iron with scrap iron and coke using hot air blast.

Nickel is purified by Mond's process and silver is extracted as anionic complex.

58. Consider the following flow sheet



So, it is clear from the flow chart that cast iron is used in the manufacture of wrought iron and steel.

Round II

1. A water soluble complex of silver with a dilute aqueous solution of NaCN is sodium argentocyanide. In the cyanide process, the native form is crushed and treated with 0.1-0.2% solution of NaCN and aerated.

$$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

Argentocyanide is soluble. Further metal is recovered from the complex by reduction with zinc.

2. CaO, K_2O cannot be reduced by carbon reduction method.

3. $$\underset{\text{Acidic impurity}}{SiO_2} + \underset{\text{Basic flux}}{CaO} \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

4. PbO and $PbSO_4$ get reduced by PbS itself which is already present in mixture. Because the reduction takes place by mixture itself, hence the process is known as self reduction.

$$2PbO + PbS \xrightarrow{\Delta} 3Pb + SO_2\uparrow$$

$$PbSO_4 + PbS \xrightarrow{\Delta} 2Pb + 2SO_2\uparrow$$

SnO_2 is reduced by C.

5. Lapis lazuli is the sodium aluminosilicate, present in earth rocks as blue stone.

6. Zinc blende is ZnS, not $ZnCl_2$.

7. Cuprite (Cu_2O) is oxide but argentite (Ag_2S) is not oxide.

8. In bauxite ore, only Al_2O_3 and SiO_2 react with conc. NaOH and forms sodium metaaluminate and silicate, respectively. Aluminate further dissolves in water.

$$Al_2O_3 + 2H_2O + 2NaOH \xrightarrow[35\text{ bar}]{500\text{ K}} 2NaAlO_2 + 3H_2O$$

$$NaAlO_2 + 2H_2O \longrightarrow 2NaAl(OH)_4$$

9. Roasting is the process in which the ore is heated strongly below its melting point in the presence of air.

11. Statements (d) is incorrect whereas all other statements are correct.

(a) Bronze is an alloy of Cu (96%) and Sn (4%).

(b) Cast iron is used to manufacture wrought iron.

(c) German silver is an alloy of 50% Cu, 30% Zn and 20% Ni.

(d) Brass is an alloy of 70% Cu and 30% Zn.

Hence, the incorrect option is (d).

12. Reaction (C) and (D) do not occur in the blast furnace during the extraction of iron.

(C) $FeO + SiO_2 \longrightarrow FeSiO_3 \Rightarrow$ (occur in Cu metallurgy)

(D) $FeO \longrightarrow Fe + \frac{1}{2}O_2$

(not possible without reducing agent like CO) whereas, both (A) and (B) reactions occur during extraction of Fe.

(A) $CaO + SiO_2 \longrightarrow CaSiO_3$
(slag formation in blast furnace)

(B) $2Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$
$\Rightarrow$ (reduction of Fe^{3+} to Fe_3O_4)

13. The explanation of given statements are as follows

(a) Zone refining process is used for the refining of B, Ga, In, Si and Ge.
Ti is refined by van Arkel method.
Thus, statement (a) is incorrect.

(b) Zincite (ZnO) is an oxide ore of Zn.
Thus, statement (b) is incorrect.

(c) NaCN is used in the hydrometallurgy of silver. It is known as Mc. Arthur Forrest process.
The reactions occuring during the process are as follows

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

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

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$$

Thus, statement (c) is incorrect.

(d) Aniline and cresol help in stabilising the froth in froth floatation process.

Thus, statement (d) is correct.

14. The correct ("leaching of bauxite using concentrated NaOH solution gives sodium aluminate and sodium silicate". 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. Al_2O_3 is leached out as sodium aluminate (and SiO_2 too as sodium silicate) leaving the impurities behind.

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

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. Here, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces precipitation.

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

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

$$Al_2O_3 \cdot xH_2O(s) \xrightarrow{1470\text{ K}} Al_2O_3(s) + xH_2O(g)$$

15. This problem involves the concept of Ellingham diagram as this diagram predicts the basis of oxidation state and stability of iron compounds.

(a) $Fe \xrightarrow{\text{Dil. } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4,\ O_2} Fe_2(SO_4)_3 \xrightarrow{\text{Heat}} Fe$

The above given reaction series is incorrect. The correct reactions series is as follows

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

$$H_2SO_4 + 2FeSO_4 + \frac{1}{2}O_2 \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3(s) + 3SO_3\uparrow$$

(b) $Fe \xrightarrow{O_2,\ heat} FeO \xrightarrow{Dil.\ H_2SO_4} FeSO_4 \xrightarrow{Heat} Fe$

This reaction series is also incorrect.

The correct reaction series is

$$F \xrightarrow[\Delta]{O_2} FeO \text{ [It could also be } Fe_2O_3 \text{ or } Fe_3O_4)$$

$$FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$$

$$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$$

(c) $Fe \xrightarrow{Cl_2,\ heat} FeCl_3 \xrightarrow{Heat,\ air} FeCl_2 \xrightarrow{Zn} Fe$

The reaction of $FeCl_3$ is not possible. Thus, the above reaction series is incorrect.

(d) $Fe \xrightarrow[O_2]{\Delta} Fe_3O_4 \xrightarrow{CO,\ 600℃} FeO \xrightarrow{CO,\ 700℃} Fe$

This reaction series is correct.

17. Flux is a substance with combine with gangue that present in the roasted or calcined ore to form fusible product, called slag.

18. Statements (A), (B), (C) and (D) are correct.

(A) $\underset{\text{Limestone}}{CaCO_3} \xrightarrow{\Delta} CaO + \underset{\text{Gas}}{CO_2}$

(B) Ag with $CN^{\ominus}$ form cyanide complex $[Ag(CN)_2]^{\ominus}$.
$Ag + CN^{\ominus} \longrightarrow [Ag(CN)_2]^{\ominus}$

(C) Mond's process is used to purification of Ni.

(D) van-Arkel method is used to purification of Zr and Ti.

19. Ellingham diagram provides information about temperature dependence of the standard Gibbs energies of formation of some metal oxides.

It predicts the feasibility of thermal reduction of the ore. The criterion of feasibility is that at given temperature, Gibbs energy of the reaction must be negative.

20. Except III, all the reduction processes are correct. Fe_2O_3 (haematite ore) is reduced into Fe, instead of FeO.

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

21. In case of auto-reduction, no reducing agent is required

(a) $\underset{\text{Haematite}}{Fe_2O_3} + \underset{\text{Reducing agent}}{3CO} \longrightarrow 2Fe + 3CO_2$

(b) $\underset{\text{Bauxite}}{Al_2O_3} + \underset{\text{Reducing agent}}{3C} + N_2 \longrightarrow 2AlN + 3CO\uparrow$

$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$

$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O \xrightarrow{Electrolysis} Al$

(c) $\underset{\text{Zinc blende}}{2ZnS} + 3O_2 \longrightarrow 2ZnO + 2SO_2$

$ZnO + \underset{\substack{\text{Reducing}\\ \text{agent}}}{C} \longrightarrow Zn + CO$

(d) $\underset{\text{Cinnabar}}{2HgS} + 3O_2 \longrightarrow 2HgO + 2SO_2$

$\underset{\text{Product}}{2HgO} \xrightarrow{\Delta} 2Hg + O_2$

23. Noble metals like Ag and Au are concentrated (or extracted) by cyanide process.

Froth floatation process is used to concentrate sulphide ore like ZnS. Ore concentration is also known as ore dressing.

Electrolytic reduction is applied in case of highly reactive metals like Al, Na, etc.

Ultrapure metals like Ge, Si, etc., are purified by zone refining.

25. The correct match is: A → 3; B → 4; C → 2; D → 1.

(A) Siderite is an ore of iron with molecular formula $FeCO_3$ (3).

(B) Kaolinite is an ore of aluminium with molecular formula $Al_2Si_2(OH)_2O_5$ (4).

(C) Malachite is an ore of copper with molecular formula $CuCO_3 \cdot Cu(OH)_2$ (2).

(D) Calamine is an ore of zinc with molecular formula $ZnCO_3$ (1).

26. Rutile has the formula TiO_2 and magnete has Fe_3O_4 or $Fe_3O_{2\times2}$. So the value of x will be 2.

27. $CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + 1 \times CO_2$

$CuCO_3 \cdot Cu(OH)_2 \xrightarrow{\Delta} 2CuO + H_2O + 1 \times CO_3$

Here, $x = 1,\ y = 2$

So, $x \times y$ will be 2.

28. Au and Pt occurs in the earth's crust in the native state.

29. Metals that can be refined by zone refining are Si, Ge and Ga.

30. P_2O_5 and $Na_2B_4O_7$ are acidic flux.

31. Zr, Ni and Ti can be refined by vapour phase refining.