6. GENERAL PRINCIPLES AND PROCESS OF ISOLATION OF ELEMENTS

Most of the metals are present in nature in the form of their compounds. The metallic compounds present in the earth crust are called **minerals**. All minerals cannot be used for the extraction of metals. A mineral from which a metal can be extracted conveniently and profitably is called **ore**.

For e.g. Bauxite is the ore of Aluminium, Haematite (Fe_2O_3), Magnetite (Fe_3O_4), iron pyrites (FeS_2) etc. are the ores of iron and copper pyrites ($CuFeS_2$), Malachite [$CuCO_3.Cu(OH)_2$], Cuprite (Cu_2O) etc. are the ores of copper.

The process of extraction of a metal from its ore is called **metallurgy**. The various steps involved in metallurgy are concentration of the ore, extraction of the metals from the concentrated ore and refining or purification of the crude metal.

i)   Concentration of the ore

The removal of impurities from the ore is called concentration of the ore. The impurities present in the ore are called gangue. Depending on the nature of the impurities, any one of the following methods can be used.

a) **Hydraulic washing**: This method is used when the gangue is lighter than the ore. The powdered ore is washed in a stream of water. The lighter gangue particles are washed away leaving behind the ore particles.

b) **Magnetic separation**: It is based on difference in the magnetic properties of the ore components. For this method either the ore or the gangue is magnetic. The powdered ore is carried on a conveyer belt which passes over a magnetic roller. The magnetic materials are collected near the magnetic roller but the non-magnetic materials are dumped away from the roller.

c) **Froth floatation**: This method is used for the concentration of the sulphide ores. In this process, a suspension of the powdered ore is made with water. To this collectors (e.g. pine oil, fatty acid, xanthates etc.) and froth stabilizers (e.g. cresols, aniline etc.) are added. The mineral particles become wet by oils while the gangue particles by water. On Agitating the mixture by passing air, froth is formed which carries the mineral particles. The froth is skimmed off and dried to get the ore particles.

This method can be used to separate two sulphide ores by adjusting the proportion of oil to water or by using depressants. For e.g. in the case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.
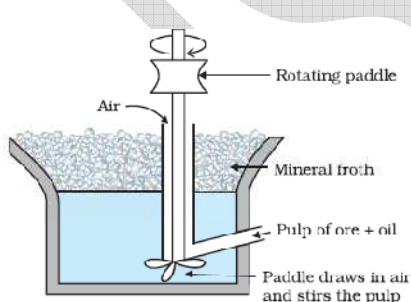

Froth Floatation   Magnetic Separation
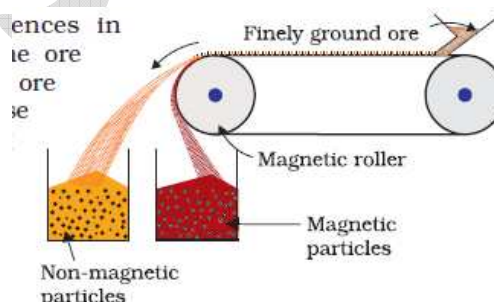
d) **Leaching**: it is often used if the ore is soluble in some suitable solvent. Here the powdered ore is treated with a suitable solvent in which ore particles alone dissolve. The impurities left undissolved are removed by filtration and the ore is recovered by precipitation.

e.g. Purification of Bauxite: Bauxite, the ore of aluminium, usually contains silica (SiO_2), iron oxides and titanium oxide (TiO_2) as impurities. Here the powdered ore is treated with a concentrated solution of NaOH at 473 – 523 K and 35 – 36 bar pressure. Alumina (Al_2O_3) dissolves in NaOH to form sodium aluminate [Silica (SiO_2) also dissolves in NaOH to form sodium silicate] leaving behind the impurities.

Al_2O_3 (s) + 2NaOH(aq) + 3H_2O(l) $\rightarrow$ 2Na[Al(OH)$_4$](aq)
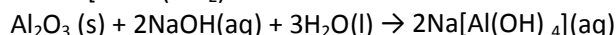
The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. The solution is seeded with freshly prepared hydrated Al_2O_3 which induces the precipitation.

$$2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3 (aq)$$

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure alumina (Al_2O_3).

$$Al_2O_3.xH_2O(s) \xrightarrow{1470 K} Al_2O_3 (s) + xH_2O(g)$$

Metallurgy of silver and gold (Hydrometallurgy)

Ag and Au are present in native state (free state) in earth crust. So we only want to remove the impurities. It is done by leaching the ore with a dilute solution of NaCN or KCN in the presence of air (O_2). These metals form soluble complexes with NaCN or KCN, which can be extracted by an electropositive metal like zinc.

$$4 Ag + 8CN^- + 2H_2O + O_2 \rightarrow 4[Ag(CN)_2]^- + 4OH^-$$
$$2 [Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Ag$$
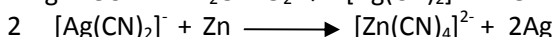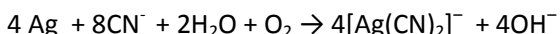
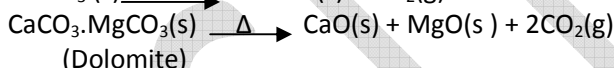### ii) Extraction of crude metal from concentrated ore

It involves the following steps:

1) Conversion to oxide and 2) Reduction of the oxide to metal

1) Conversion to oxide

Since oxide ores can easily reduced, the sulphides and carbonate ores are first converted to corresponding oxides. It can be done by calcinations or roasting.

i) **Calcination**: Here the oxide is heated in the absence of air or in limited supply of air. It is used for the conversion of hydroxide and carbonate ores to oxide ore.

$$\text{e.g. } Fe_2O_3.xH_2O(s) \xrightarrow{\Delta} Fe_2O_3 (s) + xH_2O(g)$$
$$ZnCO_3 (s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$
$$CaCO_3.MgCO_3(s) \xrightarrow{\Delta} CaO(s) + MgO(s) + 2CO_2(g)$$
$$\text{(Dolomite)}$$

ii) **Roasting**: here the ore is heated in a regular supply of air below the melting point of the metal. This method is used for the conversion of sulphide ores to oxide ore.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
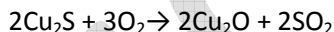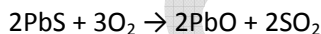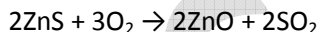
2) Reduction of the oxide to metal

It involves heating the metal oxide with suitable reducing agents like C, CO or another metal. The reducing agent combines with the oxygen of the metal oxide.

$$M_xO_y + yC \rightarrow xM + y CO$$

iii) Refining of the metal

The extracted metal often contains small amount of impurities. For getting metals of high purity, any of the following methods is used depending on the property of the metal and the impurity.

i) **Distillation**: This method is used for metals having low boiling point like Zn, mercury (Hg) etc. Here the impure metal is evaporated to obtain the pure metal as distillate.

ii) **Liquation**: It is used for metals with low melting point like tin (Sn). Here the impure metal is melted on a sloping surface of a furnace. In this way it is separated from higher melting impurities.

iii) **Electrolytic refining**: Here the impure metal is made to act as anode and a strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal. The more basic metal remains in the solution and the less basic ones go to the anode mud. The reactions are:

$$\text{Anode: } M \rightarrow M^{n+} + ne^-$$
$$\text{Cathode: } M^{n+} + ne^- \rightarrow M$$
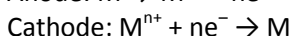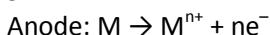
e.g. ***Refining of copper***

Here the impure copper rod is taken as the anode and a pure copper strip is used as the cathode. Acidified solution of $CuSO_4$ is used as the electrolyte. During electrolysis, the impure copper is oxidized to Cu^{2+} at anode and Cu is deposited at the cathode.

The electrode reactions are:

Anode: $Cu \rightarrow Cu^{2+} + 2\ e^-$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$
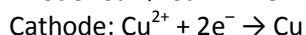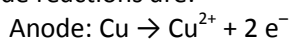
The impurities are settled down below the anode as anode mud.

iv) **Zone refining**: This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. Here a circular mobile heater is fixed at one end of a rod of the impure metal .The molten zone moves along with the heater. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off. This method is very useful for the preparation of extra pure germanium, silicon, boron, gallium and indium which are used as semiconductors.

v) **Vapour phase refining**: In this method, the metal is converted into its volatile compound and collected at another place. It is then decomposed to give pure metal.

In order to use this method there are two requirements:

(i) The metal should form a volatile compound with an available reagent,
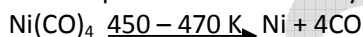
(ii) The volatile compound should be easily decomposable, so that the recovery is easy.

Examples are:

a) ***Mond's process for Refining Nickel***: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl:

$Ni + 4CO \xrightarrow{330\ -\ 350K} Ni(CO)_4$
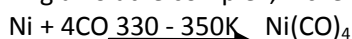
It is then decomposed to Ni and CO by heating at very high temperature.

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

b) ***van Arkel Method for Refining Zirconium or Titanium***: Here the crude metal is heated in an evacuated vessel with iodine. The metal forms it volatile iodide.

$Zr + 2I_2 \rightarrow ZrI_4$
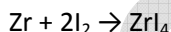
The metal iodide is decomposed electrically by using a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$ZrI_4 \rightarrow Zr + 2I_2$

vi) **Chromatographic method**: This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture is put in a liquid or gaseous medium which is moved through an adsorbent column. Different components are adsorbed at different levels on the column. They are then removed by using suitable solvents (eluant).

There are different types of chromatographic techniques like paper chromatography, column chromatography, gas chromatography etc.

Extraction of some metals

1) **Extraction of Iron**: Iron is mainly extracted from Haematite (Fe_2O_3) and Magnetite (Fe_3O_4). The sulphide ore iron pyrites (FeS_2) is not used for the extraction of iron, since the presence of sulphur corrodes the metal.

The ore is concentrated by magnetic separation and then it is calcined or roasted to remove water and to decompose carbonates. Then the ore is mixed with lime stone ($CaCO_3$) and coke (C) and fed into a blast furnace from its top. Simultaneously a blast of air is passed from bottom of the furnace. Here the oxide is reduced to the metal.

In presence of hot air blast, burning of coke takes place and the temperature is raised to about 2200K.

$C(s) + \frac{1}{2} O_2 (g) \rightarrow CO (g) + heat$
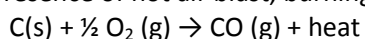
The CO and heat moves to upper part of the furnace and combines with the iron oxides and reduce them to iron.

$$3Fe_2O_3 + CO \rightarrow 2 Fe_3O_4 + CO_2$$
$$Fe_3O_4 + 4 CO \rightarrow 3Fe + 4 CO_2$$
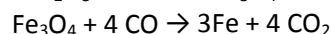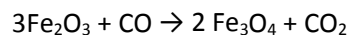
At higher temperature range in the blast furnace, lime stone ($CaCO_3$) is decomposed to CaO. It combines with silicate impurity of the ore to form slag.

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$CaO + SiO_2 \longrightarrow CaSiO_3$$
(flux)   (gangue)   (slag)
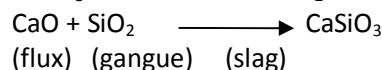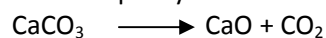
The slag is in molten state and separates out from iron. The iron obtained from blast furnace is called **pig iron**. It contains about 4% C and smaller amounts of impurities (e.g. S, P, Si, Mn etc.)

When pig iron is melted with scrap iron and coke in presence of hot air blast, *cast iron* is formed. It is extremely hard and brittle,

***Wrought iron or malleable iron** is the purest form of commercial iron.* It is prepared from cast iron by oxidizing impurities in a reverberatory furnace lined with haematite. This heamatite oxidises C to CO.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
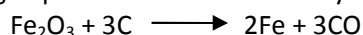
Here haematite is added as a flux.

Flux, gangue and slag

The impurities present in the ore are called *gangue*. The gangue is removed during the extraction of the metal by adding some chemical substances called *flux*. The flux combines with gangue to form an easily fusible substance called *slag*.

If the gangue is *acidic*, the flux used is *basic* in nature and vice versa.

E.g. for acidic flux are SiO_2, P_2O_5 etc. and e.g. for basic flux are CaO, MgO etc.

$$e.g. \ CaO + SiO_2 \longrightarrow Ca SiO_3$$
(Flux)   (Gangue)   (Slag)
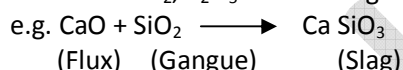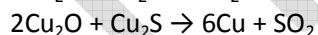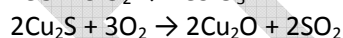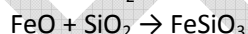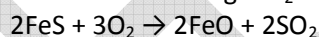
2. Extraction of Copper

The important ores of copper are cuprite (Cu_2O), Copper glance (Cu_2S), Copper pyrites ($CuFeS_2$) etc. The sulphide ores are concentrated by froth floatation and roasted to get oxides.

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

The roasted ore is heated in a reverberatory furnace after mixing it with silica (flux). Here the iron oxide (gangue) combines with silica to form iron silicate and copper is produced in the form *'copper matte'* which contains Cu_2S and FeS.

$$FeO + SiO_2 \longrightarrow FeSiO_3$$
(Flux)   (Gangue)   (Slag)
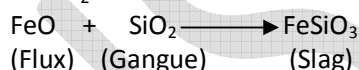
Copper matte is then transferred into a silica lined convertor. Some silica is also added and hot air blast is blown to convert the remaining FeS_2 to FeO and Cu_2S or Cu_2O to the metallic copper.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \rightarrow FeSiO_3$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called *blister copper*.

Extraction of Copper from Low Grade Ores and Scraps: Copper is extracted by hydrometallurgy from low grade ores. It is leached out using acid or bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2.

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+ (aq)$$
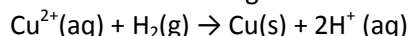
3. Extraction of zinc from zinc oxide (ZnO)

The ores of Zn are zincite (ZnO), Zinc blende (ZnS), calamine ($ZnCO_3$) etc. Zn is mainly extracted from ZnO. The reduction of zinc oxide is done using coke.
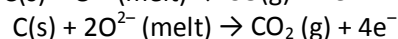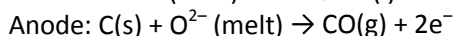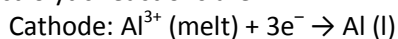
$$.ZnO + C(coke) \xrightarrow{673 \ K} Zn + CO$$
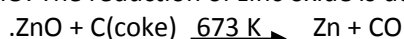
4. Extraction of Aluminium

Aluminium is extracted by Hall-Heroult process. Here the purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (to lower the melting point and to increase the conductivity) and is eletrolysed. The electrolysis is carried out in a carbon lined steel vessel, which acts as cathode. Graphite rods are used as anode. During electrolysis Al_2O_3 is reduced to Al by carbon.

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$
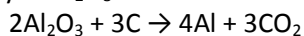
The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2.
The electrolytic reactions are:

Cathode: Al^{3+} (melt) + $3e^-$ → Al (l)
Anode: $C(s) + O^{2-}$ (melt) → CO(g) + $2e^-$
$C(s) + 2O^{2-}$ (melt) → CO_2 (g) + $4e^-$

Thermodynamic Principles of Metallurgy

The Gibbs energy change (ΔG) for a process at any specified temperature (T) is given by the equation:

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

Where, ΔH is the enthalpy change and ΔS is the entropy change for the process.

The reaction will proceed only when the value of ΔG is negative in the above equation. This can be possible in the following ways:

1.   If ΔS is positive, on increasing the temperature (T), the value of TΔS would increase (i.e. TΔS > ΔH) and then ΔG will become –ve.

2.   If two reactions having different ΔG values are coupled, the net ΔG of the reactions becomes –ve and so the overall reaction will occur. Such coupling can easily understand through Gibbs energy (ΔG^0) vs T plots for formation of the oxides.

Ellingham Diagram

The graphical representation of Gibbs energy vs Temperature was first given by H.J.T.Ellingham and these graphs are known as *Ellingham Diagram.* It gives a sound basis for considering the choice of reducing agent in the reduction of oxides. These diagrams help us in predicting the feasibility of thermal reduction of an ore. The criterion of feasibility is that at a given temperature, Gibbs energy of the reaction must be negative.
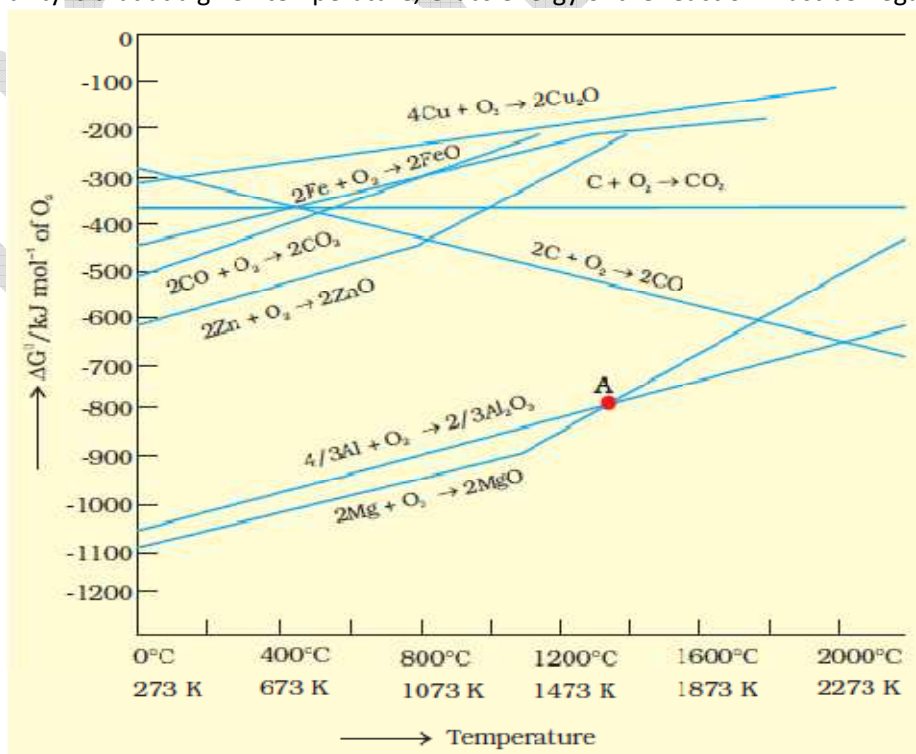
Ellingham diagram normally consists of plots of ΔG^0 vs T for formation of oxides of elements i.e., for the reaction,

$$2xM(s) + O_2(g) \rightarrow 2M_xO(s)$$
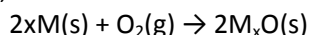
In this reaction, the no. of gaseous species decrease from left to right. This results in a –ve value of ΔS. So the sign of the second term in Gibbs equation changes to positive. The result is +ve slope in the curve.

Each plot in the diagram is a straight line, except when some state change (phase transition) occurs. The temperature at which such change occurs is indicated by an increase in the slope on +ve side.

There is a point in the curve below which ΔG is negative. Above this point, M_xO will decompose on its own.
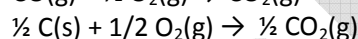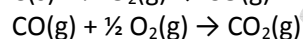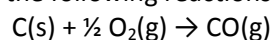

Applications of Ellingham Diagram

We know that during the reduction of the metal, the reducing agent forms its oxide. The role of reducing agent is to provide a larger ΔG^0 value and hence to make the sum of $\Delta_r G^0$ of the two reactions (oxidation and reduction) negative.
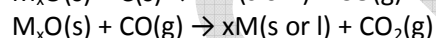
The reduction of the metal oxide can be given by:

$$M_xO(s) \rightarrow xM \text{ (solid or liq)} + \tfrac{1}{2} O_2 (g)$$
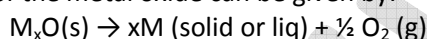
The reducing agent combines with this oxygen to form corresponding oxide. For e.g. if C or CO is the reducing agent the following reactions may occur.

$$C(s) + \tfrac{1}{2} O_2(g) \rightarrow CO(g)$$
$$CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g)$$
$$\tfrac{1}{2} C(s) + \tfrac{1}{2} O_2(g) \rightarrow \tfrac{1}{2} CO_2(g)$$

If these reactions are coupled with the above reduction reaction of the metal, we get

$$M_xO(s) + C(s) \rightarrow xM(s \text{ or } l) + CO(g)$$
$$M_xO(s) + CO(g) \rightarrow xM(s \text{ or } l) + CO_2(g)$$
$$M_xO(s) + \tfrac{1}{2} C(s) \rightarrow xM(s \text{ or } l) + \tfrac{1}{2} CO_2(g)$$

We know that on heating (i.e. when temperature increases), ΔG^0 becomes negative. Therefore the temperature of the redox reaction should be in such a way that the sum of the $\Delta_r G^0$ is negative. In Ellingham diagram, this is indicated by the point of intersection of the two curves. After that point, the $\Delta_r G^0$ becomes more negative for the combined process. The difference in the two $\Delta_r G^0$ values after that point determines whether reduction of the oxide of the upper line is feasible by the element represented by the lower line. If the difference is large, the reduction is easier.

Limitations of Ellingham Diagram

1) The graph simply indicates whether a reaction is possible or not thermodynamically. It does not say about the kinetics of the reduction process.
2) The interpretation of ΔG^0 is based on K ($\Delta G^0 = - RT \ln K$). That is the reactants and products are in equilibrium. This is not always true because the reactant or product may be solid

Q_1) The reduction of the metal oxide is easier if the metal formed is in liquid state, at the temperature of reduction. Give reason.

For a reaction to occur, the value of ΔG^0 should be negative. If the metal formed is in liquid state, the entropy is higher than that in the solid state. Thus the value of ΔG^0 becomes more negative and the reduction becomes easier.

Q_2) In the blast furnace for manufacturing iron, most of the reduction is carried out by CO rather than coke. How can you account for this?

When CO is used, the reduction can be possible at relatively low temperature. This is because, the intersection between Fe, FeO line and CO, CO_2 line in Ellingham diagram takes place at low T.

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