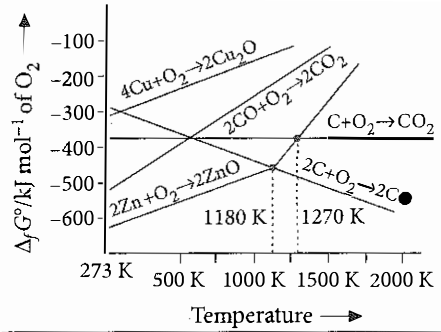


Ellingham diagram showing the formation of Cu_2O from Cu, ZnO from Zn, CO from C and CO_2 from C and CO

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, $\Delta G^\circ = nFE^\circ$
- 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 ΔG°, 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,

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

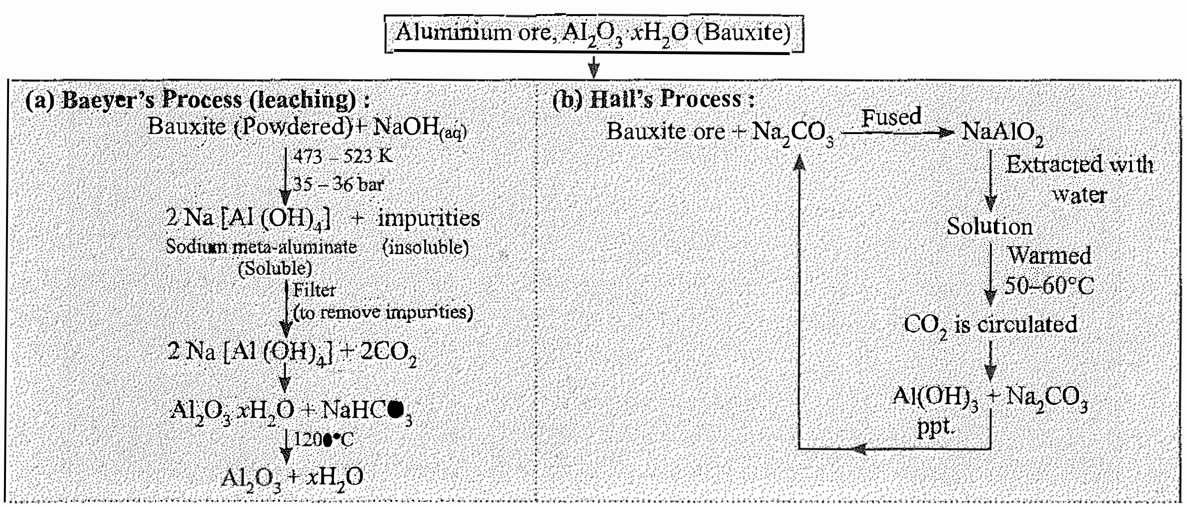
$$CO + \frac{1}{2} O_2 \longrightarrow CO_2, \Delta G_2 \text{ is negative.}$$

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. $\underset{\text{impure}}{Ni + 4CO} \xrightarrow{80^\circ C} \underset{\text{gaseous compound}}{Ni(CO)_4} \xrightarrow{200^\circ C} \underset{\text{pure}}{Ni} + 4CO\uparrow$ 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



(c) Serpeck's Process :

$$\text{Bauxite ore} + \text{Coke} \xrightarrow[N_2]{1800^\circ C} AlN \xrightarrow{H_2O} \underset{\text{ppt.}}{Al(OH)_3} + \underset{\text{By-product}}{NH_3}$$

↓

Calcination

$$Al(OH)_3 \xrightarrow{1500^\circ C} \underset{\text{Anhydrous alumina}}{Al_2O_3}$$

↓

Electrolytic Reduction (Hall - Heroult process)

Electrolyte Al_2O_3 dissolved in Na_3AlF_6 and CaF_2

Cathode — Carbon lining **Anode** — Graphite rods

$$Al_2O_3 \xrightarrow[950^\circ C]{\text{Electrolysis}} \underset{99.8\%\text{pure}}{Al} + O_2$$

↓

Electrolytic Refining

(Hoope's process)

↓

Pure Al (99.98% pure)

FLOW CHART FOR THE EXTRACTION OF COPPER

Copper pyrites

($CuFeS_2$)

↓

Crushed and sieved

↓

Concentration by froth floatation

Powdered ore + water + Potassium xanthate + pine oil ⟶ sulphide ore in the froth

↓

Roasting in reverberatory furance in presence of air

$$S + O_2 \longrightarrow SO_2\uparrow$$

$$4As + 3O_2 \longrightarrow 2As_2O_3\uparrow$$

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

↓

Silica + Coke ⟶ Roasted ore

↓

Smelting in blast furnace in presence of air

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

$$FeO + SiO_2 \longrightarrow FeSiO_3 \text{ (Slag)}$$

↓

$\xrightarrow{\text{Silica}}$ Matte (Cu_2S, FeS)

↓

Bessemerisation in bessemer converter in presence of air

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

$$FeO + SiO_2 \longrightarrow FeSiO_3 \text{ (Slag)}$$

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

$$2Cu_2O + Cu_2S \xrightarrow[\text{reduction}]{\text{Auto}} 6Cu + SO_2$$

↓