

$$K_f = 1.86$$

$$\rho_{H_2O} = 0.997 \text{ g cm}^{-3}$$

$$= 3 \times 10^{-3}$$

Chapter ORES AND METALLURGY

Page No.	
Date	

Terms

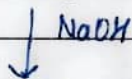
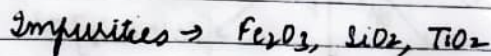
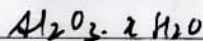
1. Minerals → substance found in earth's crust
 2. Ores → substance from which we can extract metal in a profitable way.
 3. Matrix/Gang → impurities present in ores
 4. Metallurgy → Process of extracting metal from ore in a profitable way.
- Ores of highly reactive metals exist (usually) in oxide form.

Metallurgy

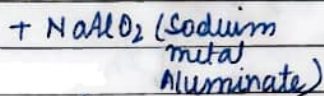
- ① concentration of ores
- ② concentrated ores converted into oxide ores.
- ③ Oxide ores $\xrightarrow{\text{Red}^n}$ Metal $\xrightarrow{\text{Red}^n}$ C, CO, Metal, self
- ④ Metal $\xrightarrow{\text{Refining}}$ Pure metal

① Conc. of ores $\xrightarrow{\text{physical/chemical}}$

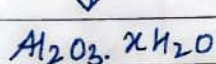
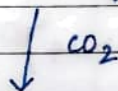
- (i) Hydraulic washing
- (ii) Magnetic separation
- (iii) Froth Floatation
- (iv) Leaching



Sodium Silicate



* Sodium Silicate
don't react with CO_2



$\xrightarrow{\text{Calcination}}$



$\xrightarrow{\text{Red}^n \text{ (electrolytic)}}$

Al

Hall-Heroult

Gravity separation or levigation

This technique utilizes the density difference between the ore and impurity to concentrate the ore. It is mainly applicable to oxide ores. For example, SnO_2 , Fe_2O_3 and FeCr_2O_4 are concentrated by this method from siliceous impurities.

In gravity separation the crushed ore is washed by a current of water on a sloping table fitted with a series of corrugated boards known as Wilfley table (Figure 6.2). The table is continuously vibrating as a result of which the lighter particles move downwards and the heavier particles are left behind the corrugations (as barriers).

A suitable arrangement is made to remove the heavier particles continuously, otherwise the separation process will become ineffective after some time as heavier and lighter particles will start passing the barrier together.

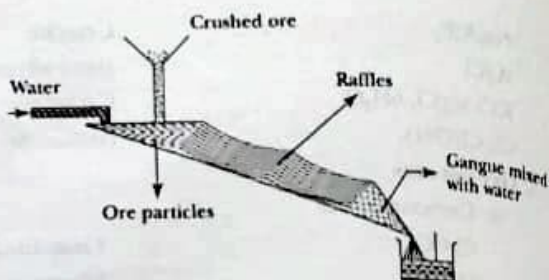


Figure 6.2 Representation of gravity separation using Wilfley table.

Magnetic separation

Generally this method is used to separate the magnetic impurities from the non-magnetic ore. For example, tin stone (SnO_2) is separated from magnetic impurity wolframite ($\text{FeWO}_4 + \text{MnWO}_4$ (minor)) by this method. In magnetic separation powdered ore is allowed to move towards magnetic roller and fall downwards. The magnetic material makes a new heap because it is held to the roller for a longer time (Figure 6.3).

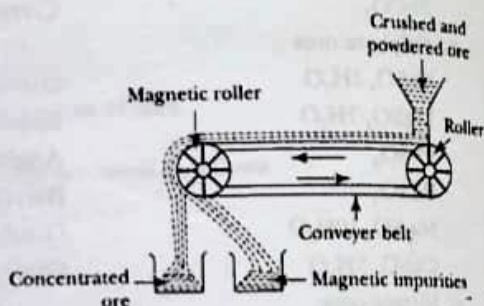


Figure 6.3 Representation of magnetic separator.

Froth floatation or oil floatation

This process is used to separate the sulphide ore from impurity in the ore. It is based upon the differential wetting of the ore by oil and the impurity by water.

In this process, the ore is ground to fine powder and mixed with water to form a slurry. Any one of the oily components such as pine oil, eucalyptus oil, crude coal tar, cresols, etc. is added to it together with sodium ethyl xanthate as collector. Air is bubbled through the mixture which acts as an agitator and creates bubbles. Finally, the ore is floated to the froth and siliceous impurities are settled at the bottom of the tank. Then the froth is collected into a separate container and washed thoroughly and dried.

The oil added acts as frothing agent. It reduces the surface tension of water and helps to produce a stable froth. Reagents such as aniline or cresol are used to stabilize the froth. The formation of bubble involves an increase in air-water surface that means doing work against surface tension. The energy

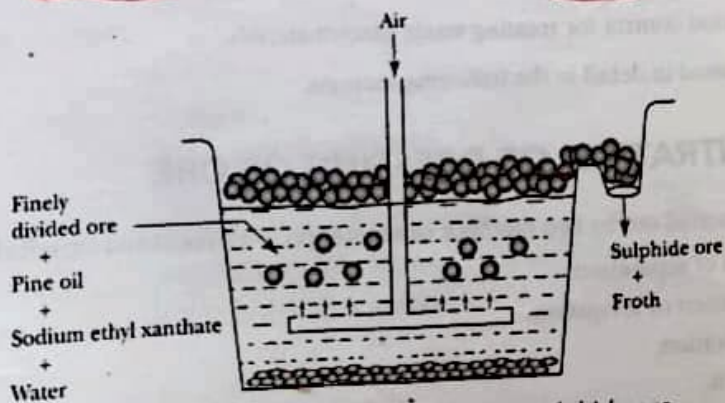
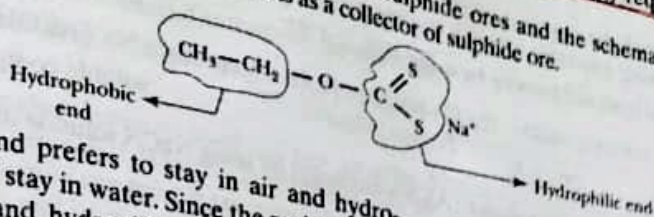


Figure 6.4 Froth floatation process for sulphide ore.

required to create a bubble of radius r is $2 \times 4\pi r^2 \times E$, where E is the energy required to create unit surface area and, is directly proportional to surface tension.

The froth floatation process is usually applied for sulphide ores and the schematic representation is shown in Figure 6.4. Sodium ethyl xanthate acts as a collector of sulphide ore.



The hydrophobic end prefers to stay in air and hydrophilic end prefers to stay in water. Since the molecule has both hydrophobic and hydrophilic part, the best place for it to stay is the air-water interface and hence it shows floating characteristics. The hydrophilic end attracts the sulphide particles and forms surface coated particles as shown in Figure 6.5.

Finally, the collected sulphide particles are floated to the froth and transferred to a separate container, washed with huge amounts of water, dried and sent for next step of extraction.

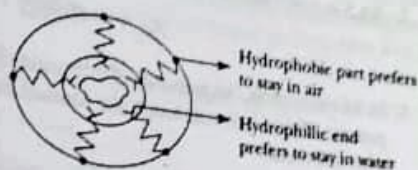


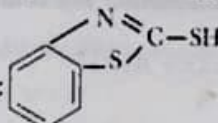
Figure 6.5 Sodium ethyl xanthate at the air-water interface.

1. The other alkyl groups in xanthate may be amyl ($C_5H_{11}-$), octyl ($C_8H_{17}-$), etc. instead of the ethyl group.
2. The other collectors that may be used are

a. Sodium lauryl sulphate: $C_{12}H_{25}-O-SO_3^- Na^+$

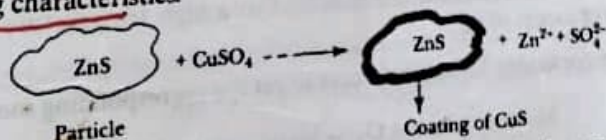
b. Trimethyl cetyl ammonium bromide: $C_{16}H_{33}N^+(Me)_3 Br^-$

c. Dicresyl dithiophosphate: $(CH_3-C_6H_4-O)_2 P(=S)(SH)$
(also called aerofloat)

d. Mercaptobenzthiazole: 
(also called as floatogen)

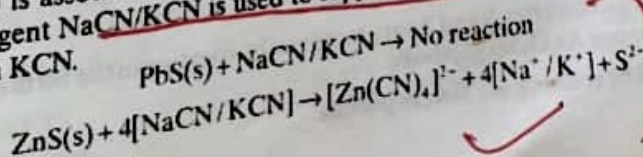
The overall ore collecting process occurs through adsorption and depends upon the unbalanced forces on the solid surface.

Activator is a substance that is added to help the collector stay attached to the particles to be floated and hence improve the floating characteristics of the ore. For example, the floating characteristic of ZnS is poor as compared to that of CuS. Hence $CuSO_4$ is used as activator to form a coating of CuS on the ZnS surface and improve its floating characteristics.

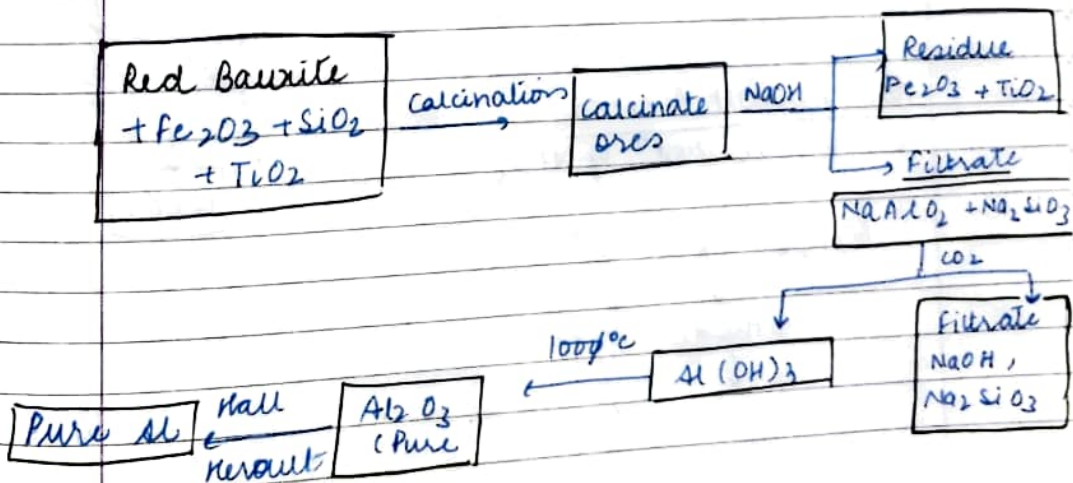
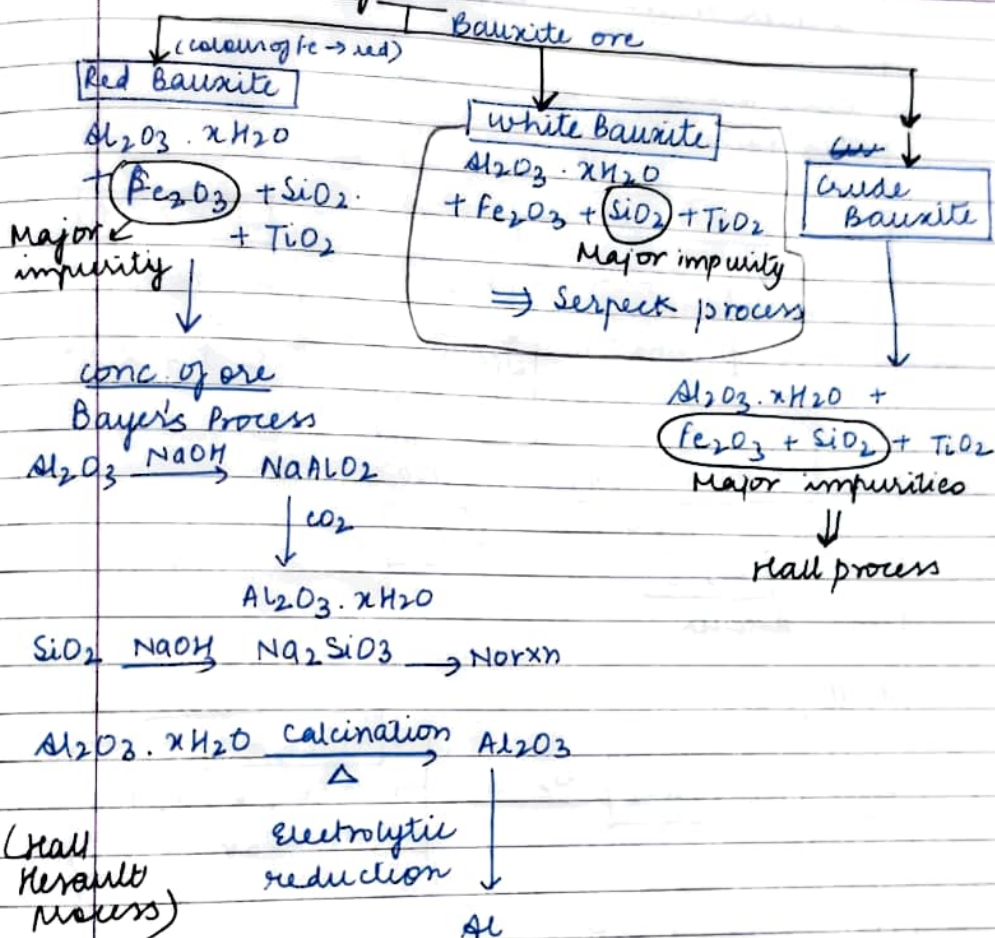


Accordingly using suitable activators, the froth floatation process can also be applied for non-sulphide ore. For example, Na_2S is suitable activator for malachite ($CuCO_3 \cdot Cu(OH)_2$) and anglesite ($PbSO_4$) in which the coatings of CuS and PbS are formed by the activator, respectively.

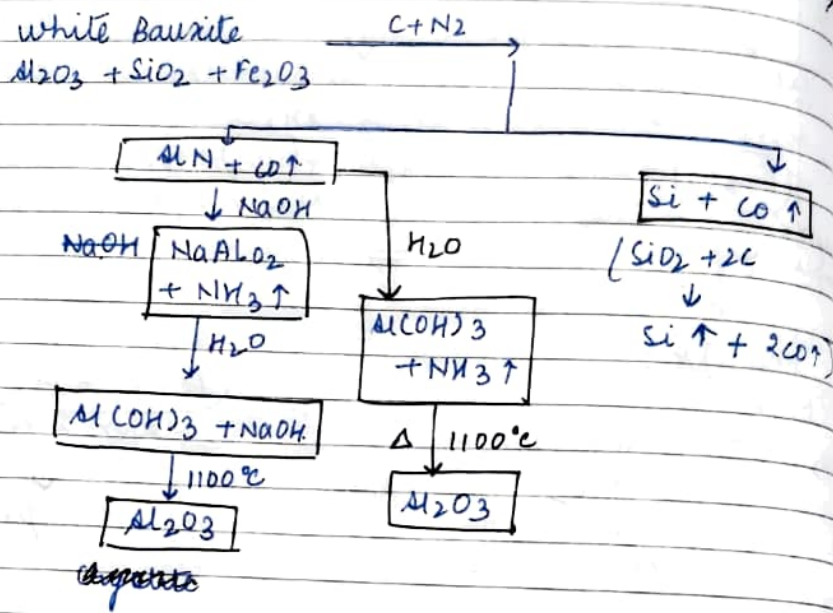
Depressant is a substance that is added to suppress the floating characteristic of the ore particles. For example, galena (PbS) is associated with another sulphide impurity ZnS which also rises to the surface with the froth. The reagent NaCN/KCN is used to suppress the floating characteristics of ZnS by forming a soluble complex with KCN.



Extraction of Al

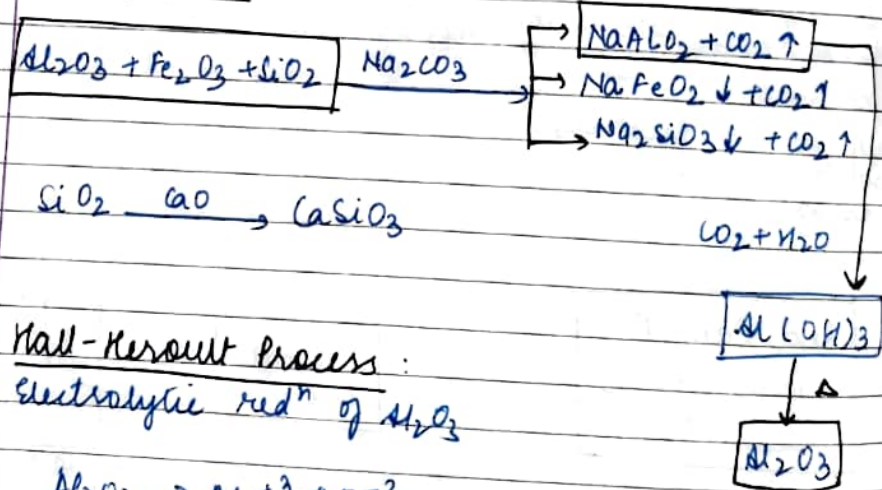


Serpent Process ($Al_2O_3 + 3C + N_2 \rightarrow AlN + CO$)

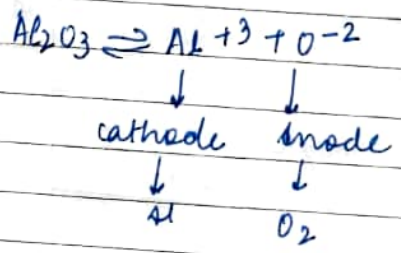


function
Cathode
Anode
 Al_2O_3

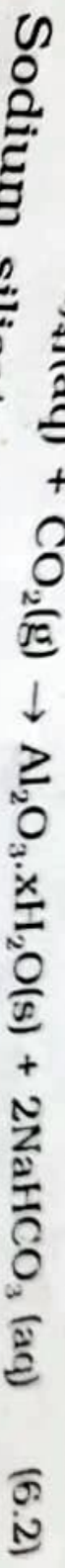
Hall process



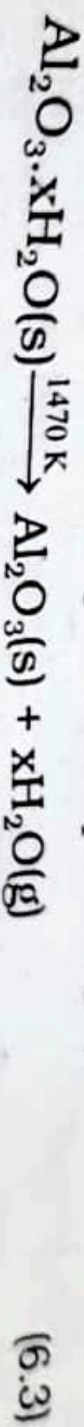
Hall-Heroult Process electrolytic redⁿ of Al_2O_3



... solution. This is called seeding. It induces the precipitation.

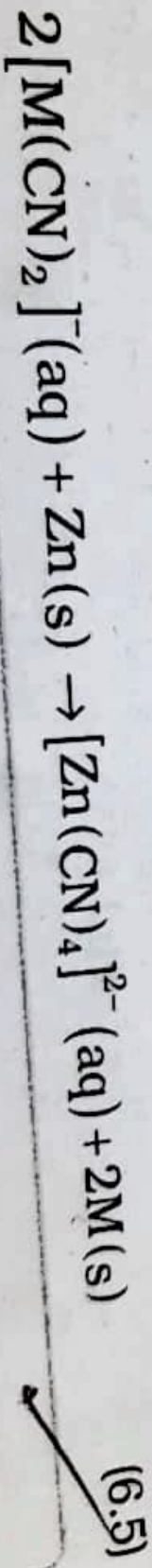
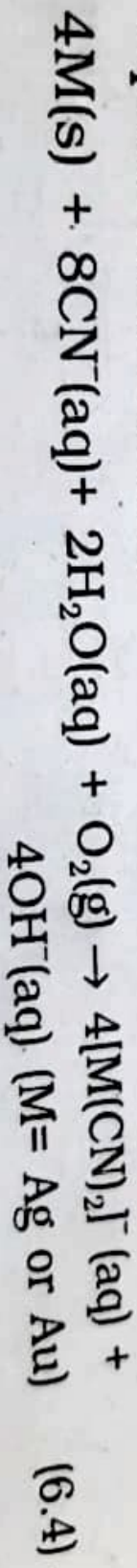


Sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3 .



(b) Other examples

In the metallurgy of silver and gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air, which supplies O_2 . The metal is obtained later by replacement reaction.



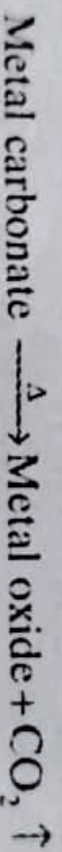
6.4 / CONVERSION OF CONCENTRATED ORE INTO ITS OXIDE

This is generally carried out by two methods — calcination and roasting.

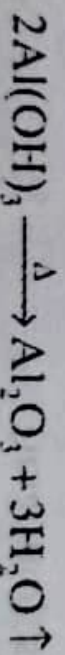
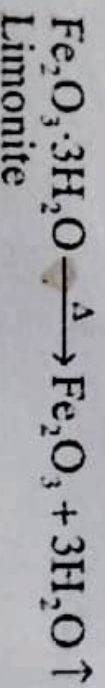
Calcination

It is the process in which the concentrated ore is heated to a high temperature (just below its fusion temperature) in the absence of air (or limited supply of air).

1. This process is mainly used for a carbonate ore to get its oxide



2. Hydrated ores or hydroxides become anhydrous by calcination. For example,

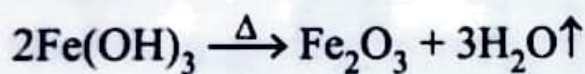


3. Impurities like S, As and Sb are removed in the form of their elemental vapours by calcination.
4. The products formed by calcination are always porous.

Roasting

General Principles and Processes of Isolation of Elements 1.11

1. Volatile impurities such as moisture, CO_2 , SO_2 , organic matter

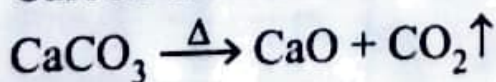


2. Water from hydrated ore

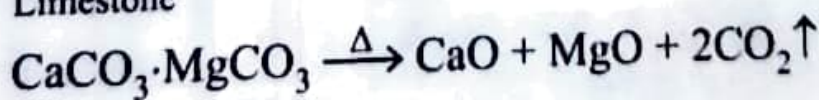


Bauxite

3. Carbon dioxide from carbonate ore



Limestone



Dolomite

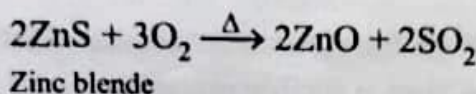
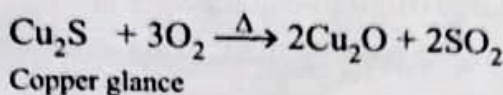
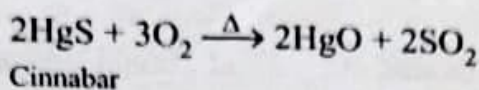
Calcination is usually done in reverberatory furnace. It makes the mass porous so that it can be easily reduced to metallic state in the next step of metallurgy.

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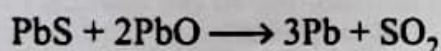
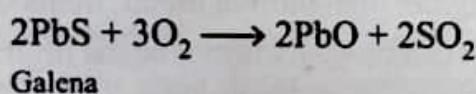
1.4.5.2 Roasting

Roasting is a process in which the ore (usually sulphide) is heated strongly in presence of air, at a temperature below the melting point of the ore. This step ensures:

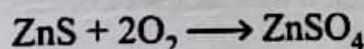
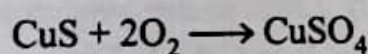
1. Conversion of the ore to the oxide form



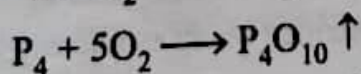
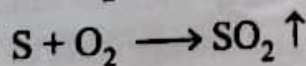
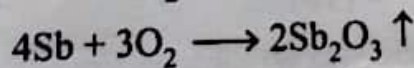
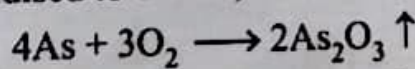
Sometimes, a part of the sulphide may act as reducing agent as in the case of extraction of lead.



Sometimes, insoluble sulphide ores are converted to corresponding sulphate ore, which are water soluble.



2. Removal of non-metallic impurities such as arsenic (As), antimony (Sb), sulphur (S) and phosphorous (P), which are oxidised to oxides, as volatile gases.



3. Removal of water from hydrated ores.

4. Makes the ore porous so that it undergoes easier reduction in the next step of metallurgy.

Roasting is usually done in reverberatory furnace or blast furnace (Figure 1.6).

1.12 Inorganic Chemistry

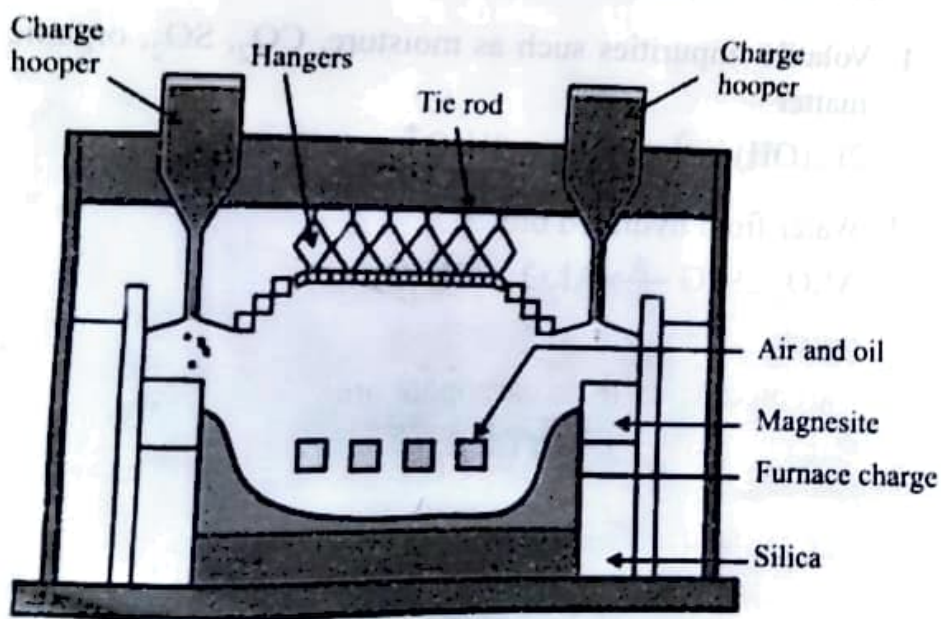


Fig. 1.6 Section of a modern reverberatory furnace

During roasting, air vents are kept open, whereas during calcination, air vents are either completely or partially closed.

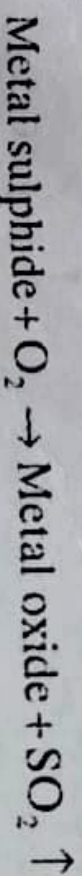
1.4.6 Reduction of Roasted/Calcined Ore to Metal

3. Impurities like S, As and Sb are removed.
4. The products formed by calcination are always porous.

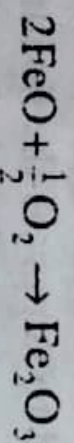
Roasting

It is the process in which the concentrated ore is heated to a high temperature (just below its fusion temperature) in presence of excess of air.

1. This process is mainly applicable for sulphide ores to get the corresponding metal oxides.

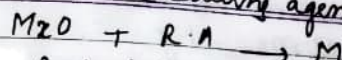


2. Sometimes the lower oxidation state oxide gets converted into higher oxidation state oxide. For example,



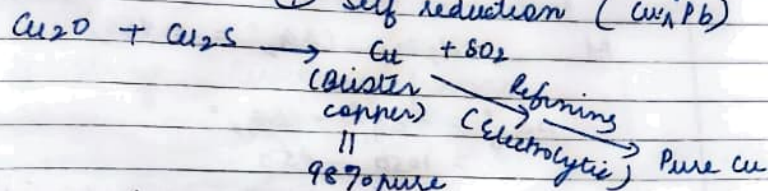
3. Hydrated ores become anhydrous through roasting.
4. The impurities like organic matter, S and As are removed by roasting in the form of their volatile oxides i.e. ($\text{CO}_2 + \text{H}_2\text{O}$), SO_2 and As_2O_3 respectively.
5. The products formed by roasting are always porous.

(Reducing agent)



Reduction :-

- ① Carbon
- ② Carbon monoxide
- ③ Other metal
- ④ Self reduction (Cu, Pb)



$$y = c + mx$$

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

$$\Delta G < 0 \text{ (rxn} \rightarrow \text{feasible)}$$

at equilibrium,

$$\Delta G = 0$$

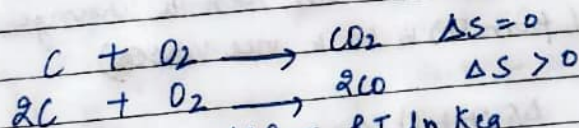
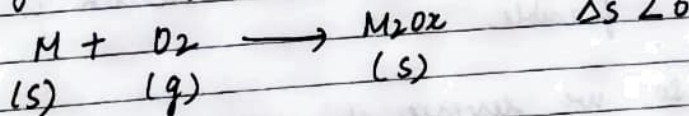
$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\text{at standard, } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

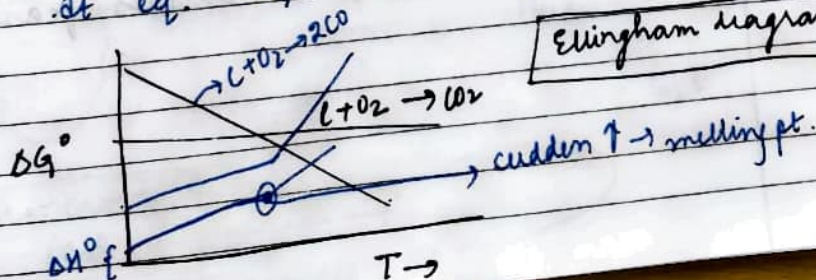
$$Q = K \text{ (at eq)}$$

$$\Delta G^\circ = RT \ln K_{eq}$$

Ellingham diagram decides whether C + oxide forms CO_2 or CO . $\Delta S < 0$



$$\text{At eq. } \Delta G^\circ = RT \ln K_{eq}$$



Ellingham diagram

(pyrometallurgy) and to predict which element will suit as the reducing agent for a given metal oxide (M_2O_x). Gibbs energy interpretations are made.

Some basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations. Gibbs energy is the most significant term here. The change in Gibbs energy, ΔG for any process at any specified temperature, is described by the equation:

$$\Delta G = \Delta H - T\Delta S \quad (6.14)$$

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:

$$\Delta G^\circ = - RT \ln K \quad (6.15)$$

where, K is the equilibrium constant of the 'reactant - product' system at the temperature, T . A negative ΔG implies a +ve K in equation 6.15. And this can happen only when reaction proceeds towards products. From these facts we can make the following conclusions:

flux' is added which combines with 'gangue' to form 'slag'. Slag separates more easily from this way, removal of gangue becomes easier.

... floats on the molten metal, floats on the molten metal, floats on the molten metal. At high temperature it can be easily removed. At high temperature it can be easily removed. At high temperature it can be easily removed.

Types of Fluxes: Fluxes are of two types:

- 1. Acidic Fluxes:** Acidic fluxes such as silica (SiO_2) and PbO , B_2O_3 , V_2O_5 , CO are added to the basic impurities, as metallic oxides (such as CaO , FeO), hence remove them as fusible slag.

$$\text{Acidic flux} + \text{Basic impurity} \longrightarrow \text{Fusible slag}$$

$$\text{SiO}_2 + \text{CaO} \longrightarrow \text{CaSiO}_3$$

$$\text{SiO}_2 + \text{FeO} \longrightarrow \text{FeSiO}_3$$
- 2. Basic Fluxes:** Basic fluxes such as limestone (CaCO_3), magnesite (MgCO_3) and haematite (Fe_2O_3) are added to remove acidic impurities such as silica (SiO_2) as fusible slag.

$$\text{Basic flux} + \text{Acidic impurity} \longrightarrow \text{Fusible slag}$$

$$\text{MgCO}_3 + \text{SiO}_2 \longrightarrow \text{MgSiO}_3 + \text{CO}_2 \uparrow$$

$$\text{CaCO}_3 + \text{SiO}_2 \longrightarrow \text{CaSiO}_3 + \text{CO}_2 \uparrow$$

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 $T\Delta S$ would increase ($\Delta H < T\Delta S$) 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 (Fig. 6.4).

Diagram

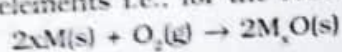
al representation of Gibbs energy was first used by H.J.T. Ellingham. is a sound basis for considering the choice of reducing agent in the oxides. This is known as Ellingham Diagram. Such diagrams help us The feasibility of thermal reduction of an ore. The criterion of feasibility given temperature, Gibbs energy of the reaction must be negative.

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 $T\Delta S$ would increase ($\Delta H < T\Delta S$) and then ΔG will become -ve.
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Ellingham Diagram

The graphical representation of Gibbs energy was first used by H.J.T. Ellingham. This provides a sound basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham Diagram. Such diagrams help us in predicting the feasibility of thermal reduction of an ore. The criterion of feasibility is that at a given temperature, Gibbs energy of the reaction must be negative.

- (a) Ellingham diagram normally consists of plots of $\Delta_f G^\circ$ vs T for formation of oxides of elements i.e., for the reaction,



In this reaction, the gaseous amount (hence molecular randomness) is decreasing from left to right due to the consumption of gases leading to a -ve value of ΔS which changes the sign of the second term in equation (6.14). Subsequently ΔG shifts towards higher side despite rising T (normally, ΔG decreases i.e., goes to lower side with increasing temperature). The result is +ve slope in the curve for most of the reactions shown above for formation of $M_xO(s)$.

- (b) Each plot is a straight line except when some change in phase (s \rightarrow liq or liq \rightarrow g) takes place. The temperature at which such change occurs, is indicated by an increase in the slope on +ve side (e.g., in the Zn, ZnO plot, the melting is indicated by an abrupt change in the curve).
- (c) There is a point in a curve below which ΔG is negative (So M_xO is stable). Above this point, M_xO will decompose on its own.
- (d) In an Ellingham diagram, the plots of ΔG° for oxidation (and therefore reduction of the corresponding species) of common metals and some reducing agents are given. The values of $\Delta_f G^\circ$, etc. (for formation of oxides) at different temperatures are depicted which make the interpretation easy.
- (e) Similar diagrams are also constructed for sulfides and halides and it becomes clear why reductions of M_xS is difficult. There, the $\Delta_f G^\circ$ of M_xS is not compensated.

Limitations of Ellingham Diagram

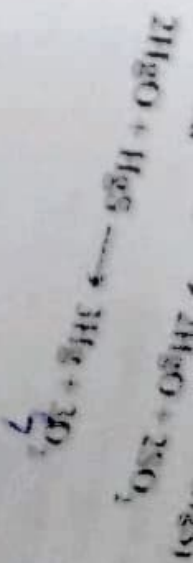
1. The graph simply indicates whether a reaction is possible or not i.e., the tendency of reduction with a reducing agent is indicated. This is so because it is based only on the thermodynamic concepts. It does not say about the kinetics of the reduction process (Cannot answer questions like how fast it could be?).
2. The interpretation of ΔG° is based on K ($\Delta G^\circ = -RT \ln K$). Thus it is presumed that the reactants and products are in equilibrium:



This is not always true because the reactant/product may be solid. [However it explains how the reactions are sluggish when every species is in solid state and smooth when

the ore melts down. It is interesting to note here that ΔH (enthalpy change) and the ΔS (entropy change) values for any chemical reaction remain nearly constant even on varying temperature. So the only dominant variable in equation (6.14) becomes T . However, ΔS depends much on the physical state of the compound. Since entropy depends on disorder or randomness in the system, it will increase if a compound melts ($s \rightarrow l$) or vapourises ($l \rightarrow g$) since molecular randomness increases on changing the phase from solid to liquid or from liquid to gas.

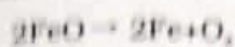
The reducing agent forms its oxide when the metal oxide



ending the
the most
e required
it as the
s energy
a thermal
ge of the
for any

As we know, during reduction, the oxide of a metal decomposes and takes away the oxygen. The role of reducing

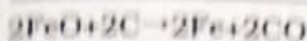
Around 1400 °C



$$\Delta_r G^\circ = +341 \text{ kJ mol}^{-1}$$



$$\Delta_r G^\circ = -447 \text{ kJ mol}^{-1}$$



$$\Delta_r G^\circ = -106 \text{ kJ mol}^{-1}$$



$$\Delta_r G^\circ = -53 \text{ kJ mol}^{-1}$$

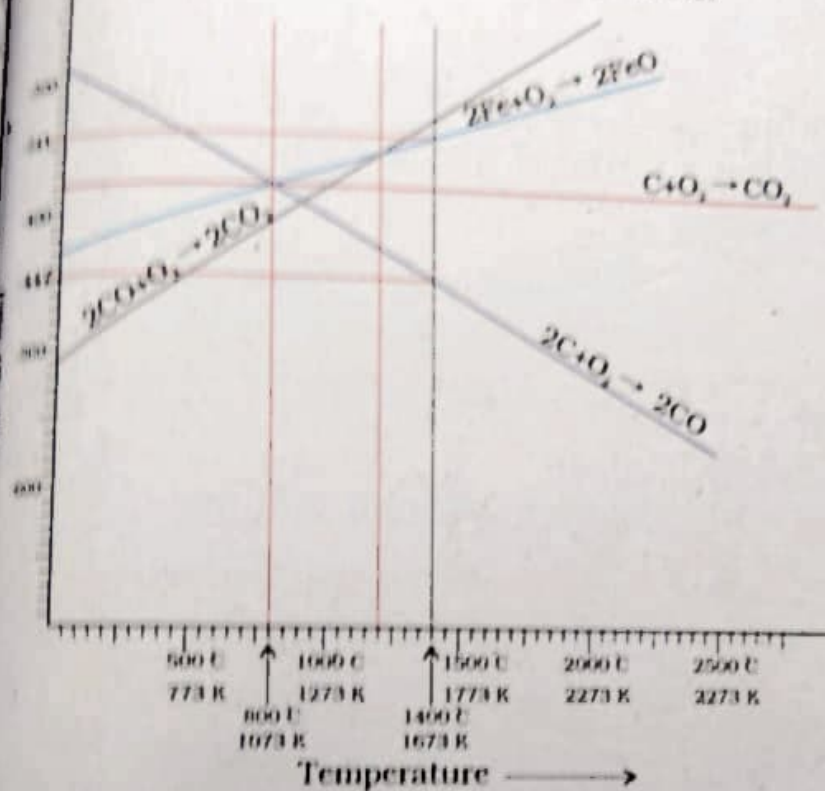
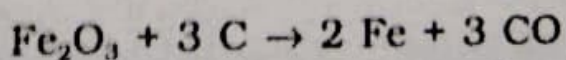


Fig. 6.6: Gibbs energy Vs T plot (schematic) for the formation of oxides of iron and carbon (Ellingham diagram)



Limestone is added as a flux and the impurities are oxidised and passed into the slag from the slag by passing through.

(b) Extraction of copper from copper ores

In the graph of $\Delta_r G^\circ$ vs T for the formation of oxides of iron and carbon, the line for the formation of iron oxide is almost at the top. So it is not feasible to reduce the iron oxide directly to the metal by heating. The oxides of carbon (C, CO₂) are at much lower positions. At 1000 – 1600 K. However, many of the ores contain iron. The sulphide ore

2FeO → 2Fe + O₂
reverse of Fe

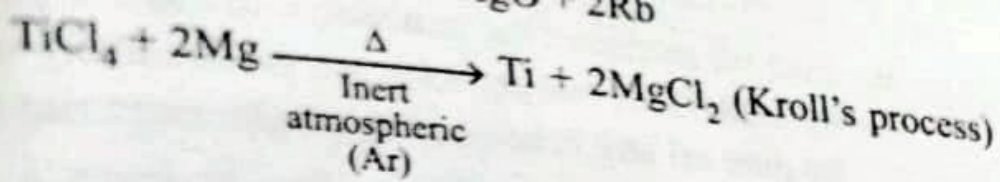
2C + O₂ → 2CO
calculate Δ_rG°
the value will be
6.27 becomes
reduction of
lower temperature
basis of low
curves with

The iron ore
contains a small
in smaller
known as
variety of
iron and is
iron and carbon
lower carbon
extremely

Further Reading

Wrought Iron

of commercial
by oxidising
lined with
to carbon

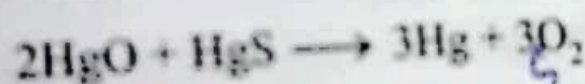
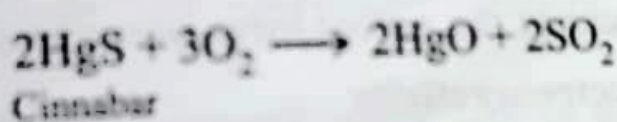


1.4.6.2 Auto-reduction or Self-reduction Process

In certain cases, no reducing agent is required. The sulphides of less electropositive metals such as mercury (Hg), copper (Cu), lead (Pb), tin (Sn) are reduced without the use of any additional reducing agent.

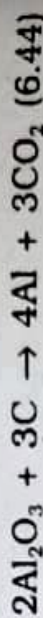
When the ores are heated in air, a part of these ores is changed into the oxide or sulphate, which then reacts with the remaining part of the ore, to give the metal and SO_2 as shown below:

1. Extraction of mercury from cinnabar (HgS)



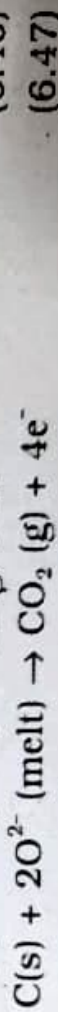
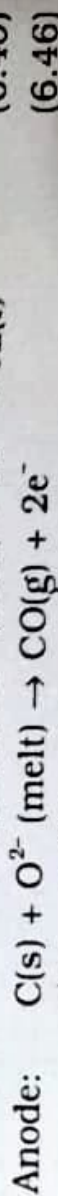
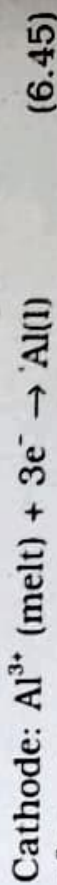
Aluminium

In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mix and brings conductivity. The fused matrix is electrolysed. Steel vessel with lining of carbon acts as cathode and graphite anode is used. The overall reaction may be written as:



This process of electrolysis is widely known as *Hall-Heroult* process.

Thus electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2 . This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are:



Copper from Low Grade Ores and Scraps

Copper is extracted by hydrometallurgy from low grade ores. The ore is leached out using acid or bacteria. The solution is then treated with scrap copper to precipitate copper.

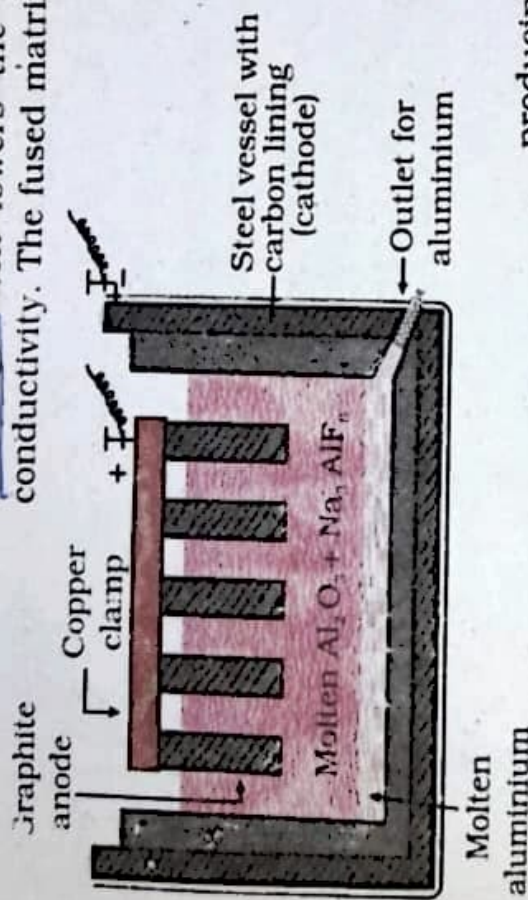
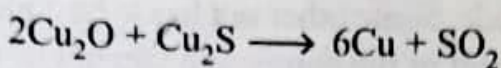
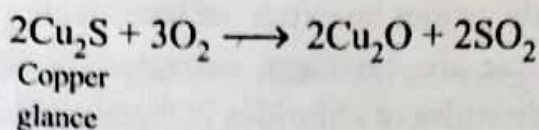
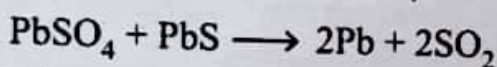
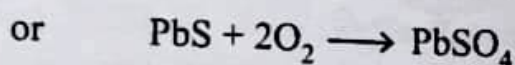
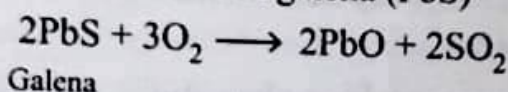


Fig. 6.6: Electrolytic cell for the extraction of aluminium

2. Extraction of copper from copper glance (Cu_2S)

Copper (Cu) so obtained is known as **blister copper** because as it solidifies, SO_2 hidden in it escapes out producing blisters on the surface.

3. Extraction of lead from galena (PbS)

Elevated temperature and the anion/s associated with the metal may bring about this change.

All roasting/smelting processes mentioned above make use of reverberatory furnaces at some stage. The diagram of such a modern furnace is shown in Figure 1.6. Oil burners shoot along intensely hot flame down the furnace and melt the charges. On the walls there are suitable tap holes for crude metals and the slag. Such a furnace may melt upto 106 kg of charge per day. Smelting operations can also be carried out in converters. Air is blown through the molten material, when the impurities are largely removed as volatile oxidation products. Also magnesite linings are used in converters to slag off any metallic impurities. Converters may be of two types:

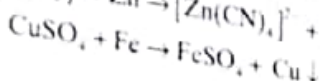
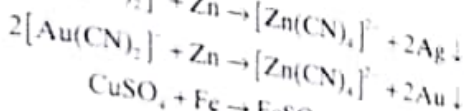
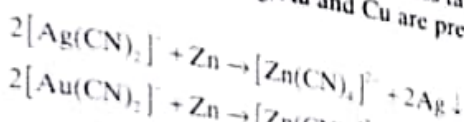
1. **Bessemer converter**, similar to that used in metallurgy of iron.

2. **Peirce-Smith converter**, which consists of a large horizontal steel drum resting upon rollers. Rolls of steel tubes (tuyeres) pass into the converter and are connected to an air duct. Air is forced into the molten bath of crude metal. The process provides its own heat due to the oxidation of impurities and the temperature rises to $\sim 2673 \text{ K}$.

are to burn together.
 $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$
 $2\text{BaO}_2 \rightarrow 2\text{BaO} + \text{O}_2$
 KClO_3 or BaO_2 provides O_2 from each and

Metal replacement method (Hydrometallurgy)

In this process, the desired metal is extracted from its solution by the addition of a more electropositive metal. The fuel cost is nil in this process because the reduction process takes place at room temperature or slightly higher temperature. Using this process, Ag, Au and Cu are precipitated from their respective solutions as follows:



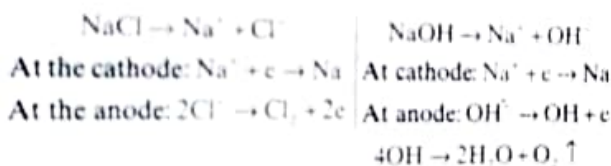
Electrolytic reduction

The oxides of strong electropositive metals such as K, Ca, Na, Al and Mg are very stable. It is difficult to reduce them into metallic state by carbon reduction process because of the following reasons.

1. The temperature requirement is very high so the fuel cost is high.
2. The collection of metals is to be done very carefully under inert environment, otherwise the metals react with air to form their respective oxides again.
3. At high temperatures, the metals being extracted may also form carbides in the presence of excess carbon taken for carbon reduction.

Such metals are extracted by passing electricity through their fused chlorides or oxides or hydroxides. For example,

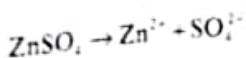
1. Na is extracted from molten NaCl or molten NaOH .



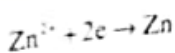
2. Al is extracted from molten Al_2O_3 (details will be discussed in the individual extraction).

Note: Aqueous solution cannot be used as electrolyte here because then these electropositive metals will react again with H_2O to liberate H_2 at the cathode.

3. The metals which come below Al in the electrochemical series can be extracted by the electrolysis of the aqueous solutions of their salts. This process is applicable for Cu, Zn, Sn, Pb, etc. For example, ZnSO_4 solution can be used to get Zn



The electrode used is Zn or Al (as cathode) and the reaction at the cathode is



Similarly, CuSO_4 and SnSO_4 solutions are used to get Cu and Sn respectively.

Electrolytic reduction of Al_2O_3

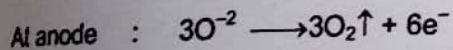
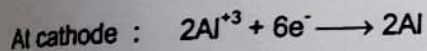
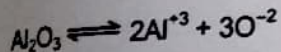
Pure alumina melts at about 2000°C and is a bad conductor of electricity. If fused cryolite and fluorspar is added, the mixture melts at 900°C and Al_2O_3 becomes a good conductor of electricity. Metallic Al is liberated at the cathode

Electrolysis of molten mixture

Cathode	:	Carbon
Anode	:	Graphite rods
Electrolyte	:	60 parts cryolite + 20 parts fluorspar + 20 parts pure Al_2O_3
Temperature	:	900°C

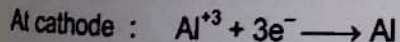
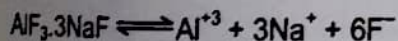
Reactions

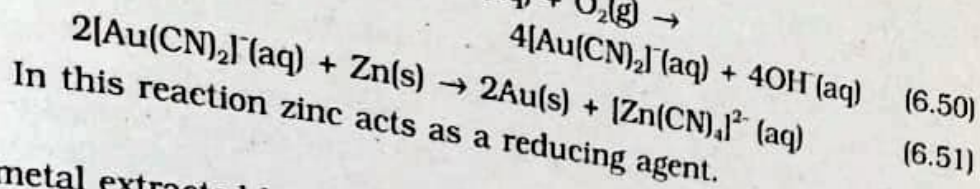
According to the 1st theory the following reaction occurs



As cryolite has greater electrochemical stability it does not dissociate. It only increases the dissociation of Al_2O_3 .

But the second theory states that, cryolite undergoes electrolytic dissociation first then Al^{+3} goes to the cathode, produces F_2 at anode then reacts with Al_2O_3 producing AlF_3 .





In this reaction zinc acts as a reducing agent.

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below.

- | | |
|---------------------------|-----------------------------|
| (a) Distillation | (b) Liquefaction |
| (c) Electrolysis | (d) Zone refining |
| (e) Vapour phase refining | (f) Chromatographic methods |

These are described in detail here.

(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) Liquefaction

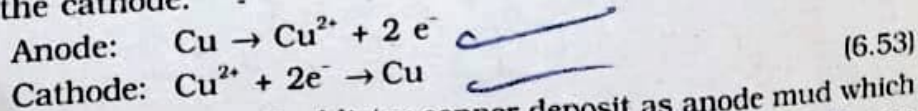
In this method a low melting metal like tin can be made to flow on a sloping surface. In this way it is separated from higher melting impurities.

(c) Electrolytic refining

In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. 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 which you have seen in previous sections. The reactions are:



Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:



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

Zinc may also be refined this way.

(d) Zone refining

This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of the impure metal (Fig. 6.7). 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

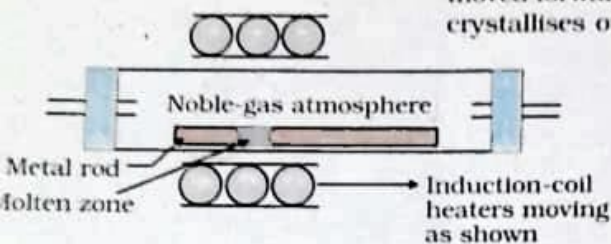


Fig. 6.7: Zone refining process

the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off. This method is very useful for producing purity, e.g., germanium, silicon, boron, gallium and indium.

(e) Vapour phase refining

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

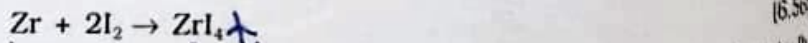
Mond Process for Refining Nickel: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl:



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



van Arkel Method for Refining Zirconium or Titanium: This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilises:



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



(f) Chromatographic methods

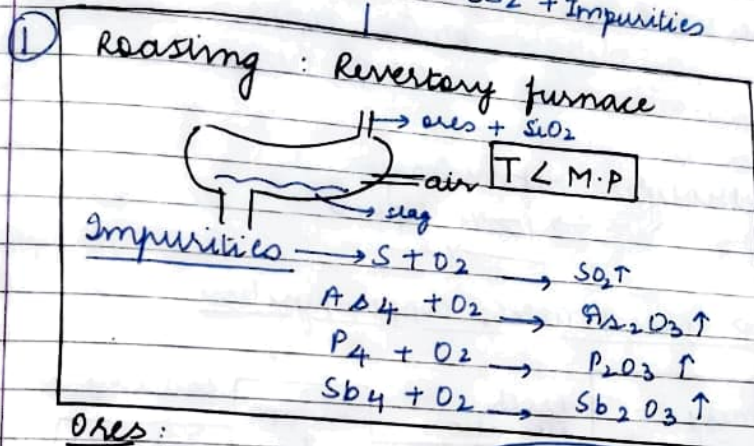
This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture is passed in a liquid or gaseous medium which is moved through the adsorbent.

Elmhurst
agarm)

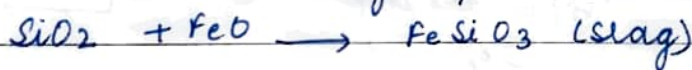
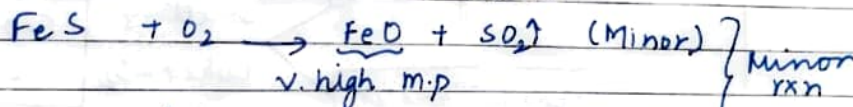
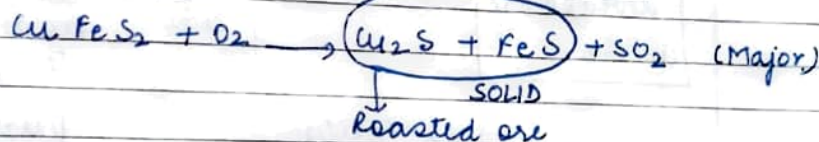
Extraction of copper

Ores \rightarrow CuFeS_2 , Copper Pyrites
concentration of ores \downarrow Froth floatation

conc. ores CuFeS_2 + Impurities

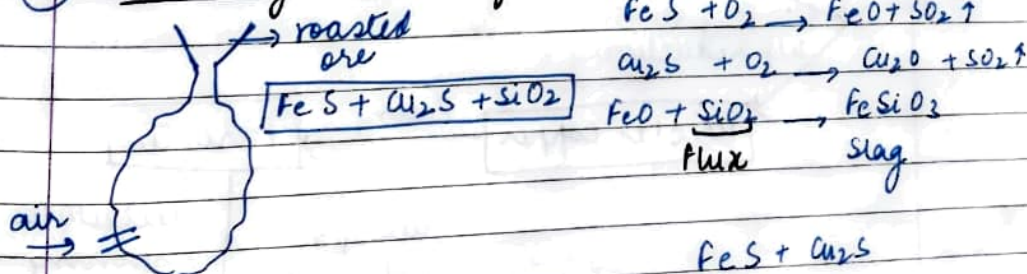


Ores:



Minor rxn

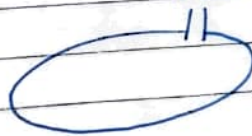
② Smelting : Blast furnace



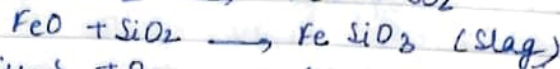
③ Besmerisation



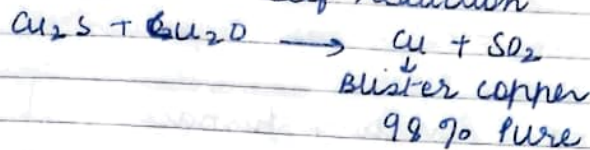
copper melt



Major here

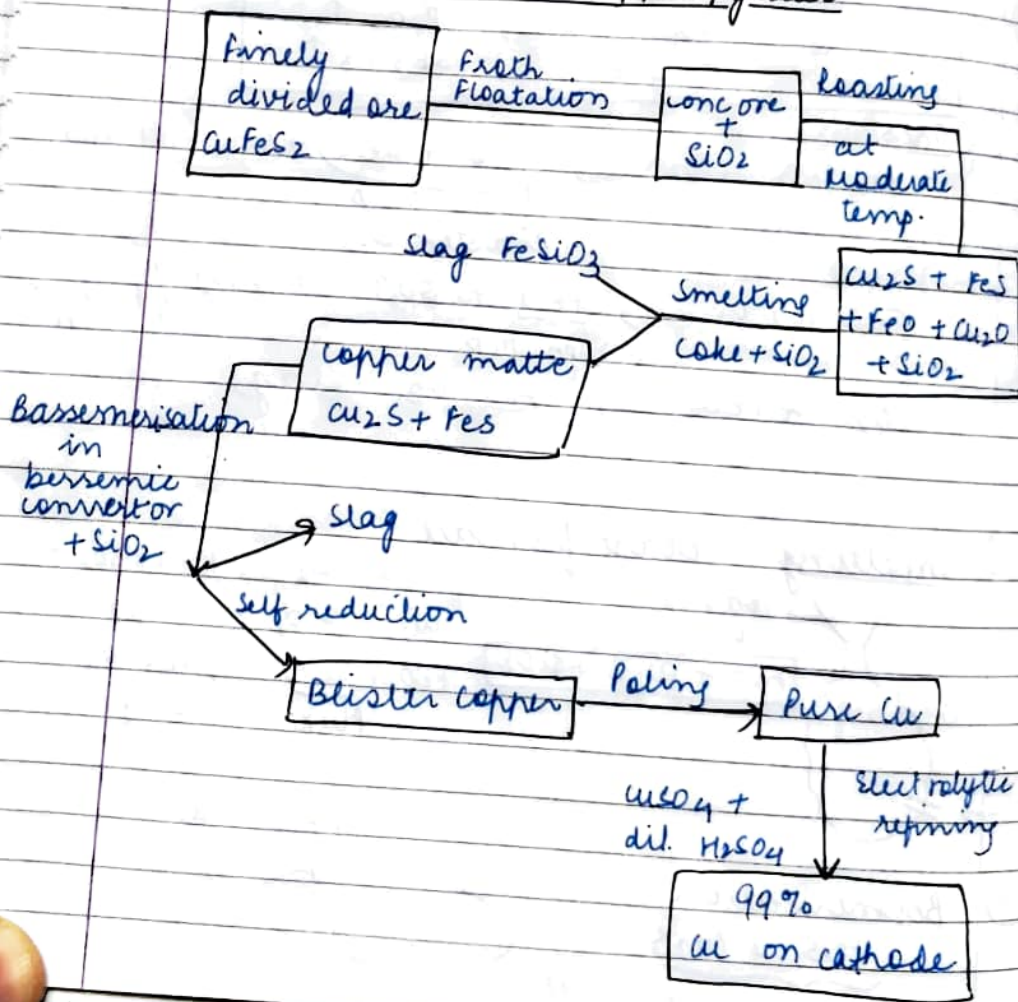


Self reduction



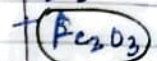
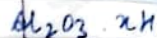
④ Electrolytic refining
→ 100% copper
— X —

Cu → ores : CuFeS_2 copper pyrites



Extract

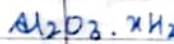
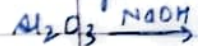
Red Bauxite



Major impurity ↓

conc of

Bayer's Pr



(Hall Herault process)

Red + Fe

Pure Al

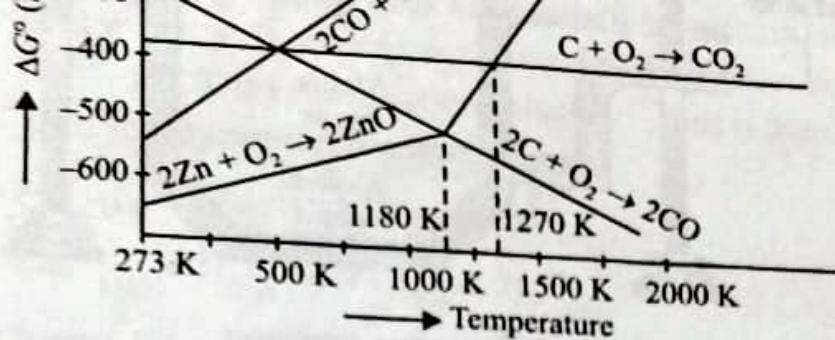
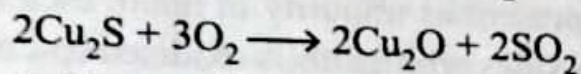


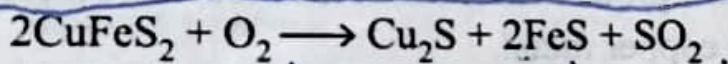
Fig. 1.11 Ellingham diagram showing the formation of Cu_2O from Cu , ZnO from Zn , Co from C , and CO_2 from C and CO



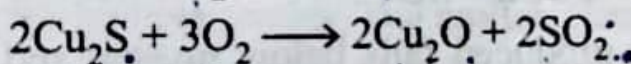
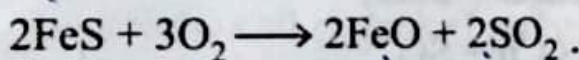
The oxides can then be reduced to metallic copper using coke as the reducing agent.



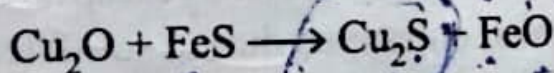
However, in actual process, the sulphide ore (i.e. copper pyrites), after concentration by froth flotation process is roasted in a reverberatory furnace when copper pyrites is converted into a mixture of FeS and Cu_2S , which, in turn, are partially oxidised.



Copper pyrites



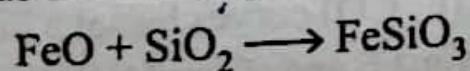
Since iron is more reactive than copper, FeS is preferentially oxidised to FeO than Cu_2S to Cu_2O . If at all any Cu_2O is formed, it combines with FeS and is changed back to Cu_2S .



Thus, the roasted ore mainly contains Cu_2S and FeO along with some unreacted FeS .

The roasted ore is then mixed with silica (flux) and some powdered coke (to check the oxidation of FeO to Fe_2O_3) and heated strongly in a blast furnace. This process is called smelting.

During smelting, FeO combines with silica to form fusible ferrous silicate slag.



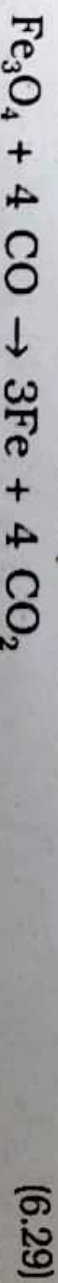
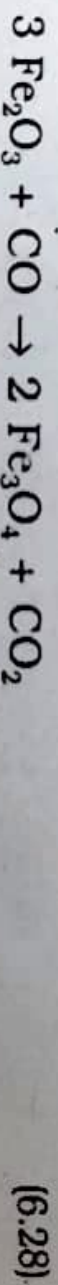
Silica

At the temperature of the furnace, the entire mass melts

Fig. 6.4: Gibbs energy (ΔG^\ominus) vs T plots (schematic) for formation of some oxides (Ellingham diagram)

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. The burning of coke therefore supplies most of the heat required in the process. The CO and heat moves to upper part of the furnace. 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. 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 $\Delta_r G^\ominus$ vs T plots. These reactions can be summarised as follows:

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



The temperature near the top of the furnace is $\sim 523\text{ K}$ while near the bottom it is $\sim 2170\text{ K}$.

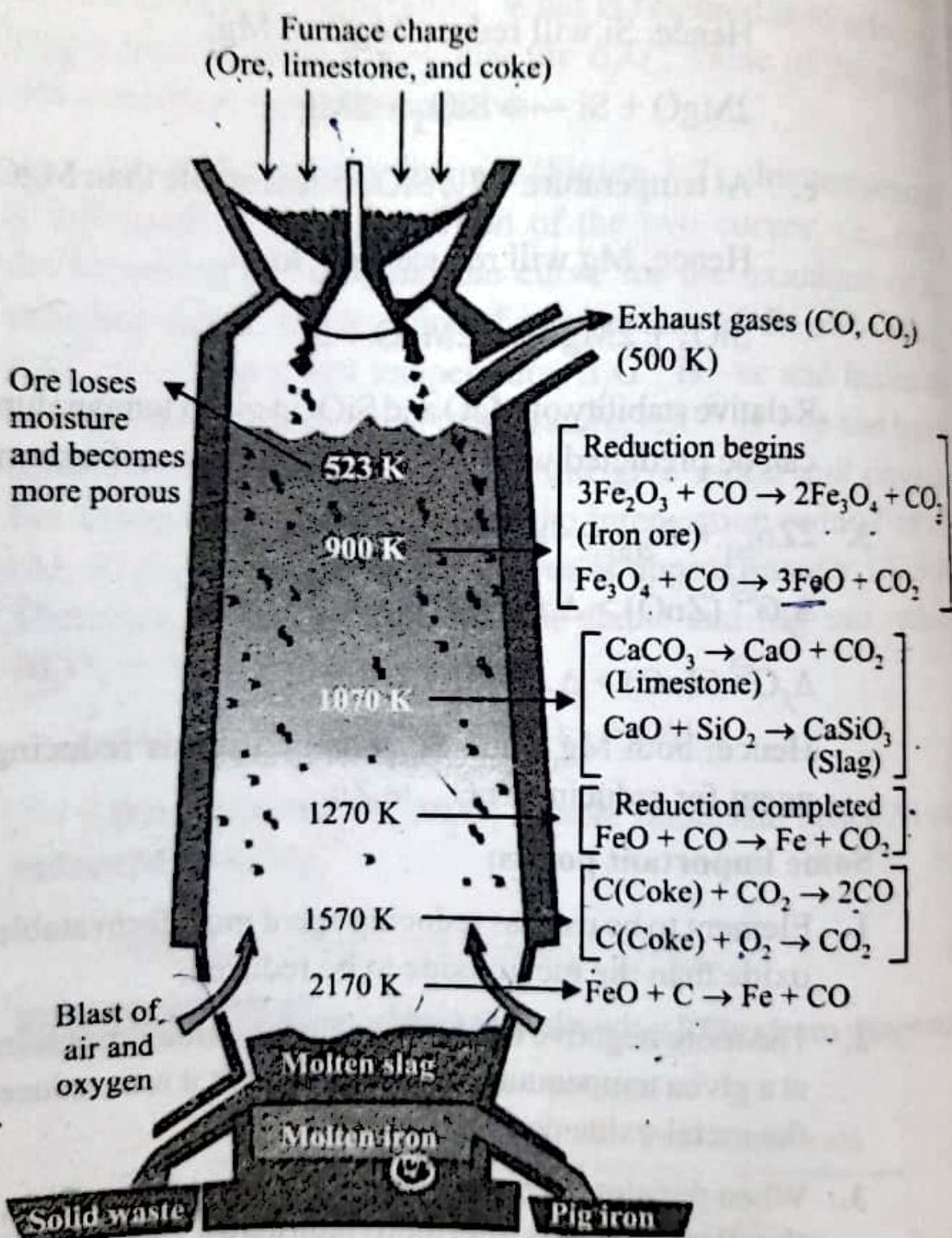


Fig. 1.9 Blast furnace

a. **Theory of reduction process:** Iron oxide is reduced to iron mainly by CO , though perhaps some reduction by C also takes place.



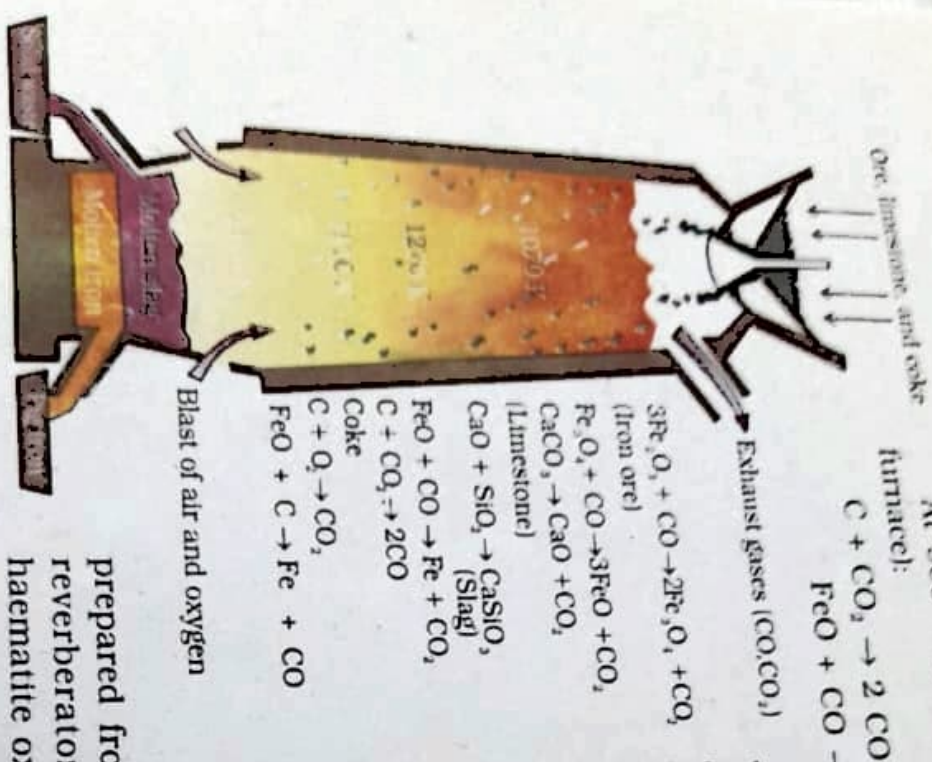


Fig. 6.5: E1 furnace

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



(6.31)

(6.32)

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

The iron obtained from Blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn). This is known as pig iron and cast into variety of shapes. Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Further Reductions

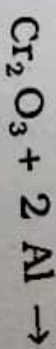
Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron, by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide:



(6.33)

Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag. The metal is removed and freed from the slag by passing through rollers.

6.3 The reaction.



is thermodynamically why does it not reduce MgO ? Why

The sc evolution

(c) Extra

The this heat

The

Electrochemical

We

Different components are adsorbed at different levels on the column. Later the adsorbed components are removed (eluted) by using suitable solvents (eluant). Depending upon the physical state of the moving medium and the adsorbent material and also on the nature of the moving medium, the chromatographic method is given the name liquid form. This is an example of column chromatography. This is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified. There are several chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc. Procedures followed in column chromatography have been depicted in Fig. 6.8.

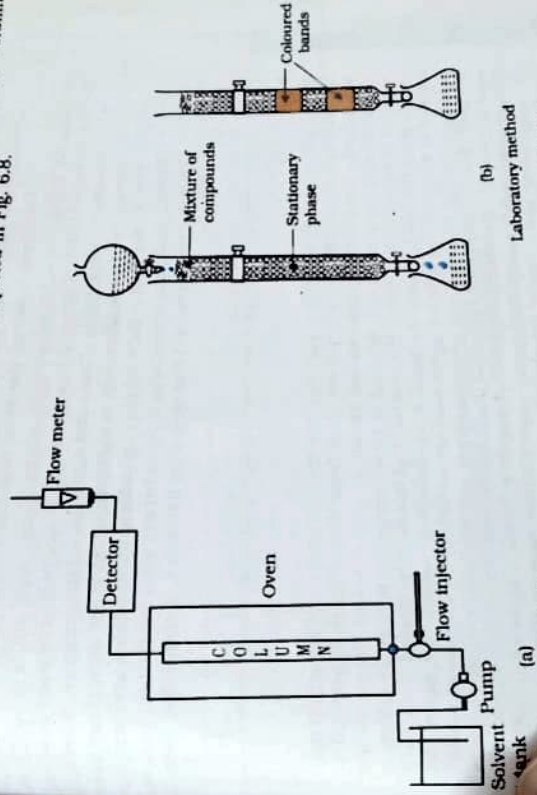


Fig. 6.8: Schematic diagram of a

Fig. 6.8: Schematic diagram illustrating the principle of column chromatography. The diagram shows a vertical column containing a stationary phase (represented by a series of horizontal lines) and a mobile phase (represented by a series of vertical lines). A sample of a mixture is applied to the top of the column. As the mobile phase moves down the column, it carries the components of the sample with it. The components are separated based on their relative affinities for the stationary and mobile phases. The more a component is attracted to the stationary phase, the slower it moves down the column. The less a component is attracted to the stationary phase, the faster it moves down the column. The components are collected in separate fractions as they move down the column.

The suitable electrolytes used in general for respective metals are:

Cu: CuSO_4 solution
Zn: ZnSO_4 solution

Sn: SnSO_4 solution
Ag: AgNO_3 solution
Au: AuCl_3 solution

Ni: $\text{Ni}(\text{NO}_3)_2$ solution
Pb: PbSiF_6 solution
Al: $(\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6)$ melt + BaF_2

6.7 | THERMODYNAMICS OF REDUCTION PROCESS

The extraction of metals from their oxides using carbon or other metals, and by thermal decomposition (Table 6.1), involves a number of points which merit detailed discussion.

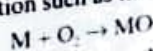
Table 6.1 Reduction potentials and extraction methods

Element	E° (V)	Materials	Extraction method
Lithium	$\text{Li}^+ \text{Li}$ -3.05	LiCl	Electrolysis of fused salts, usually chlorides
Potassium	$\text{K}^+ \text{K}$ -2.93	KCl , $\{\text{KCl}, \text{MgCl}_2, 6\text{H}_2\text{O}\}$	
Calcium	$\text{Ca}^{2+} \text{Ca}$ -2.84	CaCl_2	
Sodium	$\text{Na}^+ \text{Na}$ -2.71	NaCl	
Magnesium	$\text{Mg}^{2+} \text{Mg}$ -2.37	MgCl_2 , MgO	Electrolysis of MgCl_2
Aluminium	$\text{Al}^{3+} \text{Al}$ -1.66	Al_2O_3	High temperature reduction with C
Manganese	$\text{Mn}^{2+} \text{Mn}$ -1.08	Mn_3O_4 , MnO_2	Electrolysis of Al_2O_3 dissolved in molten $\text{Na}_3[\text{AlF}_6]$
Chromium	$\text{Cr}^{3+} \text{Cr}$ -0.74	FeCr_2O_4	Reduction with Al
Zinc	$\text{Zn}^{2+} \text{Zn}$ -0.76	ZnS	Thermite process
Iron	$\text{Fe}^{2+} \text{Fe}$ -0.44	Fe_2O_3 , Fe_3O_4	Chemical reduction of oxides by C
Cobalt	$\text{Co}^{2+} \text{Co}$ -0.27	CoS	
Nickel	$\text{Ni}^{2+} \text{Ni}$ -0.23	NiS , NiAs_2	
Tin	$\text{Sn}^{2+} \text{Sn}$ -0.14	SnO_2	
Lead	$\text{Pb}^{2+} \text{Pb}$ -0.13	PbS	Found as native metal, or compounds easily decomposed by heat (Also cyanide extraction)
Copper	$\text{Cu}^{2+} \text{Cu}$ +0.35	$\text{Cu}(\text{metal})$, CuS	
Silver	$\text{Ag}^+ \text{Ag}$ +0.80	$\text{Ag}(\text{metal})$, Ag_2S , AgCl	
Mercury	$\text{Hg}^{2+} \text{Hg}$ +0.85	HgS	
Gold	$\text{Au}^{3+} \text{Au}$ +1.38	$\text{Au}(\text{metal})$	

For a spontaneous reaction, the free energy change ΔG must be negative.

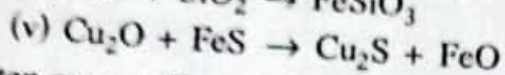
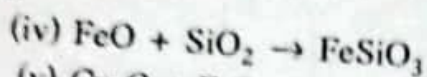
$$\Delta G = \Delta H - T\Delta S$$

ΔH is the enthalpy change during the reaction, T is the absolute temperature, and ΔS is the change in entropy during the reaction. Consider a reaction such as the formation of an oxide:



Dioxygen is used up in the course of this reaction. Gases have a more random structure (less ordered) than solids. In this reaction S decreases. Thus if the temperature is raised then $T\Delta S$ becomes less negative. Thus the free energy change ΔG becomes less negative. Thus the reaction becomes less spontaneous.

The ore is then mixed with a little coke and sand and smelted in a jacketed blast furnace. The minor reactions that occurred during roasting continue here. Ferrous oxide combines with sand to form a fusible slag. Cuprous oxide formed combines with ferrous sulphide to give ferrous sulphide and cuprous sulphide. This is because iron has more affinity for oxygen than copper.



Molten mass collected from the bottom of furnace contains largely cuprous sulphide and a little ferrous sulphide. This molten mass is known as matte.

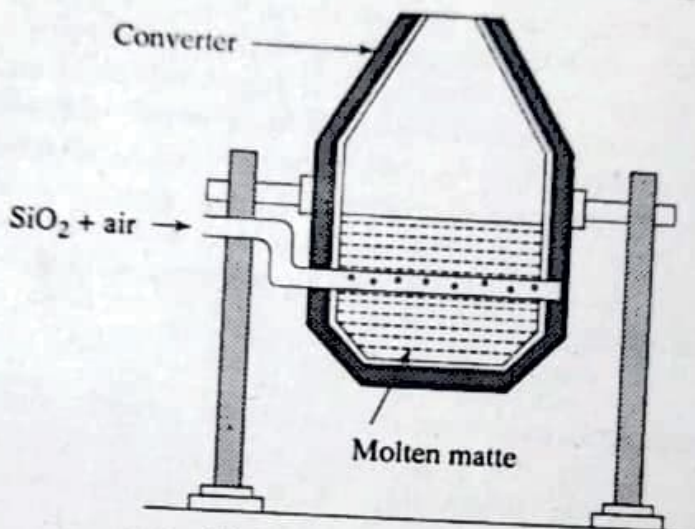
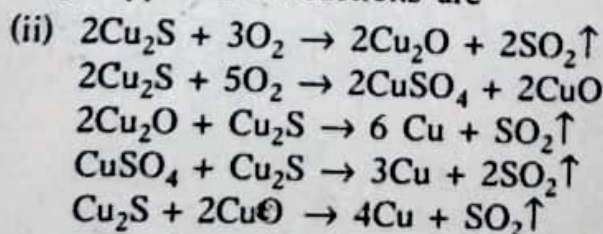


Fig. 12.2 Bessemer converter

The molten matte is finally transferred to Bessemer converter (Fig. 12.2). A blast of sand and air is blown in the converter through tuyeres which are situated a little above the bottom. This causes removal of S and As as oxides and ferrous oxide as slag (reaction iv). At the same time Cu_2S is oxidized mostly into Cu_2O (reaction ii) and partly into CuO and CuSO_4 . All these react with Cu_2S giving copper. The reactions are



Finally, copper may be refined electrolytically (electrolyte; copper sulphate; anode; impure copper and cathode; pure copper).

Extraction of lead Lead is mainly extracted from galena. After the concentration of the ore by froth flotation process, the ore is roasted in a reverberatory furnace for about six hours at a moderate temperature in a current of air. Part of galena is converted into lead oxide and lead sulphate. After this, the supply of air is stopped and small quantities of carbon, quicklime and cheap iron ore are added along with increase of temperature. At this stage, unreacted sulphide reacts with the lead oxide and sulphate giving metallic lead: