



Surface Chemistry

Adsorption

Reversible and irreversible adsorption

The adsorption is **reversible**, if the adsorbent can be easily removed from the surface of the adsorbent by physical methods. It is called **irreversible adsorption**, if the adsorbate can not be removed from the surface of the adsorbent.

A gas adsorbed on a solid surface can be completely removed in vacuum. It is, therefore, reversible adsorption. Examples of irreversible adsorption are adsorption of oxygen on tungsten adsorbate and adsorption of CO on tungsten surface

Adsorbent, Adsorbate and Interface

- The substances upon whose surface the change of concentration occurs, is called **adsorbent**.
- The substance taken up on the surface is called **adsorbate**.
- The common surface between the two phases where the adsorbed molecules concentrate is called the **interface**.

Physisorption and Chemisorption:

Physisorption	Chemisorption
Only van der Waals force are present between adsorbate and surface of adsorbent	Chemical bonds are formed between adsorbate and surface of adsorbent
Low enthalpy of adsorption i.e, in the order of 20 kJmol ⁻¹ .	High enthalpy of adsorption i.e, order of 200 kJmol ⁻¹ .
Reversible It is usually takes place at low temperature and does not require any activation energy.	Irreversible It takes place at high temperature and require activation energy..
Multi molecular layer of adsorbate are formed on the surface Not specific.	Only monomolecular layers are formed. Highly specific.



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Langmular Isotherm:

If A, B & AB represents the adsorbed, adsorbent and the adsorbed - adsorbent complex then,



k_a = Equilibrium constant for adsorption = $\frac{[AB]}{[A][B]}$

k_d = Equilibrium constant for desorption = $\frac{[A][B]}{[AB]}$

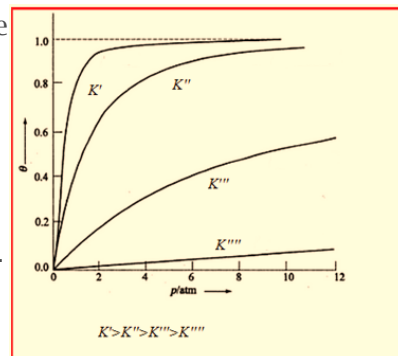
K = Distribution coefficient = k_a/k_b

Θ = Fraction of the surface of adsorbent available for adsorption.

P = pressure

So,

$$\Theta = \frac{KP}{1+KP} \quad (\text{Langmular Equation})$$



Freundlich Isotherm:

x = Mass of the gas adsorbed

m = Mass of adsorbent

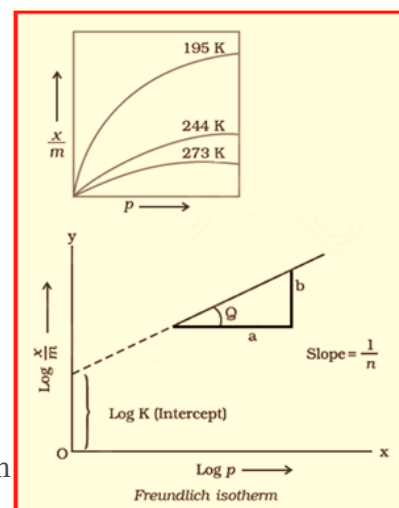
p = Pressure

K and n = constants

$$x/m = k.p^{(1/n)} \quad [n > 1]$$

or

$$\log x/m = \log k + 1/n \log P$$



Factors Affecting Adsorption:

- **Temperature:** An increase of temperature leads to a decrease in amount adsorbed and vice - versa.
- **Pressure or concentration:** It has been found that in most cases, the adsorption is reversible and an increased pressure of a gases vapour or an increase in concentration of a solute causes increased adsorption.
- **Nature of Adsorbate and Adsorbent:** The amount of the gas adsorbed depends upon the nature of adsorbent and the gas (adsorbate), which is to be adsorbed. It has been found that easily liquifiable gases such as NH_3 , HCl , Cl_2 , SO_2 , CO_2 etc. are more readily adsorbed than so the called permanent gases such as O_2 , N_2 , H_2 etc. This is because that molecules of the former type of gases have greater Vander waal's or molecular force of attraction.



Colloids

Dispersed Phase:

The phase which is dispersed or scattered through the dispersion medium is called Dispersed phase or discontinuous phase.

Dispersion Medium:

The phase in which the scattering is done is called the dispersion medium or continuous medium.

Dispersed Phase	Dispersion Medium	Name	Typical example
Solid	Liquid	Sol	Gold sol, Mud, Fe(OH) ₃ sol,
Solid	Solid	Solid sol	Gems, Ruby glass, Minerals
Solid	Gas	Aero sols	Smoke (Carbon in air) Volcanic dust
Liquid	Solid	Gel	Curd, Cheese, Jellies
Liquid	Liquid	Emulsion	Milk, water in benzene, cream
Liquid	Gas	Liquid aero sol	Clouds, fog (water in air) mist
Gas	Solid	Solid foam	Lava, Pumica
Gas	Liquid	Foam	Froth on beer , whipped cream

Lyophobic and Lyophilic Colloids:

Those substance whose colloidal solution cannot be prepared by bringing them in contact with a solvent are called Lyophobic (disliking, fearing or hating a liquid). On the other hand those substances whose colloidal solutions can be prepared by bringing them in contact with a liquid solvent are called lyophilic colloids (loving a solvent).

Emulsions:

- **Emulsion of oil in water:** Those emulsions in which the dispersed phase is oil and water is the dispersion medium. These emulsion are generally represented as O in W emulsions. Examples are milk, vanishing cream etc.
- **Emulsions of water in oil:** Those emulsion in which the dispersed phase is water while oil is the dispersion medium. These emulsion are generally represented as W in O emulsions. Examples are butter, ice cream etc.



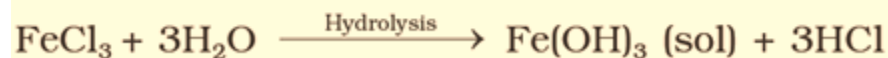
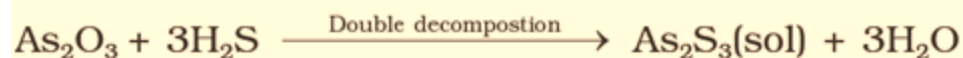
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Difference between True Solutions, Suspension & Colloids

	Suspension	Colloid
True solution		
Homogenous	Heterogeneous	Heterogeneous
Particle size less than 1nm	Particle size more than 1000nm	Particle size between 1-1000nm
Don't settle down	Settle down under the influence of gravity	Don't settle down
Complements cannot be separated out by filtration	Can be filtered	Can be filtered using special filter papers
Don't show tyndrall effect	Show tyndrall effect	Show tyndrall effect

Methods of preparation of colloids

Chemical Methods:

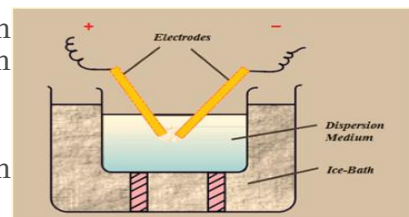


Bredig's method:

An electric arc is struck between two metallic electrodes immersed in dispersion medium. The arc produced vapourises the metal which on further condensation produces particles of colloidal size.

- **Peptization:**

Process of converting a precipitate into colloidal sol by shaking it with electrolyte in dispersion medium.



Hardy Schulze Rule:

- Ion carrying charge opposite to the colloidal particle has capacity to coagulate the colloid.



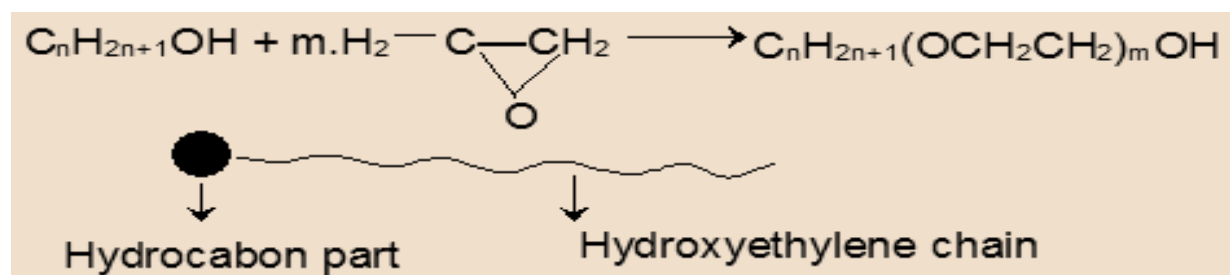
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- Greater the valency of ion, greater will be the coagulating power.
- Gold Number: The minimum amount of lyophilic colloid in milligrams which can prevent the coagulation of 10 ml gold sol against 1 ml of 10% NaCl solution.

Surfactants

substances which gets preferentially adsorbed at the air - water and solid - water interfaces forming an oriented monolayer where the hydrophilic groups point towards the aqueous phase and the hydrocarbon chain point towards the air or towards the oil phase.

- **Anionic surfactants** : Sodium salts of higher fatty acids such as sodium palmitate ($C_{16}H_{33}COONa$), sodium stearate ($C_{18}H_{37}COONa$) and sodium Oleate ($C_{17}H_{33}COONa$).
- **Cationic Surfactants**: Those which dissociates in water to yield positively charged ions **examples**: $C_{16}H_{33}N^+$, $C_{16}H_{33}(CH_3)^+$ etc.
- **Non ionogenic**: Those whose molecules cannot undergo dissociation when an alcohol having a higher molecular weight reacts with several molecules of ethylene oxide, a non - ionogenic surfactant is produced.



Micelle:

Aggregates formed when the surfactant molecules in the water air interface become so packed in the monolayer that no more molecules can be accumulated with ease they accumulate in the bulk of the solution.

At a given temperature and concentration, a micelle of a surfactant of monodispersed i.e., they contain same number of molecules usually between 25 to 100.

Critical concentration for micelle formation decreases as the molecular weight of hydrocarbon chain of surfactant grows because in this case true solubility diminishes and the tendency of surfactant molecules to associate increases.

General Principles & Processes of Isolation of Metals

Types of Ores:

Ores may be divided into four groups

- **Native Ores**: These ores contain the metal in free state eg. Silver gold etc. These are usually formed in the company of rock or alluvial impurities like clay, sand etc.



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- **Oxidised Ores:** These ores consist of oxides or oxysalts (eg. carbonates, phosphate) and silicate of metal. Important oxide ore includes, Fe_2O_3 , $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ etc. and important carbonate ores are limestone (CaCO_3), Calamine (ZnCO_3) etc.
- **Sulphurised Ores:** These ores consist of sulfides of metals like iron, lead, mercury etc. Examples are iron pyrites (FeS_2), galena (PbS), Cinnabar (HgS)
- **Halide ores:** Metallic halides are very few in nature. Chlorides are most common examples include horn silver (AgCl) carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and fluor spar (CaF_2) etc.

Metallurgy:

It is the process of extracting a metal from its ores. The following operations are carried out for obtaining the metal in the pure form.

- Crushing of the ore
- Dressing or concentration of the ore.
- Reduction of metal.
- Purification or refining of the metal

Concentration

Physical Method:-

Gravity separation:

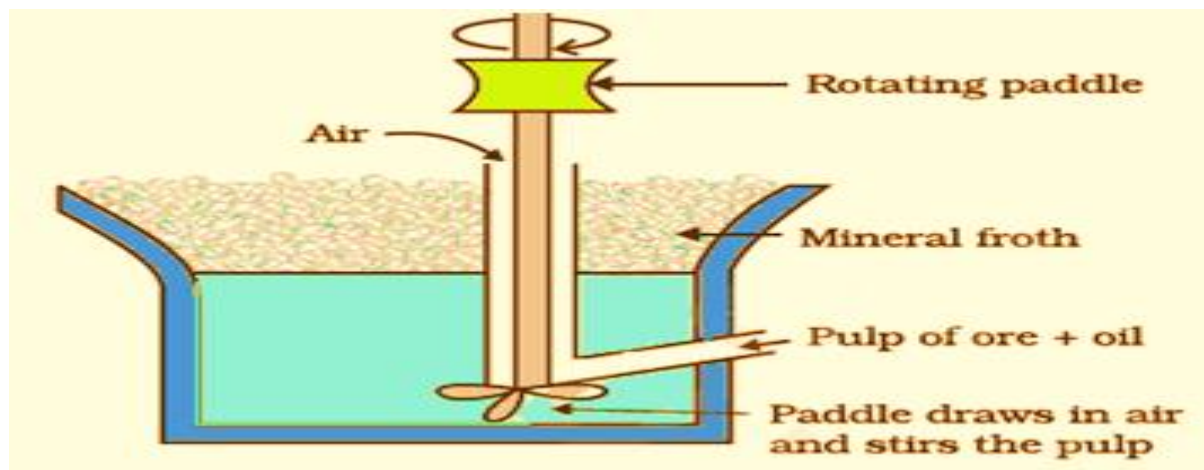
The powdered ores is agitated with water or washed with a running stream of water. The heavy ore particles of sand, clay etc. are washed away.

Froth Floatation Process:

The finely divided ore is introduced into water containing small quantity of oil (e.g. Pine Oil). The mixture is agitated violently with air a froth is formed which carries away along with it the metallic particles on account of the surface tension forces. The froth is transferred to another bath where gangue-free ore settles down.

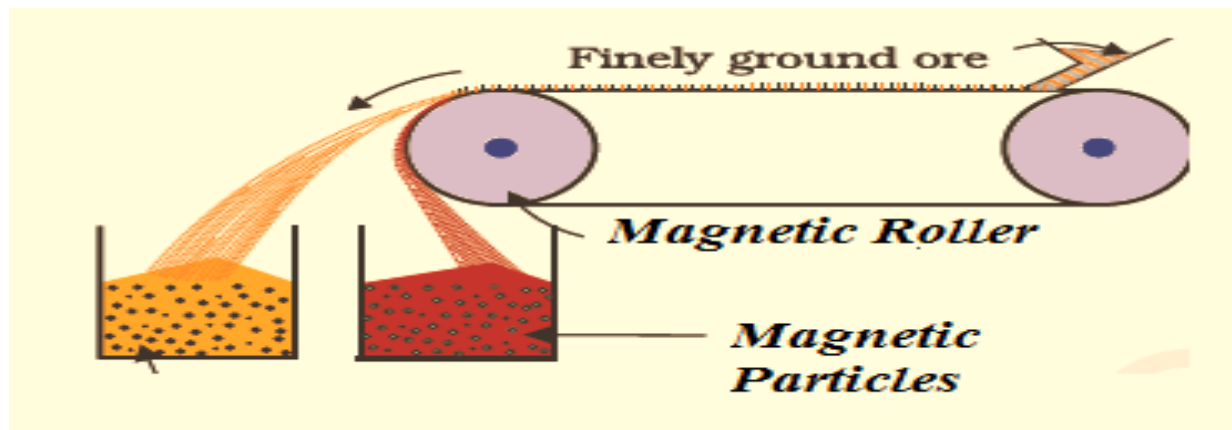


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Electro Magnetic Separator:

. A magnetic separator consists of a belt moving over two rollers, one of which is magnetic. The powdered ore is dropped on the belt at the other end. Magnetic portion of the ore is attracted by the magnetic roller and falls near to the roller while the non-magnetic impurity falls farther off

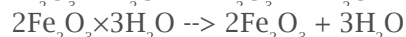
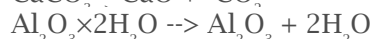


Chemical Methods:-

Calcination:

Carbonate or hydrated oxide ores are subjected to the action of heat in order of expel water from hydrated oxide and carbon dioxide from a carbonate.

Examples:



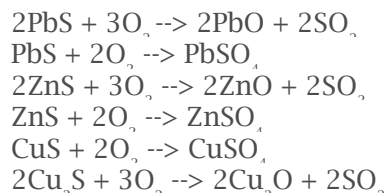
Roasting:



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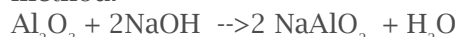
Sulphide ores either are subjected to the action of heat and air at temperatures below their melting points in order to bring about chemical changes in them.

Examples:



Leaching:-

It involves the treatment of the ore with a suitable reagent as to make it soluble while impurities remain insoluble. The ore is recovered from the solution by suitable chemical method.



Reduction of Free Metal:

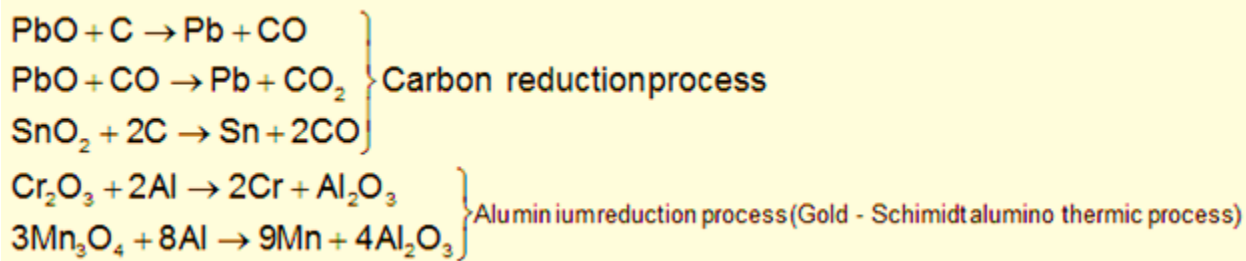
Smelting:

Reduction of a metal from its ore by a process involving melting

Several reducing agents such as sodium, magnesium and aluminum are used for reduction.

The calcinated or roasted ore is mixed with carbon (coal or coke) and heated in a reverberatory or a blast furnace.

Carbon and carbon monoxide produced by incomplete combustion of carbon reduce the oxide to the metal.



Flux:

The ores even after concentration contain some earthy matter called gangue which is heated combine with this earthy matter to form an easily fusible material. Such a substance is known as flux and the fusible material formed during reduction process is called slag.



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- **Acidic fluxes:-** like silica, borax etc are used when the gangue is basic such as lime or other metallic oxides like MnO, FeO, etc
- **Basic fluxes:-** like CaO, lime stone (CaCO_3), magnesite (MgCO_3), hematite (Fe_2O_3) etc are used when the gangue is acidic like silica, P_2O_5 etc.

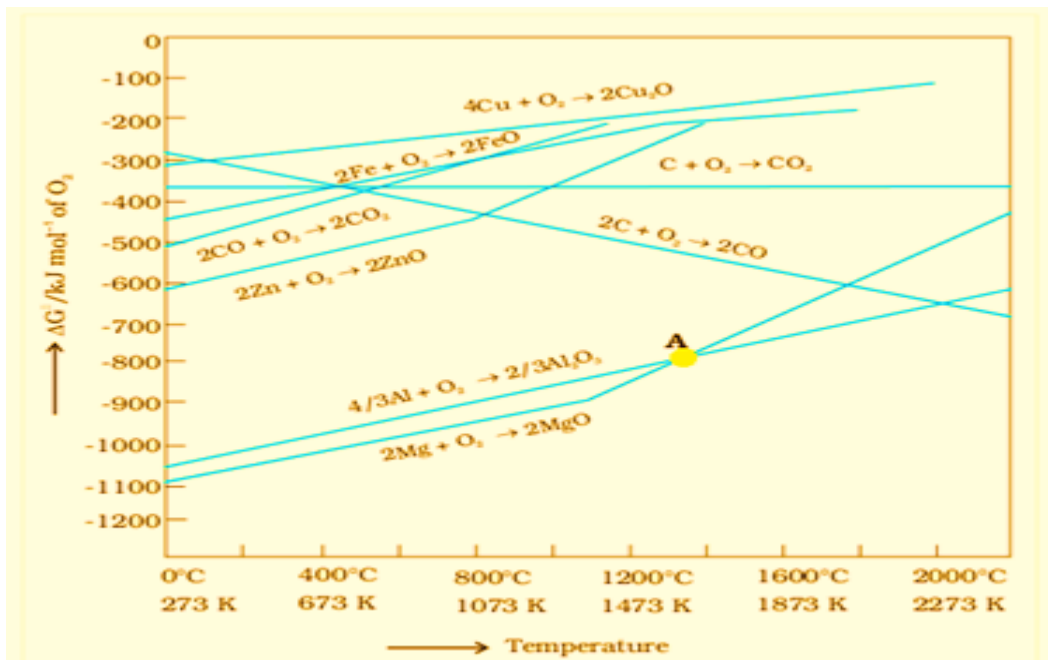
Refining

The metals obtained by the application of above reduction methods from the concentration ores are usually impure. The impure metal is thus subjected to some purifying process known as refining in order to remove undesired impurities. Various process for this are

- | | |
|--------------------------|-------------------------|
| a) Liquefaction process | b) Distillation process |
| c) Cupellation | d) Poling |
| e) Electrolytic refining | f) Bessemerisation |

Thermodynamic Principles of Metallurgy:

$\Delta G = \Delta H - TS$
or $\Delta G^\circ = -RT \ln K$



An element A can reduce element B if ΔG value for oxidation of A to AO is lower than the ΔG value for oxidation of B to BO.

i.e. $\Delta G_{(A \rightarrow AO)} < \Delta G_{(B \rightarrow BO)}$

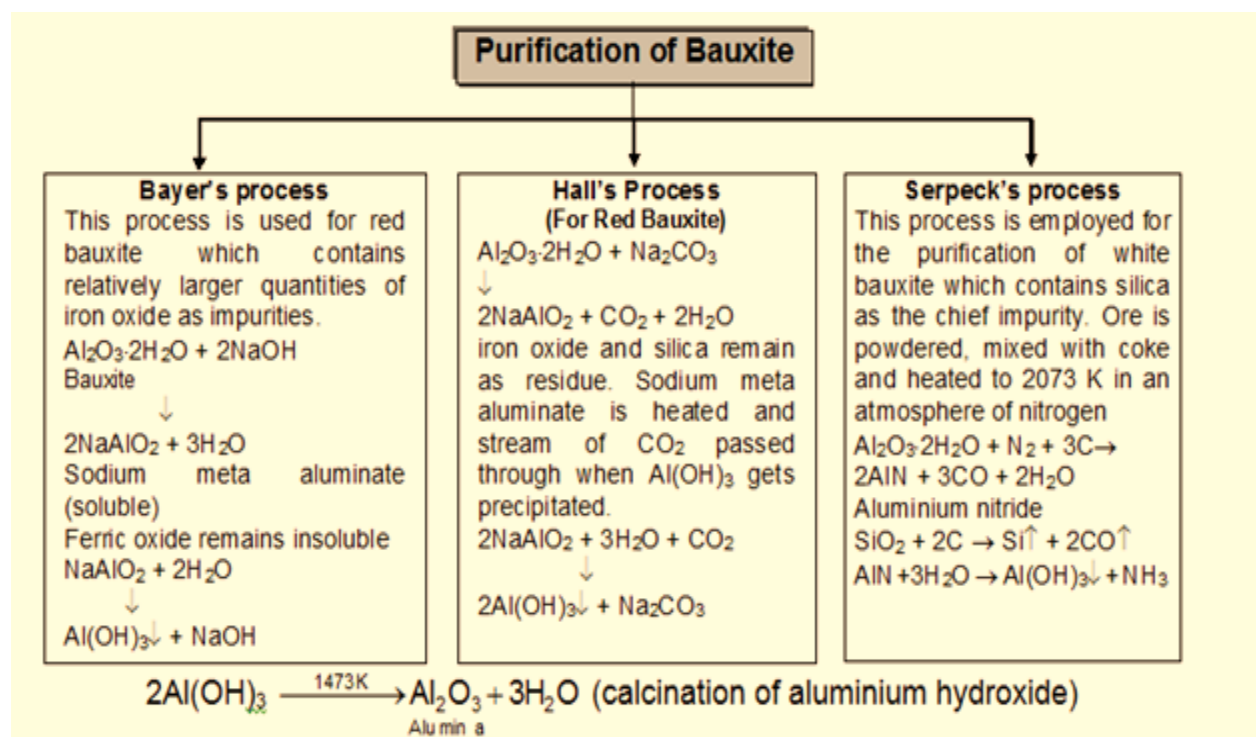
Extraction of Aluminium:



Important Ores of Aluminium:

- Bauxite : $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ Cryolite: Na_3AlF_6
- Feldspar: $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ or KAlSi_3O_8
- Mica: $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- Corundum: Al_2O_3
- Alumstone or Alunite: $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al}(\text{OH})_3$

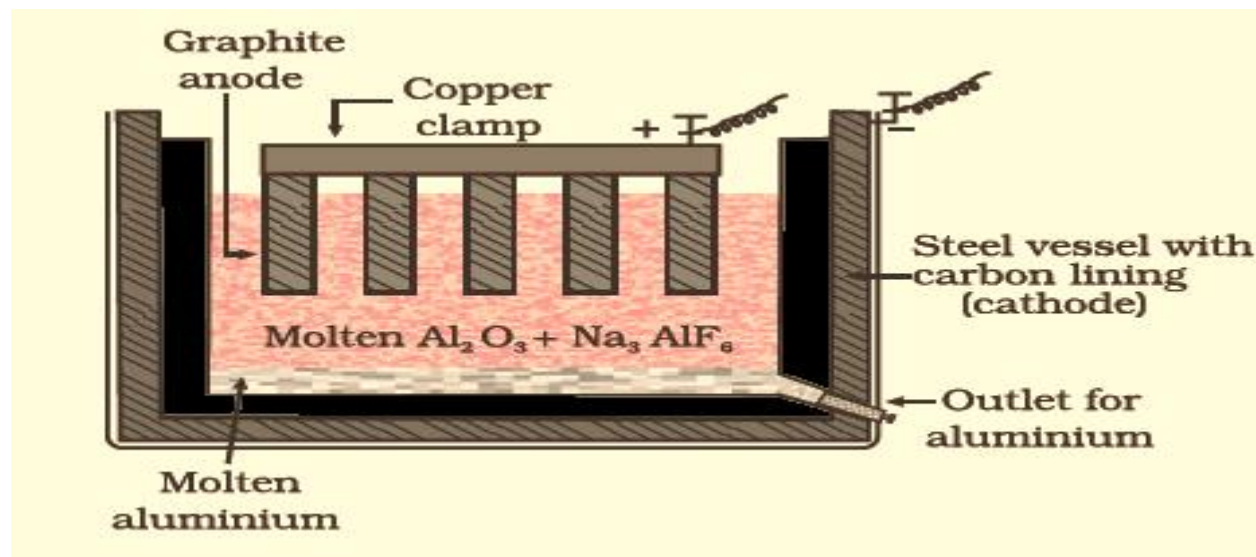
Purification of Bauxite



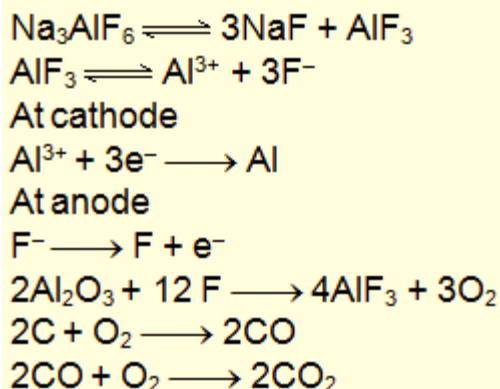
Electrolysis of fused pure alumina (Hall & Herwlt Method)



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The addition of cryolite (Na_3AlF_6) and fluorspar (CaF_2) makes alumina a good conductor of electricity and lowers its Fusion temperature from 2323 to 1140 K. the reaction taking place



during electrolysis.

Refining of Aluminium:

The graphite rods dipped in pure aluminium and Cu-Al alloy rod at the bottom in the impure aluminium work as conductors. On electrolysis, aluminium is deposited at cathode from the middle layer and equivalent amount of aluminium is taken up by the middle layer from the bottom layer (impure aluminium). Therefore, aluminium is transferred from bottom to the top layer through middle layer while the impurities are left behind. Aluminium thus obtained is 99.98% pure.

Hydrometallurgy (solvent extraction)

Solvent extraction is the latest separation technique and has become popular because of its elegance, simplicity and speed. The method is based on preferential solubility principles. Solvent or liquid-liquid extraction is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents, one of which is usually water and the other an



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organic solvent such as benzene, carbon tetrachloride or chloroform. In certain cases, the solute can be more or less completely transferred into the organic phase.

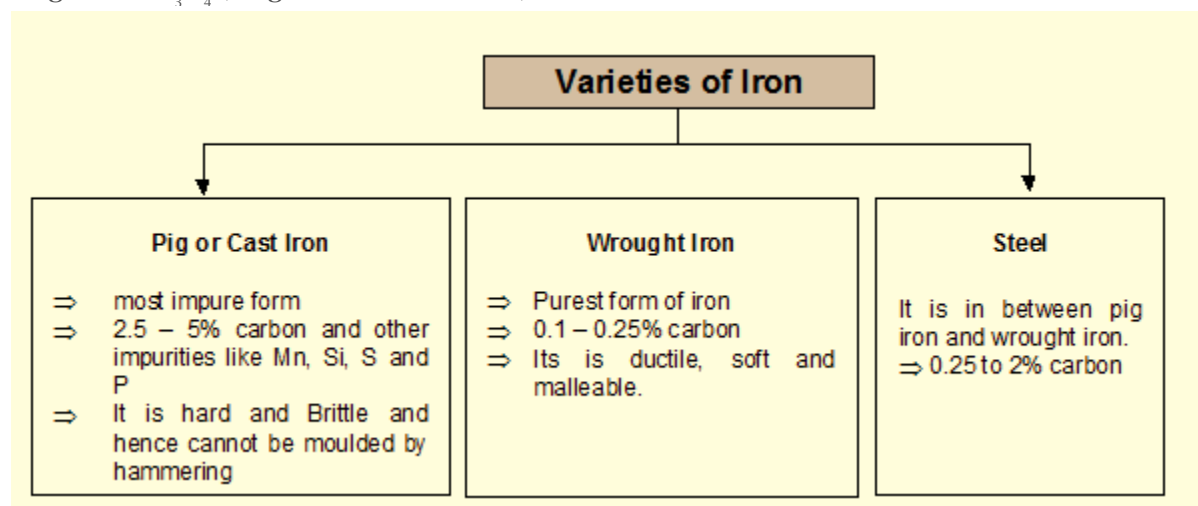
Extraction of Iron:

a) Important Ores of Iron:

Hematite Fe_2O_3 (red oxide of iron)

Limonite $\text{Fe}_2\text{O}_3 \times 3\text{H}_2\text{O}$ (hydrated oxide of iron)

Magnetite Fe_3O_4 (magnetic oxide of iron)

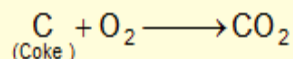


Extraction of Cast Iron:

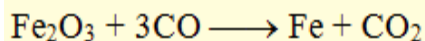


Reactions taking place in the blast furnace

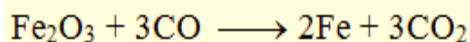
Zone of combustion



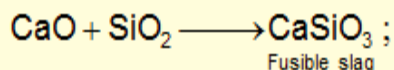
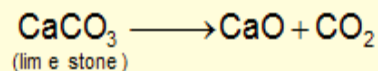
Zone of reduction



Zone of reduction



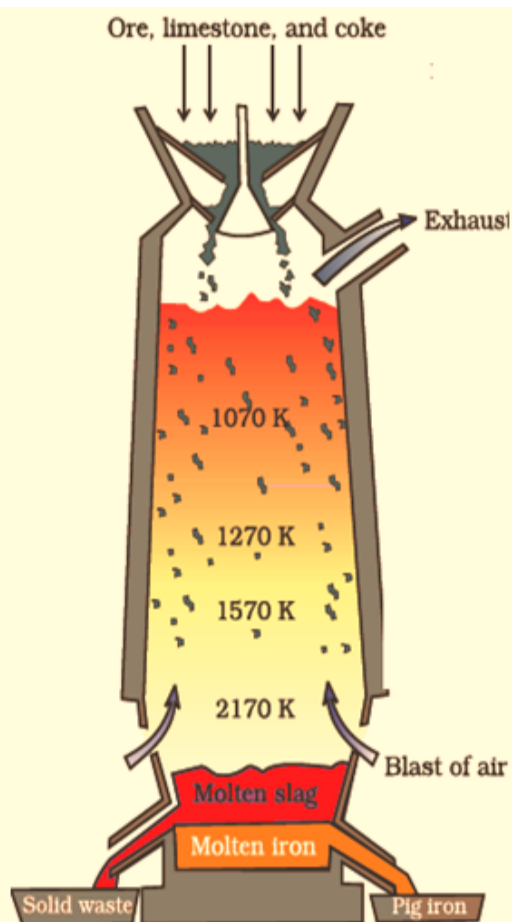
Zone of slag formation



Zone of fusion

lower part of furnace

Molten iron is heavier than molten slag. The two liquids are periodically tapped off. The molten iron tapped off from the furnace is solidified into blocks called 'pigs'.



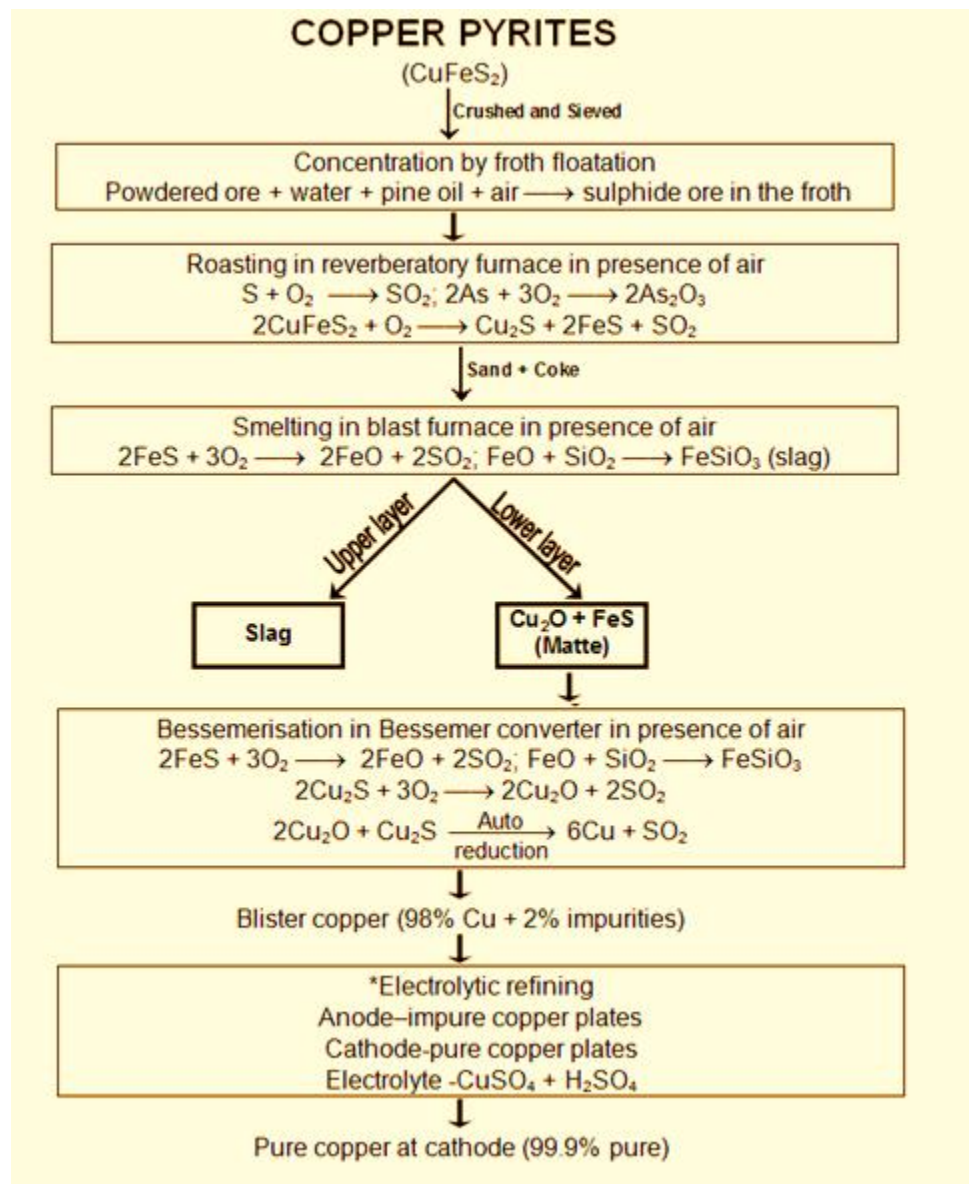
Extraction of Copper:

Ores of Copper:

- Copper glance (chalcocite) : Cu_2S
- Copper pyrites (Chalopyrites): CuFeS_2
- Malachite : $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$
- Cuprite or Ruby copper: Cu_2O
- Azurite : $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$



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Refining of Metals:

Zone refining (Fractional crystallization):

This method is employed for preparing extremely pure metals. This method is based upon the principle that when a molten solution of the impure metal is allowed to cool, the pure metal crystallises out while the impurities remain in the melt.

Electro-refining:

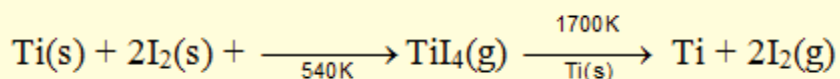


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In this method, the impure metal is converted into a block which forms the anode while cathode is a rod or plate of pure metal. These electrodes are suspended in an electrolyte which is the solution of a soluble salt of the metal usually a double salt of the metal. When electric current is passed, metal ions from the electrolyte are deposited at the cathode in the form of pure metal while an equivalent amount of metal dissolves from the anode and goes into the electrolyte solution as metal ion. The soluble impurities present in the crude metal anode go into the solution while the insoluble impurities settle down below the anode as anode mud.

Van-Arkel Method

: In this method, the metal is converted into its volatile unstable compound such as iodide leaving behind the impurities. The unstable compound thus formed is decomposed to get the pure metal.



Cupellation and Poling

are used for refining of metals, cupellation is used to remove impurities of other metals with traces of lead. Lead is removed from silver by heating impure silver with a blast of air in a cupel (an oval shaped pan made up of bone ash) in which lead is oxidised to lead oxide (PbO) which being volatile escapes leaving behind pure silver. Poling is used for refining of such metals which contain impurities of their own oxide. In this process, the molten impure metal is stored with green wooden poles. At the high temperature of the molten metal, wood liberates methane which reduces the oxide of the metal to free metal.

