Metallurgy

Mostly, the metals occur in earth crust in a combined state but sometimes they can also occur in the free state. The most abundant metals in earth crust are aluminium, iron and calcium.

Minerals are naturally occurring chemical substance obtained through mining in which metals are present in combined formed.

Ores are those minerals from which metal are extracted conveniently and profitably. These ores contain good percentage of metal.

Ores of different metal:

Ore of Aluminium: Bauxite ($Al_2O_3.2H_2O$), Cryolite (Na_3AlF_6)

Ore of Zinc: Zinc Blende (ZnS), Calamine ($ZnCO_3$), Zincite (ZnO)

Ores of Copper: Copper Glance (Cu_2S), Copper Pyrites ($CuFeS_2$), Cuprite (Cu_2O)

Ores of Iron: Haematite (Fe_2O_3), Magnetite (Fe_3O_4), Iron Pyrites (FeS_2), Siderite ($FeCO_3$)

Ore of Tin: Casseterite (SnO_2)

Ore of Lead: Gallena (PbS)

Ore of Mercury (Hg): Cinnabar (HgS)

Ore of Ag: Horn Silver, $AgCl$

Ore of Au: Calaverite, $AuTe_2$

The extraction and isolation of a metal from their combined form involves various principles of chemistry. The whole systematic, scientific and technological process used for isolation of the metal from its ore is known as **metallurgy**.

The ore obtained through mining is associated with different undesirable chemical substance is called **gangue**. We have to remove these unwanted substances and isolate the pure metals. These involve few common steps.

1) Concentration or dressing of the ore

2) Isolation of the metal from its concentrated ore and

3) Purification of the metal

Ore concentration or dressing is a process of mechanically separating the grains of ore/ minerals from the gangue minerals. Concentration of ores involves several steps that depend upon the differences in physical properties of the compound of the metal present and that of the gangue. For concentration, at first ores are graded and crushed to reasonable size.

Gravity separation: Gravity separation is the separation of ore from gangue or, two or more ores of different specific gravity by their relative movement in response to the force of gravity and one or more other forces (such as centrifugal forces, magnetic forces, buoyant forces), one of which is resistance to motion by viscous medium such as heavy media, water or, less commonly, air.
Examples: ores of Gold and Silver.

Froth-Flotation: Froth-Flotation is a process for selectively separating hydrophobic materials from hydrophilic. In some cases, for example, sulphides ores of copper, zinc and lead concentration is increased by this method.
In froth floatation pine oil, fatty acids, and xanthates are used known as collector and cresols, aniline are used as froth stabilisers those stabilise the froth. The principle of froth floatation is that sulphide ores are preferentially wetted by oil where as the gangue particles are wetted by water.
In few cases, two sulphide ores are separated by adjusting proportion of oil to water or by using 'depressants'. For example, 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.

Magnetic Separation: This involves the use of magnetic properties of either the ore or the gangue to separate them. The ore is first ground to fine pieces and then passed on a conveyor belt passing over a magnetic roller. The magnetic ore remains on the belt and the gangue falls off the belt.
Example: Being magnetic, Iron Tungstate ($FeWO_4$) gangue can be separated from Casseterite (SnO_2).

Leaching or Chemical Separation: Leaching is a process where ore is treated with chemicals to convert the metals within into soluble salts while impurity remains insoluble.
There are four types of leaching:
1) Cyanide leaching (e.g. gold ore)
$4M(s) + 8CN^{-}(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^{-}(aq) + 4OH^{-}(aq)$ (M= Ag or Au)
$2[M(CN)_2]^{-}(aq) + Zn(s) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2M(s)$

2) Alkali leaching (e.g. bauxite ore)It is used to eliminate SiO_2, iron oxide, TiO_2 etc from bauxite.
$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$
$2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3(aq)$
$Al_2O_3.xH_2O(s) \xrightarrow{heat} Al_2O_3(s)$

3) Acid leaching (e.g. sulphide ore)
$2ZnS + O_2 + 2H_2SO_4 \rightarrow 2ZnSO_4 + 2H_2O + 2S$

Isolation of metal from the concentrated ore involves the refining of metals from the compounds. It involves (a) conversion an ore into an oxide. (b) Reduction of metal oxide using a suitable reducing agent.

The first step involve Calcination and Roasting

1. Calcination: Ores are heated below the melting point in absent of O_2 to convert metal oxide by removing gangue. Examples: Oxide and carbonate ores.

$Fe_2O_3.xH_2O(s) \xrightarrow{\Delta} Fe_2O_3(s) + xH_2O(g)$; $MgCO_3 \xrightarrow{\Delta} MgO + CO_2\uparrow$

2. Roasting: During this process, extraction is done by heating the ore in a regular supply of air to convert metal oxide. Sulphide ores of Zinc, Lead and Copper etc.

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

The Second step involve:

1. Carbon Reduction Process:

Roasting ores are heated with sufficient coke (CO is also used) as reducing agent which reduces the oxides of metals (by losing oxygen) to produce metallic element like zinc, iron, copper, lead etc.

Reaction: $2PbO + C \rightarrow 2Pb + CO$

2. Goldschmidt Thermite Process:

Metal Oxides are heated above the m.p. with Al dust as reducing agent which reduces metal oxides to metals like V, Cr, Mn, Fe etc.

Reaction: $3V_2O_5 + 10\ Al \rightarrow 5\ Al_2O_3 + 6V$

3. Self Reduction Process: The sulphide ores of less electropositive metals like Hg, Pb, Cu etc., are heated in the air so as to convert a part of the ore into oxide or sulphide which then reacts with the remaining sulphide ore to give the metal.

Here sulphide ore itself acts as a reducing agent and need not necessary any additional reducing agent

$Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$; $2Cu_2O + Cu_2S \rightarrow SO_2 + 6Cu$

Ellingham Diagram: Ellingham Diagram is a graphical representation of Gibbs energy which helps to choice the reducing agent for reduction of metal oxides. This diagram helps us in predicting the feasibility of thermal reduction of an ore.

Characteristics:

(a)(i) It is a plot of ΔG^0 (M_xO) i.e., standard free energy change in the oxide formation reaction of common metals and reducing agents verses temperature (T).

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

(ii) Since, gaseous O_2 is consumed, entropy (ΔS) becomes negative resulting ΔG^0 become more positive (less negative) with increasing temperature. That means, stability of metal oxides decreases with increases of temperature.

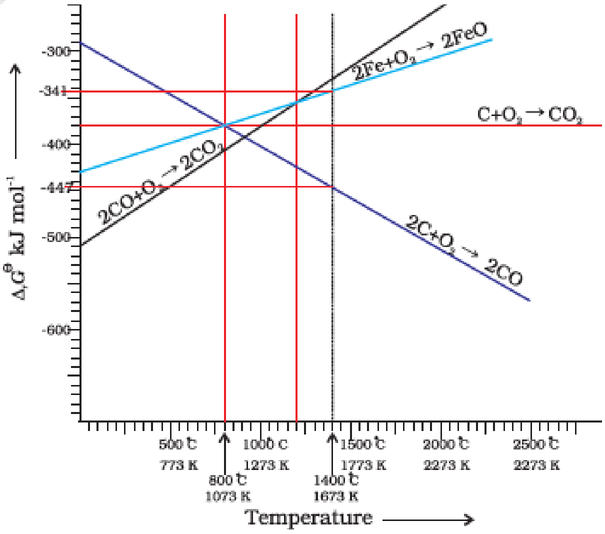
(b) Each curve is a straight line and has positive slopes except when phase change is (solid → liquid or liquid → gas) takes place.

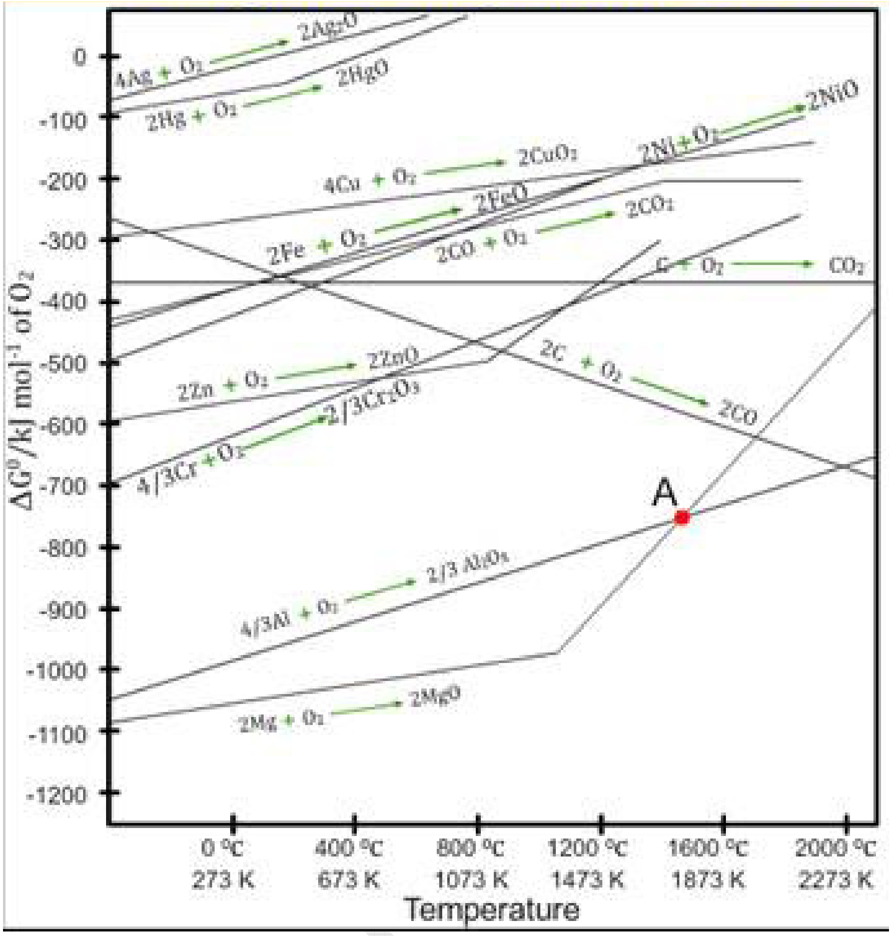
(c) A temperature is reached at which the curve crosses $\Delta G^0=0$ line. Below this temperature, ΔG^0= -ve i.e., M_xO is stable. Above this point, ΔG^0= +ve, M_xO will decomposed.

(d) A vertical line at any particular temperature provides the relative stability of the oxides. The oxide having higher in position is less stable than the oxide resides in lower position in the plot.

(e) The entropy change in the formation of CO_2 is negligible as the number of gaseous molecule does not change. So, plots of ΔG^0 versus T runs parallel to temperature axis. But, for CO formation, entropy is increased that's why ΔG^0 becomes more negative with increase of temperature. So, slope of the line is negative. This makes C as a strong reducing agent at higher temperature.

(f) A metal oxide is reduced by another metal or coke when its Ellingham line belongs at higher position than the reducing agent.





Limitation:

i)The plot indicates the reduction reaction is possible or not but, does not explain the kinetics of reduction process.

ii) It is presumed that reactants and products are in equilibrium as $\Delta G^0 = -RT\ln K_{eq}$. But, it is not always true because the reactant/product may be solid.

There are several methods of **refining or purifying** metals. These methods include:

1. Distillation: Vaporizing the metal and then allowing it to solidify outside of the impurities. Examples: Zn, Cd, Hg

2. Liquation: Metals that have particularly low melting points can use the liquation method. Liquation is similar to distillation, except the impure metal is only melted instead of vaporized.

When the other impurities have a much higher melting point, they will remain solid and can be removed from the pure liquid metal. Examples: Sn, Pb

3. Electrolysis: Metal oxide is melted and a current is passed through it. The electric current separates the metal from the oxygen.

A cathode adds electrons on the metal, making pure metal and an anode collects the extra electrons on the oxygen, combining it with carbon to form CO. Examples: Al, Zn, Sn etc.

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

Aluminium is obtained by Hall-Heroult process. In this process purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed using in an electrolytic cell using carbon electrodes. The graphite anode and steel vessel with lining of carbon acts as cathode is used. The overall reaction may be written as: $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

The electrolytic reactions are:

Cathode: Al^{3+} (melt) + 3e → Al(l)

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

C(s) + $2O^{2-}$ (melt) → CO2 (g) + $4e^-$

4. 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. In this technique a molten region travels through the material to be refined, picks up impurities at its advancing edge, and then allows the purified part to recrystallize at its opposite edge.

In purification process, the impure metal in form of rod shape is placed in a quartz tube filled with inert gas. The rod is surrounded by a movable ring acts as heater. During heating impurities are soluble in melt and carried along with the molten zone on moving the heater and pure metal crystallizes from the melt. As a result impurities are transported to one end of the rod which is cut off.

This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

5. Vapour phase refining: In this method, impure metal is first converted into its volatile compound by heating with a chemical reagent at lower temperature. After this, the volatile compound is decomposed by heating to give the pure metal. So, the two requirements are:

(i) Metal should form a volatile compound with an available reagent,

(ii) Volatile compound should be easily decomposable, so that the recovery becomes easy.

1. **Mond process for refining Nickel**: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex named as nickel tetracarbonyl. This compex is decomposed at higher temperature to obtain pure metal.

$\mathrm{Ni} + 4\mathrm{CO} \xrightarrow{330-350\,K} [\mathrm{Ni(CO)_4}]$ $[\mathrm{Ni(CO)_4}] \xrightarrow{450-470\,K} \mathrm{Ni} + 4\mathrm{CO}$.

2. **van Arkel method for refining Zirconium or Titanium**: This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti.

The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises: $Zr + 2I_2 \rightarrow ZrI_4$

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal deposits on the filament. $ZrI_4 \rightarrow Zr + 2I_2$

In Hydrometallurgy, metal is extracted from strong aqueous acidic or basic solutions of ore. Generally, Cu, Pb is extracted by hydrometallurgy.

Copper is extracted by hydrometallurgy from low grade ores. The ore is leached out using acid. Then, the solution containing Cu^{2+} is treated with scrap iron or H_2.

$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$

$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

Since, Zn is more electropositive metal than Fe and H. So, it is not reduced by them.

Kroll process

It is a pyrometallurgical process for the production metallic titanium. The extraction process involved as follows:

(i) First, powdered ilmenite or rutile is heated with carbon and chlorine.

$2FeTiO_2 + 6C + 7Cl_2 \rightarrow 2TiCl_4 + 2FeCl_3 + 6CO$; $TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$

(ii) $TiCl_4$ is separated from other volatile compounds ($FeCl_3$) by fractional distillation.

(iii) Finally, TiCl4 is reduced by liquid magnesium in inert atmosphere.

$TiCl_4 + 2Mg = Ti + 2MgCl_2$

The magnesium chloride and excess magnesium are removed by washing with water and dilute HCl.

Parting process: It is a selective leaching or corrosion process in which more reactive constituent of an alloy is preferentially removed, leaving behind the more noble metal. Parting is also known as dealloying, demetalification, selective corrosion, selective leaching or parting corrosion. For example, the preferential leaching of zinc from brass is called dezincification. In this process, selective removal of zinc leaves a relatively porous and weak layer of copper and copper oxide. In the case of gray iron, dealloying is called graphitic corrosion.

By parting process gold is separated from silver as both are chemically similar and often extracted together from the same ores or recovered as by-products from the extraction of other metal ores.

A solid mixture of the two, known as bullion, can be parted by boiling in nitric acid. The silver is dissolved as silver nitrate, leaving a residue of gold that is filtered off and washed. Silver is precipitated out of solution by the addition of ferrous sulfate.

Gold and silver are mostly parted electrolytically. The bullion is cast into anodes, which are placed into an electrolytic cell and subjected to an electric current. Silver dissolves in the electrolyte and then deposits onto the cathodes. The parting process may be achieved by boiling the bullion in sulphuric acid and potassium nitrate to dissolve the silver.

Previous year questions

2019

- ✓ Write two characteristics of Ellingham diagram.
- ✓ Outline the principle of zone refining.
- ✓ Cu can be extracted by hydrometallurgy but not Zn. Explain.

2021

- ✓ How do you prepare Ni from $Ni(CO)_4$ using Mond's process.
- ✓ What do you mean by zone refining method? How do you prepare pure Si from SiO_2 using zone refining process?

  Silicon is prepared by reduction of SiO_2 with high purity coke in an electric arc furnace. The formation of SiC can be avoided by using excess SiO_2. Pure Silicon can be obtained through the formation of $SiCl_4$ which is purified by distillation and then reduction by Mg or Zn. $Si + Cl_2 = SiCl_4$; $SiCl_4 + 2Mg = Si + 2MgCl_2$.

  Pure silicon also is produced by zone refining process. (as noted above)

2022

- ✓ Write down the principle of vapour phase refining. How Ni and Zr can be purified in this method?
- ✓ What do you know about Ellingham diagram? Illustrate with example.
- ✓ Why is carbon used for reduction of ZnO?
- ✓ What do you mean by hydrometallurgy?