6. General Principles and Processes of Isolation of Elements

Occurrence of metals:

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

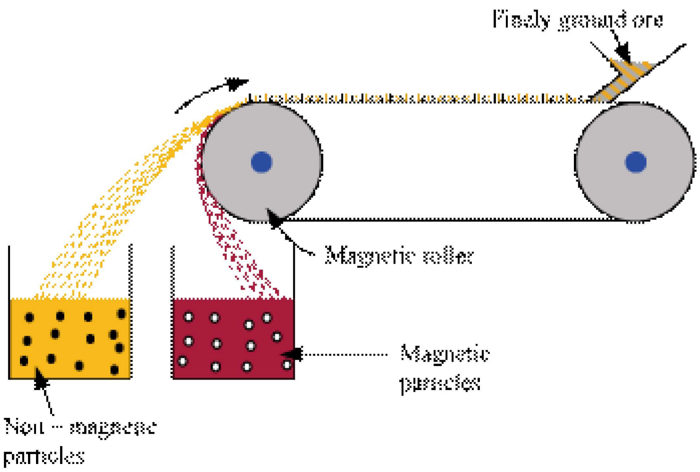
- **Metallurgy**: Process of extracting pure metal from their ore
- **Minerals**: Mixture of metal compounds, soil, sand, limestone and rock
- **Gangue**: Impurities present in ore like mud, silica etc.
- **Ores**: Minerals from which metals can be extracted economically at low cost and with minimum cost
- **Flux**: Substance added in furnace to remove gangue
- **Slag**: The fusible mass formed when flux combined with gangue
- **Smelting**: Process of extracting metal from their oxide ores by reducing the roasted oxides

The major steps involved in the extraction and isolation of metals from ores are:

1. Crushing and grinding ore
2. Concentration of the ore
3. Roasting and Calcination of the ore
4. Reduction of the metal oxide
5. Refining of the pure metal

Concentration of ores:

- Hydraulic washing: It is the washing away of lighter gangue particles from the heavier ore. It is based on the gravity difference between the ore and the gangue particles.
- Magnetic separation: This separation is carried out if either the ore or the gangue is attracted by a magnetic field.



- Froth floatation method: This method is used for removing gangue from sulphide ores. 'Depressants' are used for separating two sulphide ores. E.g., for separating ZnS and PbS, NaCN is used as the depressant.

- Leaching: If the ore is soluble in some suitable solvent, then this process is used. For example, ores of aluminium (bauxite), silver and gold
    1. **Leaching of alumina**

$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)}$ ® $2Na[Al(OH)_4]_{(aq)}$

$2Na[Al(OH)_4]_{(aq)} + CO_{2(g)}$ ® $Al_2O_3.xH_2O_{(s)} + 2NaHCO_{3(aq)}$

$$Al_2O_3.xH_2O_{(s)} \xrightarrow{1470\,K} Al_2O_{3(s)} + xH_2O_($$

Isolation of crude metal from concentrated ore: It involves two steps –
(i) Conversion into oxide and (ii) Reduction of the oxide to metal

- Conversion into oxide:

1. Calcination → Involves heating
   Generally, carbonate ores are converted into oxides by this process.

   $$ZnCO_{3(s)} \xrightarrow{\Delta} ZnO_{(s)} + CO_{2(g)}$$

1. Roasting → Involves heating in a regular supply of air, at a temperature below the melting point of the metal.

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

   Generally, sulphide ores are converted into oxides by this process.

Slag → $FeSiO_3$

- Reduction of the oxide to metal:
  Involves heating with some reducing agents such as C, CO or another metal.

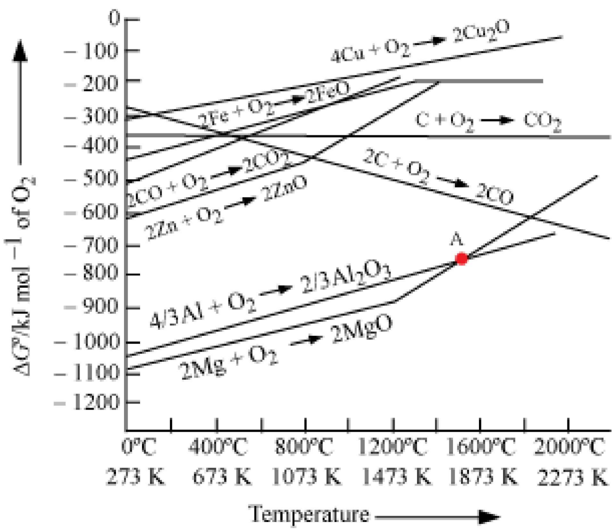
Thermodynamic principles of metallurgy: For any process, the change in Gibbs energy at a temperature is given by

$\mathbf{\Delta G} = \Delta H - T\Delta S$

and $\Delta G^{\Theta} = -RT \ln K$

A reaction will proceed when the value of ΔG is negative.

- Applications:



If $\Delta G_{(X, XO)}$ is lower than $\Delta G_{(Y, YO)}$, then X can reduce YO.

Extraction of iron from its oxides:

1. Reaction taking place in a blast furnace
2. At 500 – 800 K

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$$

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$

1. At 900 – 1500 K

$$C + CO_2 \rightarrow 2CO$$

$$FeO + CO \rightarrow Fe + CO_2$$

1. Limestone is decomposed to CaO, which removes silicate impurity as slag.

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SiO_2 \rightarrow CaSiO_3 \text{ (slag)}$$

1. Pig iron is the iron obtained from a blast furnace, which contains about 4% carbon and impurities like S, P, Si, Mn in smaller amounts.
2. Cast iron (contains about 3% carbon) is obtained by melting pig iron with scrap iron and coke, using hot-air blast.

1. **Extraction of copper from cuprous oxide:**

$$Cu_2O + C \rightarrow 2Cu + CO$$

1. Copper matte contains Cu_2S and FeS. It is put in the silica-lined converter to convert the remaining Cu_2S/Cu_2O into metallic copper.

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

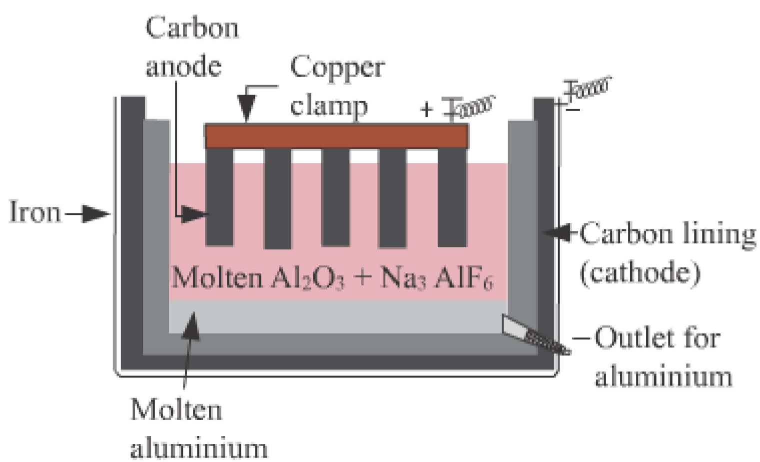
$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

1. Extraction of zinc from zinc oxide:

$$ZnO + C \xrightarrow{\text{coke, 673 K}} Zn + CO$$

Electrochemical principles of metallurgy: A more reactive metal displaces a less reactive one from its salt solution.

- **Extraction of aluminium:**



1. Purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 to lower the melting point and bring conductivity.
2. The overall reaction –

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

1. This electrolytic process is known as Hall-Heroult process.
2. The electrolytic reactions are –

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

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

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

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  - **Copper from low-grade ores and scraps:**

  Copper is extracted by hydrometallurgy from low-grade ores. The solution containing Cu^{2+} is treated with scrap iron or H_2.

  $$Cu^{2+}{}_{(aq)} + H_{2(g)} \rightarrow Cu_{(s)} + 2H^+{}_{(aq)}$$

Extraction of Chlorine from Brine

- oxidation reaction

$$2NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)} + Cl_{2(g)}$$

- $E^0 = 2.2$ V
- Requires an external emf greater than 2.2 V. But the
- Electrolysis requires an excess potential to overcome some other hindering reactions.
- Electrolysis of molten NaCl produces Na metal in the place of NaOH.

Extraction of Gold and Silver

- Metal is leached with NaCN or KCN.
- Ag is oxidised to Ag^+ and Au is oxidised to Au^+

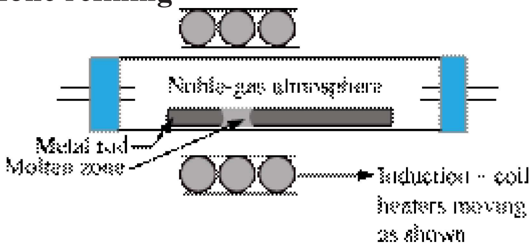
$$4M_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(aq)} + O_{2(g)} \longrightarrow 4[M(CN)_2]^-_{(aq)} + 4OH^-_{(aq)}$$
$$(M = Ag \text{ or } Au)$$
$$2[M(CN)_2]^-_{(aq)} + Zn_{(s)} \longrightarrow [Zn(CN)_4]^{2-}_{(aq)} + 2M_{(s)}$$

Refining (Purification):

- **Distillation** –
  The impure forms of low-boiling metals like zinc and mercury are evaporated to obtain pure metals as distillate.
- **Liquation** –
  Low-melting metals (like tin) are separated from higher-melting liquids by allowing them to flow on a sloping surface.
- **Electrolytic refining** –
  Anode: $M \rightarrow M^{n+} + ne^-$
  Cathode: $M^{n+} + ne^- \rightarrow M$

a. Impure metal is taken as anode and a strip of pure metal is taken as cathode.
b. Copper and zinc are refined by this process.
c. Anode mud obtained during electrolytic refining of copper contains antimony, selenium, tellurium, silver, gold and platinum.

- **Zone refining –**



a. Principle – The impurities are more soluble in the molten state than in the solid state of a metal.
b. Germanium, silicon, boron, gallium, indium are refined by this process.

- **Vapour-phase refining –**

a. **Requirements –**
b. The metal should form a volatile compound with an available reagent.
c. The volatile compound should be easily decomposed so that it can be recovered easily.

a. Mond process for refining nickel:

$$Ni + 4CO \xrightarrow{330-350\ K} Ni(CO)_4$$

$$Ni(CO)_4 \xrightarrow{450-470\ K} Ni + 4CO$$

a. van Arkel method for refining ziroconium (Zr) or titanium (Ti):
Used for removing oxygen and nitrogen present as impurities

$$Zr + 2I_2 \rightarrow ZrI_4$$

$$ZrI_4 \rightarrow Zr + 2I_2$$

- Chromatographic methods:

a. Principle – Different components of a mixture are differently adsorbed on an adsorbent.
b. Chromatography involves a mobile phase and a stationary phase.
c. There are several chromatographic techniques –
d. Paper chromatography
e. Column chromatography
f. Gas chromatography