Unit 6

General Principles and Processes of Isolation of Elements

OCCURRENCE

- The most abundant element in the earth's crust is **oxygen**. Next to oxygen is the element **silicon**.
- The most abundant metal in the earth's crust is **aluminium**.
- The most abundant transition metal in the earth's crust is **iron**.
- About 88 elements are naturally occurring while the remaining have been synthesized.
- The natural substances in which the metals or their compounds occur in the earth are called **minerals**. The minerals from which the metals can be conveniently and economically extracted are known as **ores**.
- All ores are minerals but all minerals are not ores.
- Sometimes lumps of pure metals are also found. These are termed as **nuggets**.

Principal Types of Minerals

Type	Mineral
Uncombined metals	Ag, Au, Bi, Cu, Pd, Pt
Carbonates	$CaCO_3$ (calcite, limestone), $MgCO_3$ (magnesite), $CaCO_3 \cdot MgCO_3$ (dolomite), $PbCO_3$ (cerussite), $ZnCO_3$ (smithsonite)
Halides	CaF_2 (fluorite), NaCl (halite), KCl (sylvite), Na_3AlF_6 (cryolite)
Oxides	$Al_2O_3 \cdot 2H_2O$ (bauxite), Cu_2O (cuprite), MnO_2 (pyrolusite), SnO_2 (cassiterite), Al_2O_3 (corundum), Fe_2O_3 (haematite), TiO_2 (rutile), ZnO (zincite), Fe_3O_4 (magnetite)
Phosphates	$Ca_3(PO_4)_2$ (phosphate rock), $Ca_5(PO_4)_3OH$ (hydroxyapatite)
Silicates	$NaAlSi_3O_8$ (albite), $Mg_3(Si_4O_{10})(OH)_2$ (talc)
Sulphides	Ag_2S (argentite), CdS (greenockite), Cu_2S (chalcocite), FeS_2 (pyrite), HgS (cinnabar), PbS (galena), ZnS (sphalerite)
Sulphate	$BaSO_4$ (baryte), $CaSO_4$ (anhydrite), $MgSO_4 \cdot 7H_2O$ (epsom)

- Silicates and aluminates are the most abundant minerals but are difficult to concentrate and reduce.

Metal	Occurrence
Aluminium (Most abundant metal 8.3% of earth's crust)	Bauxite ($AlO_x(OH)_{3-2x}$ or $Al_2O_3 \cdot xH_2O$) Corundum (ruby, emerald) (Al_2O_3) Diaspore ($Al_2O_3 \cdot H_2O$) Cryolite (Na_3AlF_6)
Copper Only 0.0001% of earth's crust	Chalcopyrites ($CuFeS_2$) Chalcocite (Cu_2S), Cuprite (Cu_2O) Bornite (Cu_5FeS_4), Malachite (green) ($CuCO_3 \cdot Cu(OH)_2$) Azurite (blue) ($2CuCO_3 \cdot Cu(OH)_2$)
Zinc Mainly in combined state, traces in native state found in Melbourne	Zinc blende (ZnS) Calamine ($ZnCO_3$) Zincite (ZnO) Willemite (Zn_2SiO_4)
Iron Fourth most abundant element	Magnetite (Fe_3O_4), Haematite (Fe_2O_3) Limonite ($Fe_2O_3 \cdot 3H_2O$) Siderite ($FeCO_3$), Iron pyrites (FeS_2)

METALLURGY

- The process of extraction of metals from their ores is called **metallurgy**.
- Metallic ores are often found to contain certain sand, clay, quartz, felspar, silicates, mica etc. These unwanted impurities are called gangue or matrix.

Metallurgy Involves Three Major Steps

I. Concentration of the ore
II. Isolation of the metal from concentrated ore
III. Purification of the metal

- **Concentration of ores :** It is the process of gangue removal. The common methods are :
  - **Gravity separation :** Based on the difference in the specific gravity of gangue and ore particles.

Powdered ore
↓ fed into
Stream of running water
↓ Lighter impurities washed away
↓ Heavier ore particles left behind

– Used for oxide and carbonate ores.

- **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 → Recovered from the solution by a suitable chemical method.

Impurities remains undissolved → 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

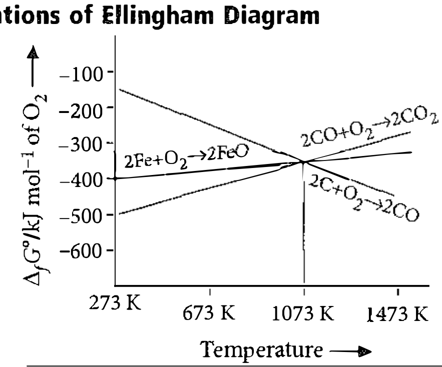
- Thermodynamics help in understanding the conditions of temperature and selecting suitable reducing agent in a metallurgical process.
- Gibb's Helmholtz equation is used to check the feasibility of a reduction.

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