

VELAMMAL MATRIC HR.SEC SCHOOL- SURAPET

DEPARTMENT OF CHEMISTRY

UNIT-1

METALLURGY

INTRODUCTION

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

MINERAL

Minerals: They are the naturally occurring chemical substances in the earth's crust obtainable by mining.

EXAMPLE : Minerals of Aluminium
Bauxite, clay, Diaspore , etc.,.

ORE

Ores: The mineral from which the metals can be economically and conveniently extracted is called an ore.

For example,

Bauxite and china clay both are minerals of Aluminium . However Aluminum can be commercially extracted from bauxite while extraction from China clay not profitable one. Hence the mineral, Bauxite is an ore of Aluminium while clay is not.

NOTE : ALL ORES ARE MINERALS BUT ALL MINERALS ARE NOT ORES

LIST OF SOME METALS AND THEIR COMMON ORES

Metal	Ore	Composition	Metal	Ore	Composition
Aluminum	Bauxite	$\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$	Zinc	Zinc blende or Sphalerite	ZnS
	Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$		Calamine	ZnCO_3
	Kaolinite	Al_2O_3		Zincite	ZnO
Iron	Haematite	Fe_2O_3	Lead	Galena	PbS
	Magnetite	Fe_3O_4		Anglesite	PbSO_4
	Siderite	FeCO_3		Cerussite	PbCO_3
	Iron pyrite	FeS_2	Tin	Cassiterite (Tin stone)	SnO_2
	Limonite	$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Silver	Silver glance (Argentite)	Ag_2S
Copper	Copper pyrite	CuFeO_2		Pyrargyrite (Ruby silver)	Ag_3SbS_3
	Copper glance	Cu_2S		Chlorargyrite (Horn Silver)	AgCl
	Cuprite	Cu_2O		Stefinite	Ag_2SbS_4
	Malachite	$\text{CuCO}_3 \cdot \text{Cu(OH)}_2$		Proustite	Ag_2AsS_3
	Azurite	$2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$			

METALLURGICAL PROCESS

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

1. Concentration of ores
2. Extraction of crude metals
3. Refining of crude metals

Concentration of the ore/ dressing or benefaction:

The process of removal of the unwanted materials (e.g., sand, clays, etc.) from the ore is known as concentration, dressing or benefaction

[Gangue: The ores are associated with non metallic impurities, rocky materials and siliceous matter which are collectively known as gangue]

Different methods of concentrations:

Hydraulic Washing,

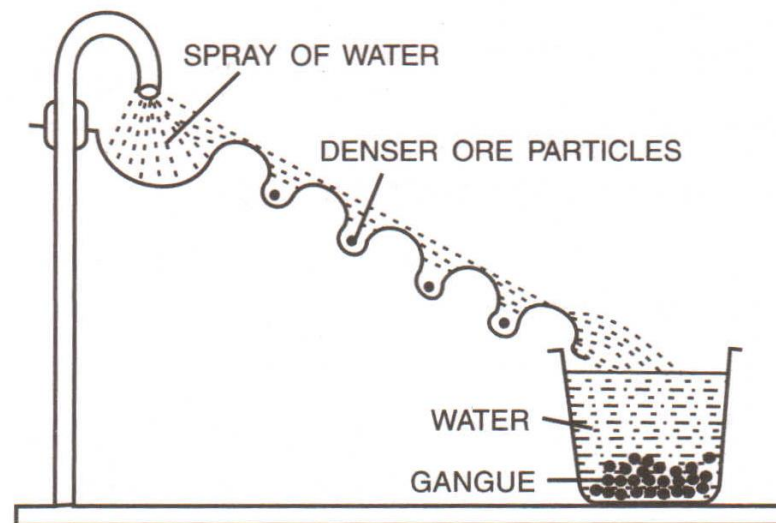
Froth Floatation.

Leaching,

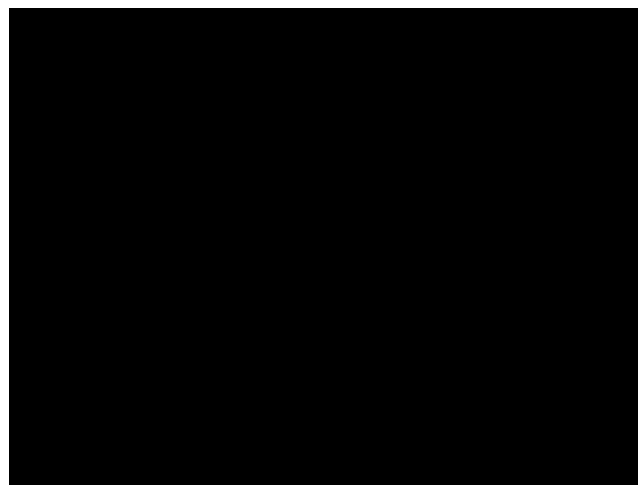
Magnetic separation,

HYDRAULIC WASHING (OR) GRAVITY SEPARATION

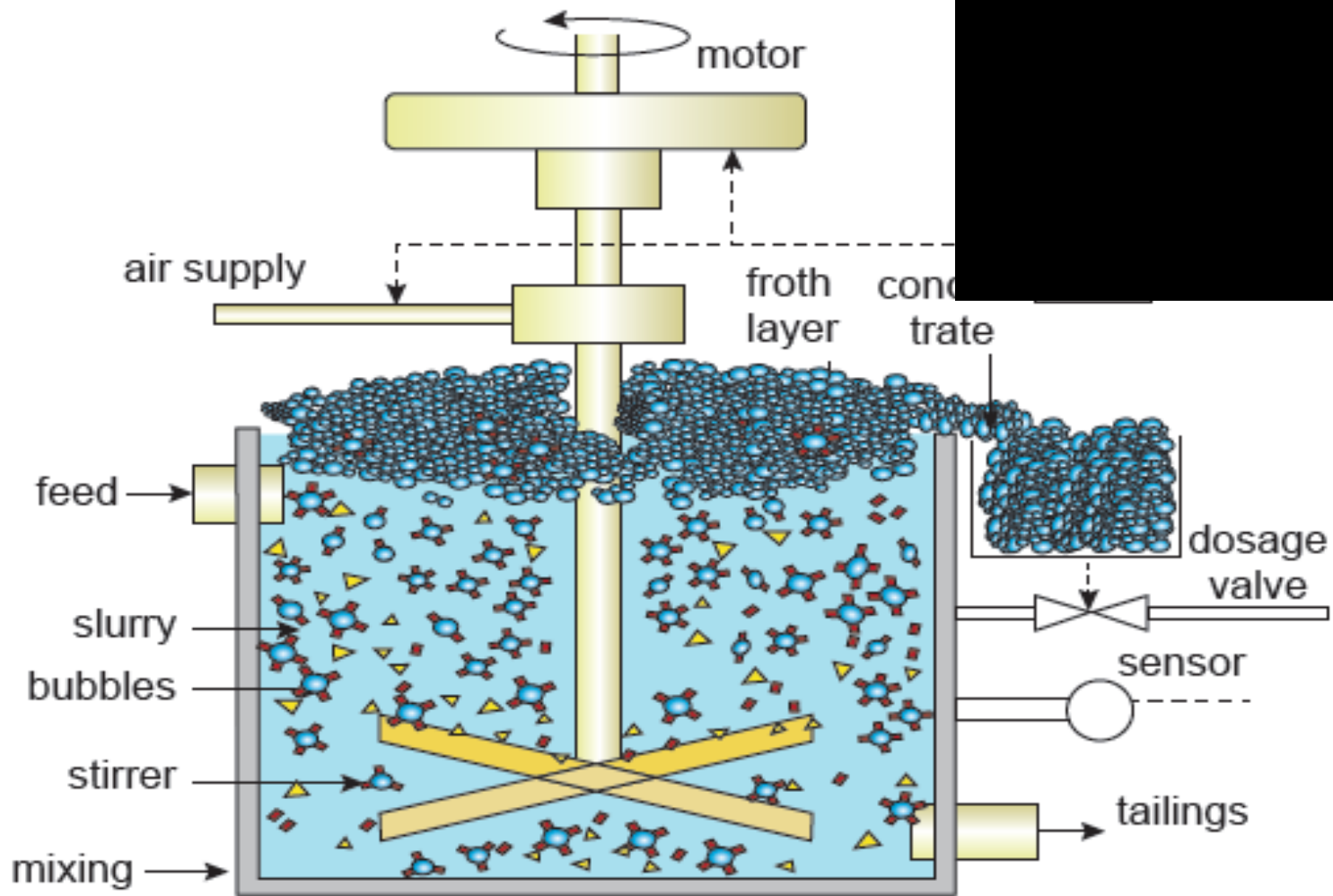
- **Principle:** This is based on the differences in gravities of the ore and the gangue particles.
- In this process, an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind.
- This method is frequently used when the ore particles are heavier than the earthly or rocky gangue particles. It is commonly used for oxide ores such as haematite, tin stone and native ores of Au, Ag.



Hydraulic washing



FROTH FLOTATION PROCESS



- **Principle:** The mineral particles are wetted by oil while the gangue particles are wetted by water
- This method has been in use for removing gangue from sulphide ores. (eg: ZnS,PbS)
- In this process, a suspension of the powdered ore is mixed with water. To it collectors and frothing agent are added.
- Collectors- Sodium ethyl xanthates, enhance non-wettability of the mineral particles

Frothing agent – Pine oil, eucalyptus oil stabilise the froth.

The mineral particles are wetted by oil while the gangue particles are wetted by water.

A rotating paddle agitates the mixture and draws air in it. As a result, the 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.

The role of a depressant in the floatation process

- When sulphide ore of a metal of interest contains other metal sulphides as impurities, depressing agent(NaCN , Na_2CO_3) is used
- Depressant selectively prevents one of the sulphide ore coming to froth by complexation
- NaCN is used as depressant when ore containing ZnS and PbS , it selectively prevents ZnS from coming to the froth but allows PbS to come with the froth

LEACHING

- This is another method of concentration of ore.

Principle:

This method is based on the solubility of the ore in a suitable solvent and the reactions in aqueous solution.

Definition:

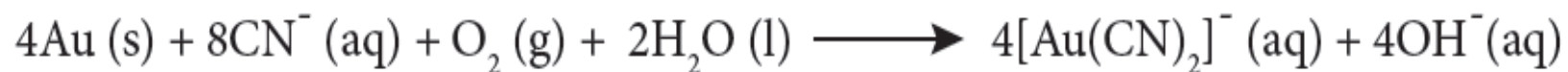
- In this method, the crushed ore is allowed to dissolve in a suitable solvent, the metal present in the ore is converted to its soluble salt or complex while the gangue remains insoluble.

TYPES OF LEACHING

- Cyanide leaching
- Ammonia leaching
- Alkali leaching
- Acid leaching

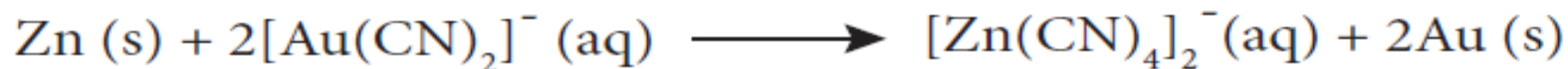
Cyanide leaching

- The crushed ore of gold is leached with aerated dilute solution of sodium cyanide. Gold is converted into a soluble cyanide complex. The gangue, alumino silicate remains insoluble.



Recovery of metal of interest from the complex by reduction:

Gold can be recovered by reacting the deoxygenated leached solution with zinc. In this process the gold is reduced to its elemental state (zero oxidation state) and the process is called **cementation**.



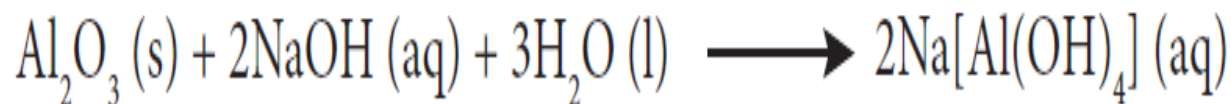
- When a crushed ore containing nickel, copper cobalt is treated with aqueous ammonia under suitable pressure, ammonia selectively leaches these metals by forming their soluble complexes viz. $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, and $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ respectively
- From the ore leaving behind the gangue, iron(III) oxides/hydroxides and aluminosilicate.

Alkali leaching

The ore is treated with aqueous alkali to form a soluble complex.

Example,

Bauxite, an important ore of aluminum is heated with a solution of sodium hydroxide or sodium carbonate in the temperature range 470 - 520 K at 35 atm to form soluble sodium meta-aluminate leaving behind the impurities, iron oxide and titanium oxide.



The hot solution is decanted, cooled, and diluted. This solution is neutralised by passing CO_2 gas, to the form hydrated Al_2O_3 precipitate.



The precipitate is filtered off and heated around 1670 K to get pure alumina Al_2O_3 .

- Leaching of sulphide ores such as ZnS, PbS etc., can be done by treating them with hot aqueous sulphuric acid.
- In this process the insoluble sulphide is converted into soluble sulphate and elemental sulphur.



Magnetic separation

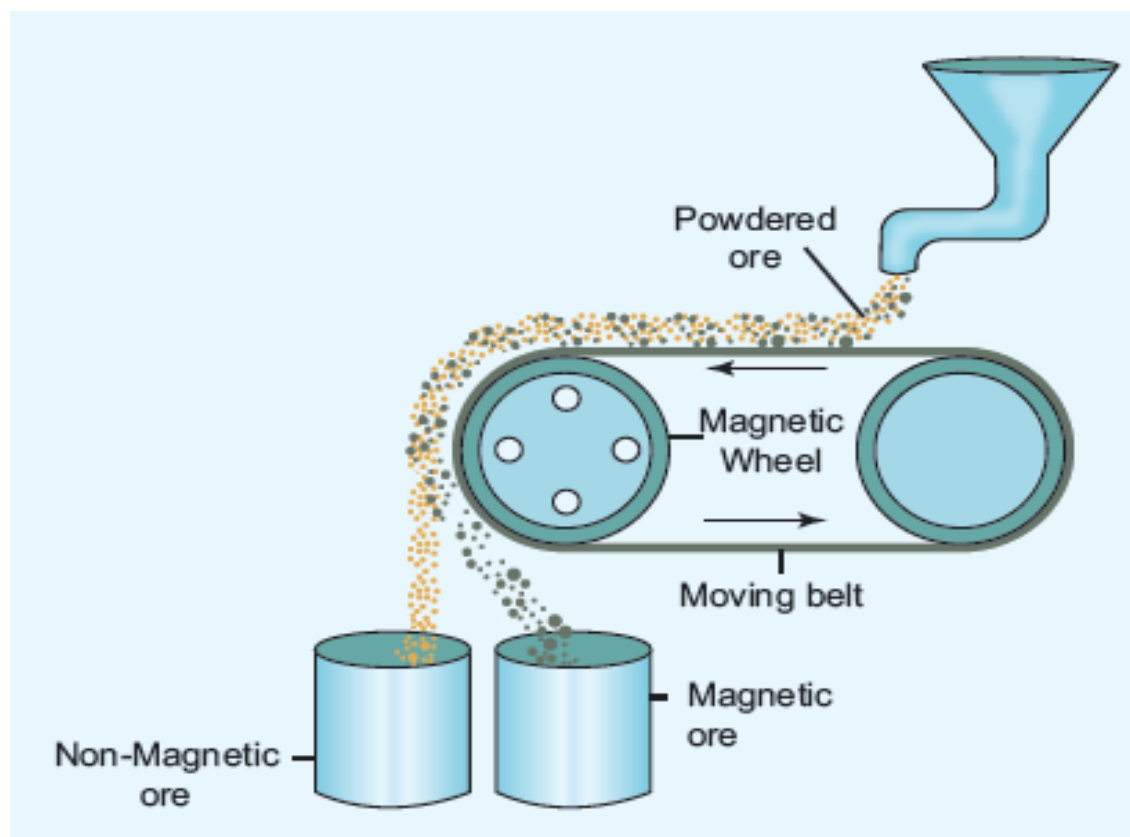
Principle:

This method is applicable to ferromagnetic ores and it is based on the difference in the magnetic properties of the ore and the impurities.

- **For example:** tin stone can be separated from the wolframite impurities which is magnetic. Similarly, ores such as chromite, pyrolusite having magnetic property can be removed from the non magnetic siliceous impurities.

The crushed ore is poured on to an electromagnetic separator consisting of a belt moving over two rollers of which one is magnetic.

The magnetic part of the ore is attracted towards the magnet and falls as a heap close to the magnetic region while the nonmagnetic part falls away from it as shown in the figure



Extraction of crude metal

- The extraction of crude metals from the concentrated ores is carried out in two steps namely,
 - (i) Conversion of the ore into oxides of the metal of interest
 - (ii) Reduction of the metal oxides to elemental metals.

Conversion of ores into oxides

Roasting:

- Roasting is the method, usually applied for the **conversion of sulphide ores into their oxides.**
- In this method, **the concentrated ore is oxidised by heating it with excess of oxygen in a suitable furnace below the melting point of the metal.**

Roasting Example



Roasting also removes impurities such as arsenic, sulphur, phosphorous by converting them into their volatile oxides.



Calcination

Calcination is the process in which the concentrated **ore is strongly heated in the absence of air.**

- During this process, the water of present in the hydrated oxide escapes as moisture.
- Any organic matter (if present) also gets expelled leaving behind a porous ore. This method can also be carried out with a limited supply of air.

During calcination of carbonate ore, carbon dioxide is expelled



During calcination of hydrated ore, the water of hydration is expelled as vapour



Reduction of metal oxides

- Metal oxide can be reduced to crude metal by using a suitable reducing agent like carbon, carbon monoxide, hydrogen, aluminium and other reactive metals such as sodium etc...
- The choice of reducing agent depends on the nature of the metal.
- For example, carbon cannot be used as a reducing agent for the reactive metals such as sodium, potassium, aluminium etc... Similarly CO cannot be used to reduce oxides such as ZnO , Al_2O_3 . Later in this, we study selection of suitable reducing agents by applying Ellingham diagram.

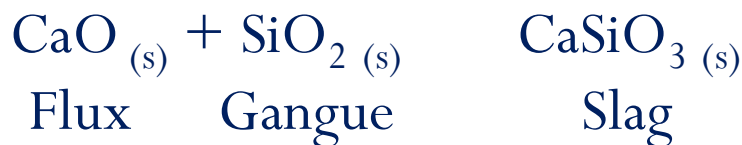
Smelting

In this method, a flux (a chemical substance that forms an easily fusible slag with gangue) and a reducing agent such as carbon, carbon monoxide (or) aluminium is added to the concentrated ore and the mixture is melted by heating at an elevated temperature (above the melting point of the metal) in a smelting furnace.

For example the oxide of iron can be reduced by carbon monoxide as follows.



In this extraction, a basic flux, limestone (CaO) is used. Since the silica gangue present in the ore is acidic in nature, the limestone combines with it to form calcium silicate (slag).



Reduction by carbon:

In this method the oxide ore of the metal is mixed with coal (coke) and heated strongly in a furnace (usually in a blast furnace).

This process can be applied to the metals which do not form carbides with carbon at the reduction temperature.

Examples:



Reduction by hydrogen:

This method can be applied to the oxides of the metals (Fe, Pb, Cu) having less electro-positive character than hydrogen.



Nickel oxide can be reduced to nickel by using a mixture of hydrogen and carbon monoxide (water gas)



Reduction by metal:

Metallic oxides such as Cr_2O_3 can be reduced by an aluminothermite process.

In this process, the metal oxide is mixed with aluminium powder and placed in a fire clay crucible.

To initiate the reduction process, an ignition mixture (usually magnesium and barium peroxide) is used.



During the above reaction a large amount of heat is evolved (temperature up to 2400°C , is generated and the reaction enthalpy is : 852 kJ mol^{-1}) which facilitates the reduction of Cr_2O_3 by aluminium powder.



Active metals such as sodium, potassium and calcium can also be used to reduce the metal oxide



Auto-reduction:

Simple roasting of some of the ores give the crude metal.

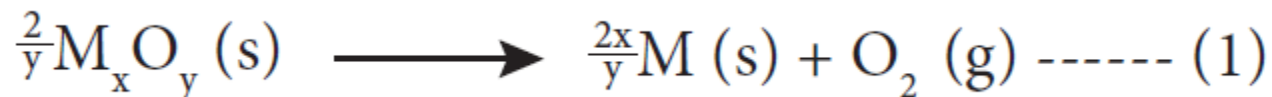
In such cases, the use of reducing agents is not necessary.

For example, mercury is obtained by roasting of its ore cinnabar (HgS)



THERMODYNAMIC PRINCIPLES OF METALLURGY

As we discussed, the extraction of metals from their oxides can be carried out by using different reducing agents. For example, consider the reduction of a metal oxide M_xO_y .



The above reduction may be carried out with carbon. In this case, the reducing agent carbon may be oxidised to either CO or CO_2 .



If carbon monoxide is used as a reducing agent, it is **oxidised** to CO_2 as follows,



The selection of reducing agent depends on the thermodynamic factor

- *A suitable reducing agent is selected based on the thermodynamics considerations.
- *For a spontaneous reaction the change in free energy should be negative.
- *Therefore thermodynamically the reaction of metal oxide with a given reducing agent can occur if the free energy change for the coupled reaction is negative.
- *Hence reducing agent is selected in such a way that it provides a large negative ΔG value for the coupled reaction.

The change in Gibbs free energy (ΔG) for a reaction is given by the expression.

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

where, ΔH - enthalpy change ,

T - temperature in kelvin

ΔS - entropy change.

For an equilibrium process, ΔG^0 can be calculated using the equilibrium constant by the following expression

$$\Delta G^0 = -RT \ln K_p$$

Harold Ellingham used the above relationship to calculate the ΔG^0 values at various temperatures for the reduction of metal oxides by treating the reduction as an equilibrium process.

Ellingham diagram

He has drawn a plot by considering the temperature (T) in the x-axis the standard free energy change (ΔG^0) for the formation of metal oxide in y-axis.

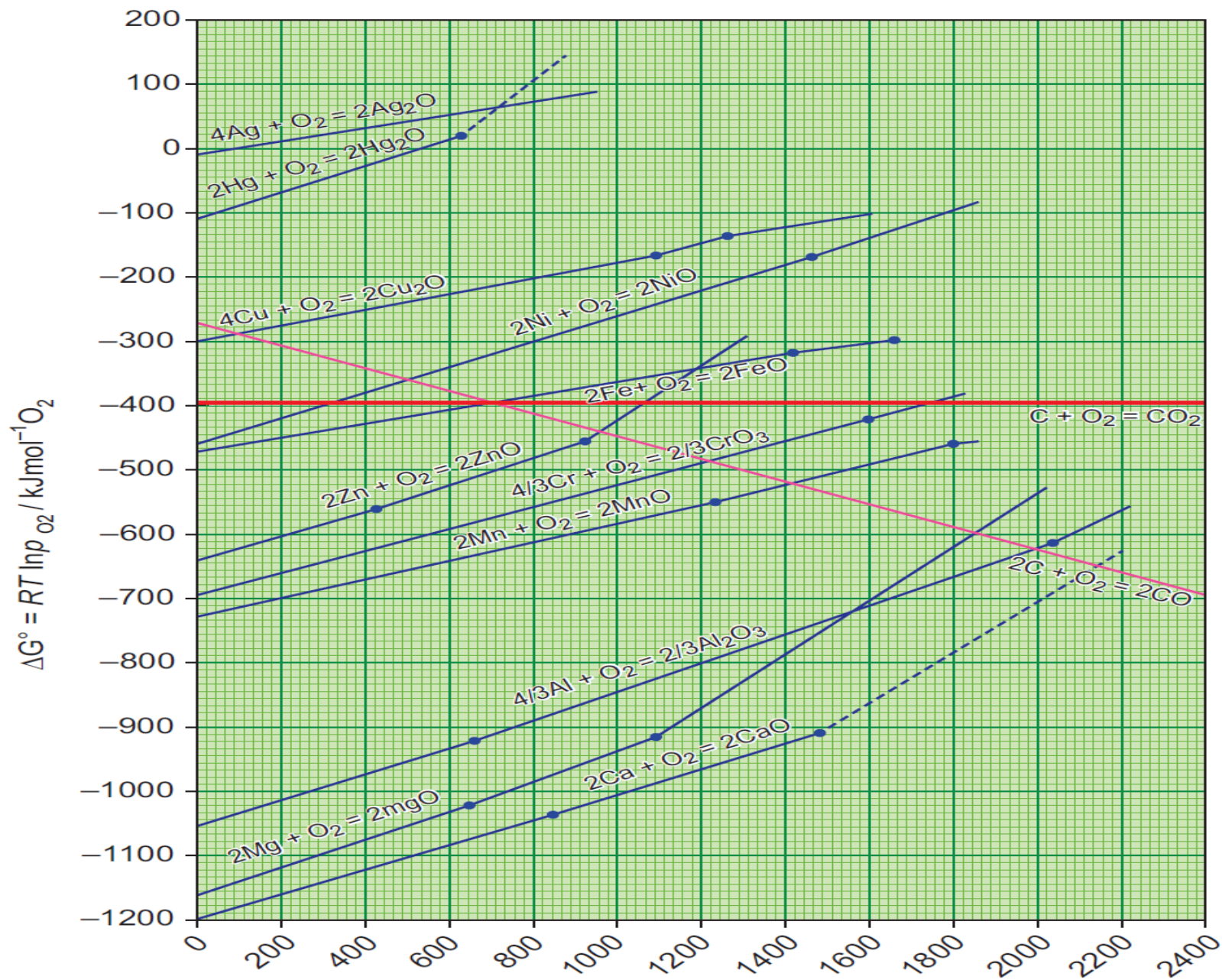
The resultant plot is a straight line with

ΔS as slope and ΔH as y-intercept.

DEFINITION :

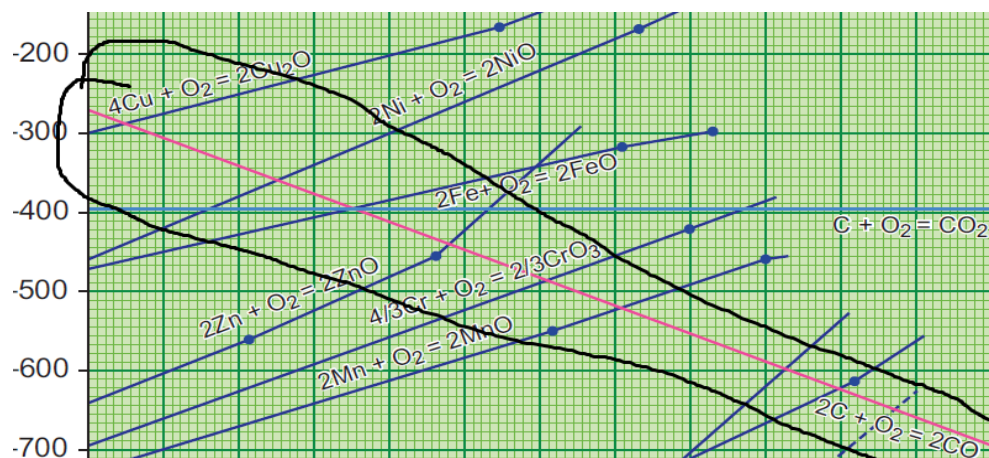
The graphical representation of variation of the standard Gibbs free energy of reaction for the formation of various metal oxides with temperature is called Ellingham diagram

1.4.1 Ellingham diagram



Observations of Ellingham diagram

1. For most of the metal oxide formation, the slope is positive. It can be explained as follows. Oxygen gas is consumed during the formation of metal oxides which results in the decrease in randomness. Hence, ΔS becomes negative and it makes the term, $T\Delta S$ positive in the straight line equation.
2. The graph for the formation of carbon monoxide is a straight line with negative slope. In this case ΔS is positive as 2 moles of CO gas is formed by the consumption of one mole of oxygen gas. It indicates that CO is more stable at higher temperature.

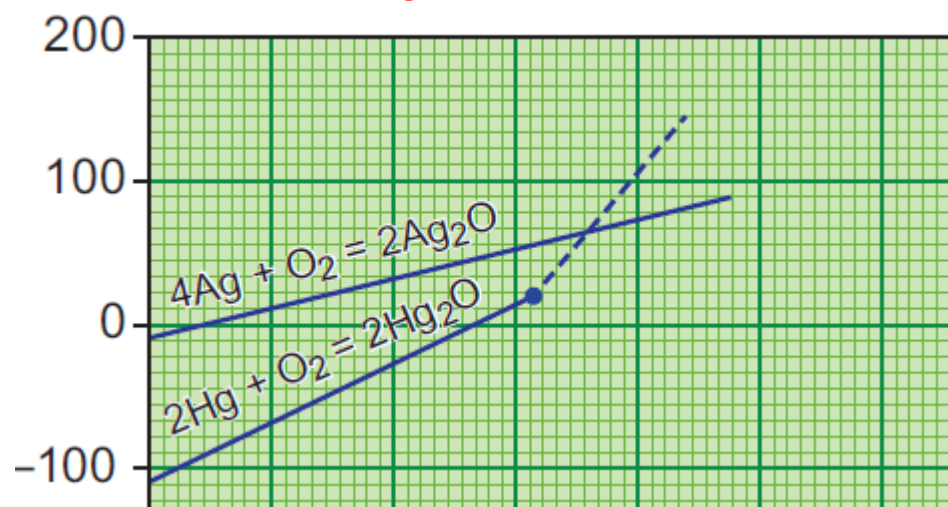


3. As the temperature increases, generally ΔG value for the formation of the metal oxide become less negative and becomes zero at a particular temperature. Below this temperature, ΔG is negative and the oxide is stable and above this temperature ΔG is positive.

This general trend suggests that metal oxides become less stable at higher temperature and their decomposition becomes easier.

4. There is a sudden change in the slope at a particular temperature for some metal oxides like MgO, HgO.

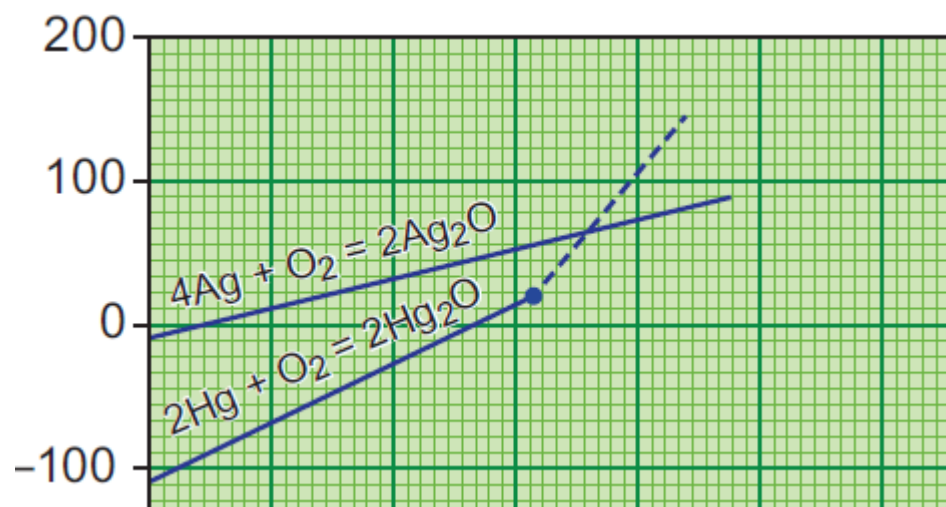
This is due to the phase transition (melting or evaporation).



Applications of Ellingham diagram

Ellingham diagram helps us to select a suitable reducing agent and appropriate temperature range for reduction.

1. Ellingham diagram for the formation of Ag_2O and HgO is at upper part of the diagram and their decomposition temperatures are 600 and 700 K respectively. It indicates that these oxides are unstable at moderate temperatures and will decompose on heating even in the absence of a reducing agent.



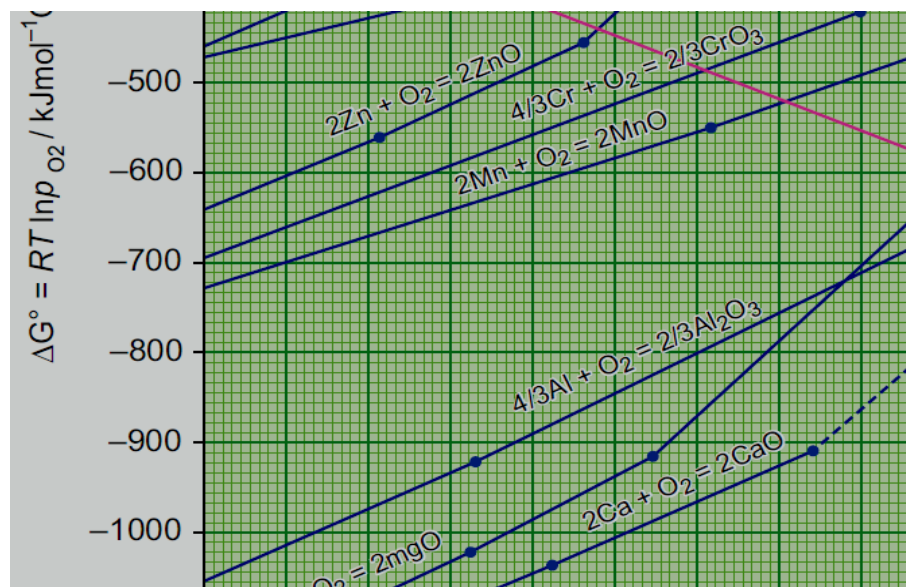
2. Ellingham diagram is used to predict thermodynamic feasibility of reduction of oxides of one metal by another metal. Any metal can reduce the oxides of other metals that are located above it in the diagram.

FOR EXAMPLE,

In the Ellingham diagram, for the formation of chromium oxide lies above that of the aluminium, meaning that Al_2O_3 is more stable than Cr_2O_3 .

Hence aluminium can be used as a reducing agent for the reduction of chromic oxide.

However, it cannot be used to reduce the oxides of magnesium and calcium which occupy lower position than aluminium oxide.

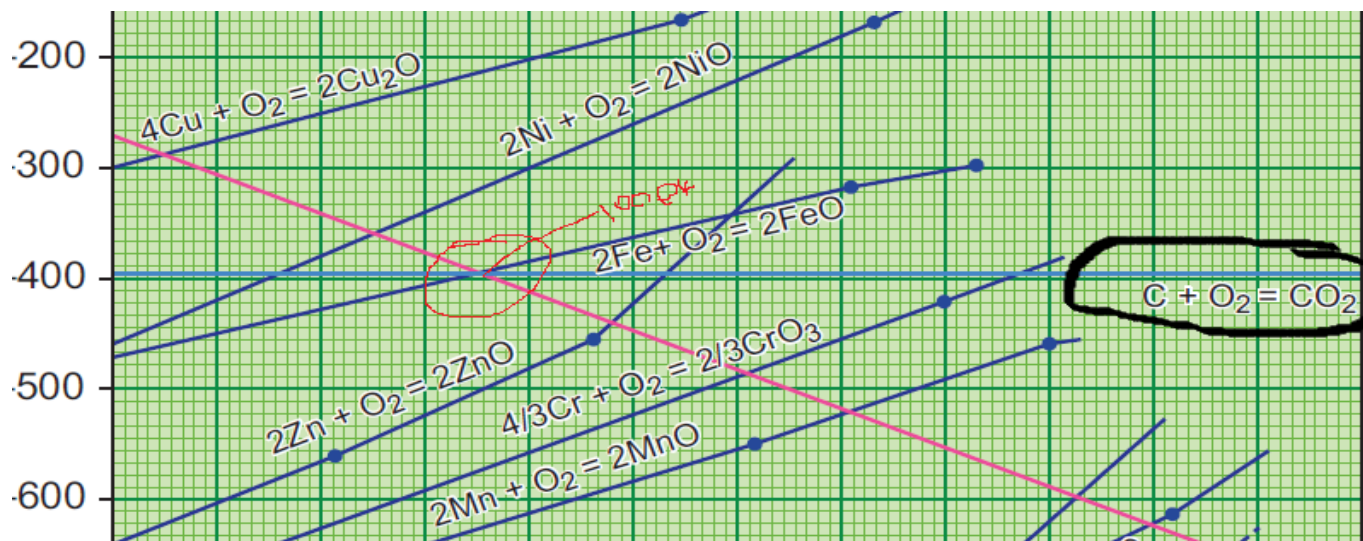


3. The carbon line cuts across the lines of many metal oxides and hence it can reduce all those metal oxides at sufficiently high temperature.

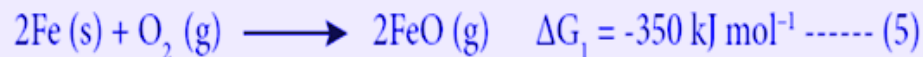
Let us analyse the thermodynamically favourable conditions for the reduction of iron oxide by carbon.

Ellingham diagram for the formation of FeO and CO intersects around 1000 K. Below this temperature the carbon lies above the iron line which indicates that FeO is more stable than CO and hence at this temperature range, the reduction is not thermodynamically feasible.

However, above 1000 K carbon line lies below the iron line and hence, we can use coke as reducing agent above this temperature. The following free energy calculation also confirm that the reduction is thermodynamically favoured.



From the Ellingham Diagram at 1500 K,



Reverse the reaction (1)



Now couple the reactions (2) and (3)



The standard free energy change for the reduction of one mole of FeO is, $\Delta G_3/2 = -65 \text{ kJ mol}^{-1}$

The limitations of Ellingham diagram.

- *It does not tell anything about the rate of the reaction.
- *It does not tell the possibility of other reactions that might be takes place.
- *The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the products which is not always true.

Electrochemical principles of metallurgy.

*Electrochemical principles also find applications in metallurgical process.

The reduction of active metals such as Na, K by carbon is thermodynamically not possible. Such metals are extracted from their ores by using electrochemical methods.

*In this method the metal salts are taken in a fused form or in solution form. The metals ion present can be reduced by treating it with some suitable reducing agent or by electrolysis.

*Gibb's free energy changes for the electrolysis process is given by $\Delta G^0 = -nFE^0$ Where n is number of electrons involved in the process,

F - is faraday and E^0 - is the standard emf of the redox reaction.

*If E^0 is positive then ΔG^0 is negative and the reduction is spontaneous and hence a redox reaction is planned in such a way that the emf of the net redox reaction is positive.

*When a more reactive metal is added to the solution containing less reactive metal ions the more reactive metal will go in to the solution.

*Ex. $\text{Cu} + 2\text{Ag}^+ \text{-----} > \text{Cu}^{2+} + 2\text{Ag}$

Hall Herold process. (purification of Al)

Anode: carbon blocks

Cathode: Iron tank lined with carbon

Electrolyte: 20% Alumina + cryolyte + 10%CaCl₂

Temperature: 1270k

Cryolite lowers the melting point and increases the conductivity of the solution.

Ionisation of alumina $\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{3+} + 3\text{O}^{2-}$

Cathode $2\text{Al}^{3+} + 6\text{e}^- \rightarrow 2\text{Al}$

Anode $6\text{O}^{2-} \rightarrow 3\text{O}_2 + 12\text{e}^-$

$\text{C} + \text{O}^{2-} \rightarrow \text{CO} + 2\text{e}^-;$

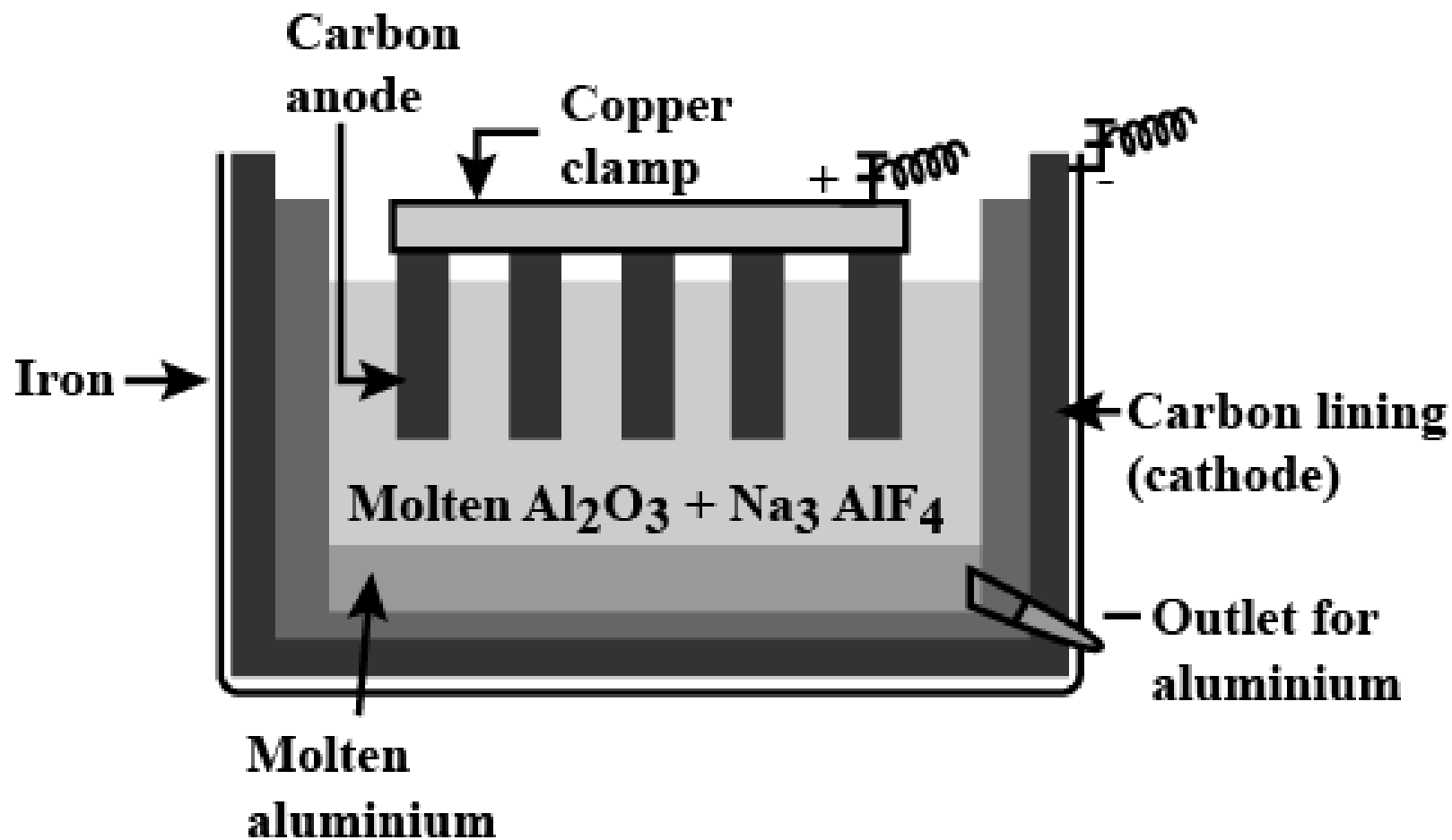
$\text{C} + 2\text{O}^{2-} \rightarrow \text{CO}_2 + 4\text{e}^-;$

Due to the above two reactions anodes are slowly consumed during the electrolysis.

Overall electrolysis reaction is



HALL HEROLT PROCESS



ZONE REFINING PROCESS

Zone refining is based on the principles of fractional crystallization. When an impure metal is melted and allowed to solidify, the impurities will prefer to be in the molten zone.

In this process the impure metal is taken in the form of rod. One end of the rod is heated using a mobile induction heater which results in melting of the metal on that portion.

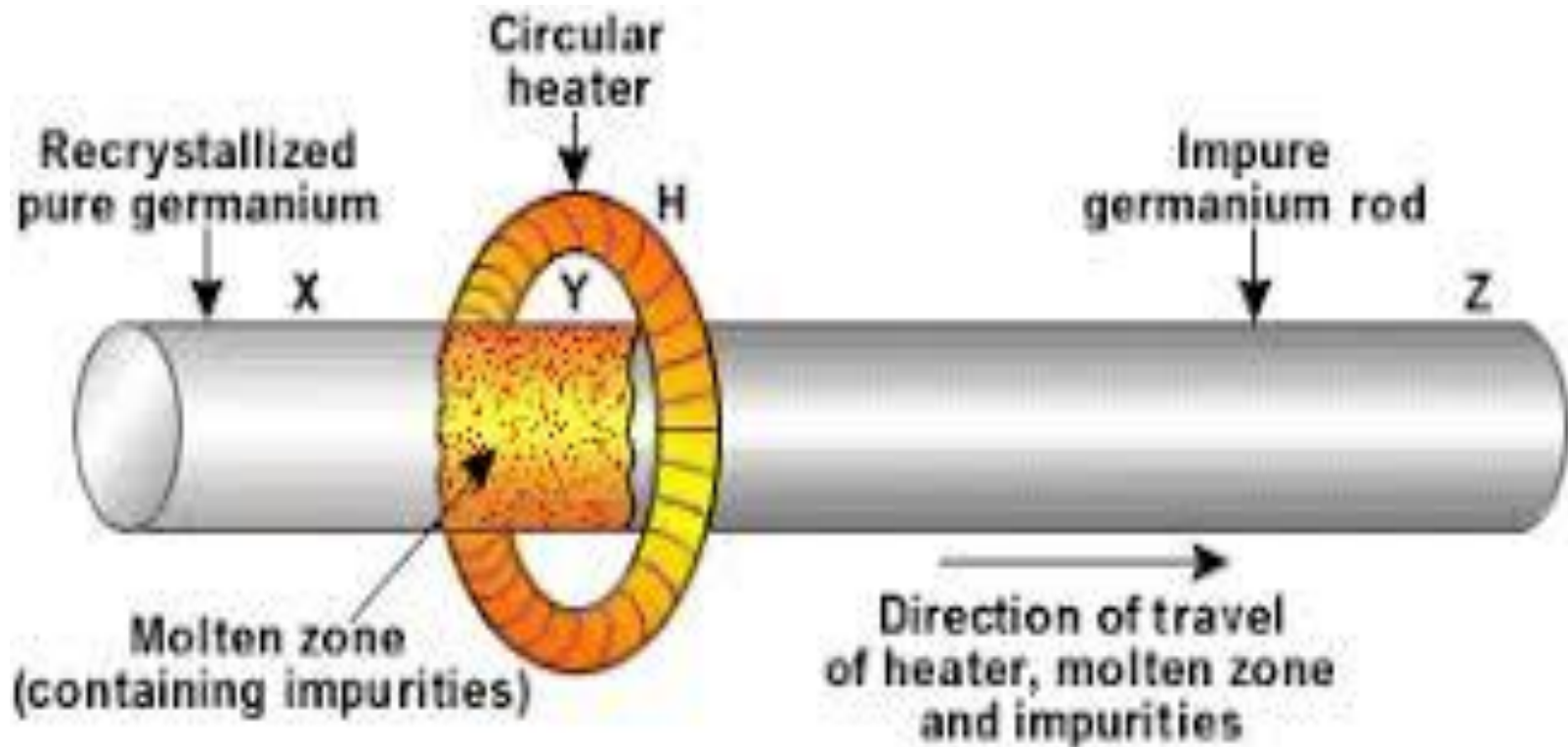
When the heater is slowly moved to the other end the pure metal crystallizes while the impurities will move on to the adjacent zone formed due to the movement of the heater.

As the heater moves further away the molten zone containing impurities also moves along with it. The process is repeated several times to get desired purity.

This process is carried out in an inert atmosphere to prevent oxidation of metals.

Ex. **germanium, silicon, and gallium** are refined by this process.

ZONE REFINING PROCESS



Zone refining of germanium metal.

Electrolytic refining.

The crude metal is purified by electrolytic refining.

Anode - Impure metal;

Cathode - Pure metal;

Electrolyte metal salt solution;

On passing current pure metal deposited on cathode and impurities settled down as anode mud.

Ex. Electrolytic refining of Ag:

Anode - Impure silver

Cathode - pure silver

Electrolyte - Acidified solution of silver nitrate (AgNO_3)

Reaction at Anode: $\text{Ag} \rightarrow \text{Ag}^+ + 1\text{e}^-$

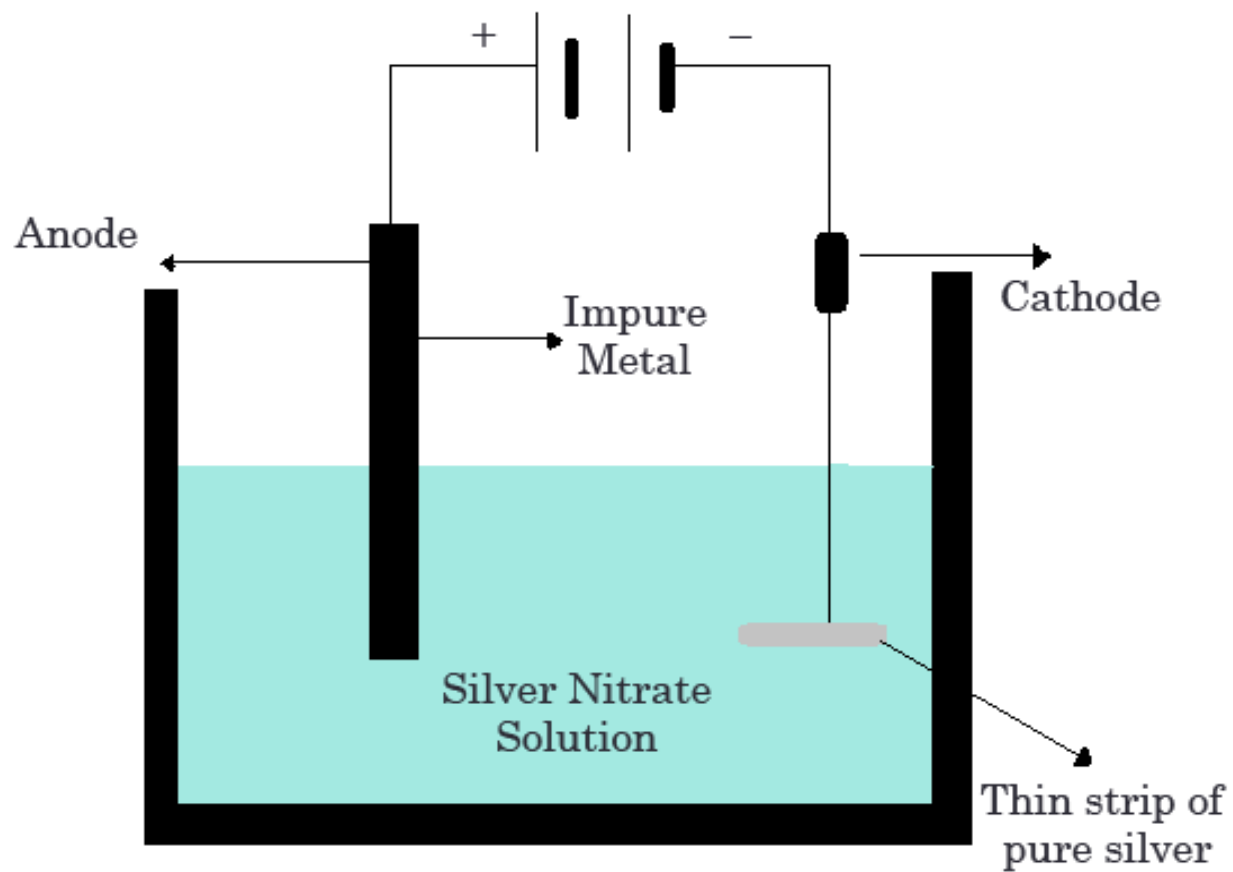
Impure Ag loss 1e^- & goes to the solution.

Cathode: $\text{Ag}^+ + 1\text{e}^- \rightarrow \text{Ag}$

The positively charged Ag^+ gain 1e^- & deposited at cathode.

Cu, Ag, Zn can also refined by this process.

ELECTROLYTIC PROCESS OF SILVER

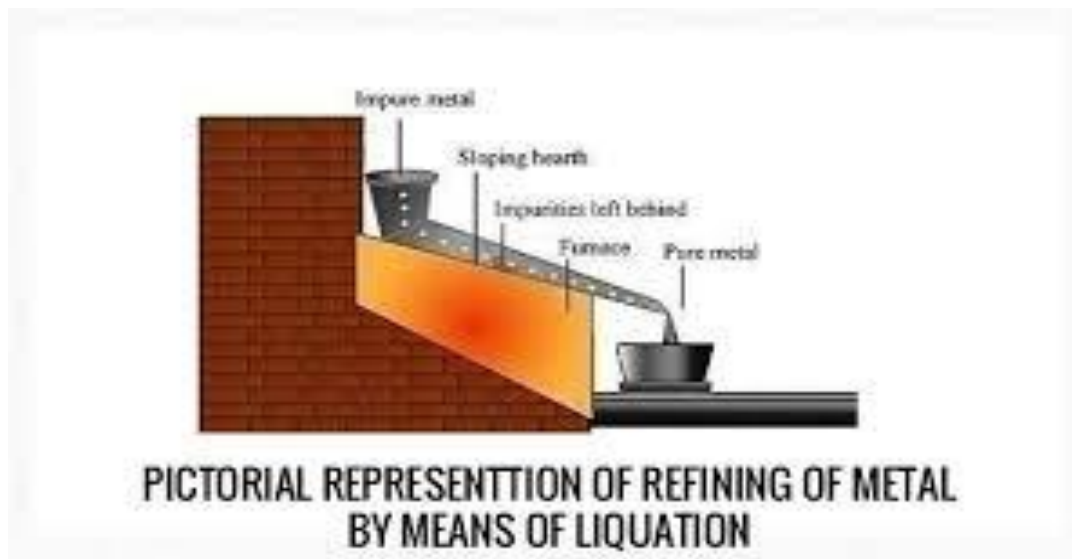


DISTILLATION

This method is employed for low boiling volatile metals like zinc (boiling point 1180 K) and mercury (630 K). In this method, the impure metal is heated to evaporate and the vapours are condensed to get pure metal.

Liquation

- This method is used to remove high melting point impurities from low melting point metals. Ex. Lead
- The impure metal is heated in the absence of air in a sloping furnace.
- Pure metal melts and flows down . And collected separately.
- The impurities remain on the slope.



Vapour phase method

The basic requirement for vapor phase refining.

The metal is treated with a suitable reagent it should form volatile compound with the metal. The volatile compound is easily decomposed to give the pure metal.

Nickel is purified by Mond's process.

The impure nickel is heated in a stream of carbon monoxide at around 350 K. The nickel reacts with the CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind



On heating the nickel tetracarbonyl around 460 K, the complex decomposes to give pure metal.



Titanium is purified by Van Arkel process

This method is based on the thermal decomposition of metal compounds which lead to the formation of pure metals.

Titanium and zirconium can be purified using this method. For example, the impure titanium metal is heated in an evacuated vessel with iodine at a temperature of **550 K** to form the volatile titanium tetra-iodide.(TiI₄). The impurities are left behind, as they do not react with iodine.



The volatile **titanium tetraiodide vapour** is passed over a tungsten filament at a temperature around **1800 K**. The titanium tetraiodide is decomposed and pure titanium is deposited on the filament. The iodine is reused.



uses of Aluminum (Al)

- Aluminum foil is used for packing food items
- Aluminium is used to make cooking vessels, heat exchangers and sinks
- Aluminum alloy is used to make Aero planes as they have light weight and strong
- Aluminium is used to make gas pipes, chemical reactors, medical equipments & refrigeration unit
- Aluminium is used to make electric cables (It is a good electrical conductor and cheap)



List the uses of Iron (Fe)

- *Used to make Bridges, electricity pylons, cutting tools, rifle barrels & cycle chain
- *Used to make pipes pumps stoves & valves
- *The alloys of iron is used to make Magnets
- *Nickel steel is used for making cables, automobiles and aero plane parts
- *Chrome steels are used for manufacture of cutting tools & crushing machines
- *Stainless steel used in architecture, bearings, cutlery, surgical instruments & jewelry

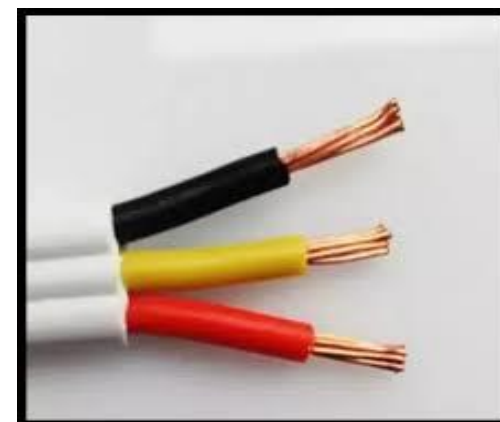


wiseGEEK



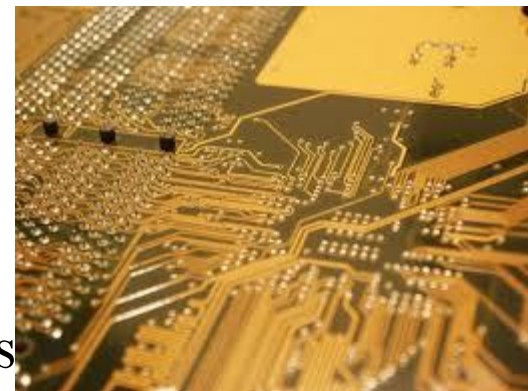
Uses of Copper (Cu)

- It is used to make coins
- It is used to make wires, electrical pipes and water pipes
- Copper and gold are used to make ornaments



Uses of Gold (Au)

- It is used to make coins
- Copper and gold are used to make ornaments
- Gold nano particles are used for increasing the efficiency of solar cells & used as catalyst
- It is used in electro plating of watches, artificial limb joints, dental fillings and electrical connectors.



Uses of zinc.

- *Metallic zinc used in galvanising metals such iron and steel to protect them from rusting and corrosion.
- *It is also used to die casting in the automobile, electrical and hardware industries.
- *Zinc oxide is used in the manufacture of many products such as paints, rubber, cosmetics, pharmaceuticals, plastics inks, batteries, textiles and electrical equipments.
- *Zinc sulphate used in making luminous paints, fluorescent lights and x ray screens.
- * Brass an alloy of zinc is used in water valves and communication equipment as it is highly resistant to corrosion.



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	Quarterly Exam	Half Yearly Exam	Public Exam	NEET		

10th Standard	Syllabus	Books	Study Materials - EM	Study Materials - TM	Practical	Online Test (EM & TM)
	Monthly Q&A	Mid Term Q&A	Revision Q&A	PTA Book Q&A	Centum Questions	Creative Questions
	Quarterly Exam	Half Yearly Exam	Public Exam	NTSE	SLAS	

9th Standard	Syllabus	Books	Study Materials	1st Mid Term	2nd Mid Term	3rd Mid Term
	Quarterly Exam	Half Yearly Exam	Annual Exam	RTE		

8th Standard	Syllabus	Books	Study Materials	1st Mid Term	2nd Mid Term	3rd Mid Term
	Term 1	Term 2	Term 3	Public Model Q&A	NMMS	Periodical Test

7th Standard	Syllabus	Books	Study Materials	1st Mid Term	2nd Mid Term	3rd Mid Term
	Term 1	Term 2	Term 3	Periodical Test	SLAS	

6th Standard	Syllabus	Books	Study Materials	1st Mid Term	2nd Mid Term	3rd Mid Term
	Term 1	Term 2	Term 3	Periodical Test	SLAS	

1st to 5th Standard	Syllabus	Books	Study Materials	Periodical Test	SLAS	
	Term 1	Term 2	Term 3	Public Model Q&A		

Exams	TET	TNPSC	PGTRB	Polytechnic	Police	Computer Instructor
	DEO	BEO	LAB Asst	NMMS	RTE	NTSE

Portal	Matrimony	Mutual Transfer	Job Portal
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Volunteers	Centum Team	Creative Team	Key Answer Team
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