

# Isolation of Metals



## 6. General Principles for Isolation of Metal

- Introduction
- Minerals, ores, concentration, benefaction, calcination, roasting, refining, etc.
- Principles of oxidation and reduction as applied to the extraction procedures
- Apply the thermodynamic concepts like that of Gibbs energy and entropy to the principles of extraction of Al, Cu, Zn and Fe
- Why reduction of certain oxides like  $\text{Cu}_2\text{O}$  is much easier than that of  $\text{Fe}_2\text{O}_3$
- Why CO is a favourable reducing agent at certain temperatures while coke is better in some other cases
- Why specific reducing agents are used for the reduction purposes.



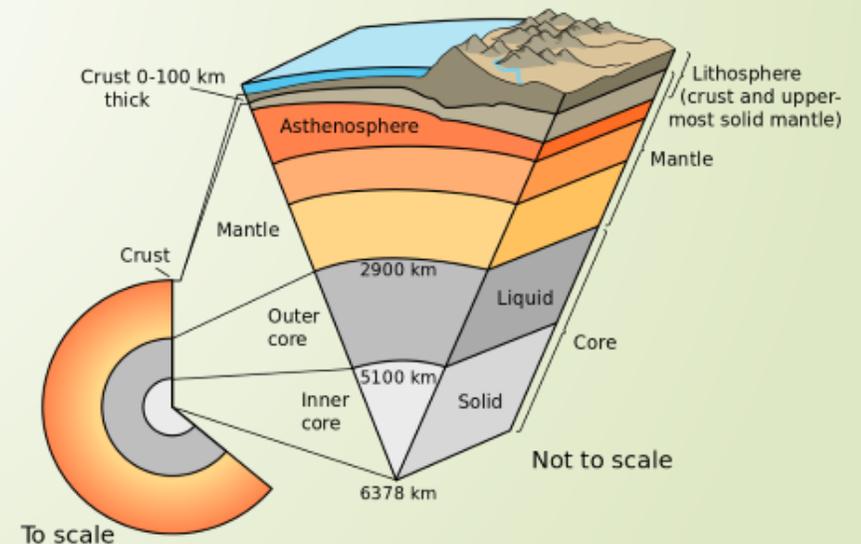


# Why study?



# Introduction

- The process of metallurgy and isolation should be such that it is **Chemically feasible** and **Commercially viable**.
- **Minerals** 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**.
- Ore is usually contaminated with earthly or undesired materials known as **Gangue**.



# Metallurgy

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

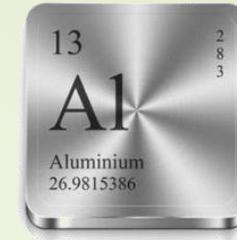
The extraction and isolation of metals from ores involves:

1. Concentration of the ore
2. Isolation of the metal
3. Purification of the metal



# Occurrence of Metals

- Aluminium is the most abundant metal.
- It is the third most abundant element in earth's crust (8.3% approx. by weight).
- Iron is the second most abundant metal in the earth's crust.
- It is one of the essential elements in biological systems as well.



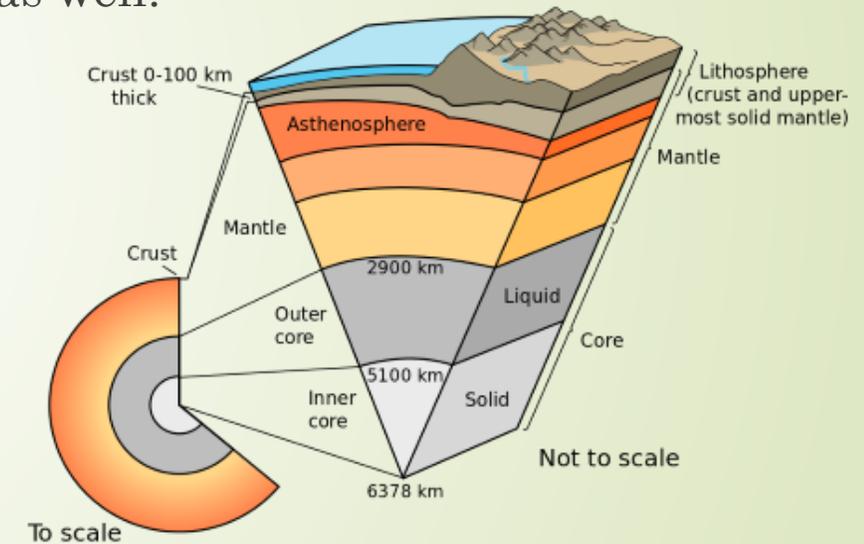
Bauxite



Ruby(Cr)



Sapphire(Co)



- Before proceeding for concentration, ores are graded and crushed to reasonable size.

## Principal Ores of Some Important Metals

Metal	Ores	Composition
Aluminium	Bauxite	$\text{AlO}_x(\text{OH})_{3-2x}$ [where $0 < x < 1$ ]
	Kaolinite (a form of clay)	$[\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5]$
Iron	Haematite	$\text{Fe}_2\text{O}_3$
	Magnetite	$\text{Fe}_3\text{O}_4$
	Siderite	$\text{FeCO}_3$
	Iron pyrites	$\text{FeS}_2$
Copper	Copper pyrites	$\text{CuFeS}_2$
	Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	Cuprite	$\text{Cu}_2\text{O}$
	Copper glance	$\text{Cu}_2\text{S}$
Zinc	Zinc blende or Sphalerite	$\text{ZnS}$
	Calamine	$\text{ZnCO}_3$
	Zincite	$\text{ZnO}$

# Ores : Concentration to Purification- steps

- Concentration of Ores
  - Hydraulic Washing
  - Magnetic separation
  - Froth floatation
  - Leaching
- Isolation of Crude Metal from Concentrated Ore
  - Conversion to Oxide
  - Electrochemical process
  - Oxidation-Reduction
- Purification of the metal
  - Distillation
  - Liquation
  - Electrolysis
  - Zone refining
  - Vapour phase refining
  - Chromatographic methods



# Concentration of Ores

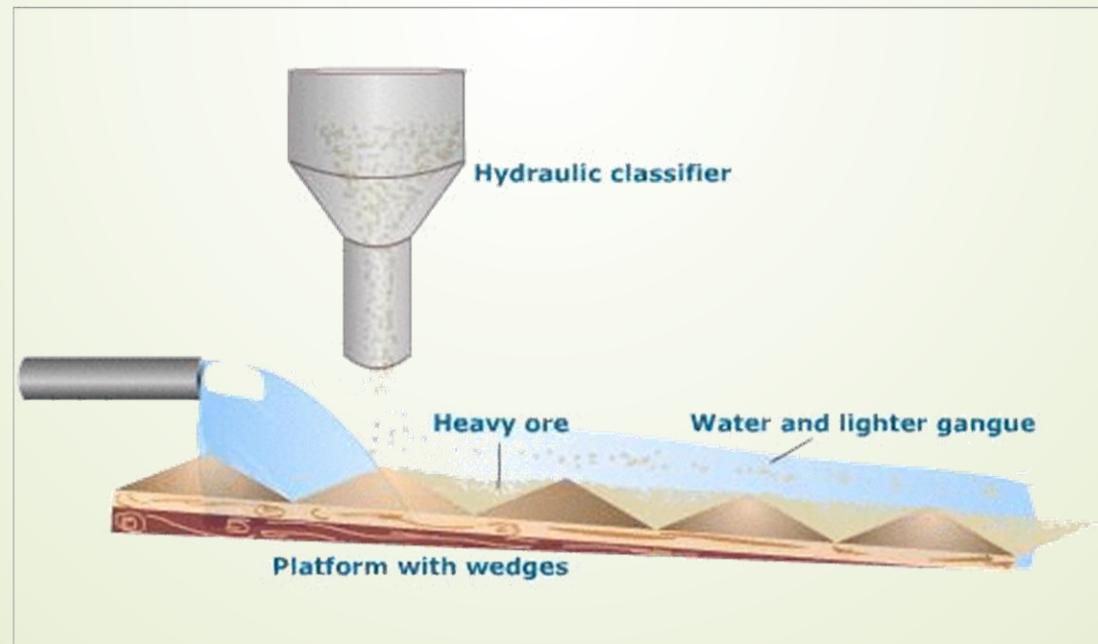
- Removal of the unwanted materials (e.g., sand, clays, etc.) from the ore is known as **Concentration, dressing or benefaction**.
- It involves several steps and selection of these steps depends upon the **differences in physical properties** of the compound of the Metal present and that of the Gangue.
- The type of the metal, the available facilities and the environmental factors are also taken into consideration.



# Concentration of Ores

## i. Hydraulic Washing

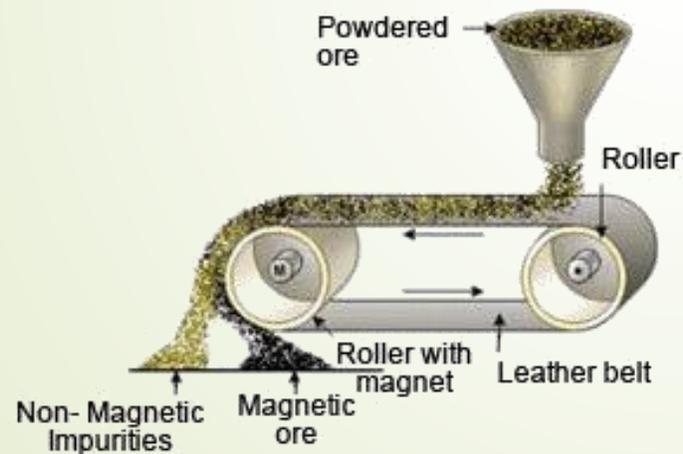
- This is based on the differences in gravities of the ore and the gangue particles.
- It is a type of **gravity separation**.
- In one such process, an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind.



# Concentration of Ores

## ii. 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



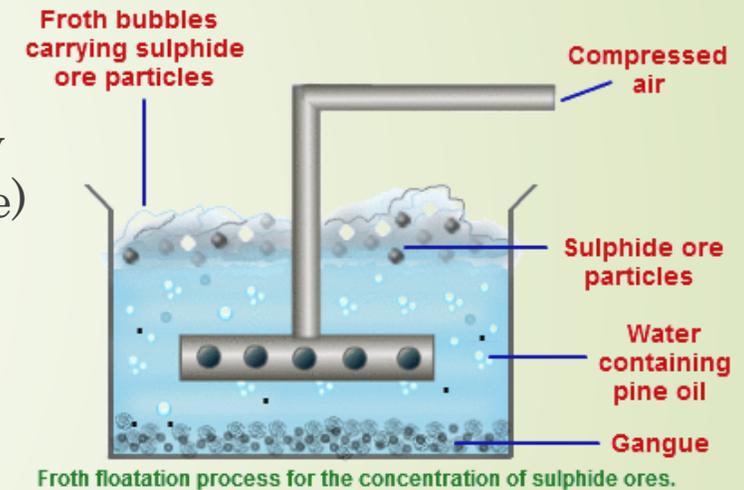
Concentration of an ore by magnetic separator



# Concentration of Ores

## iii. Froth floatation

- 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** (Pine oils, fatty acids etc.) enhance non-wettability of the mineral particles and froth **Stabilisers** (Cresols, aniline) stabilise the froth.
- The mineral particles become wet by oils while the gangue particles by water.
- A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles.
- The froth is light and is skimmed off. It is then dried for recovery of the ore particles.



## Froth floatation : cont...

- 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.



# Concentration of Ores

## iv. Leaching

- Leaching is often used if the ore is soluble in some suitable solvent.

E.g. Leaching of alumina from bauxite

- Bauxite, usually contains  $\text{SiO}_2$ , iron oxides and titanium oxide ( $\text{TiO}_2$ ) as impurities.
- Concentration is carried out by digesting the powdered ore with a concentrated solution of **NaOH**.
- This way,  $\text{Al}_2\text{O}_3$  is leached out as sodium aluminate (and  $\text{SiO}_2$  too as sodium silicate) leaving the impurities behind:



- The aluminate in solution is neutralised by passing  $\text{CO}_2$  gas and hydrated  $\text{Al}_2\text{O}_3$  is precipitated.
- At this stage, the solution is seeded with freshly prepared samples of hydrated  $\text{Al}_2\text{O}_3$  which induces the precipitation:



- The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure  $\text{Al}_2\text{O}_3$ :



E.g. In the metallurgy of Silver and Gold, the respective metal is leached with a dil. solution of NaCN or KCN in the presence of air (for O<sub>2</sub>):



- The metal is obtained later by replacement:



# Isolation of Crude Metal from Concentrated Ore

Isolation of metals from concentrated ore involves two major steps:

- (a) Conversion to oxide
- (b) Reduction of the oxide to metal

## (a) Conversion to Oxide

- The concentrated ore must be converted into a form which is suitable for reduction.
- Usually the Sulphide ore is converted to oxide before reduction as Oxides are easier to reduce.

There are 2 methods to convert to oxides:

- (i) Calcination
- (ii) Roasting

# Conversion to Oxide

## (i) Calcination:

- Calcination involves heating when the volatile matter escapes leaving behind the metal oxide:



# Conversion to Oxide

## (ii) Roasting:

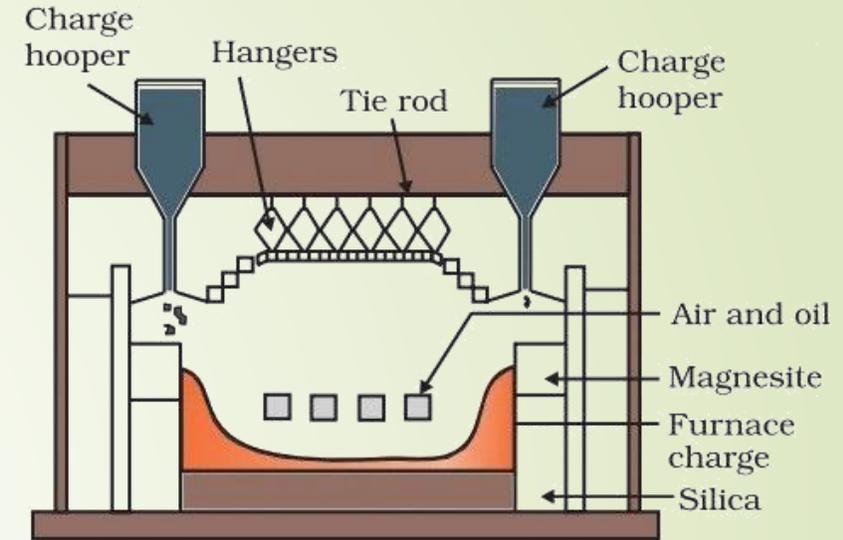
- In roasting, the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal. E.g's :



- The sulphide ores of copper are heated in Reverberatory furnace.
- If the ore contains iron, it is mixed with silica before heating.
- Iron oxide 'slags of' as Iron silicate and Copper is produced in the form of **Copper matte** which contains  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ .



- The  $\text{SO}_2$  produced is utilised for manufacturing  $\text{H}_2\text{SO}_4$  .



## Reduction of oxide to the metal

- Reduction of the metal oxide usually involves heating it with some other substance acting as a reducing agent (C or CO or even another metal).
- The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.



- Some metal oxides get reduced easily while others are very difficult to be reduced.
- To understand the variation in the temperature requirement for thermal reductions (**Pyrometallurgy**) and to predict which element will suit as the reducing agent for a given metal oxide ( $M_xO_y$ ), Gibbs energy interpretations are made.

# Thermodynamic Principles of Metallurgy

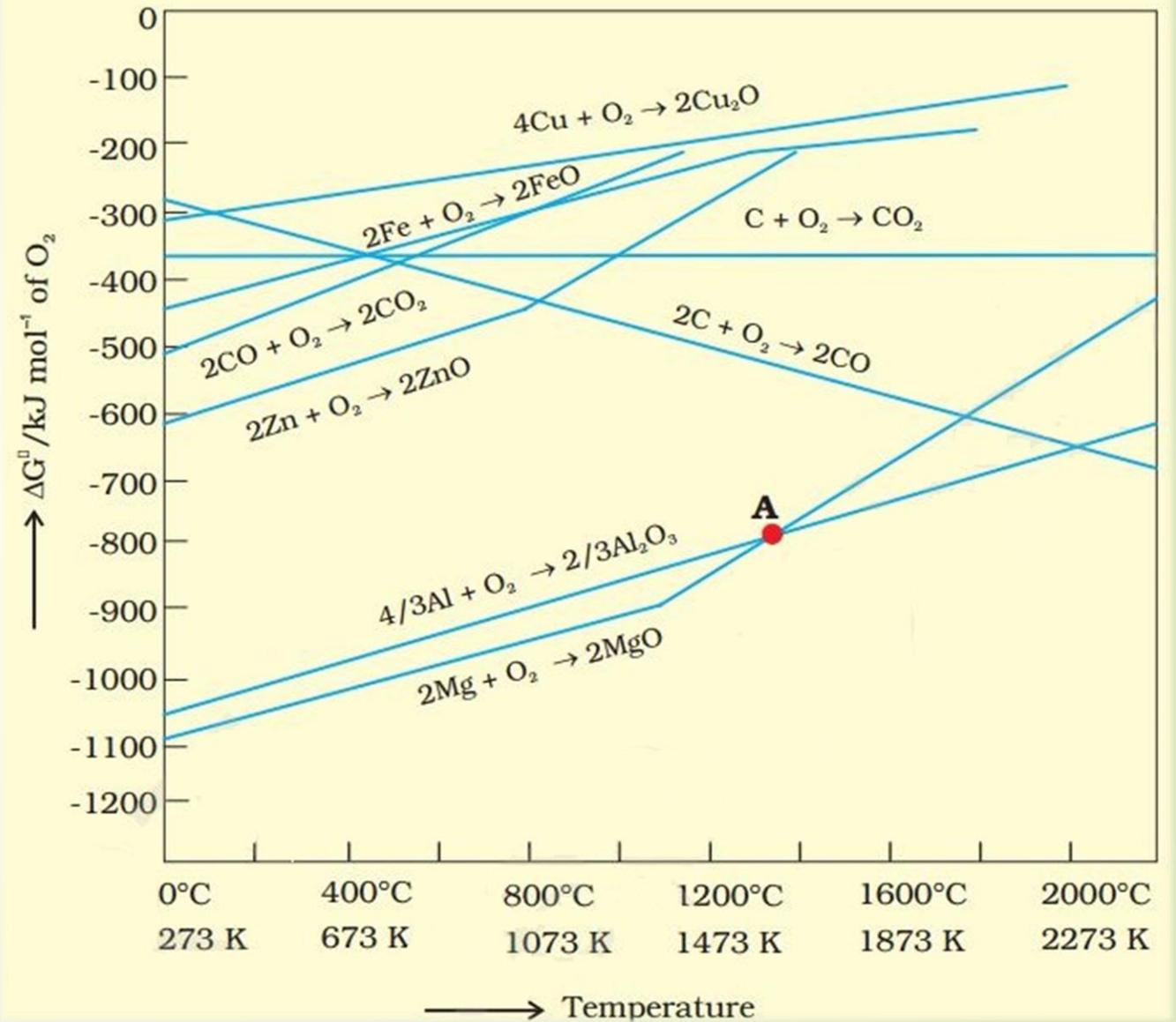
$$\Delta G = \Delta H - T\Delta S$$

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

1. When the value of  $\Delta G$  is negative in equation, only then the reaction will proceed. If  $\Delta S$  is positive, on increasing the temperature (T), the value of  $T\Delta S$  would increase ( $\Delta H < T\Delta S$ ) and then  $\Delta G$  will become -ve.
2. If reactants and products of two reactions are put together in a system and the net  $\Delta G$  of the two possible reactions is -ve, the overall reaction will occur. So the process of interpretation involves coupling of the two reactions, getting the sum of their  $\Delta G$  and looking for its magnitude and sign.

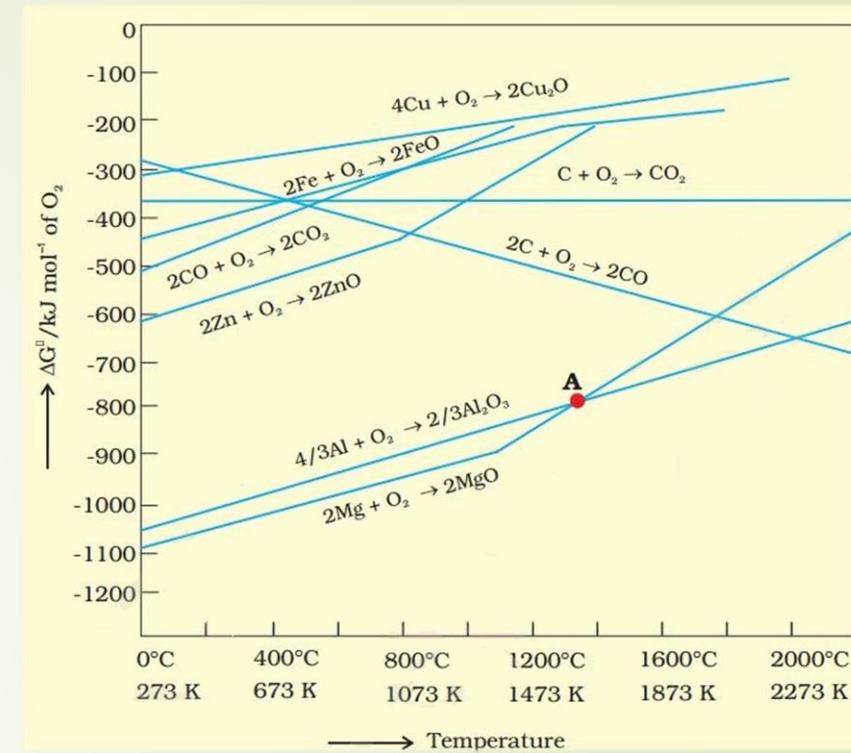
The role of reducing agent is to provide  $\Delta G$  negative and large enough to make the sum of  $\Delta G$  of the two reactions (oxidation of the reducing agent and reduction of the metal oxide) negative.

# Ellingham diagram



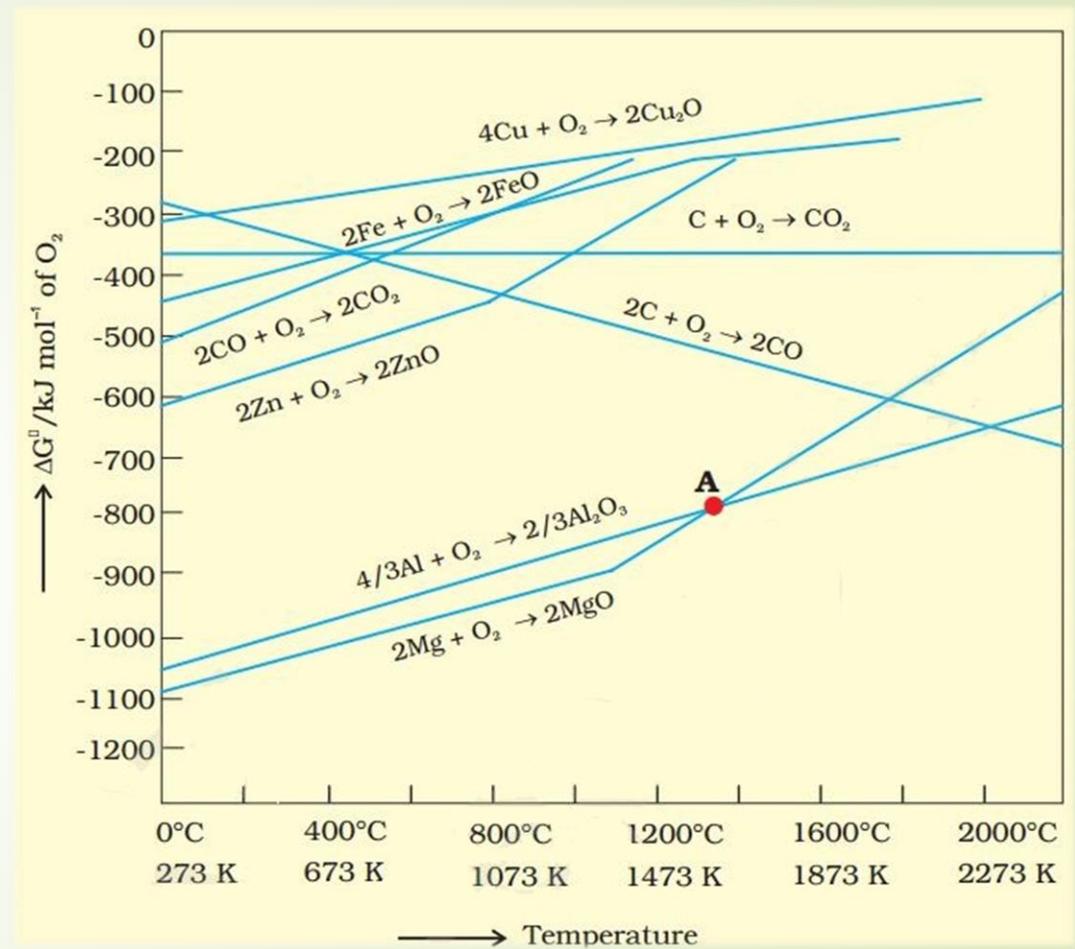
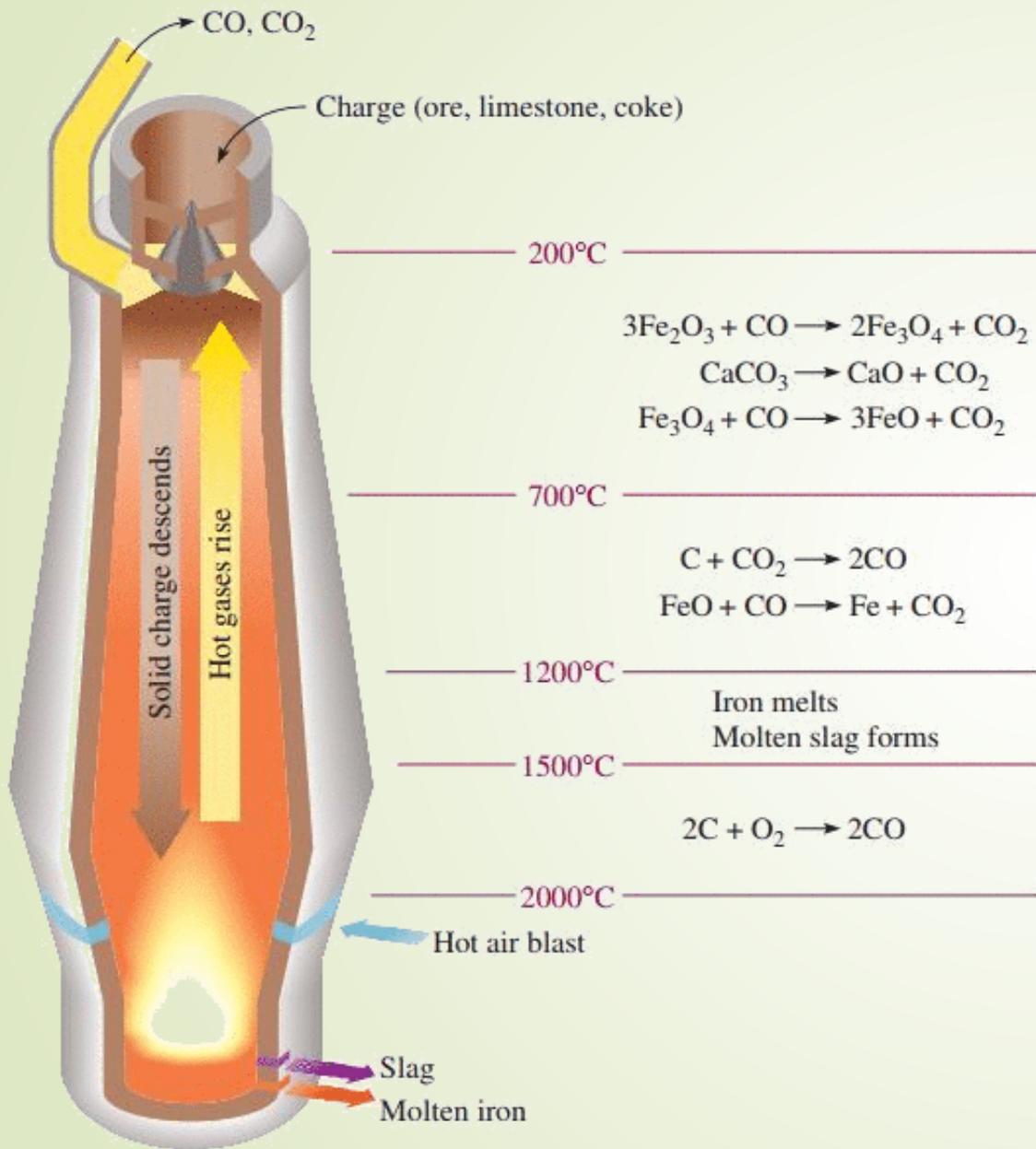
# Ellingham diagram

- Heating (incr. T) favours a negative value of  $\Delta_r G_0$ .
- Hence temperature is chosen such that the sum of  $\Delta_r G_0$  in the two combined redox process is negative.
- In  $\Delta_r G_0$  vs T plots, this is indicated by the point of intersection of the two curves.
- After that point, the  $\Delta_r G_0$  value becomes more negative the combined process including the reduction of  $M_xO$ .
- The difference in the two  $\Delta_r G_0$  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.



# Thermodynamic Principles of Metallurgy : Applications

- (a) Extraction of Iron from its oxides
- (b) Extraction of Copper from cuprous oxide [copper(I) oxide]
- (c) Extraction of Zinc from zinc oxide

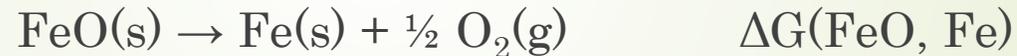


## Extraction of Iron from its oxides

- After concentration, oxide ores of **iron** are mixed with **limestone** and **coke** and fed into a Blast furnace from its top.
- The oxide is reduced to the metal.
- One of the main reduction steps in this process is:



- It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidized to CO.



- When both the reactions take place to yield the equation, the net Gibbs energy change becomes:

$$\Delta\text{G}(\text{C, CO}) + \Delta\text{G}(\text{FeO, Fe}) = \Delta_r\text{G}$$

- Above 1073K (aprx.), the C,CO line comes below the Fe,FeO line [ $\Delta\text{G}(\text{C, CO}) < \Delta\text{G}(\text{Fe, FeO})$ ]. So in this range, coke will be reducing the FeO and will itself be oxidised to CO.

## Reactions in the blast furnace

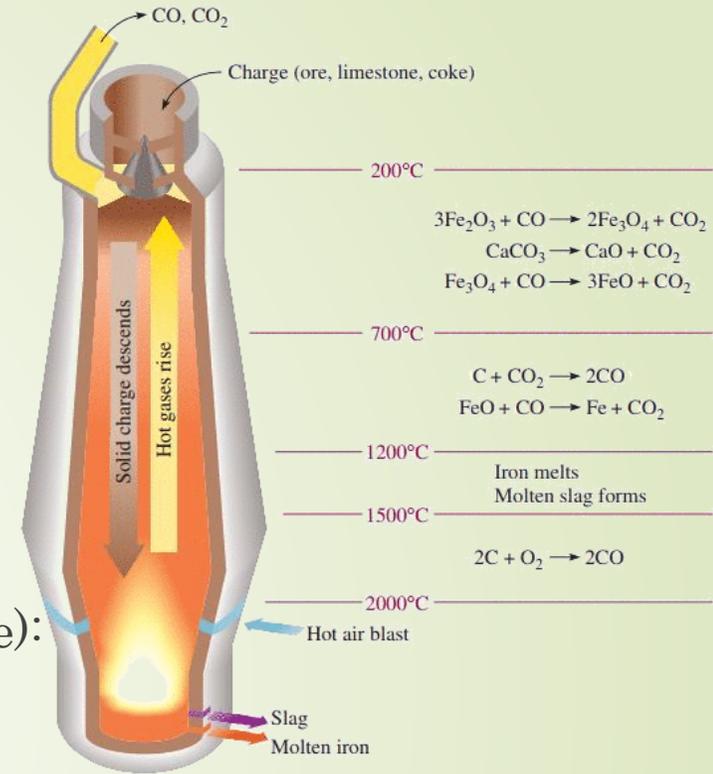
- At 500 – 800 K (lower temperature range in the blast furnace):



- At 900 – 1500 K (higher temperature range in the blast furnace):



- Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.



## Further Processing

- The iron obtained from Blast furnace contains about **4% carbon** and many impurities in smaller amount (e.g., S, P, Si, Mn). This is known as **Pig iron**.
- **Cast iron** is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (**about 3%**) and is extremely hard and brittle.
- **Wrought iron** or malleable iron is the purest form (**0.1 %**) of commercial iron and is prepared from cast iron by oxidising impurities in a **Reverberatory furnace** lined with **Haematite**.
- This haematite oxidises carbon to carbon monoxide:  
$$\text{Fe}_2\text{O}_3 + 3 \text{C} \rightarrow 2 \text{Fe} + 3 \text{CO}$$
- Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag.
- The metal is removed and freed from the slag by passing through rollers.

## Extraction of copper from cuprous oxide [copper(I) oxide]

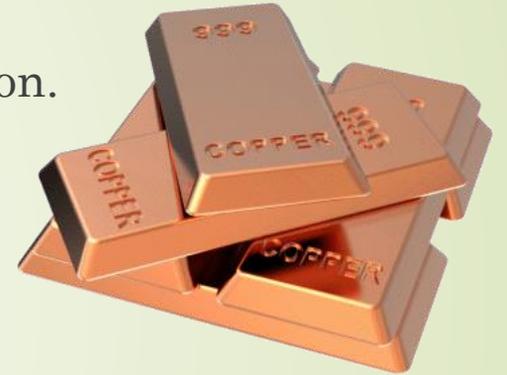
- In the graph of  $\Delta_r G_0$  vs T for formation of oxides, the  $\text{Cu}_2\text{O}$  line is almost at the top. So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke.
- But the problem most of the ores are sulphide and may also contain iron.
- The sulphide ores are first roasted/smelted to give oxides:



- The oxide can then be easily reduced to metallic copper using coke:



- In actual process, the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte. This contains  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ .



## Extraction of copper from cuprous oxide : Cont...

- Copper matte is then charged into silica lined convertor. Some silica is also added and hot air blast is blown to convert the remaining FeS, FeO and Cu<sub>2</sub>S/Cu<sub>2</sub>O to the metallic copper.
- Following reactions take place:



- The solidified copper obtained has blistered appearance due to the evolution of SO<sub>2</sub> and so it is called **Blister copper**.



## Extraction of Zinc from zinc oxide

- The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper.
- For the purpose of heating, the oxide is made into brickettes with coke and clay.



- The metal is distilled off and collected by rapid chilling.



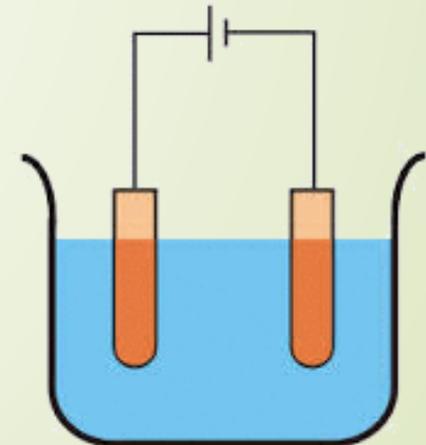
# Electrochemical Principles of Metallurgy

$$\Delta G^\circ = - nFE^\circ$$

- In simple electrolysis, the  $M^{n+}$  ions are discharged at negative electrodes (cathodes) and deposited there.
- More reactive metals have large negative values of the electrode potential, making their reduction difficult.
- If the difference of two  $E^\circ$  values corresponds to a positive  $E^\circ$  and consequently negative  $\Delta G^\circ$ , then the less reactive metal will come out of the solution and the more reactive metal will go to the solution.

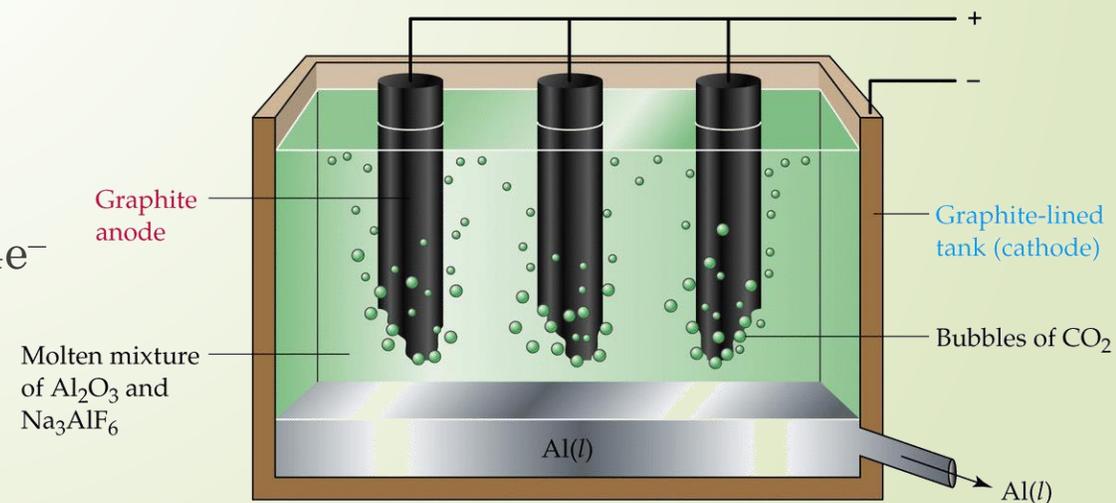
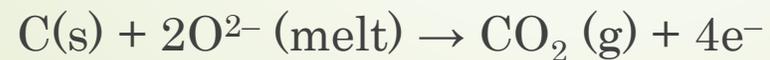
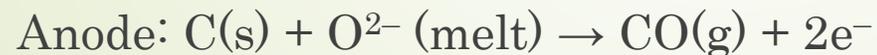


- Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes.
- Sometimes a **flux** is added for making the molten mass more conducting.



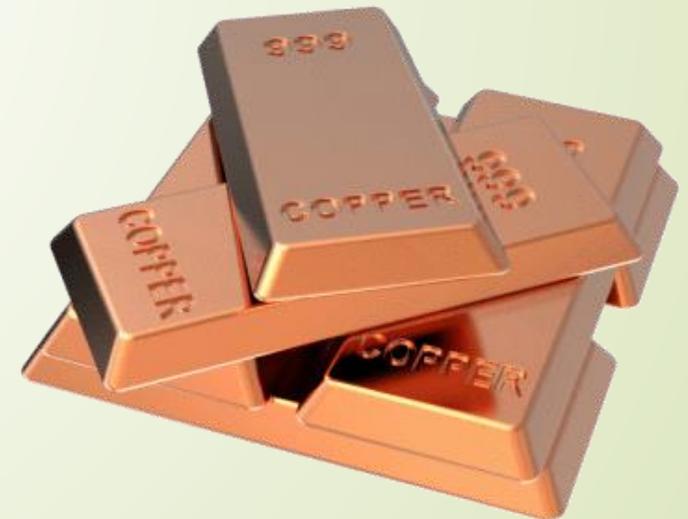
# Electrochemical Principles of Metallurgy : Aluminium

- Purified  $\text{Al}_2\text{O}_3$  is mixed with  $\text{Na}_3\text{AlF}_6$  or  $\text{CaF}_2$  which **lowers the melting point** of the mix and brings **conductivity**.
- The fused matrix is electrolyzed & is widely known as Hall-Heroult process
- **Steel vessel** with lining of carbon acts as **cathode** and graphite anode is used.
- The overall reaction may be written as:  $2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$
- The oxygen liberated at anode reacts with the carbon of anode producing CO and  $\text{CO}_2$ .
- For each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away.
- The electrolytic reactions are:



## Copper from Low Grade Ores and Scraps

- Copper is extracted by hydrometallurgy from low grade ores.
- It is leached out using acid or bacteria.
- The solution containing  $\text{Cu}^{2+}$  is treated with scrap iron or  $\text{H}_2$ .



# Oxidation-Reduction

- Besides reductions, some extractions are based on oxidation particularly for non-metals.
- A very common example of extraction based on oxidation is the extraction of chlorine from brine (chlorine is abundant in sea water as common salt) .



The  $\Delta G^{\circ}$  for this reaction is +422 kJ. When it is converted to  $E^{\circ}$ , we get  $E^{\circ} = - 2.2 \text{ V}$ .

- Naturally, it will require an external e.m.f. that is greater than 2.2 V.
- $\text{Cl}_2$  is obtained by electrolysis giving out  $\text{H}_2$  and aqueous NaOH as byproducts.
- Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH.



## Oxidation-Reduction : Gold, Silver

- As studied earlier, extraction of gold and silver involves leaching the metal with  $\text{CN}^-$ .
- This is also an oxidation reaction ( $\text{Ag} \rightarrow \text{Ag}^+$  or  $\text{Au} \rightarrow \text{Au}^+$ ).
- The metal is later recovered by displacement method.



- In this reaction zinc acts as a reducing agent.



# Purification or Refining

A metal extracted by any method is usually contaminated with some impurity.

For **obtaining metals of high purity**, several techniques are used depending upon the differences in properties of the metal and the impurity.

## Methods:

- Distillation
- Liquation
- Electrolysis
- Zone refining
- Vapour phase refining
- Chromatographic methods

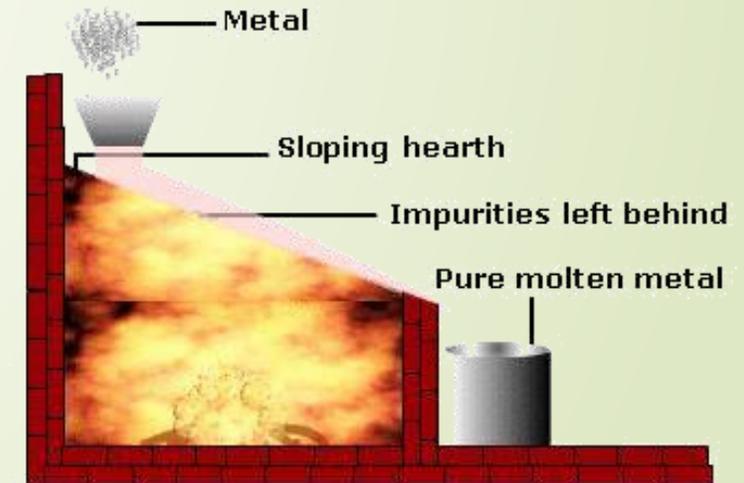
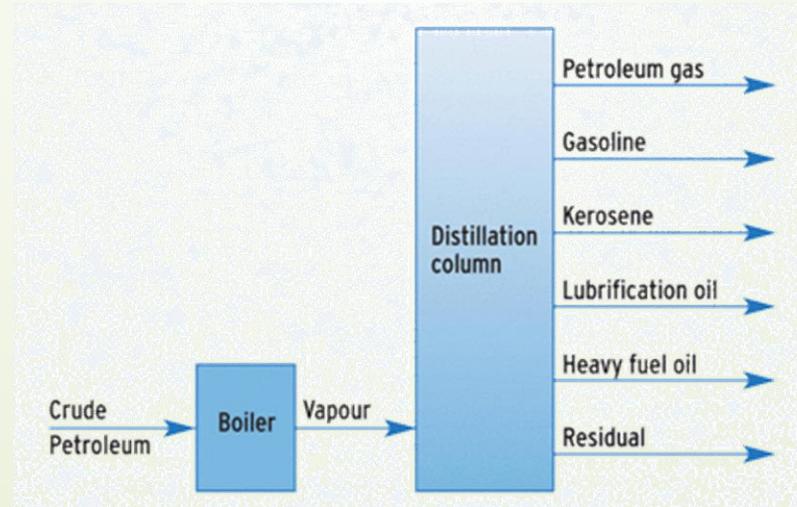
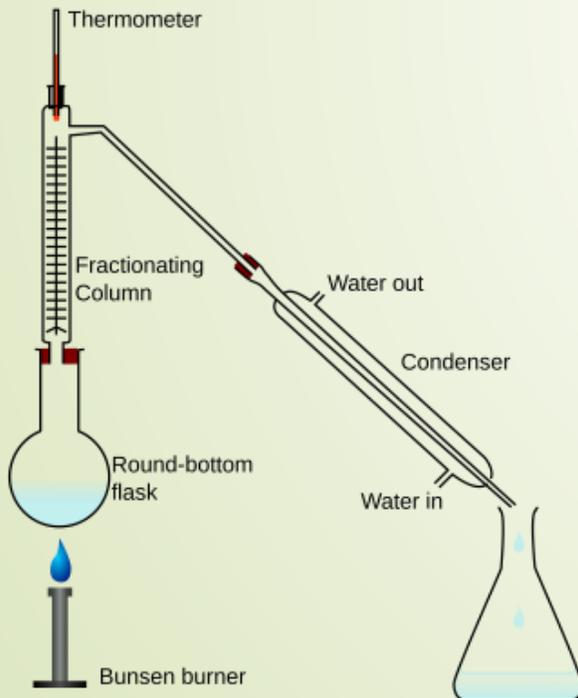
# Purification or Refining

## (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) Liqutation:

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

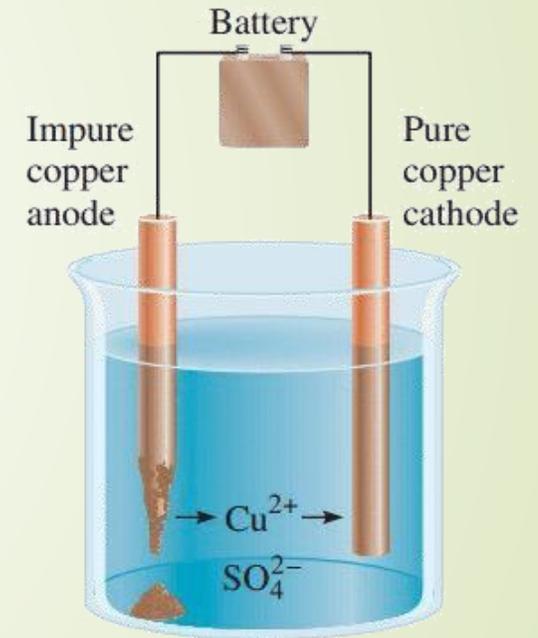
- In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode, with a suitable electrolytic bath containing soluble salt of same metal.
- This process is also explained using the concept of electrode potential, over potential, and Gibbs energy. The reactions are:



- E.g. 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 from the anode to the cathode:

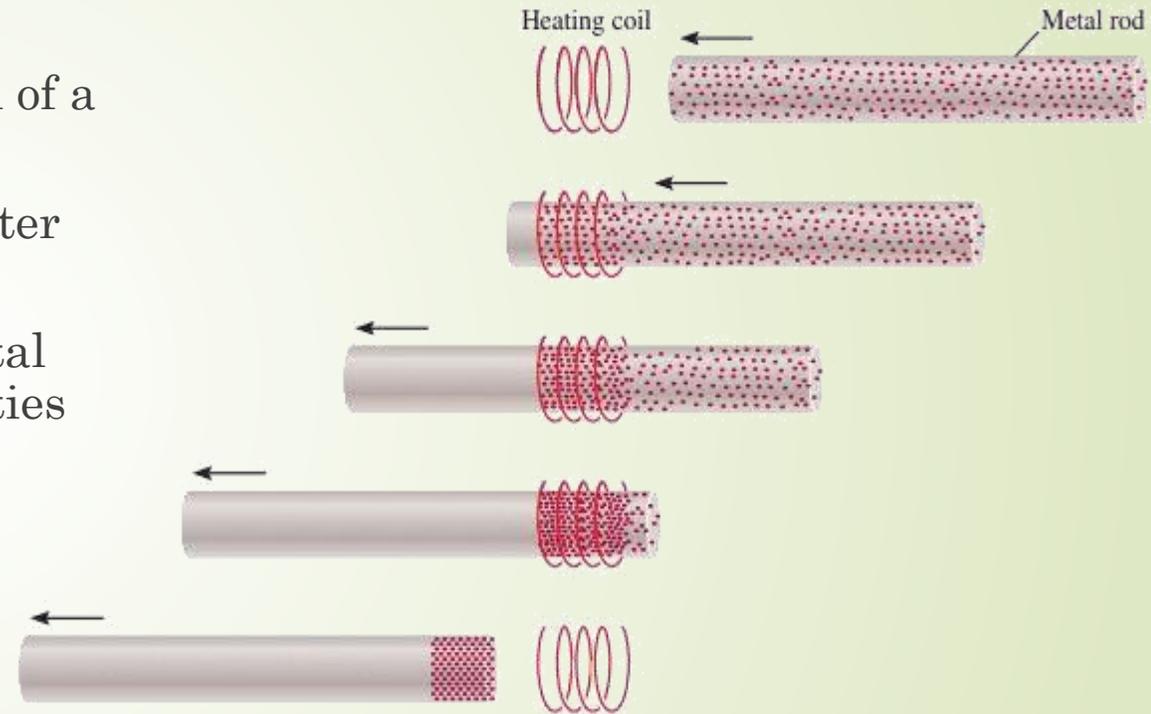


- Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; recovery of these elements may meet the cost of refining.
- Zinc may also be refined this way.



## (d) Zone refining

- This method is based on the principle that the **impurities are more soluble** in the melt than in the solid state of the metal.
- A circular mobile heater is fixed at one end of a rod of the impure metal.
- The molten zone moves along with the heater which is moved forward.
- As the heater moves forward, the pure metal 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 semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.



## (e) Vapour phase refining

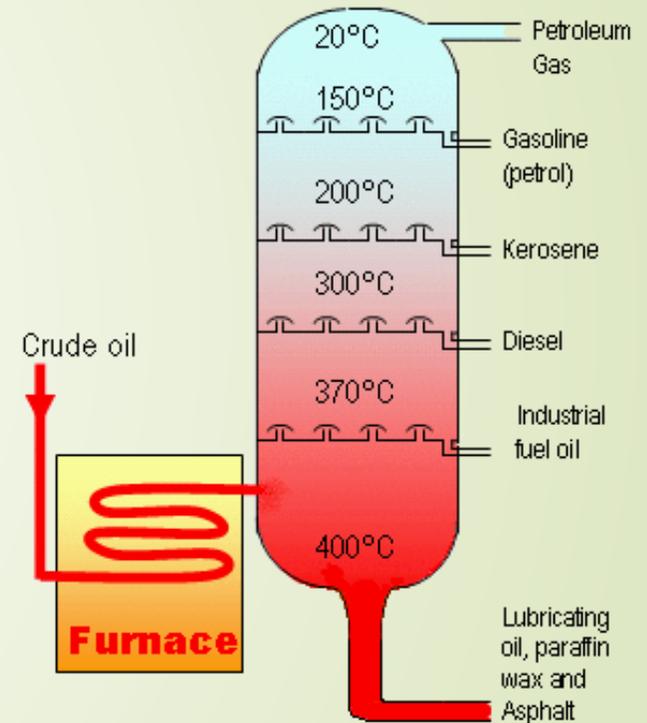
- In this method, the metal is converted into its volatile compound and collected elsewhere.
- It is then decomposed to give pure metal.
- Two requirements are:
  - (i) the metal should form a volatile compound with an available reagent
  - (ii) the volatile compound should be easily decomposable, so that the recovery is easy.

### Mond Process for Refining Nickel:

- In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl:



- The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal:



## (e) Vapour phase refining : cont...

### 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:

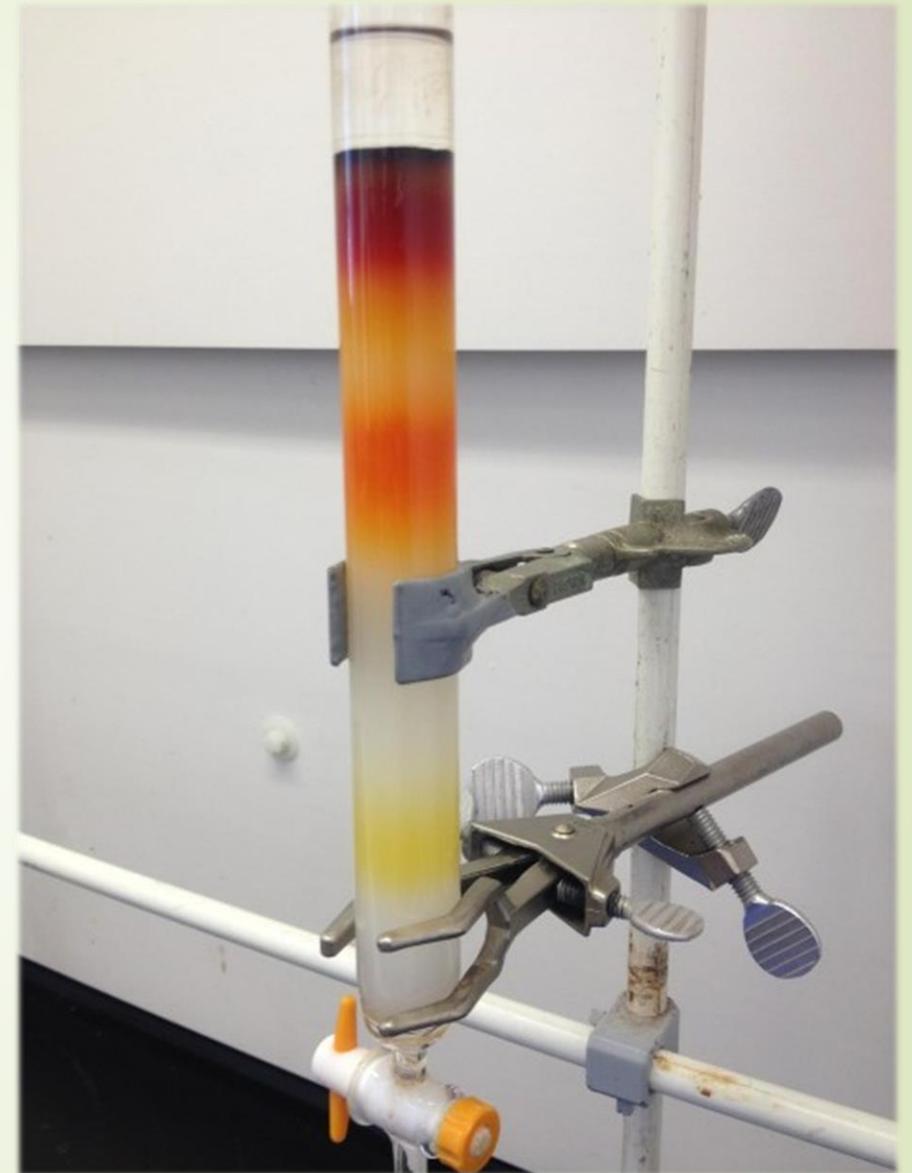
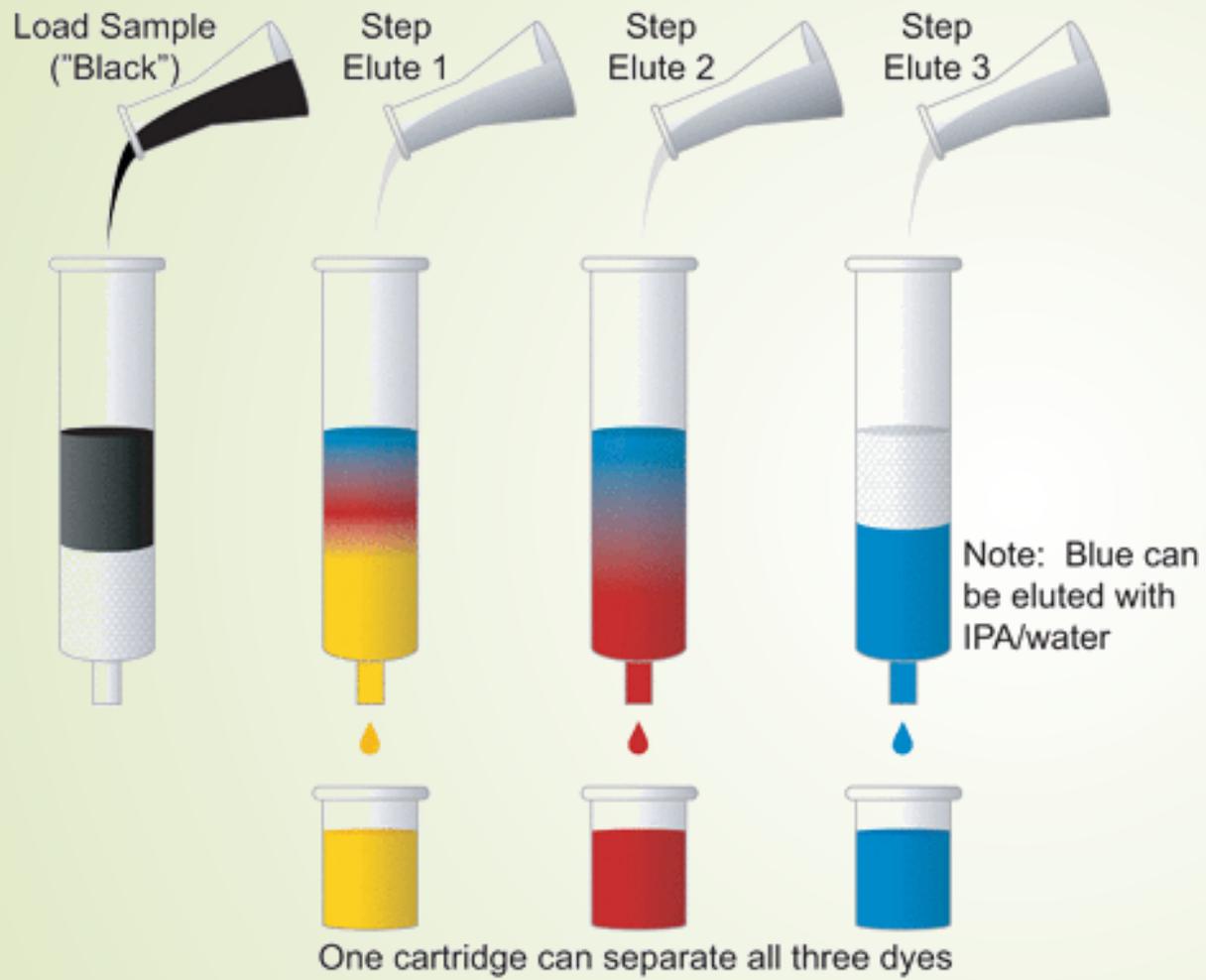


- The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K.
- The pure metal is thus deposited on the filament.



## (f) Chromatographic methods

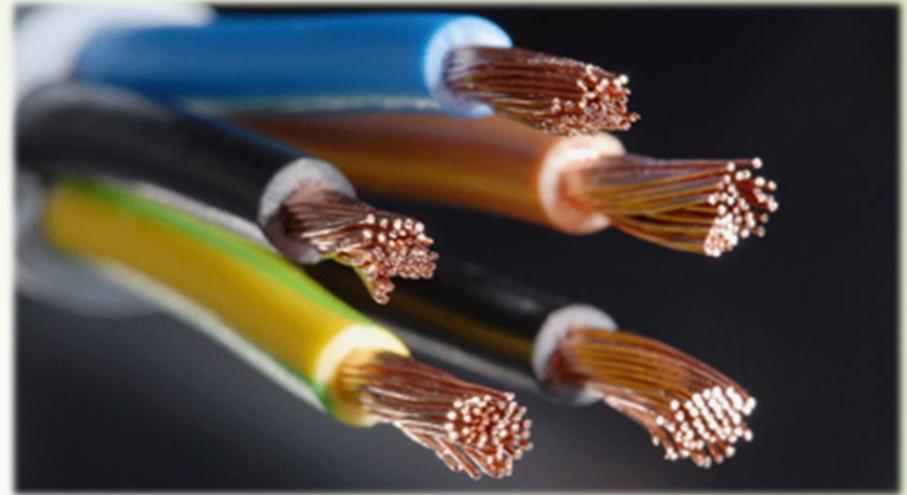
- This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent.
- The mixture is put in a liquid or gaseous medium which is moved through the adsorbent.
- Different components are adsorbed at different levels on the column.
- Later the adsorbed components are removed(eluted) by using suitable solvents(eluant).
- The column of  $\text{Al}_2\text{O}_3$  is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form (**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.



# Uses of Aluminium



# Uses of Copper



*Bronze*



**Brass**



# Uses of Zinc



**Brass**



