CLASS - XII CHEMISTRY
(General principles and processes of isolation of elements)

Topic :- Occurrence of metals, concentration methods

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

Gangue: The earthly or undesired materials which are contaminated with the ore are called gangue.

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

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

The most abundant metal is Aluminum & second most abundant metal is iron

Give some important ores of Aluminum, Iron, Copper and Zinc

Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where $0 < x < 1$]
	Kaolinite (a form of clay)	$[Al_2(OH)_4 Si_2O_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrites	FeS_2
Copper	Copper pyrites	$CuFeS_2$
	Malachite	$CuCO_3.Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

The extraction and isolation of metals from ores involve the following major steps:
- Concentration of the ore,
- converting ore into oxide
- Reduction
- Refining (Purification of the metal.)

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

Different methods of concentrations: Hydraulic Washing, magnetic separation, leaching, Froth Floatation.

Hydraulic Washing/ 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.

Magnetic separation:
- Principle: This is based on differences in magnetic properties of the ore components (Ore & gangue).
- 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 .the ground ore is carried on a conveyer belt which passes over a magnetic roller. Magnetic particles form a separate heap near the magnetic roller.
- Which of the ores mentioned in Table 6.1 can be concentrated by magnetic separation method?
- Iron ores such as Hematite, Magnetite concentrated by magnetic separation method

Leaching/chemical separation:
Leaching is often used if the ore is soluble in some suitable solvent.
Leaching of alumina from bauxite:
The principal ore of aluminum is bauxite which 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. This way, Al_2O_3 is leached out as sodium aluminate (and SiO_2 too as sodium silicate) leaving the impurities behind:

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$$
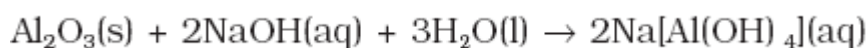
- The aluminate in solution is neutralized by passing CO_2 gas and hydrated Al_2O_3 is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces the precipitation:

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

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

$$Al_2O_3.xH_2O(s) \xrightarrow{1470 K} Al_2O_3(s) + xH_2O(g)$$
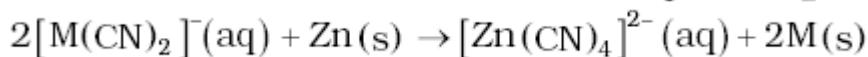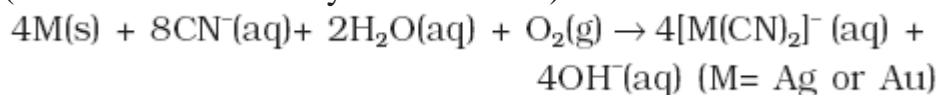
Significance of leaching in the extraction of aluminium

Leaching is significant as it helps in removing the impurities like SiO_2, Fe_2O_3, etc. from the bauxite ore.

Leaching Gold and Silver

- In the metallurgy of silver and that of gold, the respective metal 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 replacement:

  (Mac Arthur Forest Cyanide Process)

  $$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^- (aq) + 4OH^-(aq) \ (M = Ag \ or \ Au)$$

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

The role of NaCN in gold extraction

- In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN

Froth Floatation method:

- 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.

- In this process, a suspension of the powdered ore is made with water. To it collectors and froth stabilizers are added.

- Collectors- pine oil, fatty acids, xanthates, etc.-enhance non-wettability of the mineral particles

- Froth stabilizers – cresols, aniline, etc. - 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

- **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**

Topic:- Extraction of crude metal from concentrated ore

Calcination:

- **Calcinaton is a process of heating the ore strongly either in a limited supply of air or in the absence of air.** During this process the following changes take place:
  The volatile matter is removed.
  Moisture is removed.
 Water from the hydrated oxides is removed.
  The ore becomes porous.
  Carbonates decompose to oxides.

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

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

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

Roasting:

- **Roasting is the process of heating the ore strongly in the presence of excess or regular supply of air in a furnace at a temperature below the melting point of the metal.**
- Sulphide ores roasted

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

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

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
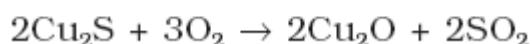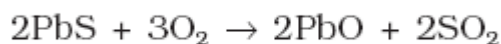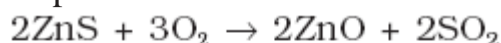
Reduction of oxide to the metal:

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

$$M_xO_y + yC \rightarrow xM + y\ CO$$
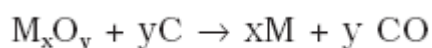
During reduction, the oxide of a metal decomposes:

$$M_xO(s) \rightarrow xM\ (solid\ or\ liq) + \frac{1}{2}O_2\ (g) \qquad\qquad (6.16)$$
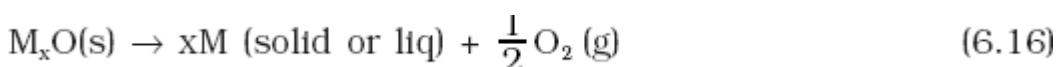
Some metal oxides get reduced easily while others are very difficult to be reduced (reduction means electron gain or electronation). In any case, heating is required. To understand the variation in the temperature requirement for thermal reductions (pyrometallurgy) and to predict which element will suit as the reducing agent for a given metal oxide (M_xO_y), Gibbs energy interpretations are made.

Basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations.

- **ΔG for any process at any specified temperature, is described by the equation:**

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

Where, ΔH is the enthalpy change and ΔS is the entropy change for the process.
- **For any reaction, this change could also be explained through the equation:**

$$\Delta G^{\ominus} = - RTlnK$$

Where, K is the equilibrium constant of the 'reactant – product' system at the temperature, T.
- **A negative ΔG implies a +ve K and this can happen only when reaction proceeds towards products. From these facts we can make the following conclusions:**

1. When the value of ΔG is negative in equation 6.14, only then the reaction will proceed. If ΔS is positive, on increasing the temperature (T), the value of TΔS would increase (ΔH < TΔS) and then ΔG will become –ve.

2. If reactants and products of two reactions are put together in a system and the net ΔG 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 ΔG and looking for its magnitude and *sign*. Such coupling is easily understood through Gibbs energy (ΔG°) vs T plots for formation of the oxides

Ellingham diagrams:

Ellingham diagrams are graphical representation of variation of ΔG vs T for the formation of oxides of elements i.e., for the reaction

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad [\Delta G_{(C, CO)}] \qquad (6.18)$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad [\Delta G_{(CO, CO_2)}] \qquad (6.19)$$

One limitation of Ellingham diagrams.
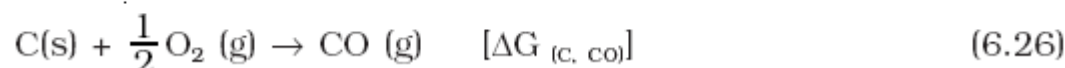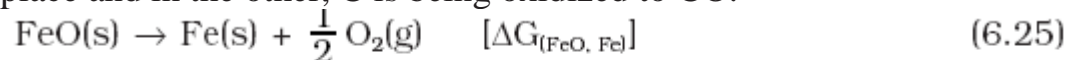
Ellingham diagrams only tell us about the feasibility of a reaction. They do not tell anything about the reaction kinetics.

Below ΔG formation of oxide values are more negative it is better reducing agent at that temperature .

**Thermodynamics helps us to understand how coke reduces the oxide**

$$FeO(s) + C(s) \rightarrow Fe(s/l) + CO (g) \qquad (6.24)$$

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:

$$FeO(s) \rightarrow Fe(s) + \frac{1}{2}O_2(g) \qquad [\Delta G_{(FeO, Fe)}] \qquad (6.25)$$

$$C(s) + \frac{1}{2}O_2 (g) \rightarrow CO (g) \qquad [\Delta G_{(C, CO)}] \qquad (6.26)$$

When both the reactions take place to yield the equation the net Gibbs energy change becomes:
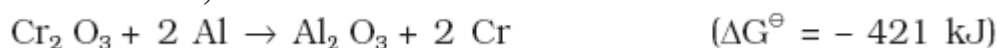
$$\Delta G_{(C, CO)} + \Delta G_{(FeO, Fe)} = \Delta_r G \qquad (6.27)$$

. At temperatures above 1073K (approx.), the C, CO line comes below the Fe,FeO line [ΔG (C, CO) < ΔG(Fe, FeO)]. So in this range, coke will be reducing the FeO and will itself be oxidised to CO.
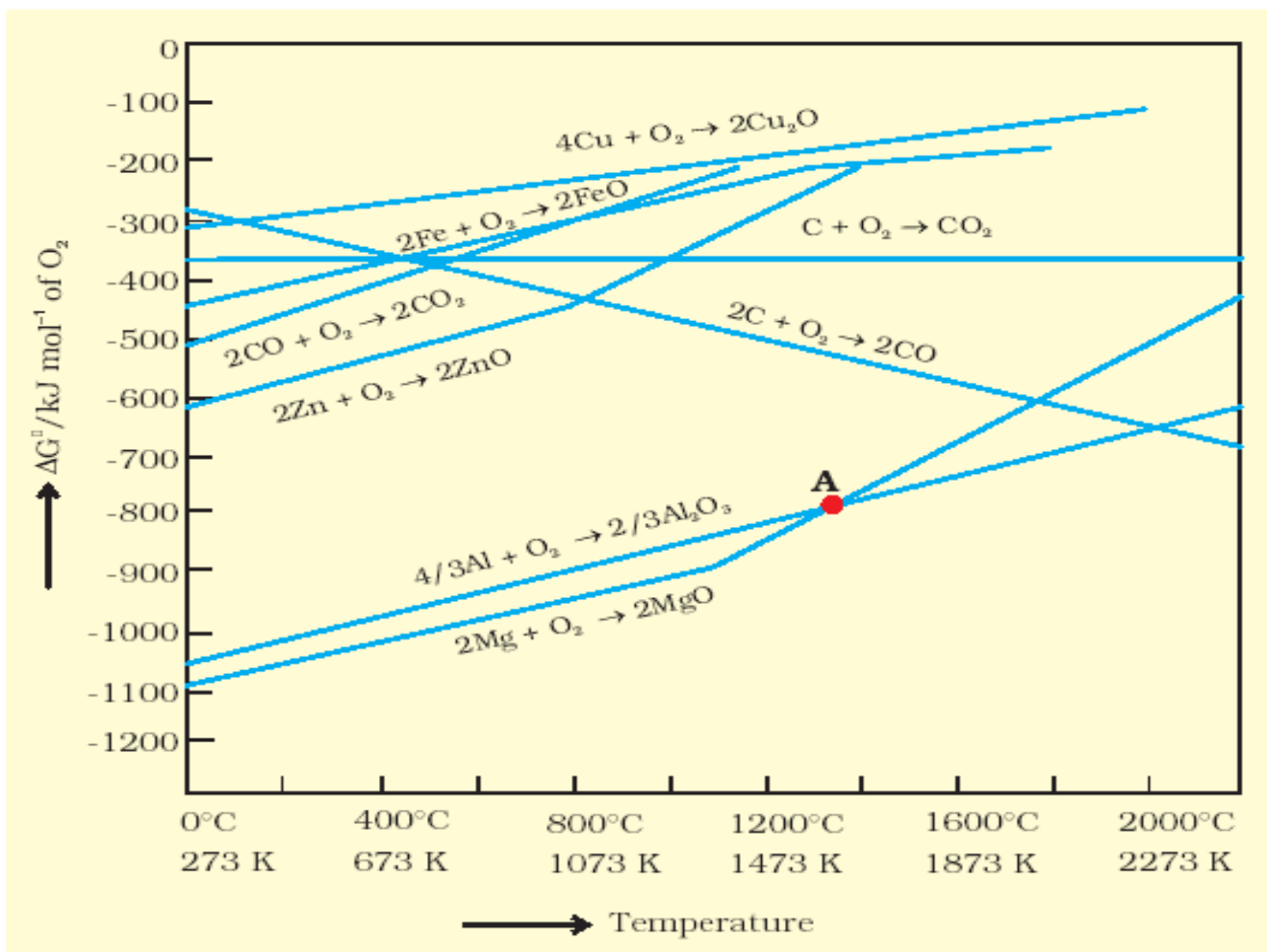
Fig. 6.4: *Gibbs energy (ΔG⊖) vs T plots (schematic) for formation of some oxides (Ellingham diagram)*

The reaction,

$Cr_2O_3 + 2\,Al \rightarrow Al_2O_3 + 2\,Cr$ $\qquad$ $(\Delta G^\ominus = -421\ kJ)$

is thermodynamically feasible as is apparent from the Gibbs energy value. Why does it not take place at room temperature?
Certain amount of activation energy is essential even for such reactions which are thermodynamically feasible, therefore heating is required.

Is it true that under certain conditions, Mg can reduce Al_2O_3 and Al can reduce MgO? What are those conditions?
Yes, below 1350°C Mg can reduce $Al_2O_3$and above 1350°C, Al can reduce MgO.

Out of C and CO, which is a better reducing agent at 673 K?
At 673 K, the value of ΔG_f (CO,CO_2)is less than that of ΔG_f (C,CO). Therefore,CO is a better reducing agent than C
Why is zinc not extracted from zinc oxide through reduction using CO?

ΔG_f (Zn,Zno) value more negative (lower) than ΔG_f (CO,CO_2)   Therefore, CO cannot reduce ZnO to Zn. Hence, Zn is not extracted from ZnO through reduction using CO

Out of C and CO, which is a better reducing agent for ZnO ?

C is a better reducing agent for ZnO because at higher temperature (above 1073k) ΔG_f (C,CO) is more negative than ΔG_f (Zn,Zno)

On the other hand, ΔG_f (CO,CO$_2$) is always higher than ΔG_f (Zn,Zno) Therefore, CO cannot reduce ZnO. Hence, C is a better reducing agent than CO for reducing ZnO.

Example 6.1 Suggest a condition under which magnesium could reduce alumina.

Solution The two equations are:

(a) $\frac{4}{3}$ Al + O$_2$ → $\frac{2}{3}$ Al$_2$O$_3$ (b) 2Mg + O$_2$ → 2MgO

At the point of intersection of the Al$_2$O$_3$ and MgO curves (marked "A" in diagram 6.4), the $\Delta G^\ominus$ becomes ZERO for the reaction:

$\frac{2}{3}$ Al$_2$ O$_3$ + 2Mg → 2MgO + $\frac{4}{3}$ Al
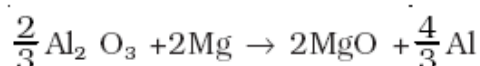
Above that point magnesium can reduce alumina.

Example 6.2 Although thermodynamically feasible, in practice, magnesium metal is not used for the reduction of alumina in the metallurgy of aluminium. Why ?

Solution Temperatures above the point of intersection of Al$_2$O$_3$ and MgO curves, magnesium can reduce alumina. But the temperature required would be so high that the process will be uneconomic and technologically difficult.
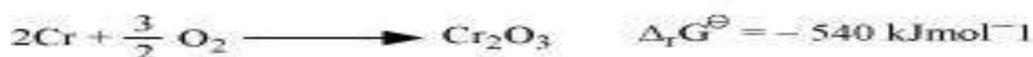
Example 6.3 Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction?

Solution The entropy is higher if the metal is in liquid state than when it is in solid state. The value of entropy change (ΔS) of the reduction process is more on +ve side when the metal formed is in liquid state and the metal oxide being reduced is in solid state. Thus the value of $\Delta G^\ominus$ becomes more on negative side and the reduction becomes easier.
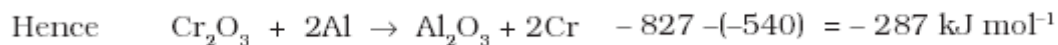
The value of $\Delta_f G^\ominus$ for formation of Cr$_2$O$_3$ is − 540 kJmol^{-1} and that of Al$_2$ O$_3$ is − 827 kJmol^{-1}. Is the reduction of Cr$_2$O$_3$ possible with Al?

The value of $\Delta_f G^\ominus$ for the formation of Cr$_2$O$_3$ from Cr (−540 kJmol^{-1}) is higher than that of Al$_2$O$_3$ from Al (−827 kJmol^{-1}). Therefore, Al can reduce Cr$_2$O$_3$ to Cr. Hence, the reduction of Cr$_2$O$_3$ with Al is possible.

Alternatively,

2Al + $\frac{3}{2}$ O$_2$ ⟶ Al$_2$O$_3$ $\Delta_r G^\ominus$ = − 827 kJmol^{-1}

2Cr + $\frac{3}{2}$ O$_2$ ⟶ Cr$_2$O$_3$ $\Delta_r G^\ominus$ = − 540 kJmol^{-1}

Subtracting equation (ii) from (i), we have

Hence $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$ $-827 - (-540) = -287$ kJ mol^{-1}

As ΔG for the reduction reaction of Cr_2O_3 by Al is negative, this reaction is possible
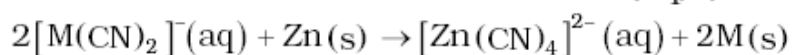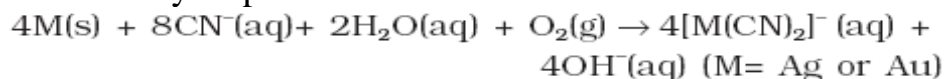
Topic:- Oxidation –Reduction; Refining.
   1. Give an example of extraction based on oxidation reduction.
      An example based on extraction by oxidation is extraction of chlorine from brine.
   2. How are gold and silver extracted?
      Gold and silver are extracted by leaching the metal with NaCN-. The metal is later recovered by displacement method in which zinc acts as reducing agent.

$$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq) \text{ (M= Ag or Au)}$$

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

Refining:
A metal extracted by any method is usually contaminated with some impurity. The process of obtaining high purity metal from impure metal.
Methods of refining :
 (a) Distillation (b) Liquation
(c) Electrolysis (d) Zone refining
(e) Vapour phase refining (f) Chromatographic methods

(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) Liquation:
In this method a low melting metal like tin can be made to flow on a sloping surface (high temperature). In this way it is separated from higher melting impurities.

(c) Electrolytic refining:
The impure metal - anode.
A strip of the same metal in pure form - cathode.
They are put in a suitable electrolytic bath containing soluble salt of the same metal. The more basic metal remains in the solution and the less basic ones go to the anode mud. This process is also explained using the concept of electrode potential, over potential, and Gibbs energy

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

The reactions are: $\text{Cathode:} \quad M^{n+} + ne^- \rightarrow M$
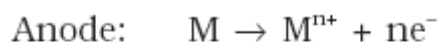
Refining of Copper:
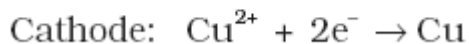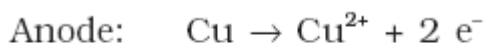Copper is refined using an electrolytic method.
Anodes - impure copper
Cathode -   Pure copper strips
Electrolyte - acidified solution of copper sulphate

The net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:

Anode: $Cu \rightarrow Cu^{2+} + 2\ e^-$
Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

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.

Use:

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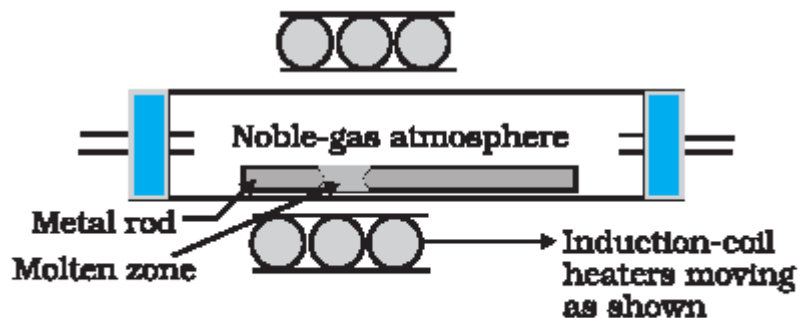

Fig. 6.7: Zone refining process

(e) Vapour phase refining:

1. In this method, the metal is converted into its volatile compound and collected elsewhere.
2. It is then decomposed to give pure metal.

So, the 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.
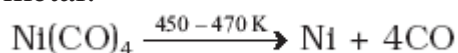Following examples will illustrate this technique.

(A) Mond Process for Refining Nickel:

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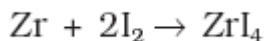tetracarbonyl:

$$Ni + 4CO \xrightarrow{330-350\ K} Ni(CO)_4$$
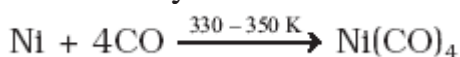
The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal:
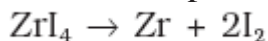
$$Ni(CO)_4 \xrightarrow{450-470\ K} Ni + 4CO$$

(B) van Arkel Method for Refining Zirconium or Titanium:

1. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:

$$Zr + 2I_2 \rightarrow ZrI_4$$

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

$$ZrI_4 \rightarrow Zr + 2I_2$$

Use:

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.

Learn role of CO and Iodine .

(f) Chromatographic methods:

This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent.

1. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent.
2. Different components are adsorbed at different levels on the column.
3. Later the adsorbed components are removed (eluted) by using suitable solvents (eluant).

In one such method the column of Al_2O_3 is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form. This is an example of **column chromatography.**

Use:

1. This is very useful for purification of the elements which are available in minute quantities.
2. The impurities are not very different in chemical properties from the element to be purified.

Types of chromatography:

There are several chromatographic techniques such as paper chromatography, column chromatography,

Gas chromatography,. etc.
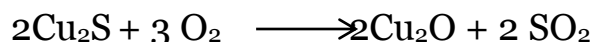

(b)
Laboratory method
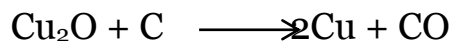
(a)
Industrial method
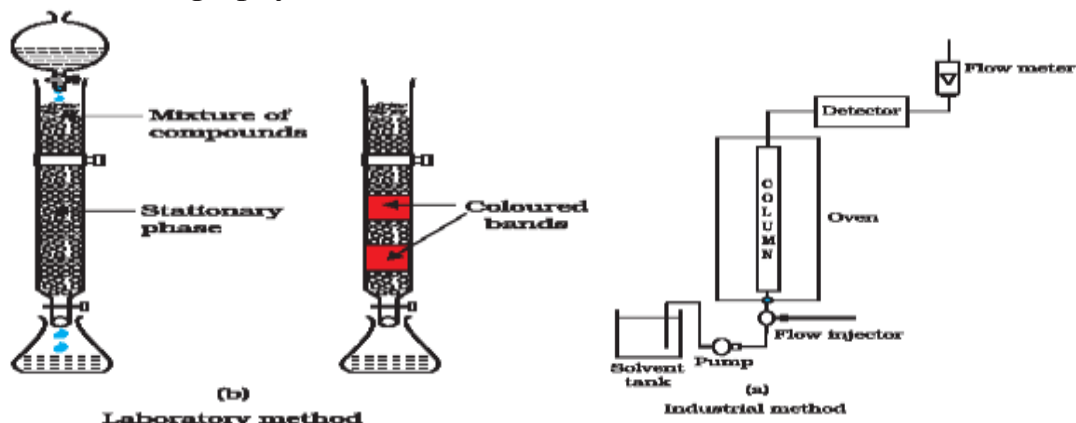
6.8 Uses of Aluminium, Copper, Zinc and Iron:

Topic:- Extraction of copper

Explain the extraction of copper?
- The sulphide ores of copper are roasted to give oxides:

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

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

    $Cu_2O + C \longrightarrow 2Cu + CO$

- The impurities like iron oxide are removed as slag by reacting with SiO2, added as flux. $FeO + SiO_2 \longrightarrow FeSiO_3$

What is Blister copper?

The solidified copper obtained after extraction has blistered appearance due to evolution of SO2 is called blister copper.

## Copper can be extracted by hydrometallurgy but not zinc. Explain.

zinc and iron are more reactive than copper. In hydrometallurgy, zinc and iron can be used to displace copper from their solution.
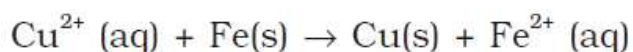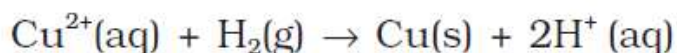
$$Fe_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + Cu_{(s)}$$

 Hence, copper can be extracted by hydrometallurgy but not zinc

How is copper extracted from low grade ores?
Copper is extracted by hydrometallurgy from low grade ores. It is leached out using acid or bacteria.

$$Cu_{(s)} + 2H^+_{(aq)} + \frac{1}{2}O_{2(g)} \longrightarrow Cu^{2+}_{(aq)} + 2H_2O_{(l)}$$
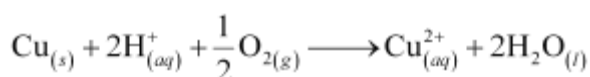
The solution containing Cu2+ is treated with scrap iron or H2

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

## At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why?

Zinc being above iron in the electrochemical series (more reactive metal is zinc), the reduction will be faster in case zinc scraps are used. But zinc is costlier metal than iron so using iron scraps will be advisable and advantageous.

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State the role of silica in the metallurgy of copper.

- During the roasting of pyrite ore, a mixture of FeO and Cu_2O is obtained
- **Silica act as flux which reacts with impurity FeO forms slag** (iron silicate)$FeSiO_3$

$$FeO + SiO_2 \xrightarrow{\Delta} FeSiO_3$$
$$(Slag)$$
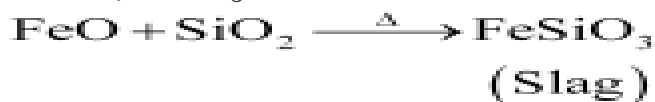
Why copper matte is put in silica lined converter?

Copper *matte* contains Cu_2S and FeS. Copper *matte* is put in a silica-lined converter to remove the remaining FeO and FeS present in the *matte* as slag ($FeSiO_3$). Also, some silica is added to the silica-lined converter. Then, a hot air blast is blown. As a result, the remaining FeS and FeO are converted to iron silicate ($FeSiO_3$) and Cu_2S is converted into metallic copper.

$$2 FeS + 3 O_2 \longrightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \longrightarrow FeSiO_3$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?

- The Gibbs free energy of formation ($\Delta_f G$) of Cu_2S is more negative than that of CS_2 and H_2S Therefore, H_2 and C cannot reduce Cu_2S to Cu.

- On the other hand, the Gibbs free energy of formation of Cu2O is less negative than that of C and CO. Hence, C can reduce Cu_2O to Cu.

$$C_{(s)} + Cu_2O_{(s)} \longrightarrow 2Cu_{(s)} + CO_{(g)}$$

Hence, the extraction of copper from its pyrite ore is difficult than from its oxide ore through reduction

Topic:- Extraction of zinc

Write chemical reactions taking place in the extraction of zinc from zinc blende.

The different steps involved in the extraction of zinc from zinc blende (ZnS) are given below:

(i) Concentration of ore

First, the gangue from zinc blende is removed by the froth floatation method.

(ii) Conversion to oxide (Roasting)

Sulphide ore is converted into oxide by the process of roasting. In this process, ZnS is heated in a regular supply of air in a furnace at a temperature, which is below the melting point of Zn.

(iii) Extraction of zinc from zinc oxide (Reduction)

Zinc is extracted from zinc oxide by the process of reduction. The reduction of zinc oxide is carried out by mixing it with powdered coke and then, heating it at 673 K.

$$ZnO + C \xrightarrow{\text{coke, 673 K}} Zn + CO$$
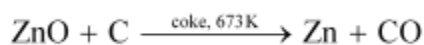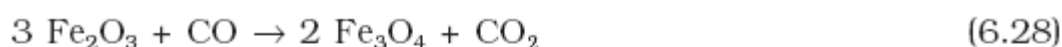
(iv) Electrolytic Refining

Distillation

Topic:- Extraction of iron

Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.

During the extraction of iron, the reduction of iron oxides takes place in the blast furnace. In this process, hot air is blown from the bottom of the furnace and coke is burnt to raise the temperature up to 2200 K in the lower portion itself. The temperature is lower in the upper part. Thus, it is the lower part where the reduction of iron oxides (Fe_2O_3 and Fe_3O_4) takes place.
The reactions taking place in the lower temperature range (500 – 800 K) in the blast furnace are:

$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2 \qquad (6.28)$$
$$Fe_3O_4 + 4\ CO \rightarrow 3Fe + 4\ CO_2 \qquad (6.29)$$
$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \qquad (6.30)$$

The reactions taking place in the higher temperature range (900 – 1500 K) in the blast furnace are:

$$C + CO_2 \rightarrow 2\ CO \qquad (6.31)$$
$$FeO + CO \rightarrow Fe + CO_2 \qquad (6.32)$$

The silicate impurity of the ore is removed as slag by calcium oxide (CaO), which is formed by the decomposition of limestone ($CaCO_3$).

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$CaO + SiO_2 \longrightarrow CaSiO_3$$
$$\text{Calcium silicate}$$
$$\text{(Slag)}$$

- **pig iron:** The iron which is obtained from blast furnace and contains about 4% carbon and many other impurities in smaller amounts like S, P, Si, Mn etc, is called pig iron.
- **Cast iron:** Iron obtained by melting pig iron with scrap iron and coke using hot air blast is cast iron.
- **Wrought iron:** Wrought iron and malleable iron is the purest form of commercial iron which is prepared from cast iron by oxidizing impurities in a reverberalory furnace lined with hematite.

What is added as flux in extraction of iron?
Limestone is used as flux in extraction of iron.

How is 'cast iron' different from 'pig iron"?

The iron obtained from blast furnaces is known as pig iron. It contains around 4% carbon and many impurities such as S, P, Si, Mn in smaller amounts.

Cast iron is obtained by melting pig iron and coke using a hot air blast. It contains a lower amount of carbon (3%) than pig iron. Unlike pig iron, cast iron is extremely hard and brittle

==**Topic:- Electrochemical Principles of Metallurgy**==

What is the basis of reduction of a molten metal salt? Explain
In the reduction of molten metal salt, electrolysis is done which is based on electrochemical principles following equation $\Delta G = -nFE^0$
Here n is the number of electrons and E0 is the electrode potential of redox couple. More reactive metals have large negative values of the electrode potential and are difficult to reduce
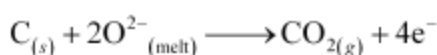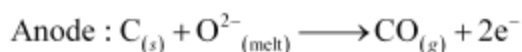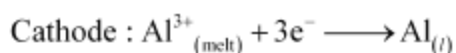
Electrolytic cell for the extraction of aluminium
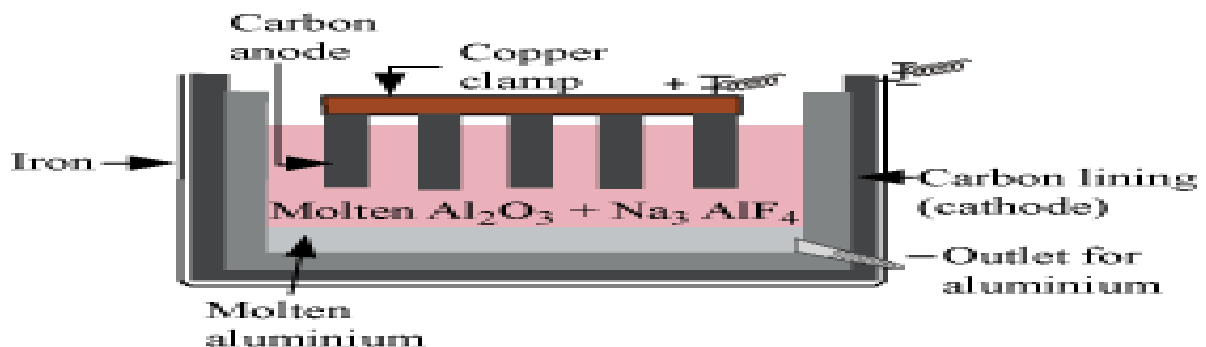
- Na$_3$AlF$_6$ or CaF$_2$ is added to alumina to lower the melting point, and to increase the conductivity of the electrolyte.
- The overall reaction is

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

- This electrolytic process is known as Hall–Heroult process.
- The oxygen liberated at the anode reacts with the carbon of the anode to produce CO and CO$_2$.
- The cell reactions are

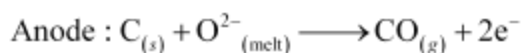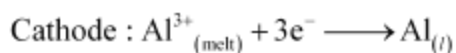Cathode : $Al^{3+}_{(melt)} + 3e^- \longrightarrow Al_{(l)}$

Anode : $C_{(s)} + O^{2-}_{(melt)} \longrightarrow CO_{(g)} + 2e^-$

$C_{(s)} + 2O^{2-}_{(melt)} \longrightarrow CO_{2(g)} + 4e^-$

What is the role of cryolite in the metallurgy of aluminium?

Cryolite (Na_3AlF_6) has two roles in the metallurgy of aluminium:

1. To decrease the melting point of the mixture from 2323 K to 1140 K.

2. To increase the electrical conductivity of Al_2O_3.

What is the role of graphite rod in the electrometallurgy of aluminium?

In the electrometallurgy of aluminium, a fused mixture of purified alumina (Al_2O_3), cryolite (Na_3AlF_6) and fluorspar (CaF_2) is electrolysed. In this electrolysis, graphite is used as the anode and graphite-lined iron is used as the cathode. During the electrolysis, Al is liberated at the cathode, while CO and CO_2 are liberated at the anode, according to the following equation.

$$\text{Cathode}: Al^{3+}_{(melt)} + 3e^- \longrightarrow Al_{(l)}$$
$$\text{Anode}: C_{(s)} + O^{2-}_{(melt)} \longrightarrow CO_{(g)} + 2e^-$$
$$C_{(s)} + 2O^{2-}_{(melt)} \longrightarrow CO_{2(g)} + 4e^-$$

If a metal is used instead of graphite as the anode, then O_2 will be liberated. This will not only oxidise the metal of the electrode, but also convert some of the Al liberated at the cathode back into Al_2O_3. Hence, graphite is used for preventing the formation of O_2 at the anode. Moreover, graphite is cheaper than other metals.

Uses of Aluminium:
1. Aluminium foils are used as wrappers for chocolates.
2. The fine dust of the metal is used in paints and lacquers.
3. Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides.
4. Wires of aluminium are used as electricity conductors.
5. Alloys containing aluminium, being light, are very useful.
Uses of Copper:
1. Copper is used for making wires used in electrical industry and for water and steam pipes.
2. It is also used in several alloys that are rather tougher than the metal itself, e.g., brass (with zinc), bronze (with tin) and coinage alloy (with nickel).

Uses of Zinc:
1. Zinc is used for galvanising iron.
2. It is also used in large quantities in batteries.
3. As a constituent of many alloys, e.g., brass, (Cu 60%, Zn40%) and german silver (Cu 25-30%, Zn 25-30%, Ni 40–50%).
4. Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

Uses of Iron:
i. Cast iron:
1. It is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes, toys, etc.
2. It is used in the manufacture of wrought iron and steel.
ii. Wrought iron:
It is used in making anchors, wires, bolts, chains and agricultural implements.
iii. Steel:
 Alloy steel is obtained when other metals are added to it
 1. Nickel steel is used for making cables, automobiles and aeroplane
parts, pendulum, measuring tapes.
2. Chrome steel for cutting tools and crushing machines.
3. Stainless steel for cycles, automobiles, utensils, pens, etc.

Exercises
6.1 Copper can be extracted by hydrometallurgy but not zinc. Explain.
Ans- Zinc is highly reactive metal; it may not be possible to replace it from a solution of $ZnSO_4$ so easily.

6.2 What is the role of depressant in froth floatation process?
Ans- It prevents one of the components from forming the froth by complexation.

6.3 Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?
Ans- The Gibbs energies of formation of most sulphides are greater than that for CS_2. In fact, CS_2 is an endothermic compound. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.

6.4 Explain: (i) Zone refining (ii) Column chromatography. Ref notes
6.5 Out of C and CO, which is a better reducing agent at 673 K?
CO

6.6 Name the common elements present in the anode mud in electrolytic refining of copper. Why are they so present?
Ans- Selenium, tellurium, silver, gold are the metals present in anode mud. This is because these are less reactive than copper.

6.7 Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.
6.8 Write chemical reactions taking place in the extraction of zinc from zinc blende.
6.9 State the role of silica in the metallurgy of copper.
 Ans- Silica removes iron oxide remaining in the matte by forming silicate, $FeSiO_3$.

6.10 What is meant by the term "chromatography"?
6.11 What criterion is followed for the selection of the stationary phase in chromatography?
6.12 Describe a method for refining nickel.

6.13 How can you separate alumina from silica in a bauxite ore associated with silica? Give equations, if any.

6.14 Giving examples differentiate between 'roasting' and 'calcination'.

6.15 How is 'cast iron' different from 'pig iron"?
Ans- Cast iron is made from pig iron by melting pig iron with scrap iron and coke. It has slightly lower carbon content (» 3%) than pig iron (» 4% C)

6.16 Differentiate between "minerals" and "ores".

6.17 Why copper matte is put in silica lined converter?
Ans- To remove basic impurities like Fe_2O_3

6.18 What is the role of cryolite in the metallurgy of aluminium?
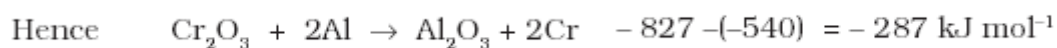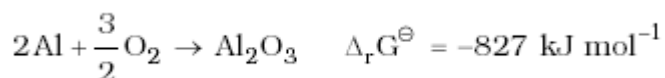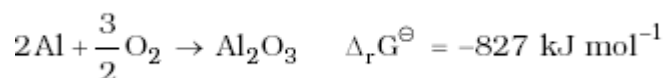**Ans-** To lower the melting point of the mixture.

6.19 How is leaching carried out in case of low grade copper ores?
6.20 Why is zinc not extracted from zinc oxide through reduction using CO?
Ans- The reduction may require very high temperature if CO is used as a reducing agent in this case.

6.21 The value of $\Delta_f G^\ominus$ for formation of Cr_2O_3 is – 540 kJmol^{-1} and that of Al_2O_3 is – 827 kJmol^{-1}. Is the reduction of Cr_2O_3 possible with Al?
Ans- Yes,

$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 \qquad \Delta_r G^\ominus = -827 \text{ kJ mol}^{-1}$$

$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 \qquad \Delta_r G^\ominus = -827 \text{ kJ mol}^{-1}$$

Hence $\qquad Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr \qquad -827 -(-540) = -287 \text{ kJ mol}^{-1}$

6.22 Out of C and CO, which is a better reducing agent for ZnO?

Ans- Carbon is better reducing agent.

6.23 The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with two examples.