6. General Principles and Processes of Isolation of Metals

General introduction and occurrence of some important ores.

Metallurgy: Extraction of crude metal and its refining.

Mineral: Naturally occurring metallic constituent.

Ore: Mineral from which a metal is economically extracted.

Gangue: Impurities associated with ore.

Concentration (ore dressing) or benification: Removal of gangue from ore.

Smelting: Production of metal in molten state by reduction of metallic constituent.

Flux: Removes gangue. Acidic flux (*Ex.* silica, SiO_2) removes basic gangue and basic flux (*Ex.* lime, CaO) removes acidic gangue.

Slag: Molten mass formed by combination of flux and gangue.

Collector: Forms thin film over ore particle. *Ex.* ethyl xanthate

Froth stabilizer: Stabilizes the froth. *Ex.* oils, soaps

Depressant: Prevents ores from forming froth. *Ex.* NaCN is a depressant for PbS.

Cupellation: Metal with a greater affinity for oxygen forms oxide scum (oxidative refining)

Vapour phase refining (van Arkel method): Involves conversion of metal into volatile compound, followed by its decomposition at high temperature. *Ex.* titanium and zirconium

Dross: Infusible matter obtained during liquation

Matte: Artificially obtained mixture of sulphides. *Ex.* Sulphides of copper and iron (Extraction of Cu).

Refractory material: Withstands high temperature without melting or becoming soft; used as furnace lining. Silica, quartz are acidic; lime, dolomite, magnesite are basic; graphite, chromite, bone-ash are neutral. For basic environment – basic refractory is used and for acidic environment – acidic refractory is used, Fire brick is used as furnace lining in blast furnace.

Desilverization of lead Separation of silver from argentiferrous lead.

Nernst's distribution law Substance distributes between two immiscible solvents until at equilibrium ratio of concentrations of substances is constant at given temperature. C_A/C_B Distribution coefficient

Parke's desilverization Silver is 300 times more soluble in molten zinc than in molten lead. Molten argentiferous lead + zinc, stir, cool; Ag present in Pb is taken up by Zn; solidifies as Zn-Ag alloy.

Ellingham's diagram Plot of variation in $\Delta G° - T$ values with temperature for reaction of metal with one mole of oxygen gas at 1 atmosphere pressure

Ores of some Important Metals

Metal	Ore	Formula
Iron	Haematite	Fe_2O_3 (red)
	Limonite	$Fe_2O_3 3H_2O$
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Pyrites	FeS_2
Copper	Chalcopyrite	$CuFeS_2$ or $Cu_2S.Fe_2S_3$
	Cuprite (Ruby copper)	Cu_2O
	Copper glance (Chalocite)	Cu_2S
	Malachite	$CuCO_3.Cu(OH)_2$
	Azurite	$2CuCO_3.Cu(OH)_2$
Aluminium	Bauxite	$Al_2O_3.2H_2O$
	Cryolite	Na_3AlF_6 or $3NaF.AlF_3$
Zinc	Calamine	$ZnCO_3$
	Zinc blende (sphalerite)	ZnS
	Willemite	Zn_2SiO_4

Concepts of general principles of metallurgy

The various steps involved in the extraction of metals from their ores are as discussed below.

Concentration of the ore: Separation of the gangue (impurities) from the ore is concentration. Ores are concentrated by the following physical methods.

1. **(a) Gravity separation (Washing or Levigation):** It is based on the differences in the densities of gangue and ore particles. *Ex.* Gold and oxide ores like haematite (Fe_2O_3).

   (b) Froth flotation: This method is used for the concentration of the sulphide ores of Zn, Cu, Pb. During froth flotation process various substances are added to the suspension in the froth flotation tank.

   i. **Collectors:** These are used to increase the non wettability of ore particles by water.
   Example : Pine oil, Xanthates and Fatty acids.

   ii. **Froth stabilizers:** These are added to stabilize the froth.
   Example : Cresols and aniline.

   iii. **Depressants:** These are the substances used when ore contains mixture of sulphides of different metals. Depressants help in the selective separation of one metal sulphide along with the froth by preventing that of the other metal sulphide from forming the froth simultaneously.
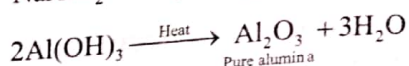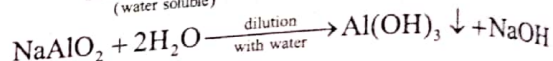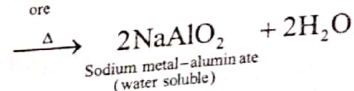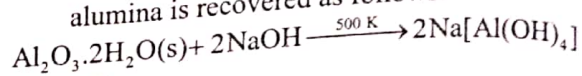   Example : NaCN is used as depressant for ZnS to prevent its separation along with the froth when PbS is present along with it.

   (c) Magnetic separation: Magnetic ore containing non magnetic impurities or vice versa is separated by this method. Example : Wolframite $FeWO_4$ a magnetic impurity is separated from the non magnetic ore cassiterite or tinstone an ore of tin.

   (d) Chemical method (Leaching)
   Ore containing impurities is leached with an aqueous solution of a suitable dissolving reagent so that the metal present in the ore is converted into a simple soluble salt or complex compound, while the impurities remain undissolved in the reagent and are removed by filtration. Metal is extracted from the complex salt.

   (i) **Concentration of bauxite (Bayer's process)**
   Bauxite $Al_2O_3 \cdot 2H_2O$ (an ore of Al) contains impurities like Fe_2O_3, TiO_2, SiO_2. The impurities can be separated either by Bayer's process or by Hall's process both of which are leaching processes. Bauxite is heated with a solution of NaOH (Bayer's process) or Na_2CO_3 (Hall's process).

Ore is converted into soluble complex compound $NaAlO_2$ and impurities remain undissolved and are removed by filtration from the solution. Pure alumina is recovered as follows.

$$Al_2O_3 \cdot 2H_2O(s) + 2NaOH \xrightarrow{500\ K} 2Na[Al(OH)_4]$$
$$\underset{ore}{} $$

$$\xrightarrow{\Delta} \underset{\substack{Sodium\ metal-aluminate \\ (water\ soluble)}}{2NaAlO_2} + 2H_2O$$

$$NaAlO_2 + 2H_2O \xrightarrow[\text{with water}]{\text{dilution}} Al(OH)_3 \downarrow + NaOH$$

$$2Al(OH)_3 \xrightarrow{Heat} \underset{Pure\ alumina}{Al_2O_3} + 3H_2O$$

(ii) **MaC –Arthur Forest cyanide process** Concentration of silver and gold is also a leaching process. (for details : Refer Hydrometallurgy)

In the physical methods of concentration there is no change in the composition of the ore during the process. During chemical methods of concentration there is a chemical change in the composition of the ore.

2. **Conversion of ore into metal oxide :** Preliminary treatment is carried out to convert an ore into metal oxide by roasting and calcination to make ore suitable for smelting or reduction.

   Roasting Generally followed for sulphide ores and ores which contain lower oxides. Ore is heated just below its fusion temperature in excess of air, sulphides are converted into oxides and lower oxides are converted into higher oxides (*Ex.* $FeO \rightarrow Fe_2O_3$).

   Calcination Followed for carbonate and hydroxide ores. Ore is heated just below its fusion temperature preferably in the absence of air. Carbonate/hydroxide present decomposes into an oxide.

   During roasting and calcination, ore becomes porous, loses volatile impurities and is chemically modified.

3. **Extraction of crude metal:** The calcined or roasted ore is reduced to free metal by any one of the following processes based on the nature of the ore.

   A. **Pyrometallurgy:** Metal is extracted from calcined or roasted ore by heating to a very high temperature. Smelting, reduction by using carbon, hydrogen or aluminium (Goldschimdt alumino thermic process), self reduction (or auto reduction process) are some of the methods which are based on pyrometallurgy principle.

   i. **Smelting**
   - Reduction of metal oxide by heating with carbon or carbon monoxide in the presence of suitable flux.
   - Metal is obtained in the molten state.
   - Less electropositive metals like Pb, Zn, Fe, Sn are extracted by this method.

Flux: It is a substance used to remove infusible gangue from roasted or calcined ore in the form of fusible mass called slag.

$$\underset{\text{(infusible)}}{\text{Flux + gangue}} \rightarrow \underset{\text{(fusible)}}{\text{slag}}$$

Different type of fluxes are used based on the nature of the gangue (or impurities)

Acidic flux: When ore is associated basic impurities such as FeO, CaO, MgO, etc acidic fluxes such as SiO_2 (silica) is used.
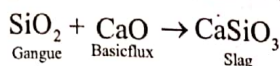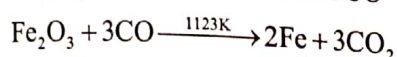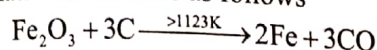
$$\underset{\text{BasicGangue}}{FeO} + \underset{\text{Flux}}{SiO_2} \rightarrow \underset{\text{slag}}{FeSiO_3}$$
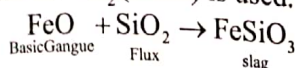
Basic flux: When ore is associated with acidic impurities such as SiO_2, P_2O_5, etc basic fluxes such as CaO and MgO are used.

$$\underset{\text{acidic gangue}}{SiO_2} + \underset{\text{basic gangue}}{CaO} \rightarrow \underset{\text{gangue}}{CaSiO_3}$$
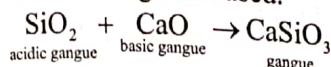
Concentrated ore + flux + gangue + reducing agent → metal + slag + volatile gaseous impurities.

For example, extraction of iron from haematite ore is done as follows

$$Fe_2O_3 + 3C \xrightarrow{>1123K} 2Fe + 3CO$$

$$Fe_2O_3 + 3CO \xrightarrow{1123K} 2Fe + 3CO_2$$

$$\underset{\text{Gangue}}{SiO_2} + \underset{\text{Basicflux}}{CaO} \rightarrow \underset{\text{Slag}}{CaSiO_3}$$

ii. **Self reduction (Auto reduction):** Sulphide ores of less electropositive metals like Hg, Pb, Cu etc are heated in air to partially convert sulphide ore into an oxide which then reacts with remaining sulphide to give metal and sulphur dioxide. No additional substance is used as reducing agent. For example extraction of Cu from copper glance occurs as follows

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

$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$
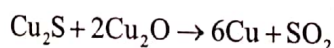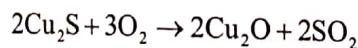
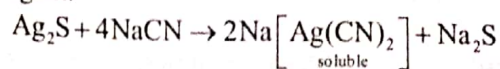iii. **Alumino thermic process (Goldschimdt alumino thermic process)**
Metal oxides such as Cr_2O_3, Mn_3O_4 are reduced by heating with powdered aluminium. A mixture of concentrated ore and aluminium powder is called thermite.
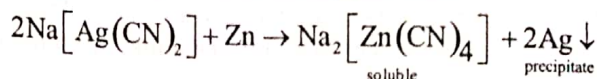
$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$$
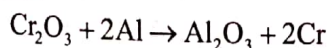
A mixture of Fe_2O_3 and aluminium powder in 3 : 1 is also called thermite and is used in welding.

B. **Hydrometallurgy:** Ore is converted into a soluble complex by digesting with an aqueous solution of a suitable reagent. From the solution, metal is precipitated by adding a more electropositive metal.

For example, Silver is extracted from its ore argentite (Ag_2S) using NaCN as a complexing agent.

$$Ag_2S + 4NaCN \rightarrow 2Na\underset{\text{soluble}}{\left[Ag(CN)_2\right]} + Na_2S$$

Ag is precipitated on adding Zn dust.

$$2Na\left[Ag(CN)_2\right] + Zn \rightarrow Na_2\underset{\text{soluble}}{\left[Zn(CN)_4\right]} + \underset{\text{precipitate}}{2Ag\downarrow}$$

C. **Electrometallurgy:** Highly electropositive metals like alkali metals Na, K and alkaline earth metals like Mg, Ca and also aluminium are extracted by this method. Fused salts of the metals on electrolysis form the metal at cathode. Sodium is extracted from fused NaCl and aluminium is extracted from Al_2O_3 in the presence of cryolite Na_3AlF_6.
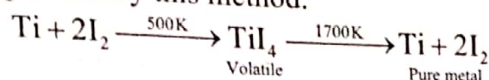
4. **Refining of crude metals**
i. **Liquation:** This method is based on the difference in melting points of metal and impurities and followed to separate high melting impurities from the low melting metals.
Examples : Bi, Sn, Hg, Pb, etc.

ii. **Distillation:** This method is based on difference in boiling points of metal and the impurities. More volatile metals like Zn, Hg are purified by this method.

iii. **Poling:** This method is used for the purification of metals which contain their own oxides as impurities. Impure molten metal is stirred with green wooden logs to remove traces of oxygen from oxides.
Example: copper and tin.

iv. **Oxidation method**
(a) **Bessemerisation:** Non metallic impurities like C, S, P are removed by this method. Impure metal is heated with trace amounts of its own oxide to oxidise the non metals into volatile oxides. Example : Iron.
(b) **Cupellation:** Lead present as impurity in silver is oxidised to volalite oxide by heating impure silver in a cupella.

v. **Electrolytic refining:** Crude metal is taken as anode; A thin sheet of pure metal is cathode, salt solution of same metal is electrolyte. Upon electrolysis, metal at anode gets deposited on cathode. Impurities collect as anode mud or enter into solution.

vi. **Zone refining:** Ultra pure metals and non-metals are obtained by zone refining. Impure metal is taken in the form a rod and is heated by a moving circular electrical coil. Impurities are more soluble

in molten metal and move into molten region. The process is repeated to separate impurities which are collected at one extreme end of the rod. *Ex.* Si, Ge.

vii. **Vapour phase refining:** Metal is separated from impurities by converting it into a volatile compound by heating with a suitable reagent.

Van Arkel Method: Titanium and Zirconium are purified by this method.

$$Ti + 2I_2 \xrightarrow{500K} TiI_4 \xrightarrow{1700K} Ti + 2I_2$$
$$\qquad\qquad \underset{\text{Volatile}}{} \qquad\qquad \underset{\text{Pure metal}}{}$$

Mond's process: Nickel is purified by this method.

$$Ni + 4CO \rightarrow \underset{\text{volatile}}{Ni(CO)_4} \rightarrow \underset{\text{pure metal}}{Ni} + 4CO$$

viii. **Chromatographic method:** This method is followed when elements are obtained in very small quantities and that the element and associated impurities have nearly the same properties.

The method is based on selective distribution of various constituents of a mixture between two phases, i.e., stationary phase and a moving phase. The stationary phase can either be a solid or it can be a tightly bound liquid on a solid support. The moving phase may be a liquid or a gas. Most common types of chromatographic methods are

1. Column chromatography
2. Thin layer chromatography
3. Paper chromatography
4. Gas chromatography

Column chromatography is a widely used modern technique. In column chromatography Al_2O_3 is used as stationary phase and acts as an adsorbent. Mobile phase is a solution containing the mixture the constituents of which are to be separated. A solution containing the mixture in a suitable solvent is passed over the column from the top. Different components of the mixture are adsorbed to different extent depending upon their polarity. The adsorbed components are extracted (eluted) from the column with a suitable solvent (eluent). Weakly adsorbed components (which are at the lower part of the column) are extracted first and strongly adsorbed component (which are present at the top of the column) are extracted at the end.

Thermodynamic principles of metallurgy

Thermodynamic principles help in deciding the temperature and the selection of the reducing agents in the reduction process. The feasibility of the process can be predicted in terms of Gibb's free energy change (ΔG) at a specified temperature (T) which is related to enthalpy change (ΔH) and entropy change (ΔS) as

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

For any reaction Gibb's free energy ($\Delta G°$) is also related to equilibrium constant (K) at a given temperature (T) as :

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

If ΔG is $-ve$, then K will be positive and that the reaction is spontaneous.
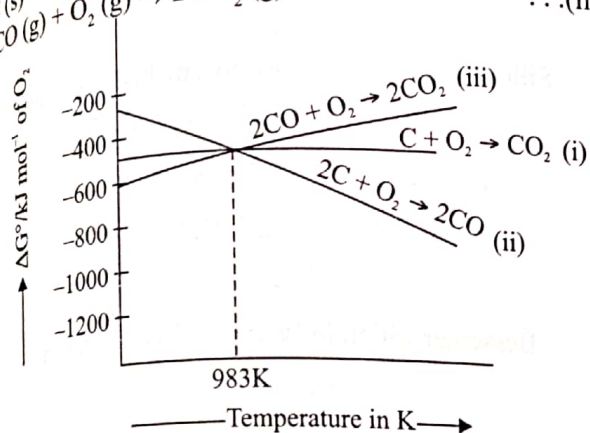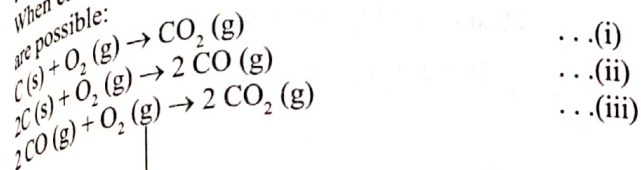
- The criterion for the feasibility of a reaction at any temperature is that, the ΔG of the reaction must be **negative.**

- A reaction with positive ΔG value (or less $-ve$ value of ΔG) can be made to occur by coupling with another reaction having larger negative ΔG value so that, the net ΔG of the two reactions is negative. Such couplings can be understood with the help of Ellingham diagram which are the plots of Gibb's free energy change $\Delta G°$ for the formation of oxides versus temperature (T). Ellingham diagrams help in predicting the feasibility of thermal reduction of an oxide ore by using a suitable reducing agent.

- Each plot is a straight line directing upwards with increase is temperature. These plots show deviation at the temperature when some phase change (solid to liquid or liquid to gas) takes place.

- The feasibility of a reduction process can be predicted from the diagram by looking at the position of the plots of free energy change for the formation of oxides of various metals.

- A metal for which free energy of formation of its oxide $\Delta G_f°$ is more negative can reduce all the metal oxide whose $\Delta G_f°$ value is less negative or which lies above it as indicated in the Ellingham diagram.

- Greater the difference is the $\Delta G_f°$ values of two plots more easier will be the reduction process.
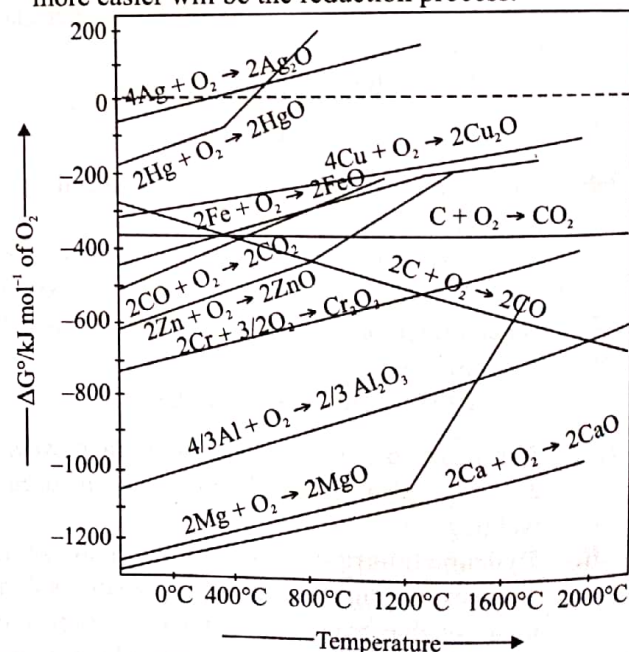
Ellingham diagram $-\Delta G_f°$ vs T plots for formation of oxides of some metals

Reducing behaviour of carbon.

When carbon reacts with dioxygen, three types of reactions are possible:

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \ldots(i)$$
$$2C(s) + O_2(g) \rightarrow 2CO(g) \qquad \ldots(ii)$$
$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \qquad \ldots(iii)$$

Ellingham diagram showing the variation of $\Delta G_f°$ for three reactions

(i) $C \rightarrow CO_2$; (ii) $C \rightarrow CO$; (iii) $CO \rightarrow CO_2$

For reaction (i), the volume of CO_2 formed is almost equal to the volume of O_2 consumed, so ΔS does not change significantly and Ellingham plot is almost horizontal to the temperature axis. For reaction (ii), the plot slopes downwards and $\Delta G°$ value becomes more negative with increase in temperature. Here two volumes of CO are produced for one volume of O_2 consumed, thus ΔS becomes positive. In the reaction (iii) two volumes of CO_2 are formed for every three volumes of reactants used. Thus, ΔS is −ve, hence $\Delta G_f°$ becomes increasingly +ve as the temperature increases. Consequently, CO, CO_2 plot slopes upwards.

The three plots intersect at 983 K. Below this temperature, formation of CO_2 from C as well as from CO is energetically more favourable and above this temperature formation of CO from C is energetically more favourable. In other words, below 983 K, both C and CO can act as reducing agents. Since CO can be more easily oxidised to CO_2 than C to CO_2, **below 983 K carbonmonoxide is a more effective reducing agent than C.** However, above 983 K, CO is more stable, hence its oxidation to CO_2 is less rapid than that of C to CO_2. Therefore, **above 983 K, carbon is a better reducing agent than CO.**
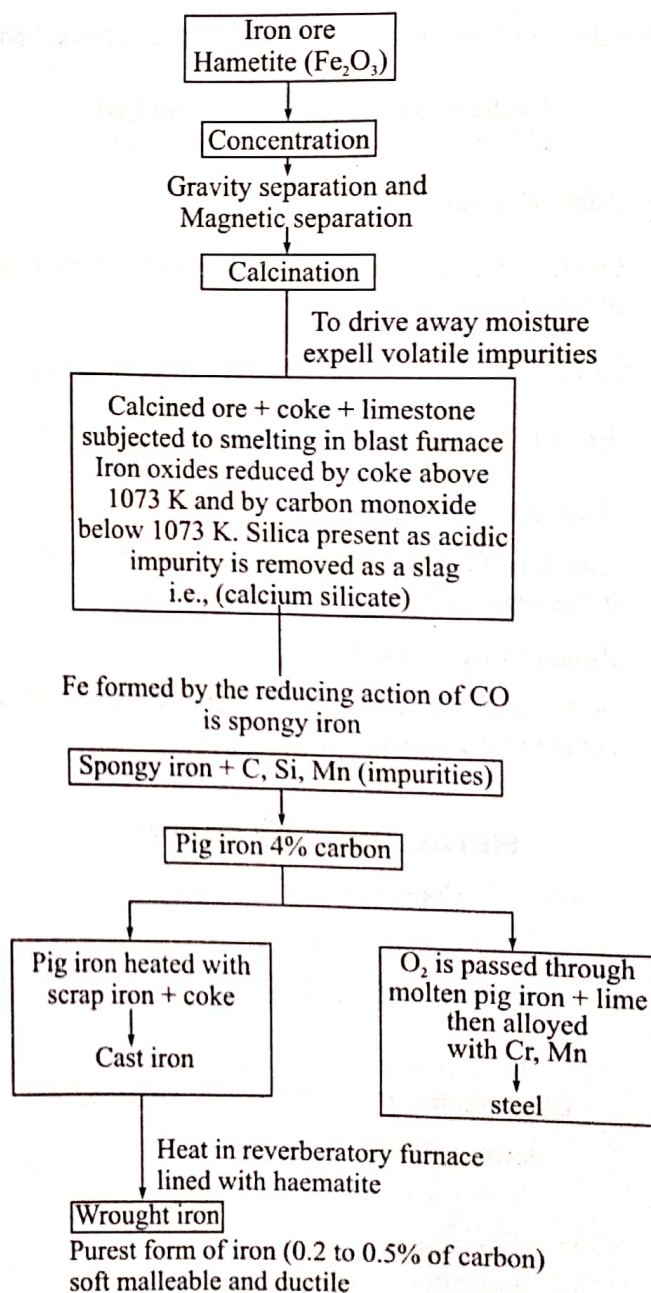
Effect of Temperature on the Free Energy Change ($\Delta G_r°$) of the overall reduction process

According to the Gibb's free energy equation $\Delta G = \Delta H - T\Delta S$, with the increase in the temperature, the values of ΔH and ΔS remain constant, and the value of $\Delta G_r°$ becomes more negative. If a particular reduction process

does not occur at a lower temperature then, such a process can be made to occur at high temperature by selecting a suitable temperature in such a way that $\Delta G_r°$ of the overall redox reaction becomes −ve $\Delta G°$. In the Ellingham diagram, this temperature is indicated by a point of intersection of the two plots (i.e., plots for formation of metal oxide to be reduced and the other plot corresponding to the formation of the oxide of the reducing agent). For example, the temperature corresponding to the intersection of the two plot of Al→Al_2O_3 and Mg → MgO is approx. 1623 K. Below 1623 K, magnesium has greater −ve value than Al and can reduce Al_2O_3 to Al. Above 1623 K, aluminium has greater −ve $\Delta G°$ value than Mg, hence it can reduce MgO to Mg.

METALLURGY OF IRON

```
        ┌─────────────────────────┐
        │     Iron ore            │
        │  Hametite ($Fe_2O_3$)   │
        └─────────────────────────┘
                    ↓
        ┌─────────────────────────┐
        │     Concentration       │
        └─────────────────────────┘
          Gravity separation and
           Magnetic separation
                    ↓
        ┌─────────────────────────┐
        │      Calcination        │
        └─────────────────────────┘
                         To drive away moisture
                         expell volatile impurities
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Calcined ore + coke + limestone subjected to smelting in blast furnace Iron oxides reduced by coke above 1073 K and by carbon monoxide below 1073 K. Silica present as acidic impurity is removed as a slag i.e., (calcium silicate)

Fe formed by the reducing action of CO is spongy iron

Spongy iron + C, Si, Mn (impurities)

Pig iron 4% carbon

Pig iron heated with scrap iron + coke
↓
Cast iron

O_2 is passed through molten pig iron + lime then alloyed with Cr, Mn
↓
steel

Heat in reverberatory furnace lined with haematite

Wrought iron

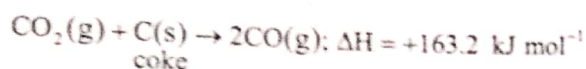Purest form of iron (0.2 to 0.5% of carbon) soft malleable and ductile

Blast furnace can be visualized to have different zones depending upon the approximate ranges of temperature and types of reactions occurring in these regions as indicated below ;
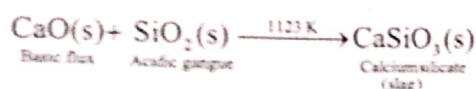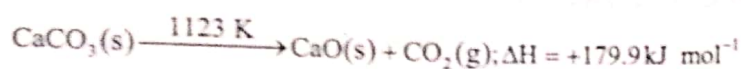
(i) Zone of combustion (2173 K)

$$\underset{\text{coke}}{C(s)} + \underset{\text{hot air}}{O_2(g)} \rightarrow CO_2(g); \Delta H = -393 kJ\ mol^{-1}$$
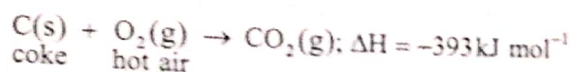
(ii) Zone of heat absorption (1673-1473K)

$$CO_2(g) + \underset{\text{coke}}{C(s)} \rightarrow 2CO(g); \Delta H = +163.2\ kJ\ mol^{-1}$$

(iii) Zone of slag formation (1473K-1123K)

$$CaCO_3(s) \xrightarrow{1123\ K} CaO(s) + CO_2(g); \Delta H = +179.9 kJ\ mol^{-1}$$

$$\underset{\text{Basic flux}}{CaO(s)} + \underset{\text{Acidic gangue}}{SiO_2(s)} \xrightarrow{1123\ K} \underset{\substack{\text{Calcium silicate}\\ \text{(slag)}}}{CaSiO_3(s)}$$

(iv) Zone of reduction (973K-500K)

Oxides of iron from the ores are reduced by carbon monoxide.

$$3Fe_2O_3(s) + CO(g) \xrightarrow{573K-673K} 2Fe_3O_4(s) + CO_2(g)$$

$$Fe_3O_4(s) + 4CO(g) \xrightarrow{773K-873K} 3Fe(s) + 4CO_2(g)$$

$$Fe_2O_3(s) + CO(g) \xrightarrow{773-473K} 2FeO(s) + CO_2(g)$$
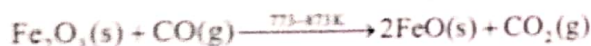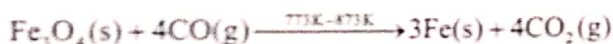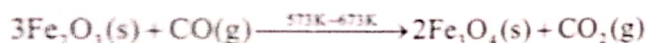
Unreduced oxides of iron are directly reduced by coke in the region above 1973 K temperature.

(v) Zone of fusion (1423-1673 K)

In this zone, the iron and the solid slag both melt and collect in the hearth of the furnace.

METALLURGY OF COPPER

Copper pyrites ($CuFeS_2$)

↓

Crushed and sieved the ore

↓

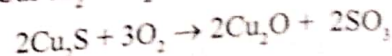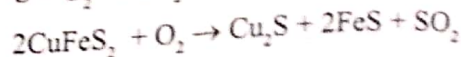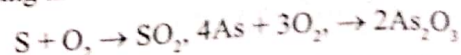Concentration by Froth Floatation Method
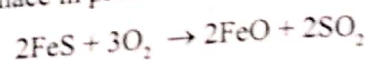
Powdered Ore + water + pine oil + air

↓

Sulphide ore in the froth

↓

Roasting in reverberatory furnace in presence of air

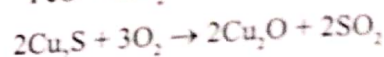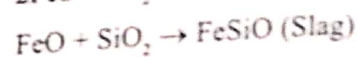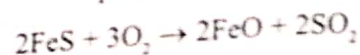$$S + O_2 \rightarrow SO_2,\ 4As + 3O_2, \rightarrow 2As_2O_3$$

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

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_3$$

↓

Silica, Coke, Roasted ore are smelted in a blast furnace in presence of air to get matte.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

Matte (Cu_2S, FeS)

↓

Bessemerization in Bassemer's converter in presence of air

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \rightarrow FeSiO\ (Slag)$$

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

$$2Cu_2O + Cu_2S \xrightarrow{\text{Autoreduction}} 6Cu + SO_2$$

Blister Copper (98% Cu + 2% Impurities)

Electrolytic refining

Anode: impure copper plates.

Cathode: Pure copper plates

Electrolyte; $CuSO_4$ solution + dilute H_2SO_4

Pure copper deposits at cathode (99.6-99.9% pure)

METALLURGY OF SILVER

Argentite (Ag_2S)

↓

Concentration by froth floatation process

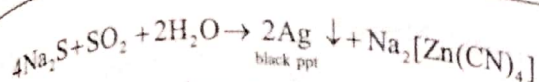Powdered ore + water + pine oil + air

↓

Froth carrying sulphide ore particles
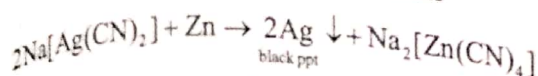
↓

Cyanidation

Concentrated ore + aq. NaCN solution

(0.4 - 0.6 %) + Air

↓

$$Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$$

sodium argento cyanide

$$4Na_2S + SO_2 + 2H_2O \rightarrow 2Ag \underset{\text{black ppt}}{\downarrow} + Na_2[Zn(CN)_4]$$

↓ Filtration

Precipitation of Silver with Zinc

$$2Na[Ag(CN)_2] + Zn \rightarrow 2Ag \underset{\text{black ppt}}{\downarrow} + Na_2[Zn(CN)_4]$$

↓ Filtration

Electrolytic Refining

Anode: Impure silver,

Cathode: Pure silver plate,

Electrolyte: $AgNO_3$ solution + HNO_3

Pure silver deposits on cathode

METALLURGY OF TIN (Sn)

Cassiterite (SnO_2)

Concentration by Levigation and

Electromagnetic separation

Crushed powdered ore is washed with

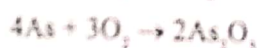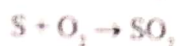water to remove lighter siliceous

impurities and the impurities of $FeWO_4$ and $MnWO_4$

are removed by electromagnetic separation

↓

Roasting in reverberatory furnace

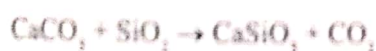Here, the impurities like S, As are removed

as SO_2 and As_2O_3

$$S + O_2 \rightarrow SO_2$$

$$4As + 3O_2 \rightarrow 2As_2O_3$$

↓

Smelting

Roasted ore + carbon + lime stone are heated

in reverberatory furnace at 1200-1300° C

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

$$SnO_2 + 2C \rightarrow Sn + 2CO$$

Black tin (99.5%)

Purification by liquation or poling

or electrolytic method
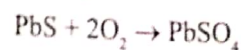
↓

Pure Sn

METALLURGY OF LEAD

Galena (PbS)

Concentration by Froth Floatation Process

(i) Air Reduction Process (or auto reduction method)

It is carried out in reverberatory

furnace and in presence of air.

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

$$PbS + 2O_2 \rightarrow PbSO_4$$

↓
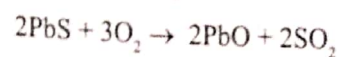
Mixed with more galena and is smelted

in blast furnace

↓

PbO and $PbSO_4$ are reduced by PbS into

crude lead metal (auto reduction)

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

$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2$$
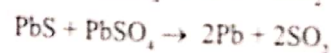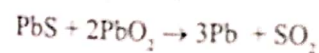
Purification: By Parke's method and Cupellation

(ii) Carbon Reduction Process

The ore is mixed with lime and heated in sinterer

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

$$PbS \rightarrow PbO$$

↓
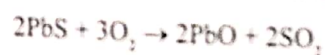
Mixed with C and CaO and is heated to

higher temperature to get crude lead.

METALLURGY OF ZINC

Zinc Blende (ZnS)

↓

Concentration by Froth Floatation Process

Powdered ore + water + pine oil ——agitation by air——→

Froth carrying sulphide ore particles

↓

Roasting in reverberatory furnace

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

$$ZnS + 2O_2 \rightarrow ZnSO_4$$

$$2ZnSO_4 \rightarrow 2ZnO + 2SO_2 + O_2$$
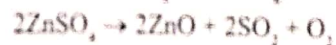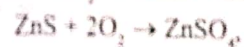
Reduction → $ZnO + C \rightarrow Zn + CO$

Purification by distillation at 950°C -1000°C

(by Electrolytic Refining)

↓

Anode: made up of impure metal,
Cathode: made up of pure Al sheet,
Electrolyte: solution of Zn sulphate
Pure Zn deposits at cathode

METALLURGY OF ALUMINIUM

$Al_2O_3 .2H_2O$ (Bauxite)
Electrolytic method

↓

Concentration of Bauxite

(a) Baeyer's Method: Bauxite ore $\xrightarrow{\text{roasted}}$
to convert FeO into Fe_2O_3

Roasted ore + NaOH $\xrightarrow[\text{solution} \quad 80 \text{ atm.}]{150°C}$ $NaAlO_2$

$\underset{\text{Sod.meta aluminate}}{NaAlO_2}$ $\xrightarrow[\text{In the presence of little } Al(OH)_3]{\text{Hydrolysis}}$ $\underset{\text{ppt.}}{Al(OH)_3}$ + NaOH

(b) Hall's Method

Bauxite ore + Na_2CO_3 $\xrightarrow{\text{Fused}}$ $NaAlO_2$

| Extract with water

Solution

| Heat to 50-60°C

CO_2 is circulated

↓

$Al(OH)_3 + Na_2CO_3$

Pure Al_2O_3 ← Heat to dryness

(c) Serpeck's Method

Bauxite ore + Coke + $\underset{\text{(from air)}}{N_2}$ $\xrightarrow{1800°C}$ AlN

$\xrightarrow{3H_2O}$ $\underset{\text{ppt.}}{Al(OH)_3}$ ↓ + NH_3 ↑

↓

Calcination

$2Al(OH)_3$ $\xrightarrow{1500°C}$ $\underset{\text{Anhydrous alumina}}{Al_2O_3}$ + $3H_2O$

↓

Electrolytic Reduction

Al_2O_3 is dissolved in Na_3AlF_6 and CaF_2

Cathode → Carbon lining

Anode → Graphite rods

$2Al_2O_3$ $\xrightarrow[950°C]{\text{Electrolysis}}$
→ Al (at cathode) 99.8% pure
→ O_2 (at anode)

electrolytic refining
liquation
distillation
refining by distribution law — ⑤ Refining
zone refining
Mond process / vapour-phase refining
van Arkel method

① crushing and grinding

(i) gravity separation or levigation or hydraulic washing
(ii) magnetic separation
(iii) hand picking
(iv) electrostatic separation
(v) froth floatation
(vi) leaching

smelting
auto reduction
reduction with hydrogen
electrolytic reduction
reduction with powerful reducing agent
aluminothermy
hydrometallurgical process — ④ conversion of metal oxide to free metal
amalgamation
poling
puddling — oxidation of impurities
bessemerisation
cupellation

metallurgy — ② concentration

③ conversion of metal to oxide — calcination / roasting

General principles of metallurgy

- Pyrometallurgy
- Hydrometallurgy
- Electrometallurgy

Thermodynamics of carbon reduction use of Ellingham diagrams in the selection of reducing agents

Pyrometallurgy → Smelting
- Extraction of tin from cassiterite
- Extraction of iron from haematite
  - concentration
  - calcination
  - smelting is carried out in presence of flux (lime stone) and coke (reducing agent)
  - Bessemerisation

Self reduction
- Extraction of copper from copper pyrites
  - Concentration
  - Roasting
  - Bessemerisation
  - Electrolytic refining
- Extraction of lead from galena
  - Concentration
  - Roasting
  - Reduction
    - self reduction
    - carbon reduction
  - Refining
    - Liquation method
    - Desilveration of lead
    - Electrolytic method

Extraction of silver from Argentite
- Concentration
- Roasting
- Cyanide process of complexation using NaCN
- Recovery of silver from solution
- Refining
  - Cupellation
  - Electrolytic

Extraction of gold
- Concentration
- Roasting
- Cyanide process of complexation using NaCN
- Recovery of gold from solution
- Cupellation
- Refining
  - Parting
  - Miller's process
  - Electrolytic

Extraction of low grade copper

Extraction of aluminium
- Baeyer's method
- Hall's method
- Serpeck's process
- Concentration
- Electrolytic reduction