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An Initiative by अमर उजाला

GENERAL PRINCIPLES OF METALLURGY

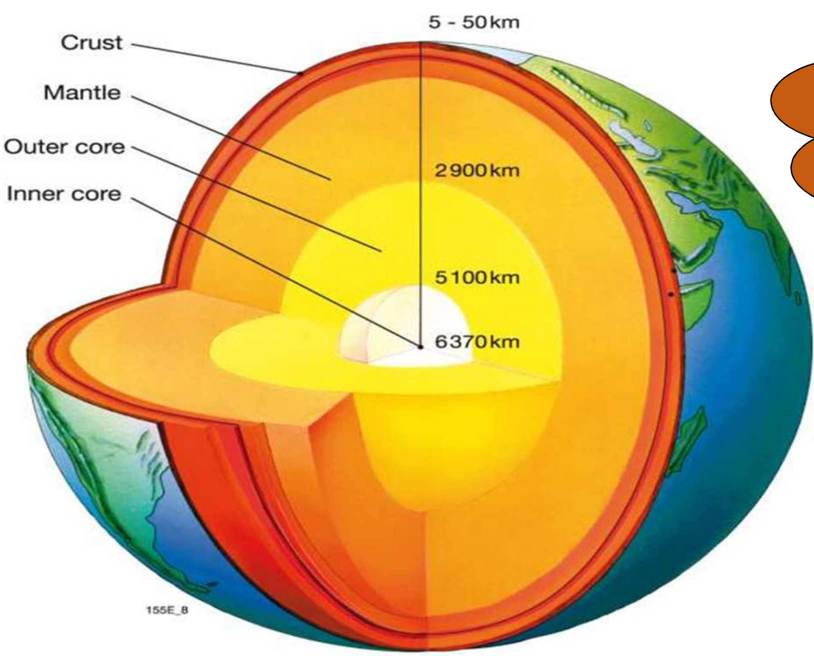
INTRODUCTION
TO
MINERALS & ORES

Metal usage is part and parcel of our life. i.e. We use them for all our needs.

[illegible]

A few of them for your eyes only

Metals are used for all our needs in all our applications of modern world.



Most of the metals do not occur in free state. They occur in combined state in the earth crust.

Let us observe the stages involved getting the pure metal from an ore.

Stage-I — SELECTION OF ORES

Stage-II — CONCENTRATION OF ORE

Stage-III — EXTRACTION OF METAL

Stage-IV — REFINING OF METAL

PURE METAL

MINERAL :

Do you know what an ore is!

- **The naturally occurring substances on the earth's crust which are obtained by mining which contains the metal in free state or combined state.**
- **A mineral containing a high percentage of the metal, from which the metal can be profitably extracted.**

ORE:

What does ore contain?

Ore has metal in the combined state and is usually contaminated with earthy impurities and undesirable chemicals

MCQs

1) **The natural materials from which an element can be extracted economically are called…**

   a) ores

   b) minerals

   c) gangue

   d) flux

2) Earth crust extends up to

a) 50km

b) 1000km

c) 3000Km

d) 6500Km

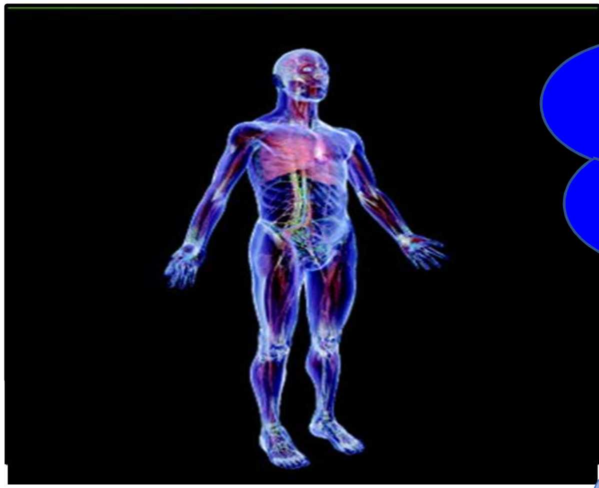
MINERALS & ORES OF A FEW METALS

Occurrence of Metals

Aluminum

Aluminium is the 3rd most abundant element in earth's crust (8.3% approx. by weight)

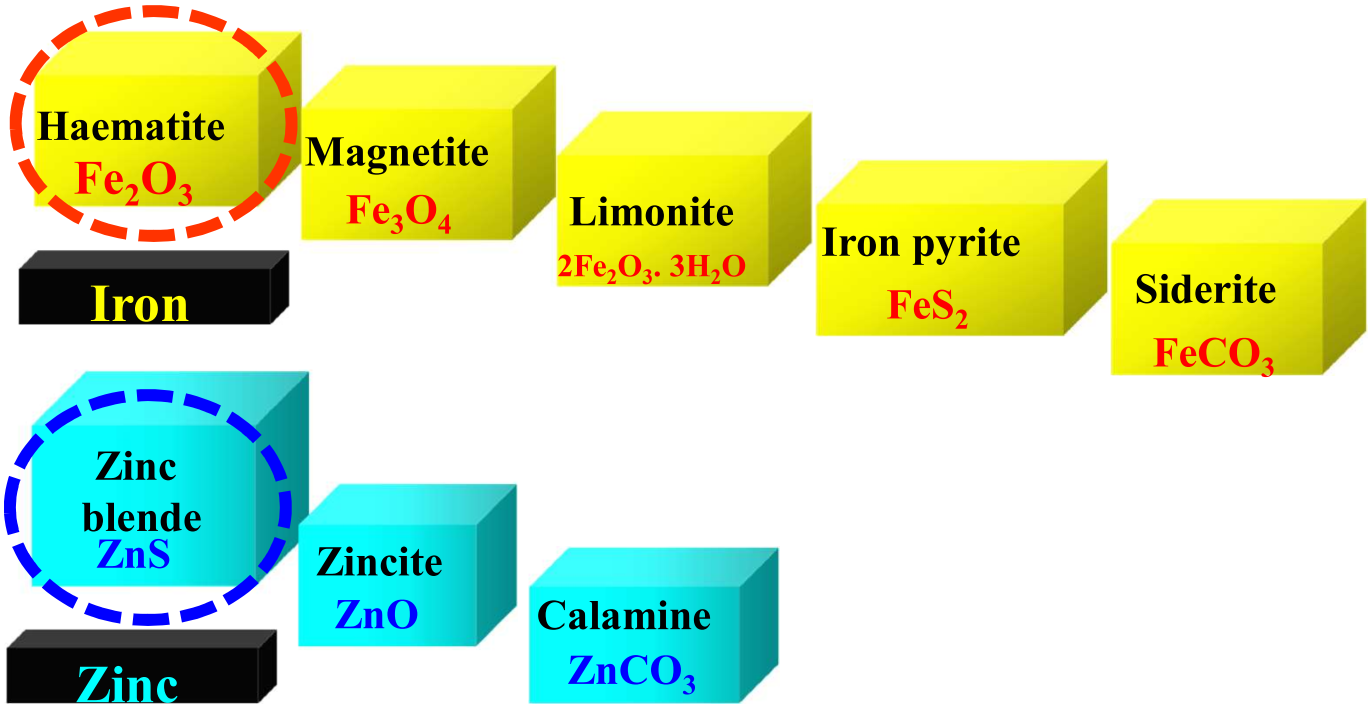
Occurrence of Metals



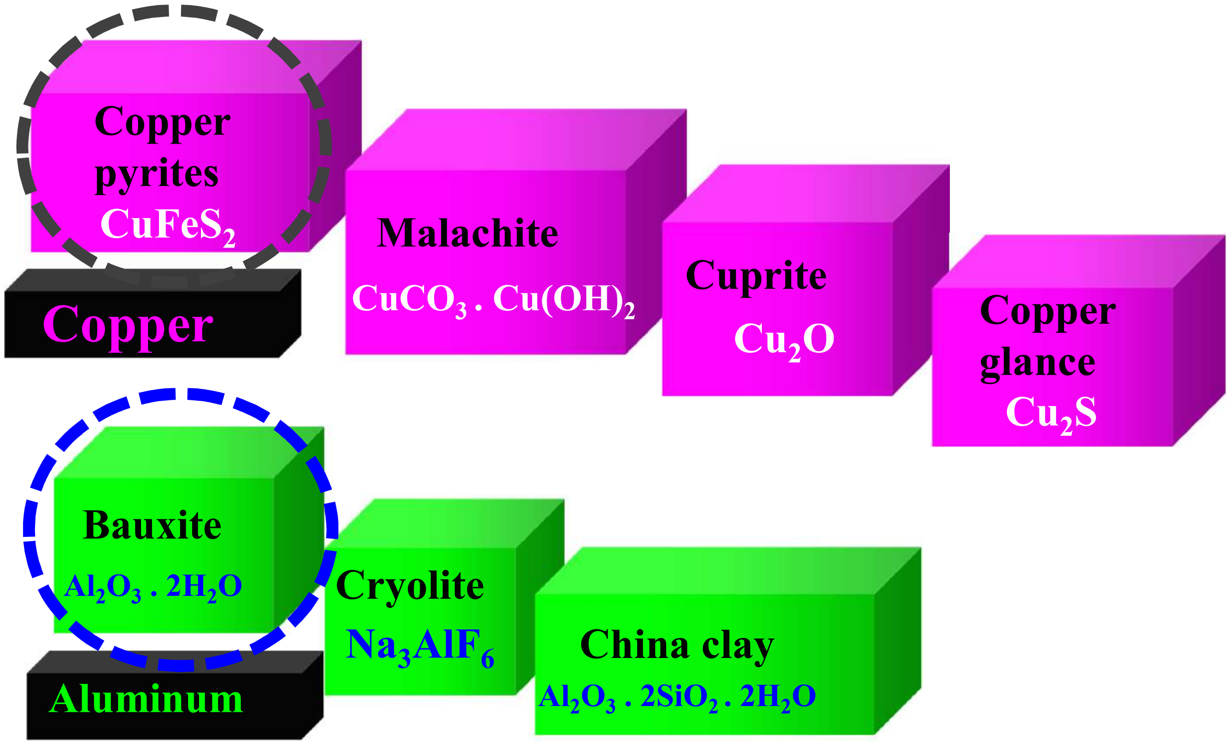
Fe is one of the most important essential elements used in highly evolved plants and animals. Fe is present in haemoglobin to supply oxygen through blood.

Cu, Ag, Au, pt, Fe are the metals that occur to some extent in native state as they are less reactive metals.

Minerals & Ores of a few metals



Minerals & Ores of a few metals



Minerals & Ores of a few metals

Magnesite
$MgCO_3$

Magnesium

Dolomite
$MgCO_3 . CaCO_3$

Epsom Salt
$MgSO_4 . 7H_2O$

MCQs

1) Haematite formula

a) ZnS

b) $MgCO_3$

c) Fe_3O_4

d) Fe_2O_3

2) Magnesite formula

a) **ZnS**

b) **$MgCO_3$**

c) **Fe_3O_4**

d) **Fe_2O_3**

3) The number of water molecules present in Epsom salt

a) 4

b) 5

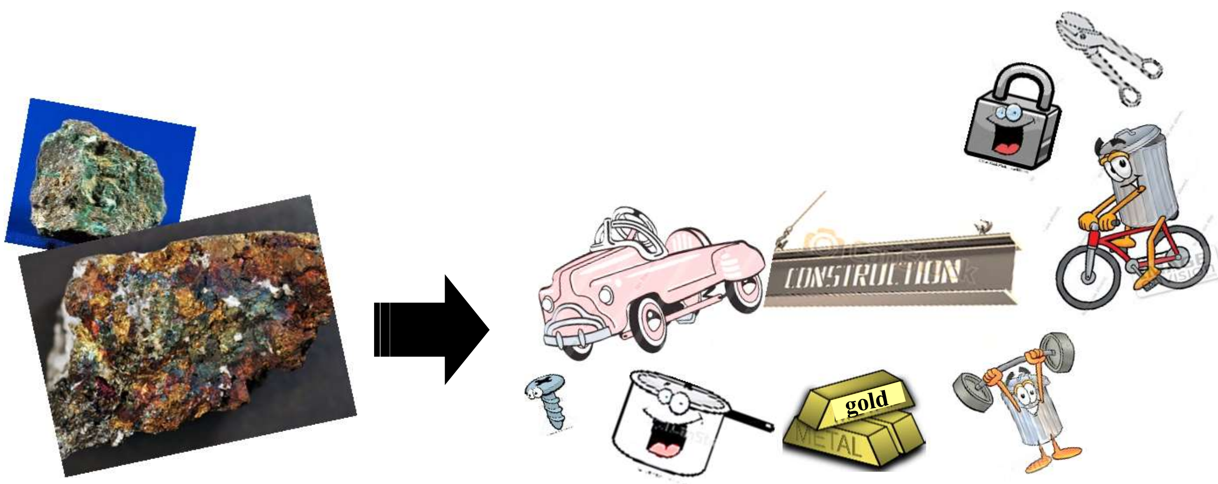
c) 6

d) 7

DEFINITION OF METALLURGY

What is metallurgy?

The process of extraction and isolation of metal from its naturally occurring compounds is called *metallurgy*. And it should be chemically and commercially viable.



The selection of a mineral as an ore depends on following factors :

- **The percentage of metal in the mineral.**
- **Nature and magnitude of impurities in the mineral.**
- **The expenditure involved in the extraction of metal from the mineral.**
- **The industrial utility of bye – products produced in the metal extraction.**

The extraction and isolation of metals from ores involve the following major steps:

Concentration of the ore *(Removal of gangue)*,

Isolation of the metal from its concentrated ore,

- **Purification of the isolated metal.**

MCQs

1. Metallurgy is …

a) Isolation of ore from the metal

b) Isolation of mineral from metal

c) Isolation of metals from its ore

d) None of these

2. Which of the following is not a reactive metal?

a) Na

b) Ag

c) Mg

d) Fe

3. Which of the following ores do not represent the ore of iron?

a) Casseterite

b) Haematite

c) Limonite

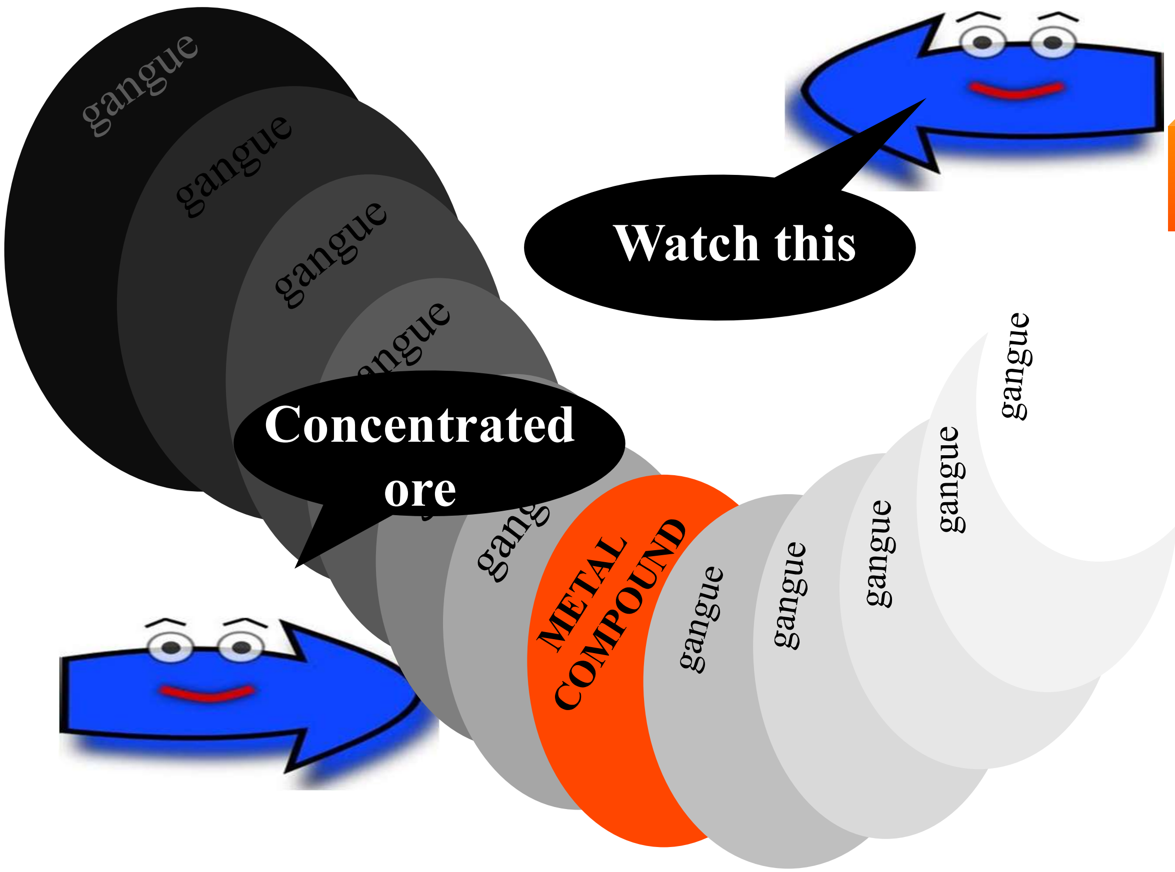
d) Magnetite

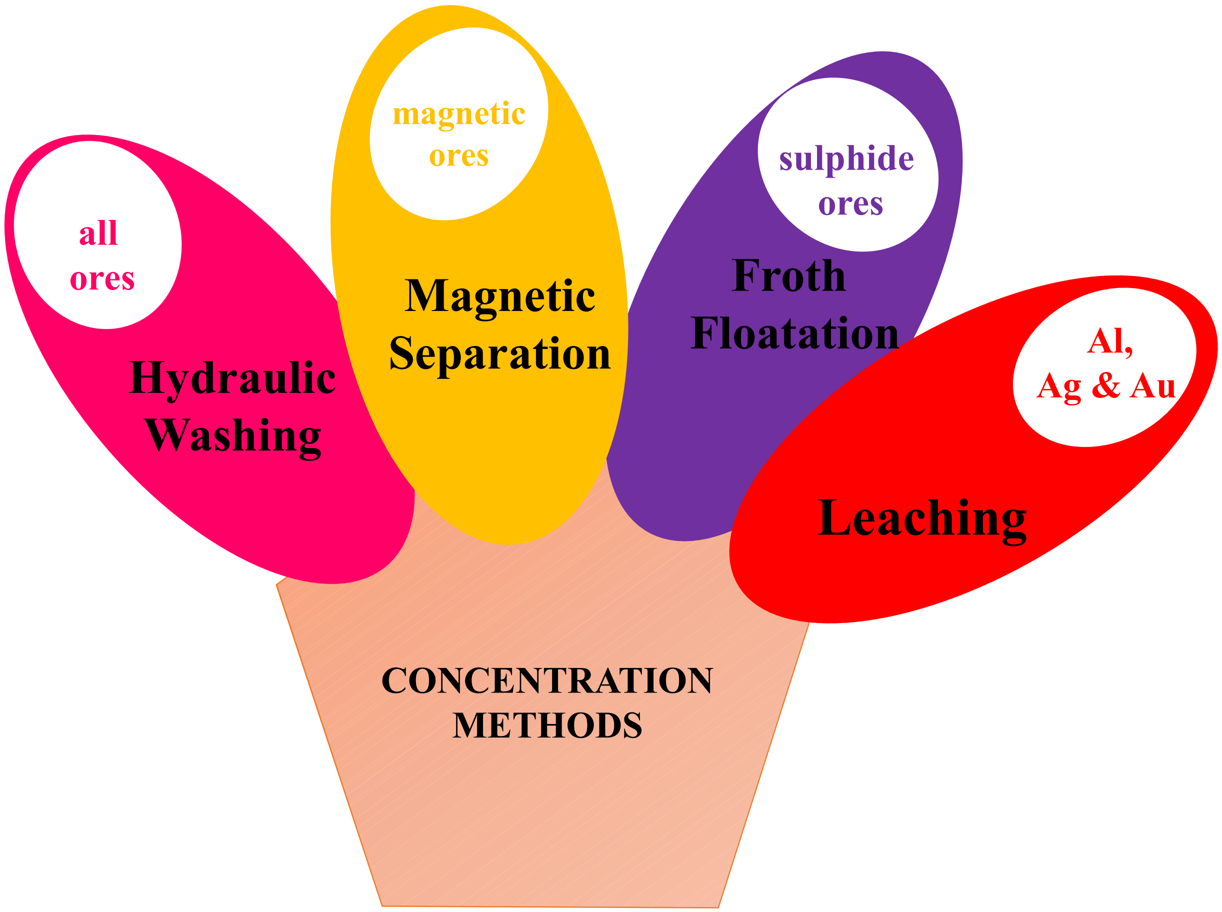
CONCENTRATION OF ORES
1. HYDRAULIC WASHING

Concentration of Ores

Some of the important procedures are described as follows..

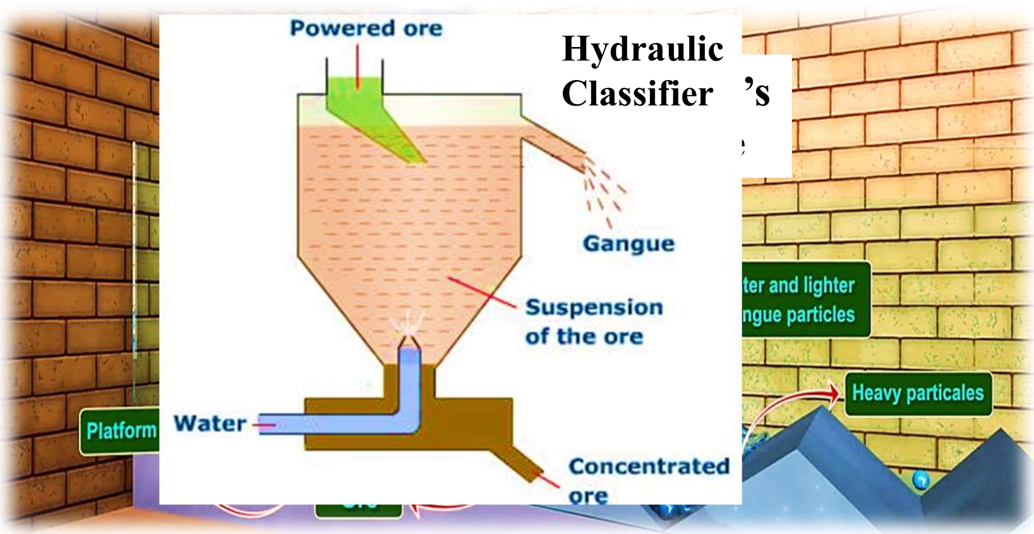
CONCENTRATION




all ores
Hydraulic Washing
magnetic ores
Magnetic Separation
sulphide ores
Froth Floatation
Al, Ag & Au
Leaching
CONCENTRATION METHODS

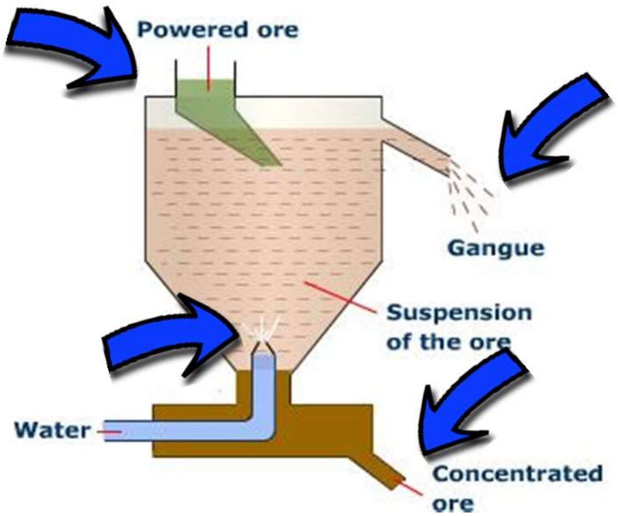
I) Hydraulic Washing or Levigation

- It is a type of gravity separation. In one such process, an upward stream of running water is used to wash the powdered ore.



I) Hydraulic Washing or Levigation

Working & using of hydraulic classifier method



The heavier ore particles are collected at the apex of the cone which is at the bottom of the reservoir.

MCQs

1) The earthy impurities present in the mineral are called

a) flux

b) gangue

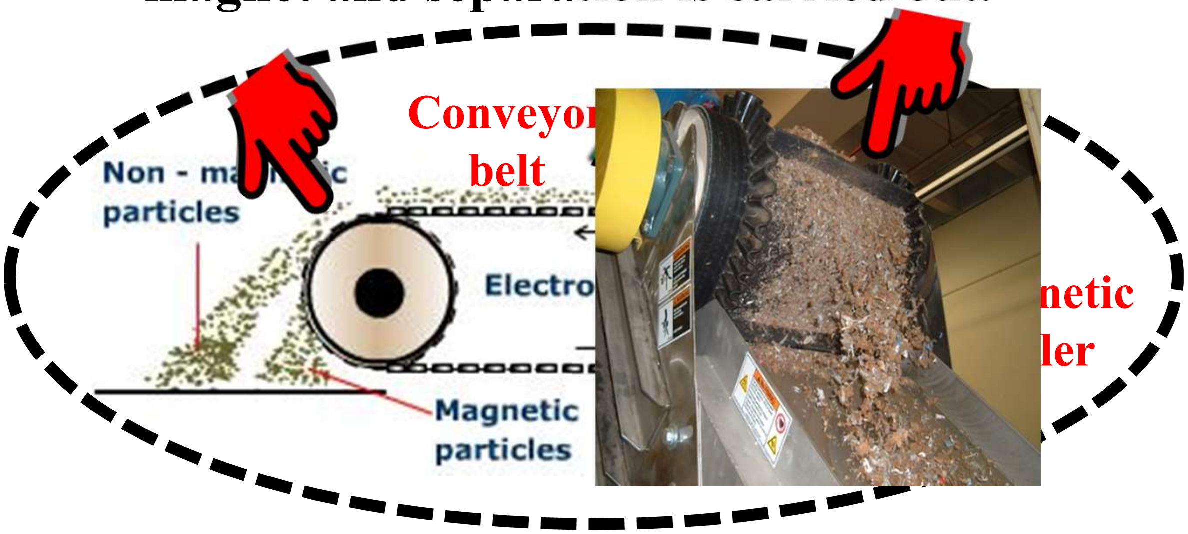
c) slag

d) Refractory material

MAGNETIC SEPARATION

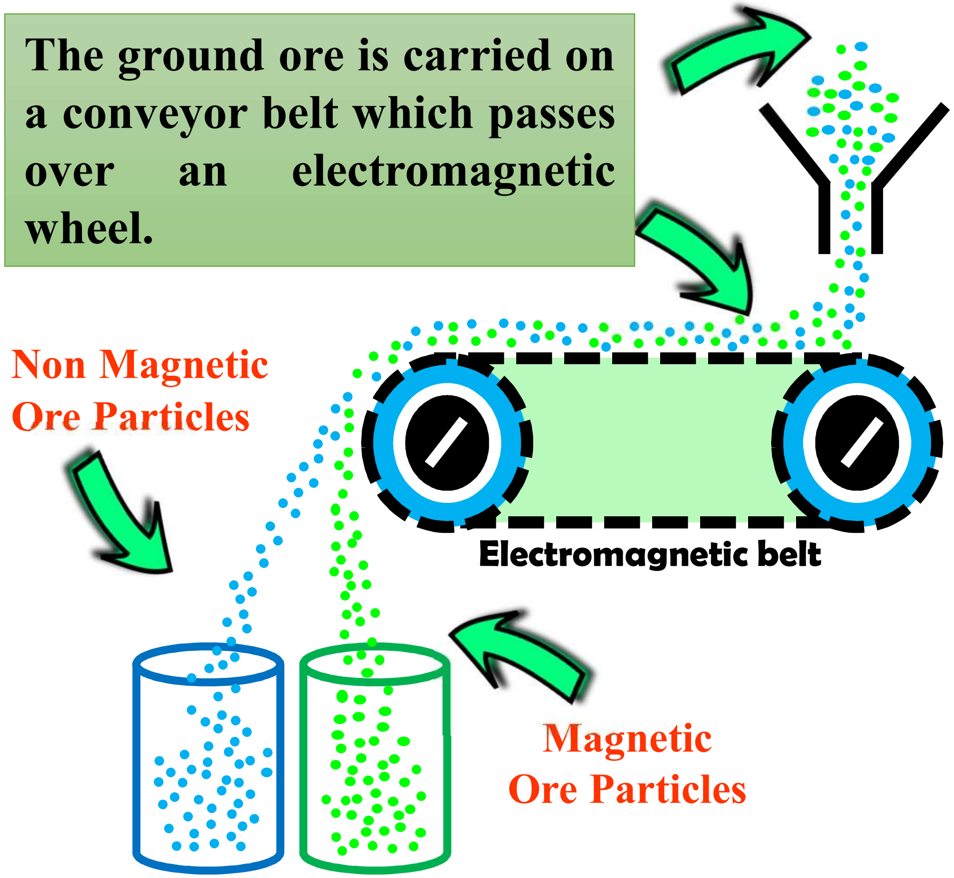
II) Magnetic Separation

- **This is based on the differences in magnetic properties of the ore and gangue. One of them is attracted by magnet and separation is carried out.**



The ground ore is carried on a conveyor belt which passes over an electromagnetic wheel.

Electromagnetic wheel of the conveyor attracts only magnetic particles into a separate heap.



1.Chromite ore is separated from non – magnetic silicon impurities.

MCQs

1. Electromagnetic separation method is based upon…

a) Preferential washing of ores & gangue particles

b) Difference in densities of ore particles & impurities

c) Difference in magnetic Properties of ore particles & impurities

d) None of these

2.Magnetic separation is used for increasing concentration of following…

a) Horn silver

b) Calcite

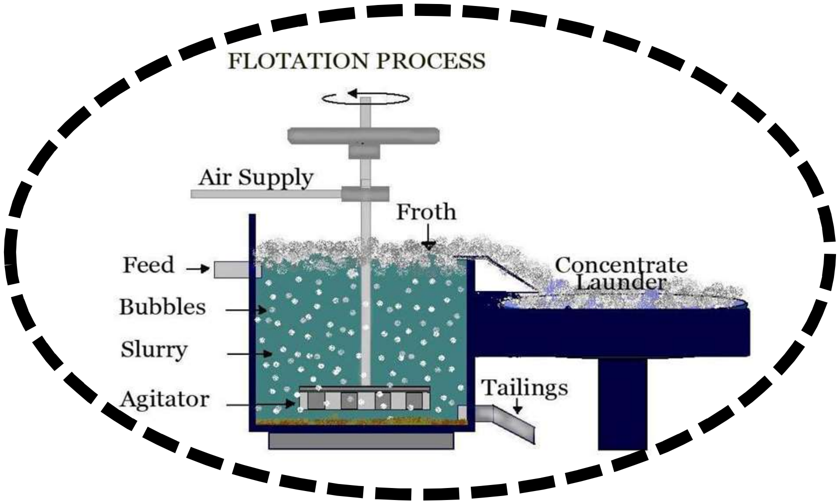
c) Haematite

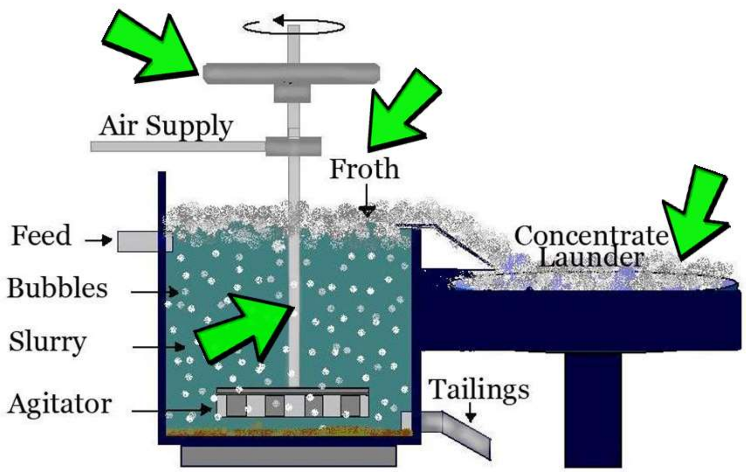
d) Magnesite

FROTH FLOATATION METHOD

III) Froth floatation method

- ‘The surface of sulphide ores is preferentially wetted by oils while that of gangue is preferentially wetted by water.’

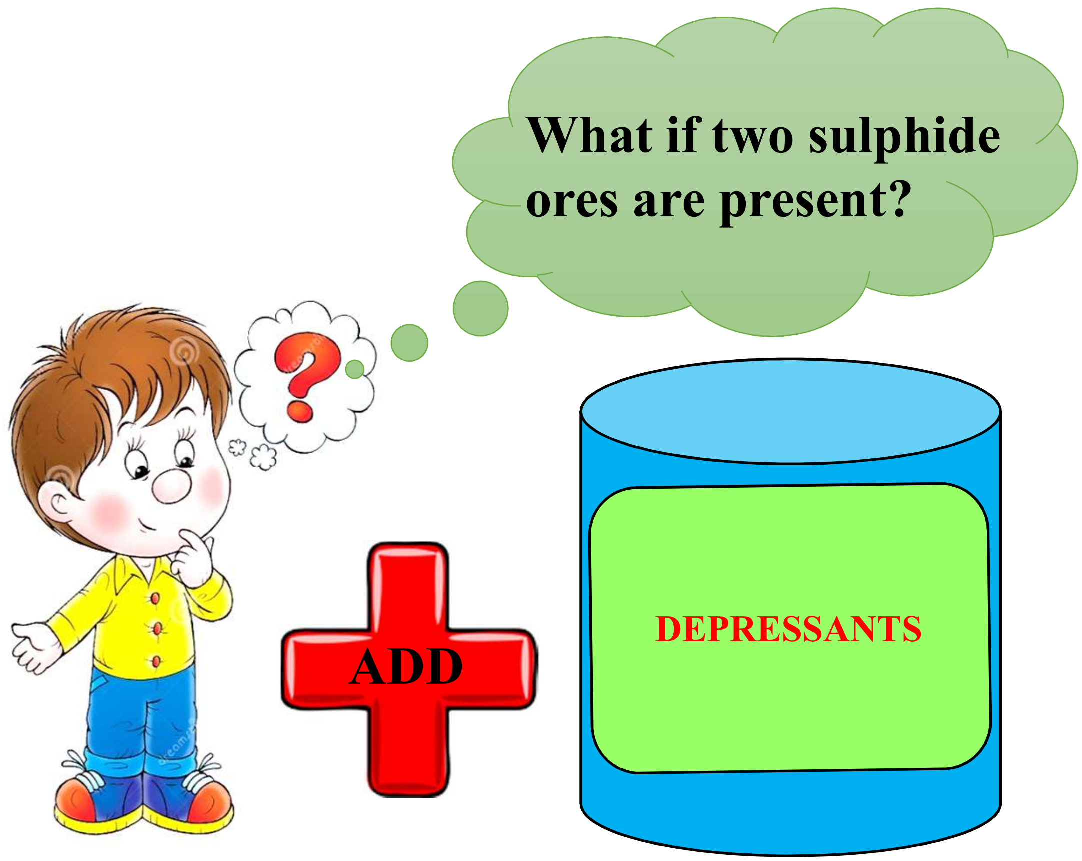


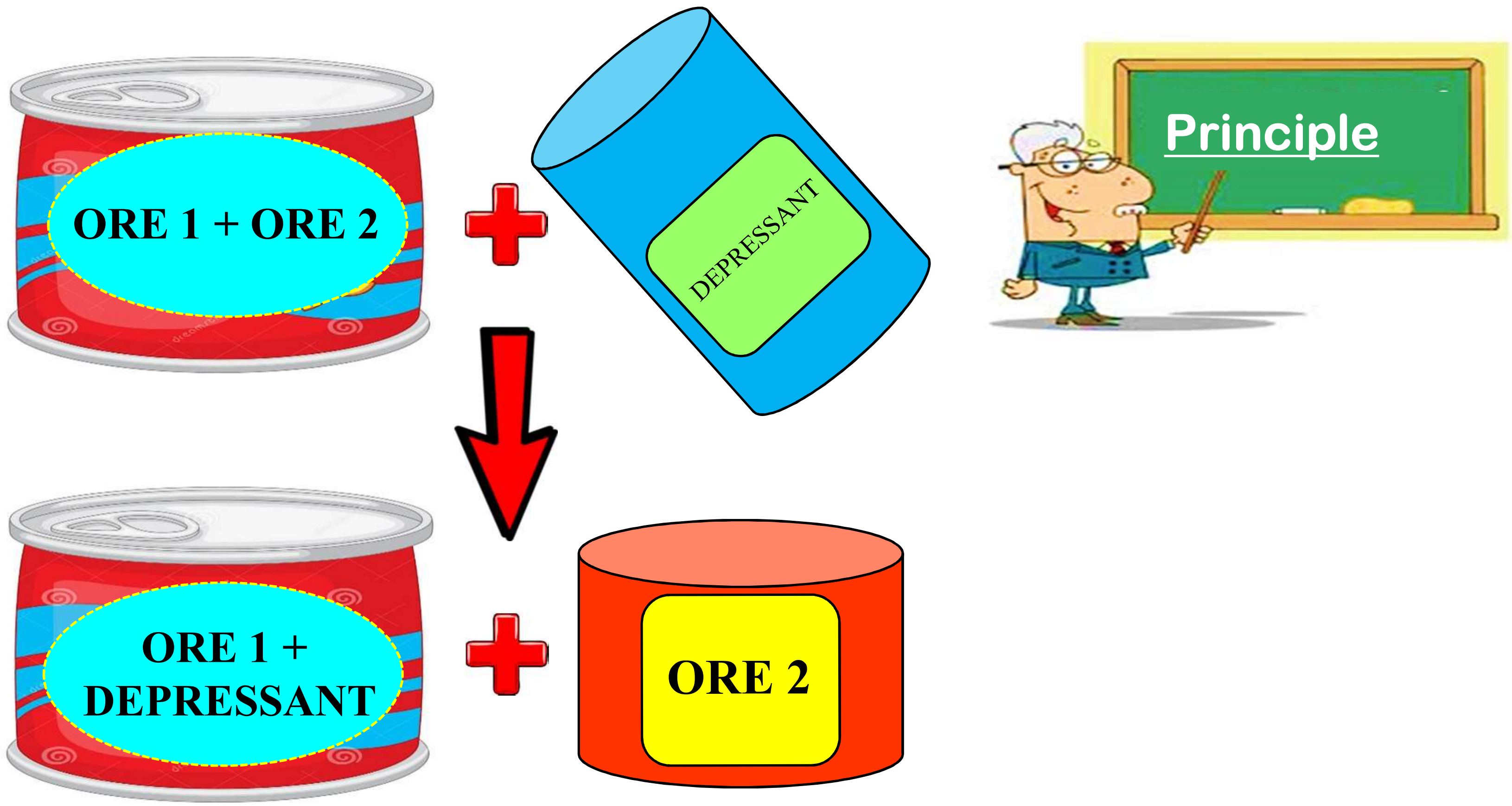


WORKING
using
Floatation cell

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

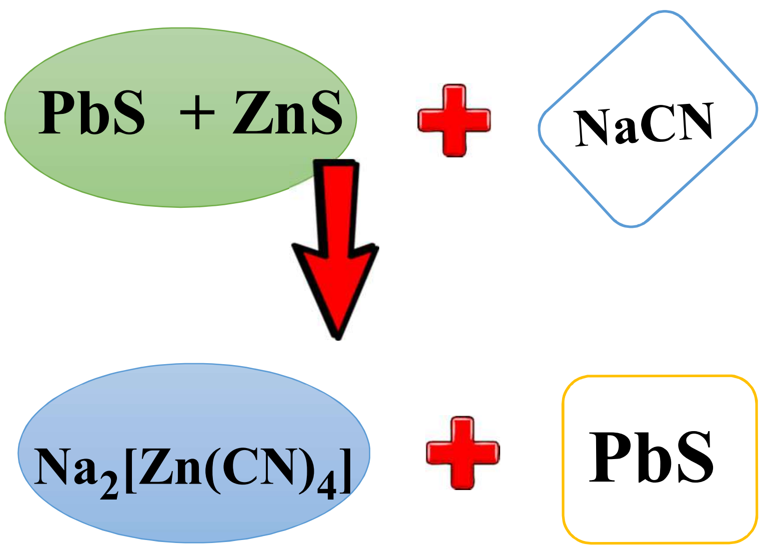
Froth Floatation


What if two sulphide ores are present?
ADD
DEPRESSANTS


ORE 1 + ORE 2
DEPRESSANT
Principle
ORE 1 +
DEPRESSANT
ORE 2

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**



MCQs

1. The froth-floatation process is based upon…

a) Magnetic properties of gangue

b) Specific gravity of ore particles

c) Preferential wetting of ore particles by oil

d) Preferential wetting of gangue particles by oil

2. Which of the following is used as a foaming agent in Froth Floatation process ?

a) KCN

b) $CuSO_4$

c) Nitric acid

d) Pine oil

3. **Which one of the following ores is not concentrated by Froth Floatation process ?**

a) Copper pyrites

b) Pentlandite

c) Iron Oxide

d) Zinc blende

LEACHING OF ALUMINA FROM BAUXITE

IV) Leaching

The following examples illustrate the procedure

The process of extracting minerals from a solid by dissolving them in a liquid. It is used if the ore alone but not the gangue is soluble in some suitable solvent.

(a) Leaching of alumina from bauxite

Bauxite

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.**

$$Al_2O_3\,(s) + 2NaOH\,(aq) + 3H_2O\,(l) \rightarrow \boxed{2Na[Al(OH)_4]\,(aq)}$$

This way, Al_2O_3 is leached out as sodium aluminate (and SiO_2 too as sodium silicate) leaving the impurities behind

- **Sodium aluminate is neutralized by passing CO_2 gas and hydrated Al_2O_3 is precipitated.**

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

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

$$Al_2O_3.xH_2O\ (s) \xrightarrow{1470\,K} Al_2O_3\ (s) + xH_2O\ (g)$$

(b) Other examples

- silver and gold is leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by the replacement by zinc.

$$4M\ (s) + 8CN^{-}\ (aq) + 2H_2O\ (aq) + O_2\ (g)$$

$$\longrightarrow 4[M(CN)_2]^{-}\ (aq) + 4OH^{-}\ (aq)$$

(M= Ag or Au)

$$2\left[M(CN)_2\right]^{-}(aq) + Zn(s) \rightarrow \left[Zn(CN)_4\right]^{2-}(aq) + 2M(s)$$

MCQs

1) The impurities present in Bauxite …

a) SiO_2

b) iron oxides

c) TiO_2

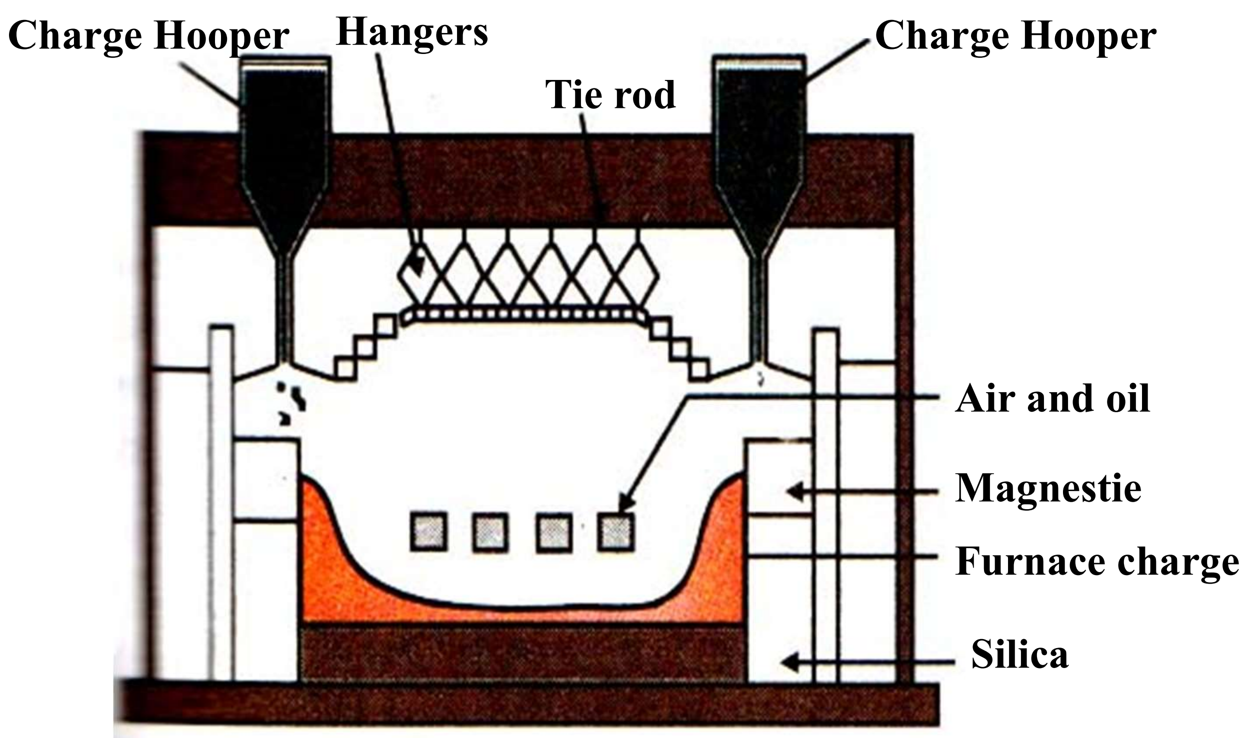
d) All the above

2) Which of the following aqueous solution is used in Leaching of Alumina…

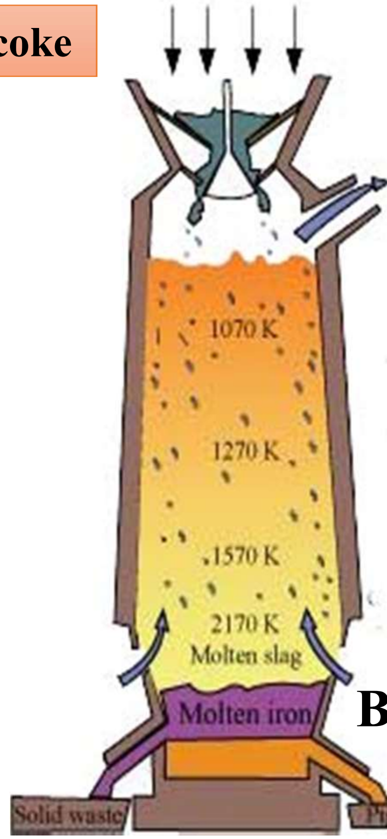
- **a) NaOH**
- **b) $Ca(OH)_2$**
- **c) CsOH**
- **d) $B(OH)_3$**

EXTRACTION OF CRUDE METAL FROM CONCENTRATED ORE

A SECTION OF A MODERN REVERBERATOR FURNACE



Ore. Limestone and coke



Exhaust gases (CO, CO_2)

$3Fe_2O_3 + CO \rightarrow 3FeO + CO_2$

(Iron ore)

$Fe_2O_4 + CO \rightarrow 3FeO + CO_2$

$CaCO_3 \rightarrow CaO + CO_2$

(Limestone)

$CaO + SiO_2 \rightarrow \underbrace{CaSiO_3}_{\text{Slag}}$

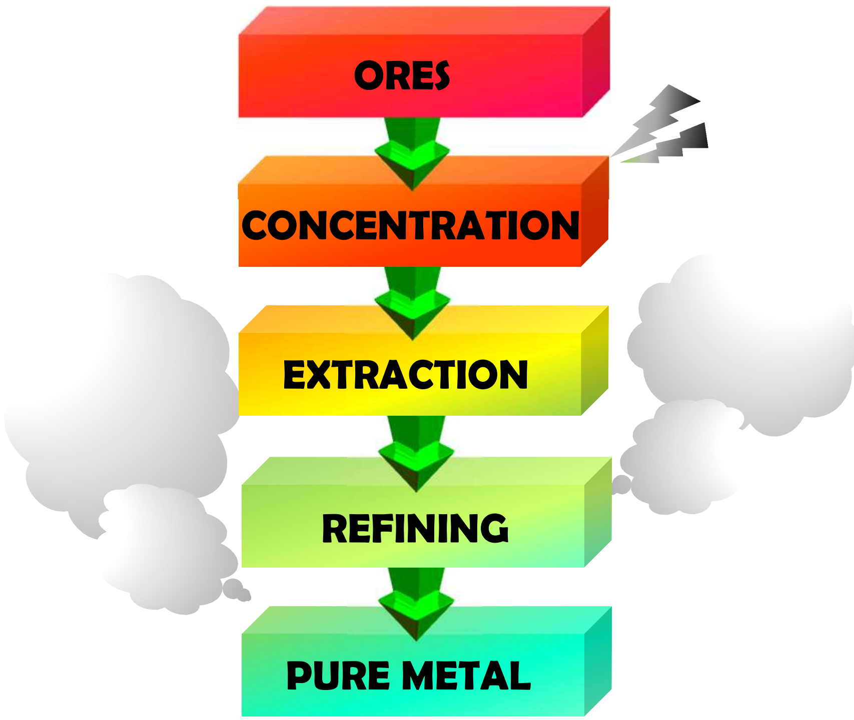
$FeO + CO \rightarrow Fe + CO_2$

$C + CO_2 \rightarrow 2CO$

$C + O_2 \rightarrow CO_2$

$FeO + C \rightarrow Fe + CO$

Blast of air and oxygen


ORES
CONCENTRATION
EXTRACTION
REFINING
PURE METAL

Extraction of Crude Metal from Concentrated Ore:

- **Isolation of metals from concentrated ore involves two major steps viz.,**

a) Conversion of ore into oxide if the ore is not an oxide

b) Reduction of the oxide to metal

a) Conversion to oxide.

I) Calcination:

After heating the metal oxide is formed

- Calcination involves heating of the ore in the absence of air just below its fusion temperature in a reverberatory furnace.

$$Fe_2O_3.xH_2O\ (s) \xrightarrow{\Delta} \boxed{Fe_2O_3\ (s) +} xH_2O\ (g)$$

$$ZnCO_3\ (s) \xrightarrow{\Delta} \boxed{ZnO\ (s) +} CO_2\ (g)$$

$$CaCO_3.MgCO_3\ _{(s)} \xrightarrow{\Delta} \boxed{CaO\ (s) +} MgO\ (s\ ) + 2CO_2\ (g)$$

II) Roasting:

- In roasting, the ore is heated in a regular supply of air in a reverberatory furnace at a temperature below the melting point of the metal.

The SO_2 produced is utilized for manufacturing of H_2SO_4

- Some of the reactions involving sulphide ores are…

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

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

- The sulphide ores of copper are heated in reverberatory furnace.

If the ore contains iron oxide, it is mixed with silica and roasted.

$$FeO + SiO_2 \rightarrow \underset{\text{(slag)}}{FeSiO_3}$$

Iron oxide is converted into iron silicate, called slag

A mixture of Cu_2S and little FeS is know as

Copper matte

Smelting :

- The process of separating molten metal in crude form (or) mixture of metal sulphides in molten form from ore is called smelting.

Example :

A mixture of copper iron pyrites, coke and sand on heating in blast furnace gives matte.

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

b) Reduction of oxide to the metal

- **Reduction of the metal oxide usually involves heating it with some other substance acting as a reducing agent (Carbon or coke or CO)**

- **The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide to form CO**

$$M_xO_y + yC \rightarrow xM + y\,CO$$

To study the temperature dependence for thermal reduction and choice of reducing agent at high temperature can be made from Gibbs energy and temperature curves called Ellingham diagrams.

MCQs

1) **Which gas is liberated during roasting?**

a) SO_2

b) O_2

c) SO_3

d) H_2

2) **Reducing agent used in reduction of oxide to the metal**

a) CO_2

b) O_2

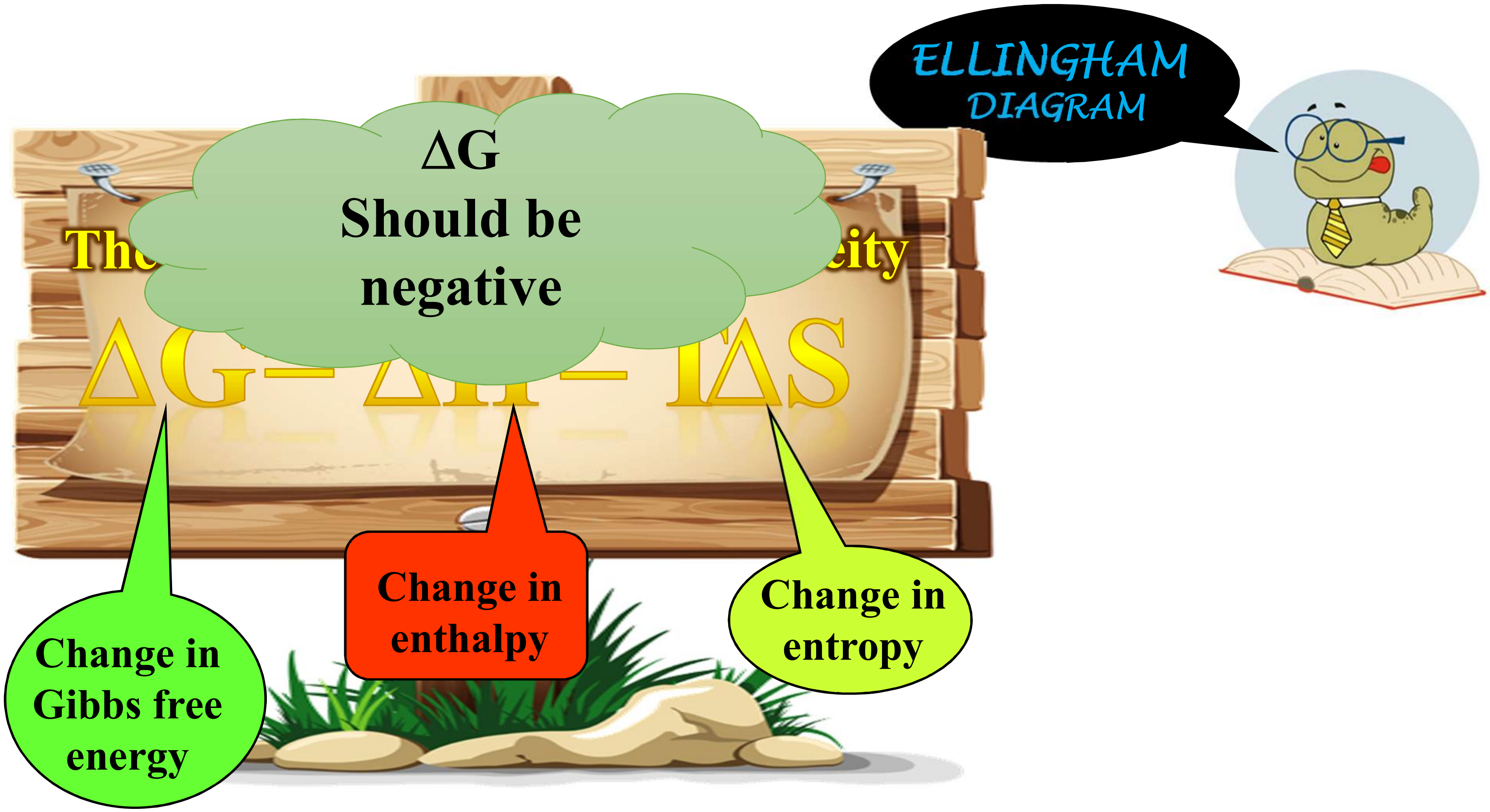
c) N_2

d) C

ELLINGHAM DIAGRAM

Ellingham Diagram

- **The graphical representation of Gibbs energy was given by H.J.T.Ellingham.**
- **It provides the choice of taking reducing agent in the reduction of oxides.**
- **It also provides the information whether a particular reaction is feasible at particular temperature or not.**



ΔG
Should be
negative
Change in Gibbs free energy
Change in enthalpy
Change in entropy
ELLINGHAM
DIAGRAM

$$M_{(s)} + O_{2(g)} \Rightarrow 2MO_{(s)}$$

Gas

Solid

Thermodynamics principle of Metallurgy

ΔH = –ve

ΔS = –ve

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

$$= \quad - \; T$$

at HIGH temp $\Rightarrow$ $\Delta G \Rightarrow$ +ve

at LOW temp $\Rightarrow$ $\Delta G \Rightarrow$ –ve

$$C_{(s)} + O_{2(g)} \Rightarrow 2CO_{(g)}$$

1 Gas

2 Gas

Thermodynamics principle of Metallurgy

ΔH = –ve

ΔS = +ve

ΔG Decreases with increase in temp.

Higher the temp

$\Delta G \Rightarrow$ decreases

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

Thermodynamics principle of Metallurgy

Gas

$\Delta H = -ve$

ΔG is independent of temp.

Independent of temperature

$$MO + C \rightarrow M + CO$$

Metal oxide is STABLE → Reaction will not happen

Carbon monoxide is STABLE → Reaction will happen

MCQs

1) Ellingham diagram represents

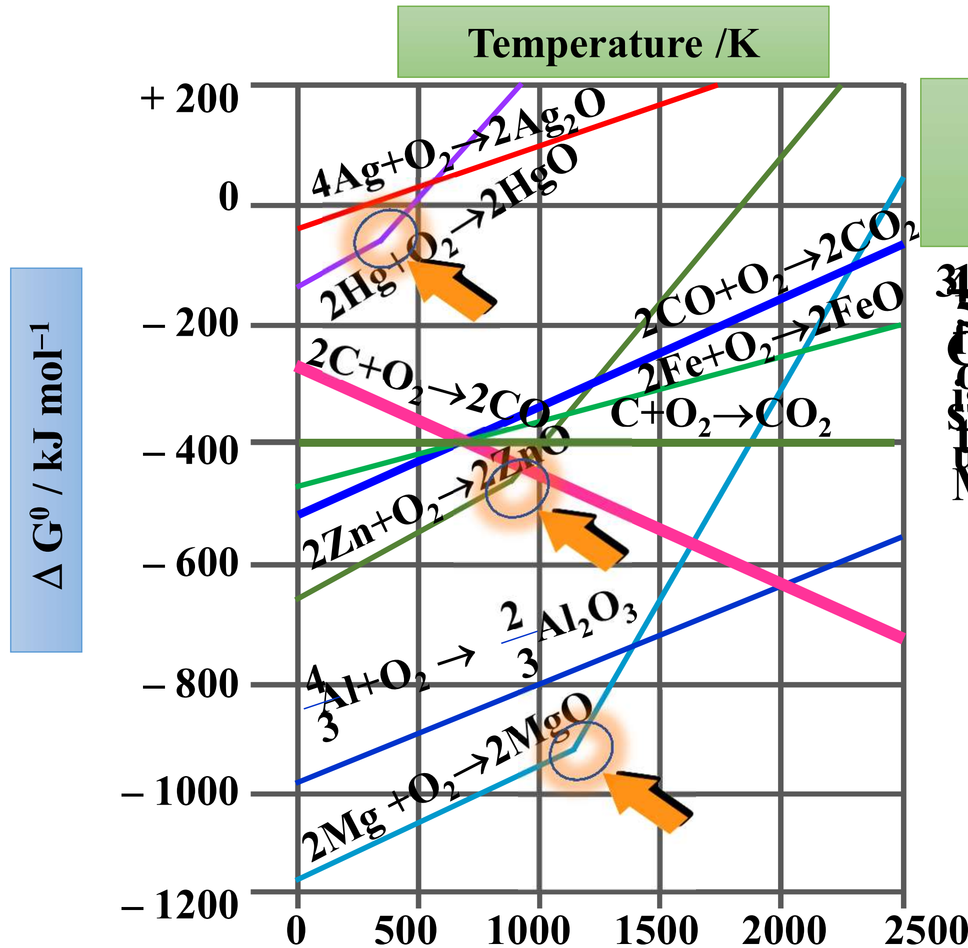
a) Change of ΔG with temperature

b) Change of ΔH with temperature

c) Change of ΔG with pressure

d) Change of $\Delta G - T \Delta S$ with temperature

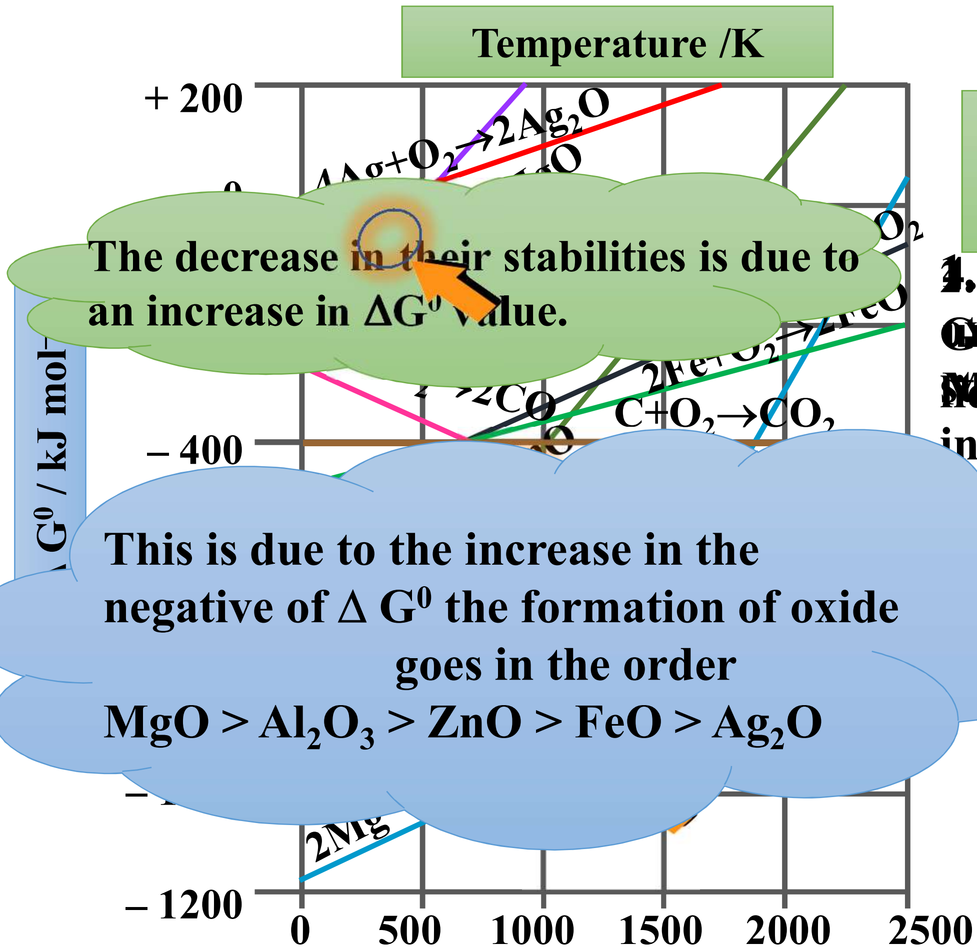
FEATURES & IMPORTANCE OF ELLINGHAM DIGRAM



Features of Ellingham diagram

5. The graph for the formation of CO_2 is straight line parallel to temperature axis.

MgO, ZnO and HgO.



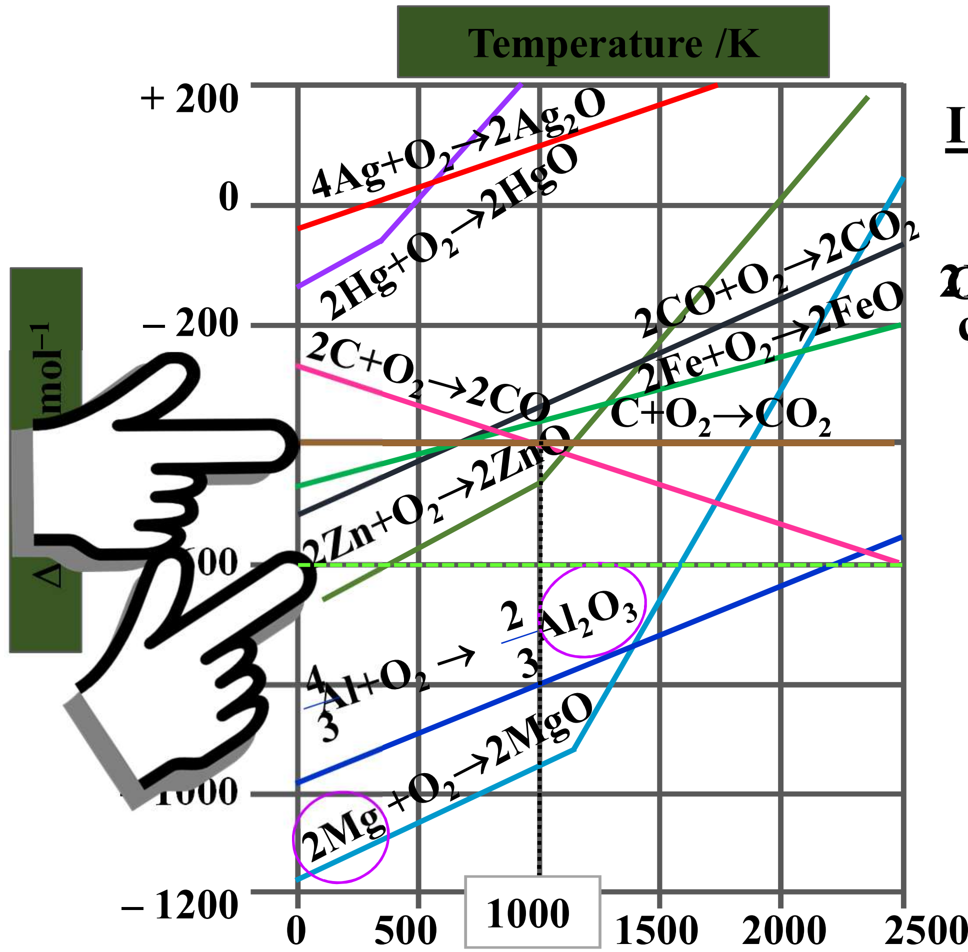
The decrease in their stabilities is due to an increase in ΔG^0 value.

This is due to the increase in the negative of ΔG^0 the formation of oxide goes in the order

$MgO > Al_2O_3 > ZnO > FeO > Ag_2O$

Significance of Ellingham diagram

increase in temperature.



Importance of Ellingham diagram

At Low temperature

Ag$_2$O and HgO

can be easily decomposed at

900K

$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO$

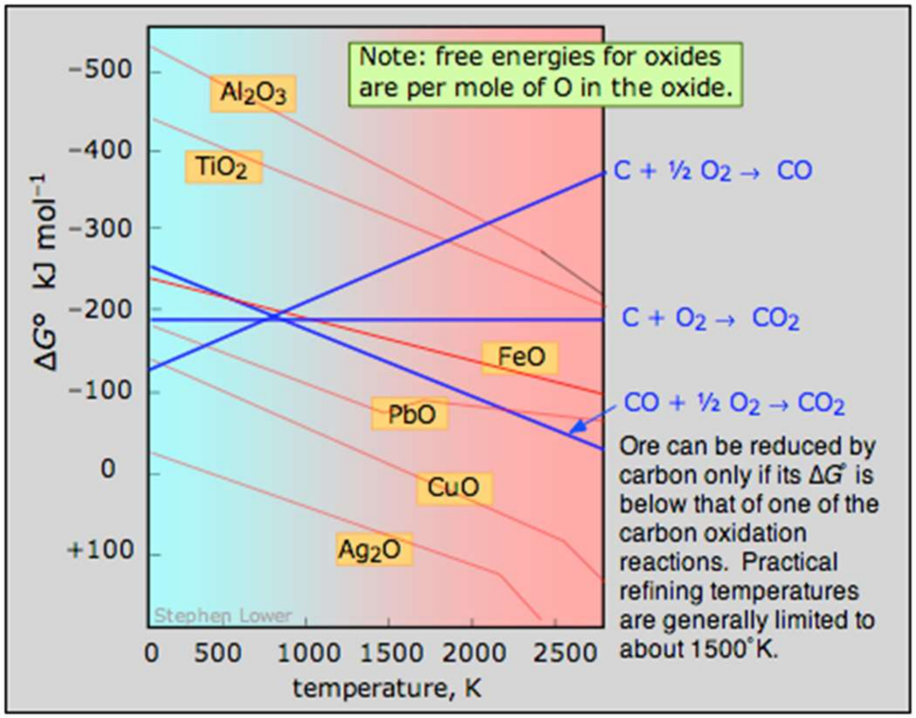
CO_2 is the better reducing agent

$Al_2O_3 + 3Mg \rightarrow 3MgO + 2Al$

1500K

$ZnO + C \rightarrow Zn + CO$

600 K and 700 K



Note: free energies for oxides are per mole of O in the oxide.
-500
-400
-300
-200
-100
0
+100
ΔG° kJ mol-1
Al2O3
TiO2
FeO
PbO
CuO
Ag2O
C + ½ O2 → CO
C + O2 → CO2
CO + ½ O2 → CO2
Ore can be reduced by carbon only if its ΔG° is below that of one of the carbon oxidation reactions. Practical refining temperatures are generally limited to about 1500°K.
Stephen Lower
0 500 1000 1500 2000 2500
temperature, K

ELLINGHAM
DIAGRAM

Question

Suggest a condition under which magnesium could reduce alumina.

Answer:

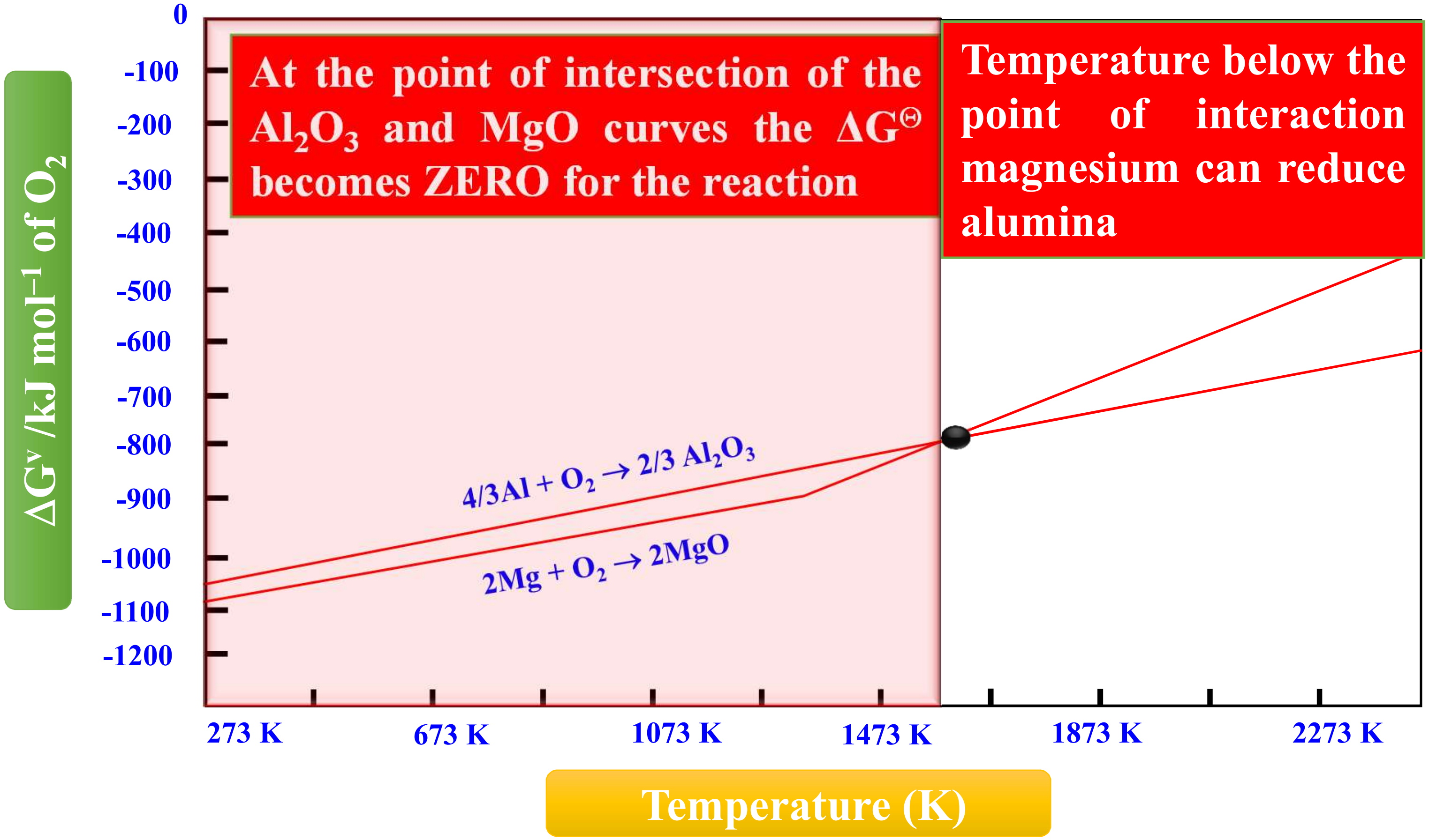
The two equations are:

$$\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3 \quad \text{..........} \quad (1)$$

$$2Mg + O_2 \rightarrow 2MgO \quad \text{..........} \quad (2)$$

$$\frac{2}{3}Al_2O_3 + 2Mg \rightarrow 2MgO + \frac{4}{3}Al$$

Overall reaction



At the point of intersection of the Al_2O_3 and MgO curves the $\Delta G^{\ominus}$ becomes ZERO for the reaction
Temperature below the point of interaction magnesium can reduce alumina
$4/3Al + O_2 \rightarrow 2/3\ Al_2O_3$
$2Mg + O_2 \rightarrow 2MgO$
$\Delta G^{\ominus}$ /kJ mol^{-1} of O_2
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
-1100
-1200
273 K
673 K
1073 K
1473 K
1873 K
2273 K
Temperature (K)

Question

Although thermodynamically feasible, in practice, magnesium metal is not used for the reduction of alumina in the metallurgy of aluminium, Why?

Answer:

The temperatures above the point of interaction of Al_2O_3 and MgO curves, magnesium can reduce alumina but the process will be uneconomical.

Question

Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction?

Answer:

- **The entropy is higher if the metal is in liquid state than when it is in solid state because randomness increases**
- **As ΔS will be high, change in Gibbs energy will be more negative and the reduction becomes easier.**

MCQs

1) ΔG^0 vs T plot in Ellingham diagram slopes downward for the reaction --

a) $Mg + \frac{1}{2} O_2 \rightarrow MgO$

b) $2Ag + \frac{1}{2} O_2 \rightarrow Ag_2O$

c) $C + \frac{1}{2} O_2 \rightarrow CO$

d) $C + \frac{1}{2} O_2 \rightarrow CO_2$

THERMODYNAMIC PRINCIPLES OF METALLURGY

1. EXTRACTION OF IRON FROM ITS OXIDES

Thermodynamic Principles of Metallurgy : Applications

(a) Extraction of iron from its oxides

- **Oxide ores of iron, after concentration through calcination/roasting are mixed with limestone and coke and fed into a blast furnace.**
- **Here, the oxide is reduced to the metal**
- **Thermodynamics helps us understand how coke reduces the oxide and selection furnace.**

Applications

(a) Extraction of iron from its oxides

One of the main reduction steps in this process is:

$$FeO\,(s) + C\,(s) \rightarrow Fe\,(s/l) + CO\,(g)$$

- **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 oxidised to CO:**

$$FeO\,(s) \rightarrow Fe\,(s) + \frac{1}{2}O_2\,(g) \quad [\Delta G_{(FeO,\,Fe)}] \text{ ------------ } (1)$$

$$C\,(s) + \frac{1}{2}O_2\,(g) \rightarrow CO\,(g) \quad [\Delta G_{(C,\,CO)}] \text{ ------------ } (2)$$

Applications

(a) Extraction of iron from its oxides

- **When both the reactions take place to yield the equation (1) the net Gibbs energy change becomes:**

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

- **Naturally, the resultant reaction will take place when the right hand side in equation is negative**

Applications

(a) Extraction of iron from its oxides

- In $\Delta G^{\ominus}$ vs T plot representing equation (2) the plot goes upward and that representing the change $C \rightarrow CO$ (C,CO) goes downward

Applications

(a) Extraction of iron from its oxides

- **At temperatures above 1073K (approx.), the C,CO line comes below the Fe, FeO line [$\Delta G_{(C, CO)} < \Delta G_{(Fe, FeO)}$]**
- **So, in this range, coke will be reducing the FeO and will itself be oxidized to CO**

Applications

(a) Extraction of iron from its oxides

- **In a similar way the reduction of Fe_3O_4 and Fe_2O_3 at relatively lower temperatures by CO can be explained on the basis of lower lying points of intersection of their curves with the CO, CO_2 curve.**

Applications

(a) Extraction of iron from its oxides

- **In the Blast furnace, reduction of iron oxides takes place in different temperature ranges.**
- **Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto about 2200K in the lower portion itself.**

Applications

(a) Extraction of iron from its oxides

- **The burning of coke, therefore, supplies most of the heat required in the process.**
- **The CO and heat move to upper part of the furnace.**

Applications

(a) Extraction of iron from its oxides

- **In upper part, the temperature is lower and the iron oxides (Fe_2O_3 and Fe_3O_4) coming from the top are reduced in steps to FeO.**
- **The CO and heat moves to upper part of the furnace.**

1. It is used for the concentration of oxide carbonate and native ores.

Applications

(a) Extraction of iron from its oxides

- **Thus, the reduction reactions taking place in the lower temperature range and in the higher temperature range, depend on the points of corresponding intersections in the $\Delta_r G^\Theta$ vs T plots**

Applications

(a) Extraction of iron from its oxides

- **These reactions can be summarized as follows:**
- **At 500 – 800 K (lower temperature range in the blast furnace):**

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$$

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$