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Unit - I - [B]

B- Extraction of Elements

The metals are found in nature in free state or combined state

① **Free state OR Native state:**

The metals which does not reacts with air, water carbondioxides OR surroundings are called as native metal or native or free state.

eg platinum, gold

② **Combined state:**

The metals which are found in the form of compound are called as combined state.

These elements are found in the nature in the form of minerals or ores.

Minerals:-

The naturally occuring substance in which metals are present in free state or combined state is called minerals.

ores:

A mineral containing high percentage of metal, from which the metal can be extracted economically and profitabally is called as ores.

That means ores are minerals but minerals are not ores.

The process of extraction of pure metals from its ore is called as **Metallurgy**.

Depending upon nature of ore, % of metal in ore, different methods for seperation methods are used.

Principles involved in Extraction of Elements.

The different methods for seperation and extraction are divided into five classes.

① **Mechanical separation of elements that exist in the native form:**

The less reactive elements like Pt, Au, Ag, Cu, Ru, Pd can be seperated by this method.

liquid mercury associated with cinnabar (HgS) can be seperated by this method. also
Diamonds found in earth crust can be seperated by this method.
The atmosphere contain traces of noble gases like argon, helium, neon can be seperated by fractional distillation of liquid air.

(ii) Thermal decomposition methods:-
When compounds are heated, they decomposes into its elements.
eg(1) When sodium azide (NaN_3) is heated, they decompose into sodium and pure nitrogen. This method is useful for making pure nitrogen in the laboratory.
eg (2) Mond process for purification of nickel.
When nickel tetracarbonyl [$Ni(CO)_4$] is heated 400K, it decomposes to give pure nickel and CO gas.

$$Ni(CO)_4 \xrightarrow{400K} Ni + 4CO$$

(iii) Displacement of one metal by another
SOP → Standard potential
The basic principle involved in the displacement reaction is that the element having higher SOP displaces the element having lower SOP from solution. That can be explain on the basis of electrochemical series.
eg Scrap iron can be used for displacement of copper from copper sulphate by

$$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu$$

(IV) High temperature chemical reduction method.
This is the commercial method for the extraction of the elements. Generally carbon is used as reducing agent. A very high temp.

is required therefore blast Furnace is generally used.

Some examples are

(a) Reduction by carbon :-

$$Fe_2O_3 + C \xrightarrow[\text{Furnace}]{\text{Blast}} Fe$$

$$ZnO + C \xrightarrow{1200^\circ c} Zn$$

$$MgO + C \xrightarrow{2000^\circ c} Mg$$

$$Ca_3(PO_4)_2 + C \xrightarrow[\text{Furnace}]{\text{Electric}} P$$

(b) Reduction of oxides - with hydrogen

$$Co_3O_4 + 4H_2 \longrightarrow 3Co + 4H_2O$$

$$NH_4[MoO_4] + 2H_2 \longrightarrow Mo + 4H_2O + NH_3$$

$$GeO_2 + 2H_2 \longrightarrow Ge + 2H_2O$$

(c) Self Reduction :-

The sulphide type of ore (PbS, CuS, Sb_2S) is roasted in air and converted into oxide and then futher heated in absence of air called as self reduction.

eg $$CuS \xrightarrow[\text{in air}]{\text{Roasted}} [2CuO + CuS]_{\text{mixture}} \xrightarrow[\text{in absence of air}]{\text{Roasted}} 3Cu + SO_2$$

(d) Reduction by another method :

If carbon as a reducing agent is not suitable for reduction then reduction is carried out by highly electropositive metals like Al.

eg Aluminum metal liberate large amount of energy (1675 KJ/mol). This is the basis for Thermite process.

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

$$B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3$$

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$$

(V) Electrolytic Reduction

The strongest reducing agent is an electron and reduction occurs at cathode. It may be performed

(a) In aqueous solution, copper and zinc are obtained by electrolysis of aq. solution of their sulphates

(b) In solvents other than water, It may be carried out eg. Fluorine reacts violently with water. so it is produced by electrolysis of KHF_2 dissolved in anhydrous HF

(c) In fused ionic salt

eg NaCl, both sodium and chlorine are obtained from the electrolysis of fused NaCl.

Factors influencing the choice of extraction process

For the selection of extraction process, following points should be ~~rembered~~ remembered.

(i) Reactivity of metal to exist in free state for mechanical separation process.

(ii) Stability of their compounds to heat, for decomposition process.

(iii) If the element exist in an ionic compound and is stable in water then one has to select proper elements in the electrochemical series for displacement process.

(iv) occurance of element as sulphide ore for roasting or as oxide for reduction - using carbon or other reducing agents eg Mg, Al, Na. etc.

(v) If all the above methods cannot be employed then electrolytic reduction is to be carried out

Thermodynamics of Reduction process

We know that metal exist in combined state in the form of ore and for obtaining the metal from its ore, reducing agent at high temp. is used. But to choose most economical reducing agent and reaction conditions, the concept of thermodynamic is used.

Entropy of solid and liquid = 0
—"— gas = +ve

Thermodynamics can be used to identify which reactions are spontaneous (i.e have a natural tendency to occur)

For spontaneous process, free energy change (ΔG) must be negative.

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

where ΔH is enthalpy change = $(H_2 - H_1)$
T is absolute Temp.
ΔS is entropy change = $(S_2 - S_1)$

(1) Consider the reaction of formation of oxide

$$M_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow MO_{(s)}$$

for this reaction, ΔH is negative.

$\Delta S = S_2 - S_1$
= Entropy of product − Entropy of reactant
= $0 - [0 + \frac{1}{2}]$
= $-\frac{1}{2}$
= −ve

ΔS is also negative ~~Therefore~~ because volume of gaseous product is less than volume of gaseous reactant. Therefore at low temperature, ΔG is ~~negative~~ positive
But with increase in temperature, ΔG becomes +ve.
Therefore oxide formation takes place with increase in temp.

(2) Consider the formation of CO from carbon

$$2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)}$$

| $\Delta S = S_2 - S_1$
| $= 2 - [0+1]$
| $= 1 = +ve$

For this reaction. ΔH is −ve, ΔS is +ve because volume of gaseous product is greater than vol^m of gaseous reactant

$\because \Delta G = \Delta H - T\Delta S$

In this eq^n, $T\Delta S$ becomes −ve so ΔG decrease with increase in temparature

(ii) Consider the formation of CO_2 from carbon

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$

For this reaction, ΔH is –ve and $\Delta S = 0$ because vol^m of gaseous product is equal to vol^m of gaseous reactant

$\Delta S = S_2 - S_1 = 1 - (0+1) = 0$

Ellingham diagram for oxides and its importance

When we plot a graph of free energy change (when one gram ~~molecule~~ molecule of O_2 is used) with temperature for the reaction of metal to their oxide is called as Ellingham diagram.

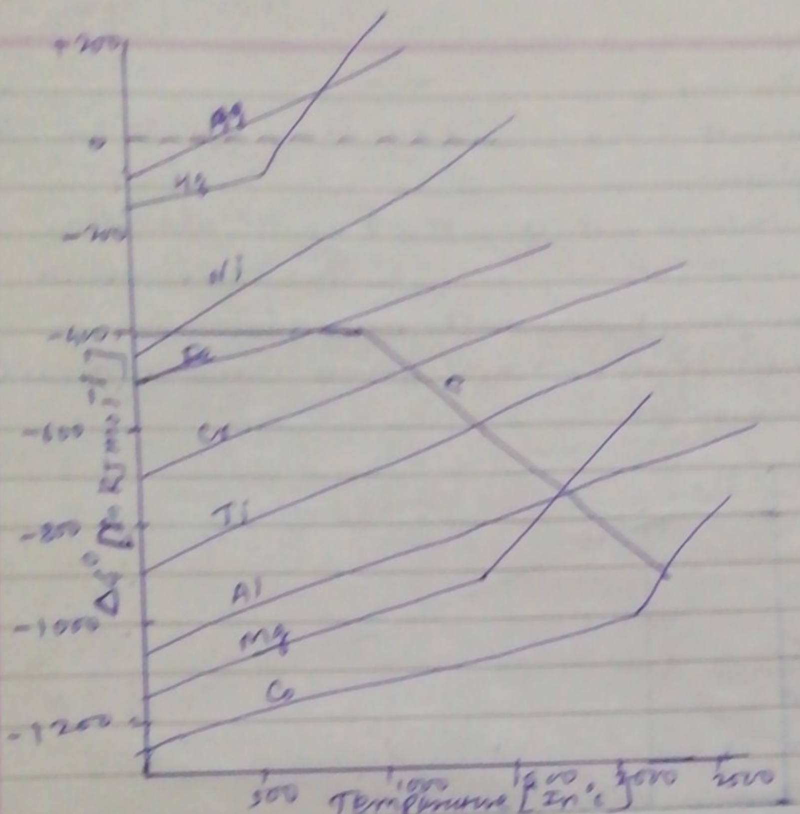
Important features of Ellingham diagram

1. The graph for formation of metal oxide is straight line with upward slope because free energy change (ΔG) increases with increase in temparature.
2. There is sudden change in slope, this indicate that there is change in phase.
3. The temperature, where a line crosses $\Delta G = 0$, the free energy change for formation of oxide is +ve and oxides becomes unstable and decompose into metal and oxygen

Below this temparature, the free energy change for the formation of oxide is –ve and oxide becomes stable.

For oxides of Ag, Au and Hg, the graph is at upper part in Ellingham diagram which can decomposed easily at lower temp. Therefore they can be extracted by thermal decomposition of their oxides.

4. The metal can reduce the oxide of other metal which is present above in the Ellingham diagram. because free energy becomes more negative by an amont equal to difference between two graphs at perticular temperature. eg Al reduces FeO, CrO and NiO in the Thermite process but Al cannot reduces MgO below 1500°c because Mg is present above Al.



Carbon reacts with oxygen in ways as

$$C + O_2 \longrightarrow CO_2 \quad \text{—— (i)}$$

$$2C + O_2 \longrightarrow 2CO \quad \text{—— (ii)}$$

(i) In first reaction, the vol^m of CO_2 produced is same as that of ~~oxygen~~ volume of oxygen used Therefore entropy change is negligible and ΔG slightly changes with temp. Therefore graph is horizontal.

(ii) In second reaction, ΔS is +ve and therefore ΔG is −ve with increase in Temp. so the line on Ellingham diagram for $C \rightarrow CO$ slopes downwards.

(iii) The two lines for $C \longrightarrow CO$ and $C \rightarrow CO_2$ crosses at about 710°C. ~~Above~~ Below this temp. formation of CO_2 is preferred but above 710°C, formation of CO is preferred.

(iv) From this it is cleared that. Carbon is used as reducing agent in many metal oxide because $\Delta G^\circ/T$ line for $C \rightarrow CO$ slopes ~~downward~~ downward and present below all other graphs for metal/metal oxides at sufficiently high temperature.

(v) But use of carbon for extracting metals has some limitations

(a) The reduction of very stable oxides like TiO_2, Al_2O_3, MgO is theoretically possible but requirement of high temperature cannot be fullfilled.

(b) At high temp., many metals reacts with carbon & forms carbides.