- **Magnetic separation :** Impurities, magnetic in nature are passed over magnetic roller. The ore and the magnetic impurity are collected as two separate heaps. Used for haematite (ore of iron), chromite, etc.
- **Froth floatation :** On the basis of difference in wetting properties of the ore and the gangue particles with water and oil.

Powdered ore + water + collectors (pine oil) + Froth stabiliseres (*e.g.*, aniline)

↓ agitated by blowing air violently

Froth formed

↓ ↓

Lighter ore particles carried to the surface by foam | Heavier impurities sink to the bottom

- **Leaching (Chemical method) :**

Powdered ore treated with suitable reagent

↓ ↓

Ore gets dissolved | Impurities remains undissolved

↓ ↓

Recovered from the solution by a suitable chemical method. | Removed by filtration

– Used for ores of Al, Ag, Au, etc.

- **Extraction of metal from concentrated ore :**
  - **Conversion of the concentrated ore into oxides :**
    - **Calcination :** Commonly used for hydroxide or carbonate ores, it involves heating of the ore below its fusion temperature in absence of air in a reverberatory furnace.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$
$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

    - **Roasting :** Sulphide ores convert into oxides or sulphates when heated in a regular supply of air at a temperature below the melting point of the metal. In a reverberatory furnace, part of sulphide may also act as a reducing agent.

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$
$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$$

  - **Reduction of the oxide to metal :** For this reduction, various processes can be used which are called pyrometallurgical processes. These are
    - **Chemical reduction :** Reduction with Na and Mg metals.

$$TiO_2 + 2Mg \longrightarrow Ti + 2MgO$$
$$TiO_2 + 4Na \longrightarrow Ti + 2Na_2O$$

    - **Auto-reduction :** The metal is obtained either by simple roasting or by the reduction of its partially oxidised form. *e.g.*

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

    - **Aluminothermic reduction or Gold-Schmidt thermite process.**

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$
$$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn$$

    - **Smelting :** Reduction by carbon (as coal, coke, charcoal, CO, etc),

$$\underset{\text{Cassiterite}}{SnO_2} + 2C \xrightarrow{1473\text{-}1573\ K} Sn + 2CO$$
$$M_xO_y + yC \longrightarrow xM + yCO$$

  - **Displacement method :** Some metals are reduced through displacement by a more reactive metal, from the complexes.

e.g. $2M(CN)_2^- + Zn \longrightarrow Zn(CN)_4^{2-} + 2M$

where, M = Ag or Au

  - **Electrolytic method :** Used for highly electropositive elements of group 1 and 2, which are found as their chlorides or oxosalts (converted to chlorides later) and their electrolysis is done in fused or molten form. The metal ions are deposited at negative electrode (cathode).

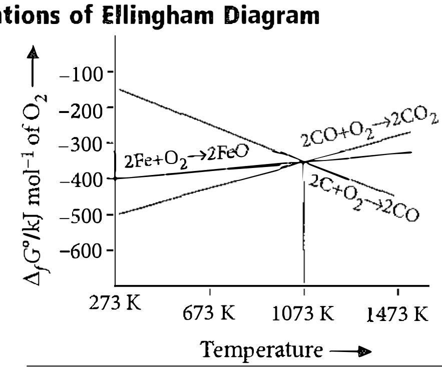
Thermodynamic Principles of Metallurgy

- Thermodynamics help in understanding the conditions of temperature and selecting suitable reducing agent in a metallurgical process.
- Gibb's Helmholtz equation is used to check the feasibility of a reduction.

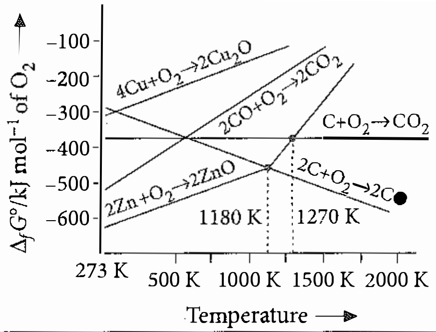
  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ if $\Delta G^\circ < 0$, the reduction is feasible.

  For a reaction, enthalpy change is fixed but temperature factor could be controlled and be the deciding factor for feasibility of that reaction.
- **Ellingham diagrams :** The plots between $\Delta_f G^\circ$ of oxides of elements *vs*. temperature are called Ellingham diagrams.
  - It provides a sound idea about selecting a reducing agent in reduction of oxides.
  - Such diagrams help in predicting the feasibility of thermal reduction of an ore. ΔG must be –ve at a given temperature for a reaction to be feasible.

Applications of Ellingham Diagram



Ellingham diagram for formation of FeO from Fe, CO from C and CO_2 from CO



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

Electrochemical Principles of Metallurgy

- Electrolysis is used to carry out the reduction of a molten metal salt.
- The electrochemical principles of this method can be understood through the equation, $\Delta G° = nFE°$
- More reactive metals have large negative values of the electrode potential so, their reduction is difficult.
- If the difference of two $E°$ values corresponds to a positive $E°$ and consequently negative $\Delta G°$, then the less reactive metal will come out of the solution and the more reactive metal will go to the solution.

Key points

At times, a coupled reaction helps the reduction feasible. For example,

$$MO + C \longrightarrow M + CO,\ \Delta G_1 \text{ is positive.}$$

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2,\ \Delta G_2 \text{ is negative.}$$

This reaction may be of great metallurgical use, if $\Delta G_1 + \Delta G_2$ = negative

- **Purification or refining of crude metals**

	Methods	Metals purified
1.	Distillation	Used for easily volatile metals like Zn, Cd, Hg, etc.
2.	Electrolysis	Copper, gold, silver, lead, aluminium. Impure metal is made anode and the pure metal is cathode. The net result is the transfer of pure metal from anode to cathode.
3.	Liquation	Impure metal can be made to flow on a sloping surface and thus separated from higher melting impurities. Used for metals like Sn, Bi, Pb, Hg, etc.
4.	Zone refining	Metals of high purity are obtained. Silicon, germanium, boron, gallium, indium are purified (which are used in semiconductors). It is based on the fact that impurities are more soluble in the melt than in the pure metal.
5.	Vapour phase refining	In Mond's process for the refining of nickel. $\underset{\text{impure}}{Ni + 4CO} \xrightarrow{80°C} \underset{\text{gaseous compound}}{Ni(CO)_4} \xrightarrow{200°C} \underset{\text{pure}}{Ni} + 4CO\uparrow$ In van Arkel method for zirconium $\underset{\text{impure}}{Zr} + 2I_2 \xrightarrow{600\ K} \underset{\text{vapour}}{ZrI_4} \xrightarrow{1800\ K} \underset{\text{pure}}{Zr} + 2I_2$
6.	Chromatographic methods	This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent *e.g.*, lanthanoids are purified by using ion exchange as adsorbent.

FLOW CHART FOR THE EXTRACTION OF ALUMINIUM

Aluminium ore, $Al_2O_3 \cdot xH_2O$ (Bauxite)

(a) Baeyer's Process (leaching) :

Bauxite (Powdered) + $NaOH_{(aq)}$

↓ 473 – 523 K, 35 – 36 bar

$2\,Na[Al(OH)_4]$ + impurities
Sodium meta-aluminate (Soluble) (insoluble)

↓ Filter (to remove impurities)

$2\,Na[Al(OH)_4] + 2CO_2$

↓

$Al_2O_3 \cdot xH_2O + NaHCO_3$

↓ 1200°C

$Al_2O_3 + xH_2O$

(b) Hall's Process :

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

↓ Extracted with water

Solution

↓ Warmed 50–60°C

CO_2 is circulated

↓

$Al(OH)_3$ ppt. + Na_2CO_3 (→ Na_2CO_3 returned to the start)