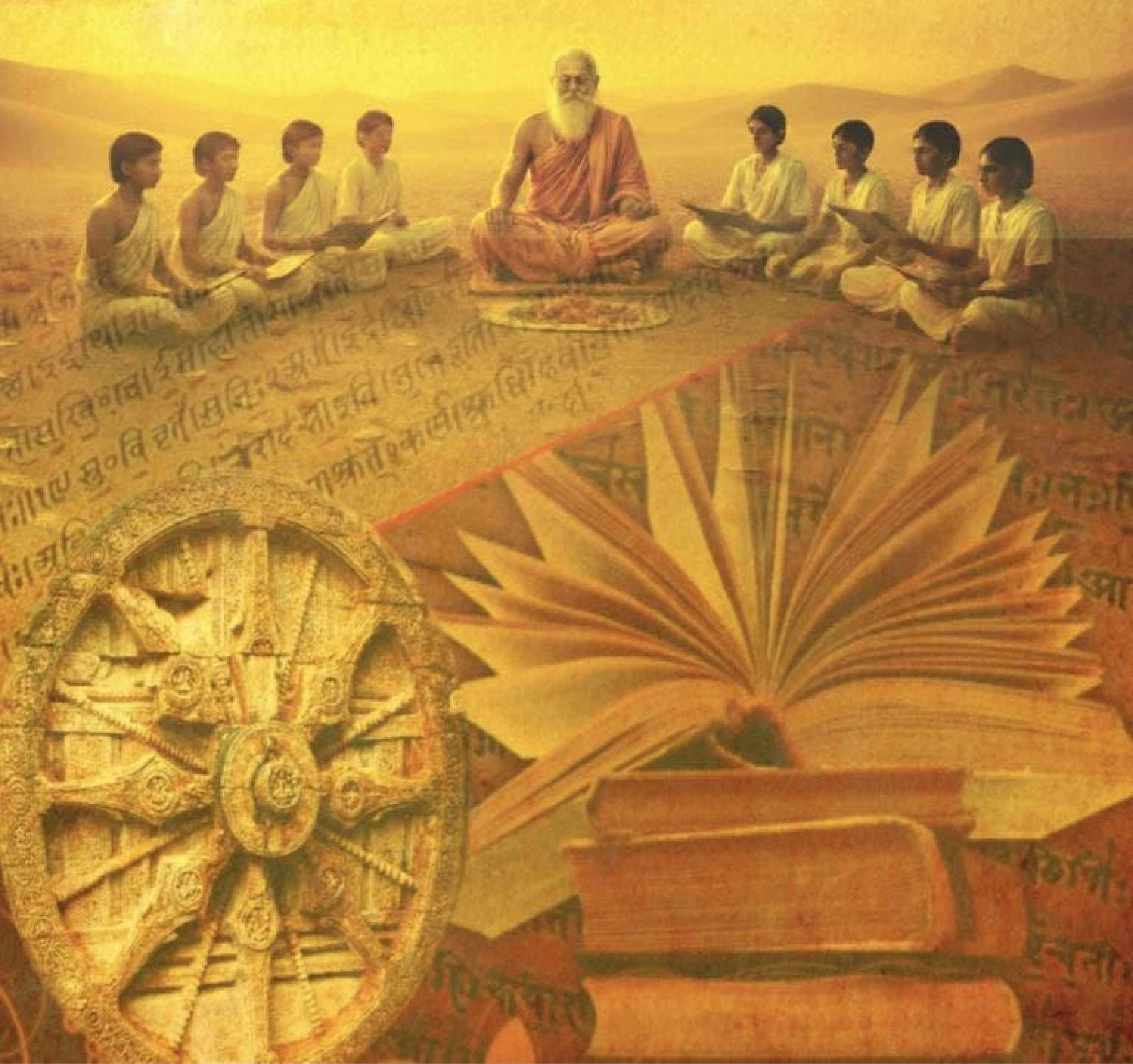
भारतीय ज्ञान प्रणाली उद्‌गम और विकास

सम्पादक :
डॉ. दिनेश चन्द्र शर्मा



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30

Processes of Isolation of Elements

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A few elements like carbon, sulphur, gold and noble gases, occur in free state while others in combined forms in the earth's crust. The extraction and isolation of an element from its combined form involves various principles of chemistry. A particular element may occur in a variety of compounds. The process of metallurgy and isolation should be such that it is chemically feasible and commercially viable. Still, some general principles are common to all the extraction processes of metals. For obtaining a particular metal, first we look for minerals which are naturally occurring chemical substances in the earth's crust obtainable by mining. Out of many minerals in which a metal may be found, only a few are viable to be used as sources of that metal. Such minerals are known as ores.

Rarely, an ore contains only a desired substance. It is usually contaminated with earthly or undesired materials known as gangue. The extraction and isolation of metals from ores involve the following major steps:

Concentration of the ore, Isolation of the metal from its concentrated ore, and Purification of the metal.

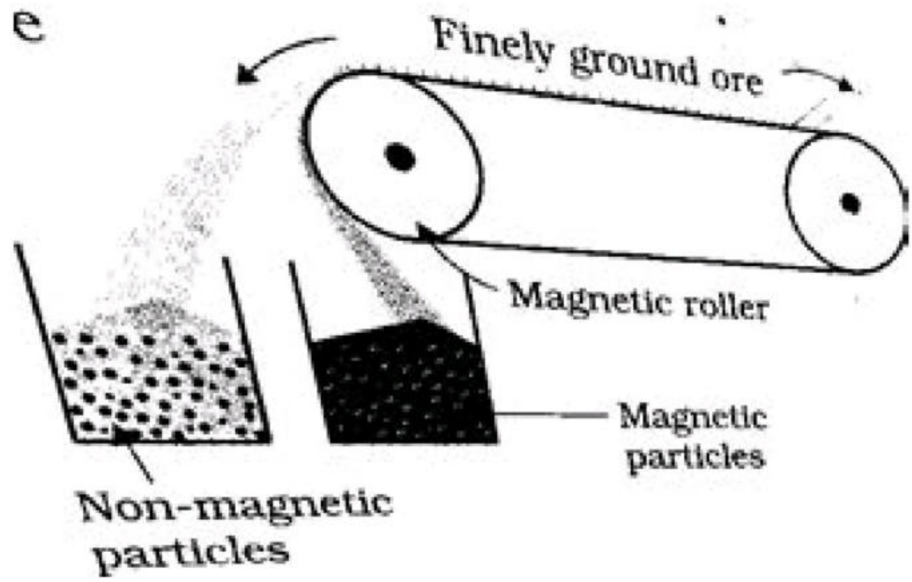
The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

Concentration of Ores

Removal of the unwanted materials (e.g., sand, clays, etc.) from the is known as concentration, dressing or benefaction. It involve steps and selection of these steps depends upon the differ physical properties of the compound of the metal present and the the gangue. The type of the metal, the available facilities environmental factors are also taken into consideration. Some of the Important procedures are described below.

Magnetic Separation

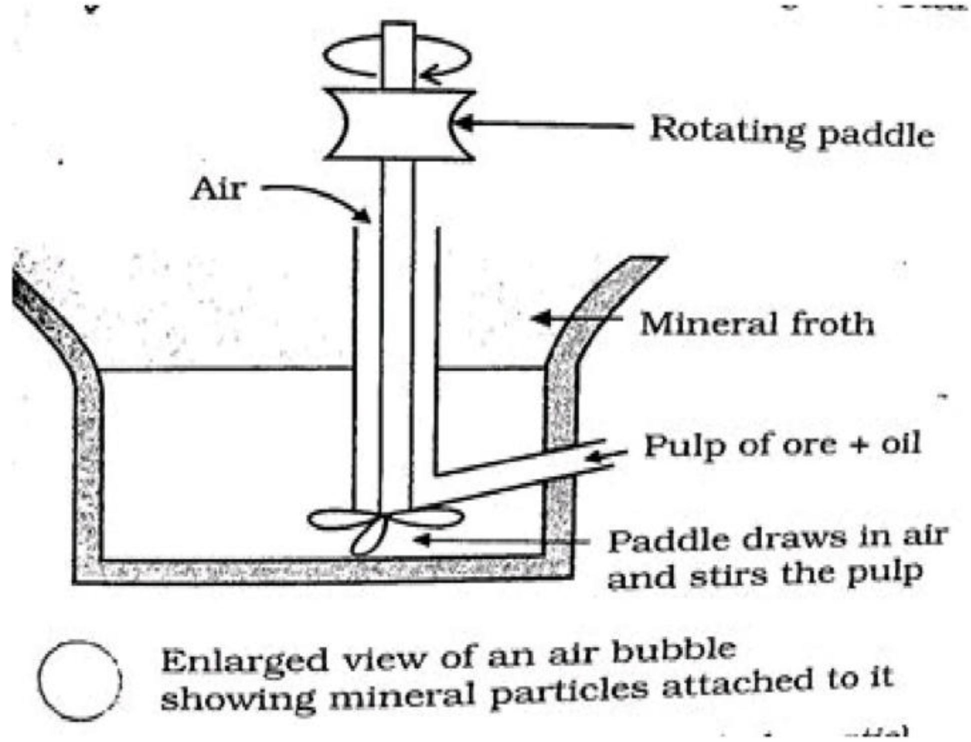
This is based on differences in magnetic properties of the ore components. If either the ore or the gangue (one of these two) is capable of being attracted by a magnetic field, then such separations are carried out (e.g.. in case of iron ores). The ground ore is carried on a conveyer belt which passes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



Froth Flotation Method

This 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 glycresols, 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. Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using depressants. For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.



Leaching

Leaching is often used if the ore is soluble in some suitable The following examples illustrate the procedure:

(a) Leaching of alumina from bauxite

Iron oxides and titanium oxide (TiO_2) as impurities, Concen The principal ore of aluminium, bauxite, usually contains is carried out by digesting the powdered ore with a concent wav, Al_2O, is leached out as sodium aluminate (and SIO, solution of NaOH at 473-523 K and 35-36 bar pressure sodium silicate) leaving the impurities behind:

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(I) \rightarrow 2Na[Al(OH))(aq)$

Al_2O, is precipitated. At this stage, the solution is seeded with filterate. The aluminate in solution is neutralised by passing CO_2 gas and hyd prepared samples of hydrated Al_2O, which induces the precipitatio

$2Na[Al(OH),] (aq) + CO_2(g) \rightarrow Al_2O_2.xH_2O(s)+2NaHCO, (aq)$

The sodium silicate remains in the solution and hydrated alum is filtered, dried and heated to give back pure Al_2O:

Al_2O_3 $XH_2O(s)$ 1470K, $Al_2O_3(s) + xH_2O(g)$

(b) Other examples

In the metallurgy of silver and that of gold, the respective met leached with a dilute solution of NaCN or KCN in the presence air (for O_2) from which the metal is obtained later by replacement

$4M(s) + 8CN (aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2] (aq) + 4OH(aq)$ (M= Ag or Au)

$2[M(CN)_2] (aq) + Zn(s) \rightarrow [Zn (CN)] (aq) + 2M(s)$

Thermodynamic Principles of Metallurgy

Some basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations. Gibbs energy is the most significant term here. The change in Gibbs energy, ΔG for any process at any specified temperature, is described by the equation:

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

where, ΔH is the enthalpy change and ΔS is the entropy change for the process. For any reaction, this change could also be explained through the equation:

$$\Delta G^{\Theta} = -RT \ln K$$

where, K is the equilibrium constant of the 'reactant - product system at the temperature, T. A negative ΔG implies a +ve K in equation 6.15. And this can happen only when reaction proceeds towards products. From these facts we can make the following conclusions:

When the value of ΔG is negative in . only then the reaction will proceed. If AS is positive, on increasing the value of TΔS would increase ΔH < TΔS and then ΔG become-ve.

If reactants and products of two reactions are put together in a system and the net ΔG of the two possible reactions is-ve, the overall reaction will occur. So the process of interpretation involves coupling of the Iwo reactions, getting the sum of their ΔG and looking for its magnitude and sign. Such coupling is easily understood through Gibbs energy (ΔG) vs T plots for formation of the oxides .

The reducing agent forms its oxide when the metal oxide is reduced. The role of reducing agent is to provide ΔG^0 negative and large enough to make the sum of ΔG® of the two reactions (oxidation of the reducing agent and reduction of the metal oxide) negative.

These reactions describe the actual reduction of the metal oxide. M_2O that we want to accomplish. The ΔG values for these reactions in general, can be obtained by similar subtraction of the corresponding ΔG, G^a values.

As we have seen, heating (1.e.. Increasing T) favours a negative value of $\Delta G''$. Therefore, the temperature is chosen such that the sum of ΔG in the two combined redox process is negative. In ΔG vs T plots, this is indicated by the point of intersection of the two curves (curve for M_2O and that for the oxidation of the reducing substance). After that point, the A,G° value becomes more negative for the combined process including the reduction of M_2O. The difference in the two ΔG values after that point determines whether reductions of the oxide of the upper line is feasible by the element represented by the lower line. If the difference is large, the reduction is easier

Refining

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are Insed depending upon the differences in properties of the metal and the impurity. Some of them are listed below.

(a) Distillation. (b) Liquation. (e) Electrolysis

(d) Zone refining. (e) Vapour phase refining

(f) Chromatographic methods

These are described in detail here.

(a) Distillation - This is very useful for low boiling metals like zinc and mercury. The Impure metal is evaporated to obtain the pure metal as distillate.

(b) Liquation - In this method a low melting metal like tin can be made to flow on a sloping surface. In this way it is separated from higher melting impurities.

(c) 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 electrolytic bath 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. This process is also explained using the concept of electrode potential, over potential, and Gibbs energy which you have seen in previous sections. The reactions are:

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

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

Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form the anode to the cathode:

Anode : $Cu \rightarrow Cu^{2+} + 2e^-$

Cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; recovery of these elements may meet the cost of refining.

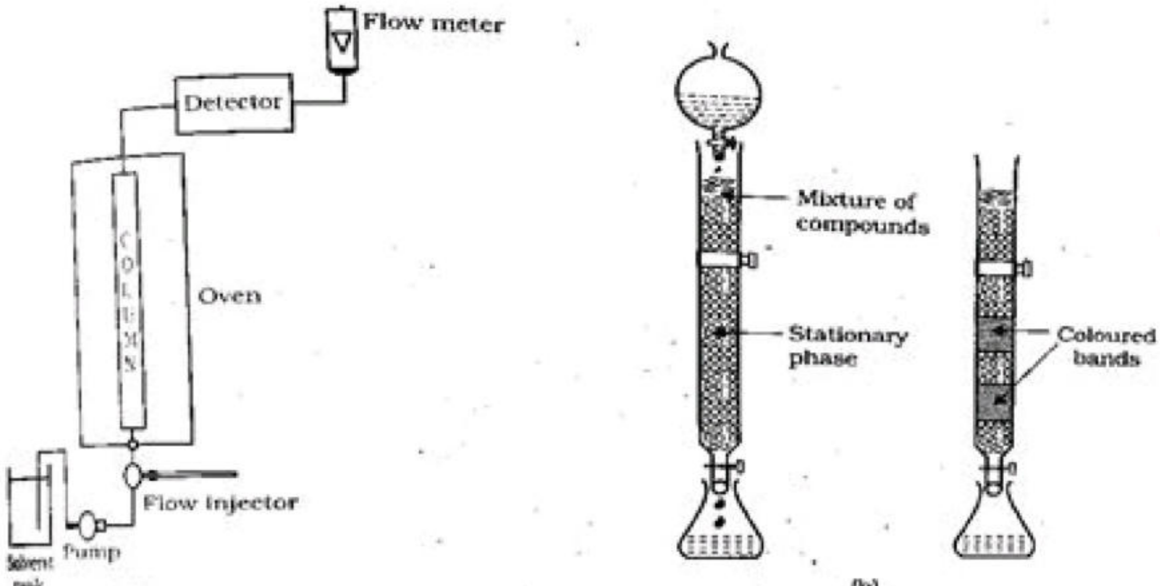
Zinc may also be refined this way.

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. The molten zone moves along with the heater which is mobile heater is fixed at one end of a rod of the impure metal moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on Into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off. This method is very useful for producing purity, e.g.. germanium, silicon, boron. gallium and indium.

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 (cluted) by using suitable solvents (eluant). Depending upon the physical state of the moving medium and the adsorbent material and also on the process of passage of the moving medium, the chromatographic method is given the name. In one such method the column of Al_2O, is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form. This is an example of column chromatography. This is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified. There are several chromatographic techniques such as paper chromatography, column chromatography. gas chromatography, etc.



(a) Industrial method

(b) Laboratory method

Procedures followed in column chromatography have been depicted.

Uses of Aluminium, Copper, Zinc and Iron

Aluminium foils are used as wrappers for chocolates. The fine the metal is used in paints and lacquers. Aluminium, being reactive, is also used in the extraction of chromium and man from their oxides Wires of aluminium are used as electricity cont Alloys containing aluminium, being light, are very useful.

Water and steam pipes. It is also used in several alloys that are Copper is used for making wires used in electrical industry tougher than the metal itself. e.g., brass (with zinc), bronze and coinage alloy (with nickel).

Zinc is used for galvanising iron. It is also used in large qua in batteries, as a constituent of many alloys, e.g., brass, (Cu 60% dust is used as a reducing agent in the manufacture of dye 40%) and german silver (Cu 25-30%, Zn 25-30%. Ni 40-50% paints, etc.

Cast iron, which is the most important form of iron, is used casting stoves, railway sleepers, gutter pipes, toys, etc. It is used in manufacture of wrought iron and steel. Wrought iron is used in ma anchors, wires, bolts, chains and agricultural implements Steel a number of uses. Alloy steel is obtained when other metals are a to it. Nickel steel is used for making cables, automobiles and aer parts, pendulum, measuring tapes, chrome steel for cutting tools crushing machines, and stainless steel for cycles, automobiles, ulers pens, etc.

A Summary of the Occurrence and Extraction of some Metals is Presented in the following Table :

Metal	Occurrence	Common Method	Remarks
Aluminium	1. Bauxtie, Al_2, xH_2O 2. Cryolite, Na, AIF_6	Electrolysis of Al_2O_2 dissolved in molten Na, AIF_6	For the extraction, a good source of electricity is required.
Iron	1. Haemattle, Fe_2O_2 2. Magenttle, Fe_2O_4	Reduction of the oxide with CO and Coke in Blast Furnace	Temperature approaching 2170 K is required.
Copper	1. Copper pyrties $CuFeS_2$ 2. Copper glance. Cu_2S 3. Malachite, $CuCO_2.Cu(OH)_2$ 4. Cuprtie, Cu_2O	Roasting of sulphide partially and reduction	It is self reduction in a specially designed converter. The reduction takes place easily
Zinc	1. Zinc blende or Sphalertie, ZnS 2. Calamine, $ZnCO_2$ 3. Zinctie, ZnO	Roasting Following by reduction with coke	The metal may be purified by fractional distillation.

Metals are required for a variety of purposes. For this, we need their extraction from the minerals in which they are present and from which their extraction is commercially feasible. These minerals are known as ores. Ores of the metal are associated with many impurities. Removal of these impurities to certain extent is achieved in concentration steps. The concentrated ore is then treated chemically for obtaining the metal. Usually the metal compounds (e.g., oxides, sulphides) are reduced to the metal. The reducing agents used are carbon, CO or even some metals. In these reduction processes, the thermodynamic and electrochemical concepts are given due consideration. The metal oxide reacts with a reducing agent: the oxide is reduced to the metal and the reducing agent is oxidised. In the two reactions, the net Gibbs energy change is negative, which becomes more negative on raising the temperature. Conversion of the physical states from solid to liquid or to gas, and formation of gaseous states favours decrease in the Gibbs energy for the entire system. This concept is graphically displayed in plots of ΔG vs T

(Ellingham diagram) for such oxidation/reduction reactions at different temperatures. The concept of electrode potential is useful in the isolation of metals (e.g., Al. Ag. Au) where the sum of the two redox couples is +ve so that the Gibbs energy change is negative. The metals obtained by usual methods still contain minor impurities. Getting pure metals require refining. Refining process depends upon the differences in properties of the metal and the impurities. Extraction of aluminium is usually carried out from its bauxite ore by leaching it with NaOH. Sodium aluminate, thus formed, is separated and then neutralised to give back the hydrated oxide, which is then electrolysed using cryolite as a flux. Extraction of iron is done by reduction of its oxide ore in blast furnace. Copper is extracted by smelting and heating in a reverberatory furnace. Extraction of zine from zinc oxides is done using coke. Several methods are employed in refining the metal. Metals, in general, are very widely used and have contributed significantly in the development of a variety of industries.

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