Chapter 18

General Principles and Processes of Isolation of Metals

IMPORTANT ORES AND MINERALS

Iron

(i) Magnetite	:	Fe_3O_4
(ii) Haematite	:	Fe_2O_3
(iii) Limonite	:	$Fe_2O_3.3H_2O$
(iv) Iron pyrite	:	FeS_2
(v) Copper pyrites	:	$CuFeS_2$
(vi) Siderite	:	$FeCO_3$

Copper

(i) Cuprite	:	Cu_2O
(ii) Copper pyrites	:	$CuFeS_2$
(iii) Copper glance	:	Cu_2S
(iv) Bornite	:	Cu_2FeS_3
(v) Malachite	:	$CuCO_3.Cu(OH)_2$
(vi) Azurite	:	$[2CuCO_3].Cu(OH)_2$

Zinc

(i) Zincite	:	ZnO
(ii) Calamine	:	$ZnCO_3$
(iii) Zinc blende	:	ZnS
(iv) Willemite	:	Zn_2SiO_4

Aluminium

(i) Corundum	:	Al_2O_3
(ii) Diaspore	:	$Al_2O_3.H_2O$
(iii) Bauxite	:	$Al_2O_3.2H_2O$
(iv) Cryolite	:	Na_3AlF_6
(v) Feldspar	:	$KAlSi_3O_8$
(vi) Mica	:	$K_2O.3Al_2O_3.6SiO_2.2H_2O$

ALUMINIUM

Al is most abundant metal in earth crust. Important ores are Bauxite $Al_2O_3.2H_2O$; Diaspore $Al_2O_3.H_2O$; Corundum Al_2O_3; Feldspar $KAlSi_3O_8$; Cryolite Na_3AlF_6. It is usually extracted from bauxite through the following steps:

Purification of Bauxite

Bayer's Process

(a) Red bauxite containing the impurity of iron oxide is concentrated by leaching with NaOH.

$$2NaOH + Al_2O_3 \rightarrow 2NaAlO_2 + H_2O$$

(b) Sodium meta aluminate thus obtained is soluble in water while impurities of iron oxides remain insoluble. The solution is diluted with water and agitated to get a precipitate of $Al(OH)_3$.

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$$

(c) On strong heating this precipitate gives alumina.

Hall's Process

(a) **Electrolysis of alumina (Hall Heroult's process) :** purified alumina is then mixed with cryolite to lower down its melting point, cryolite also increases, the conductance and molten cryolite acts as solvent.

$$Na_3AlF_6 \rightarrow 3NaF + AlF_3$$

$$AlF_3 \rightarrow Al^{3+} + 3F^-$$

At cathode : $Al^{3+} + 3e^- \rightarrow Al$

At anode : $2F^{\ominus} \rightarrow F_2 + 2e^-$

(b) Aluminium thus obtained is refined by Hoope's electrolytic process using molten cryolite and BaF_2 as electrolyte.

IRON

Ores : Haematite Fe_2O_3, Magnetite Fe_3O_4; Limonite $Fe_2O_3.3H_2O$; Iron pyrites FeS_2; Siderite $FeCO_3$.

1. **Types**

   (a) Pig iron or cast iron : 2 to 4.5% C with some impurities like S, Si, P, Mn. It cannot be welded.

   (b) Wrought iron : purest form of Fe (0.2 - 0.5% C).

   (c) Steel : 0.1 to 1.5% C along with some other elements like Cr, Mn, Ni etc.

2. **Extraction from Haematite :** It is concentrated by washing with water. Then it is roasted with a little of coal in a reverberatory furnace. During roasting moisture is removed. Impurities of As, S and P are converted into their gaseous oxides. Roasted mass is then reduced by mixing with coke and limestone in a blast furnace in the ratio of 8 : 4 : 1 (Smelting).

THERMODYNAMICS OF METALLURGY

The method employed for extracting a metal from its ores depends on the nature of the metals and that of the ore may be related to the position of the metal in the electrochemical series. In general, metals with $E° < -1.5$ volt yield compounds which are very difficult to reduce and electricity is usually used for the isolation of such metals. On the other hand, noble metals with $E° > 0.5$ volt form easily reducible compounds. A metal higher up in the electrochemical series should be more difficult to reduce to metallic form. As we move down in the electrochemical series, the reduction becomes more and more easy. E° of metal provides some idea regarding the selection of an appropriate method for extracting the metal from its compounds.

Free energy is related to standard cell potential

$\Delta G° = -nF E°_{cell}$

$n \rightarrow$ Number of moles electrons

$F \rightarrow$ Faraday constant 96500 C.

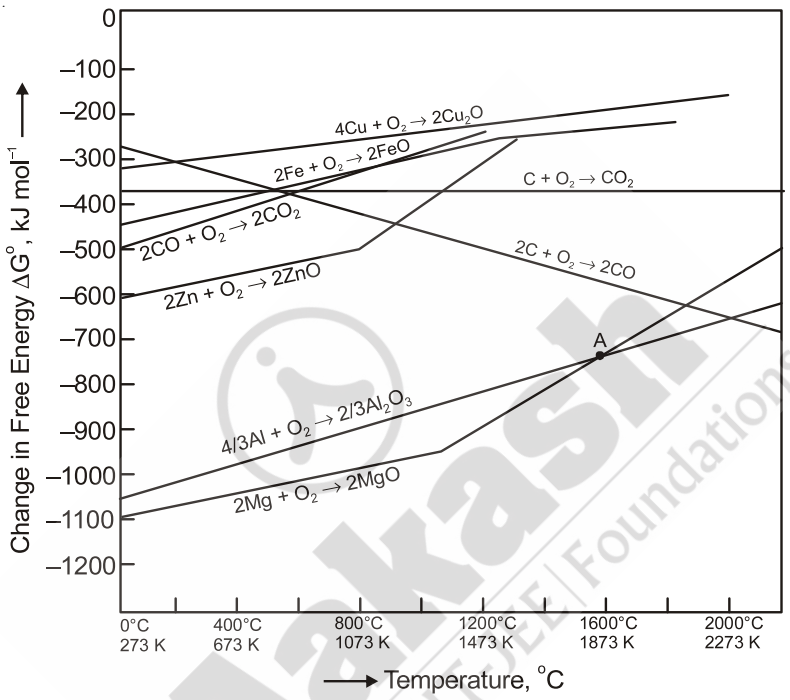
In order that the reduction of oxide, halide or sulphide ore by an element may take place simultaneously at a given temperature and pressure, there is decrease in the free energy of the system ($-\Delta G$).

More the negative value of ΔG, higher is the reducing power of an element. The free energy change (ΔG) is related to the heat change (ΔH) as well as to the product of temperature. [$\Delta G = \Delta H - T\Delta S$]

For a reaction, $2M + O_2 \rightarrow 2MO$

ΔG becomes smaller with the increase in temperature. This is because the gaseous reactant oxygen is consumed in the reaction leading to the decrease in randomness or entropy of the system hence ΔG becomes negative. With further increase in temperature, $T\Delta S$ becomes more negative value. Since the term $T\Delta S$ is high ΔG is less.

$\therefore$ Reaction becomes more feasible.



Ellingham diagram showing the change in free energy ΔG with temperature for oxides (based on 1 g mole of dioxygen in each case)

❑ ❑ ❑