



CHEMISTRY

METALLURGY

Target : JEE (Main)



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METALLURGY

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JEE (MAIN) SYLLABUS

General Principles and Processes of Isolation of Metals

Modes of occurrence of elements in nature, minerals, ores; steps involved in the extraction of metals- concentration, reduction (chemical and electrolytic methods) and refining with special reference to the extraction of Al, Cu, Zn and Fe ; Thermodynamic and electrochemical principles involved in the extraction of metals.

JEE(ADVANCED) SYLLABUS

Extractive metallurgy: Chemical principles and reactions only (industrial details excluded); Carbon reduction method (iron and tin); Self reduction method (copper and lead); Electrolytic reduction method (magnesium and aluminium); Cyanide process (silver and gold).



Metallurgy

Introduction :

The compound of a metal found in nature is called a mineral. The minerals from which metal can be economically and conveniently extracted are called **ores**. An ore is usually contaminated with earthy or undesired materials known as gangue. So all minerals are not ores but all ores are minerals. Ores may be classified mainly into following four classes.

- (a) **Native ores** : They contain the metal in free state. Silver, gold, platinum etc, occur as native ores.
 (b) **Oxidised ores** : These ores consist of oxides or oxysalts (e.g. carbonates, phosphates, sulphates and silicates) of metals.
 (c) **Sulphurised ores** : These ores consist of sulphides of metals like iron, lead, zinc, mercury etc.
 (d) **Halide ores** : These ores consist of halides of metals.

Important ore :

1. Oxide ore :

- (i) Bauxite $\rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (Major ore of Al)
 (ii) Haematite $\rightarrow \text{Fe}_2\text{O}_3$
 (iii) Zincite = ZnO
 *** (iv) Cassiterite or tin stone $\rightarrow \text{SnO}_2$ (Black Tin = 60 – 70% SnO_2)

2. Carbonate ore :

- (i) Lime stone $\rightarrow \text{CaCO}_3$ (ii) Dolomite $\rightarrow \text{CaCO}_3 \cdot \text{MgCO}_3$
 (iii) Siderite $\rightarrow \text{FeCO}_3$ (iv) Malachite $\rightarrow \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
 (v) Azurite $\rightarrow 2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ *** (vi) Calamine $\rightarrow \text{ZnCO}_3$
 *** (vii) Cerussite $\rightarrow \text{PbCO}_3$

3. Sulphate ore : Epsom salt $\rightarrow \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

4. Silicate ore : Feldspar $\rightarrow \text{KAlSi}_3\text{O}_8$

5. Sulphurised ore : Consist of sulphides of metal like Iron, lead, zinc & mercury.

- (i) Iron pyrites $\rightarrow \text{FeS}_2$ (ii) Copper glance $\rightarrow \text{Cu}_2\text{S}$
 (iii) Copper pyrite or chalcopyrite $\rightarrow \text{CuFeS}_2$ (iv) Zinc Blende $\rightarrow \text{ZnS}$
 (v) Galena $\rightarrow \text{PbS}$ (vi) Cinnabar $\rightarrow \text{HgS}$

6. Halide ore :

- (i) Cryolite $\rightarrow \text{Na}_3\text{AlF}_6$ (ii) Sylvine $\rightarrow \text{KCl}$
 ** (iii) Carnallite $\rightarrow \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (iv) Fluorspar $\rightarrow \text{CaF}_2$
 (v) Horn silver $\rightarrow \text{AgCl}$

Note : Mg obtained from both sea water & earth crust.

Solved Examples

Example-1 Which metals are supposed to occur in the native state in nature ?
Solution Elements below hydrogen in the electrochemical series like Cu, Ag, Au etc, exist native ores.

Example-2 Match the ores listed in Column-I with their correct chemical formula listed in Column-II.

Column I

- (A) Cassiterite
 (B) Siderite
 (C) Cerussite
 (D) Anglesite

Column II

- (p) FeCO_3
 (q) SnO_2
 (r) PbSO_4
 (s) PbCO_3

Solution SnO_2 is called as cassiterite or tin stone, FeCO_3 is called as siderite, PbCO_3 is called as cerussite and PbSO_4 is called anglesite. So correct match is (A) \rightarrow (q), (B) \rightarrow (p), (C) \rightarrow (s) and (D) \rightarrow (r).



Metallurgy :

The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

The isolation and extraction of metals from their ores involve the following major steps:

- (A) Crushing of the ore.
- (B) Dressing or concentration of the ore.
- (C) Isolation of the crude metal from its ore
- (D) Purification or refining of the metal.

Chart1:

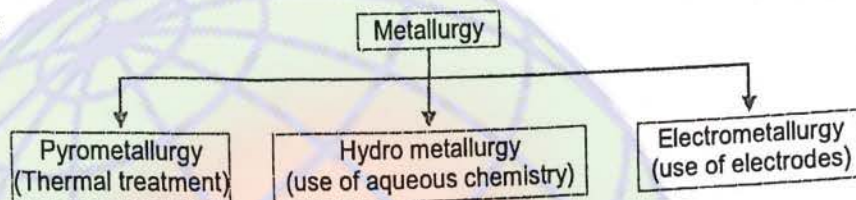
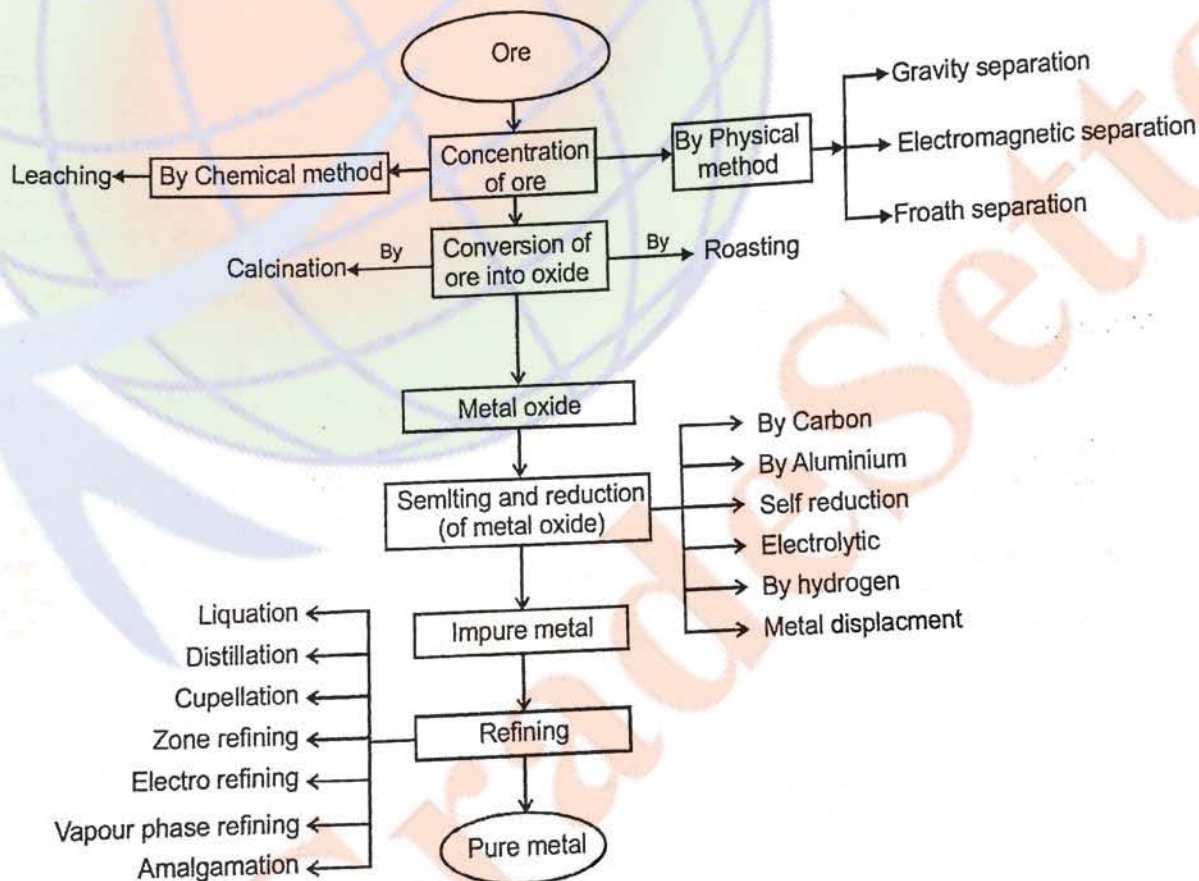


Chart2: Steps involved in metallurgy.



1. Physical Method :

(A) **Crushing and Grinding** : The ore is first crushed by jaw crushers and ground to a powder (pulverisation of the ore) in equipments like ball mills and stamp mills.

(B) **Concentration** : The removal of unwanted useless impurities from the ore is called **dressing, concentration or benefaction of ore**.

It involves several steps and selection of these steps depends upon the difference in physical properties of the compound of metal and that of gangue. Some of the important procedures are described below.

Metallurgy

(i) Hydraulic washing or Gravity separation or Levigation method : It is based on the difference in the densities of the gangue and ore particles. In this, the powdered ore is agitated with water or washed with a upward stream of running water, the lighter particles of sand, clay etc are washed away leaving behind heavier ore particles. For this either hydraulic classifier or Wilfley table is used. This method is generally used for the concentration of oxide and native ores.

(ii) Electromagnetic separation :

It is based on differences in magnetic properties of the ore components.

It is used when either the ore or the impurities associated with it are magnetic in nature. A magnetic separator consists of a belt (of leather or brass) moving over two rollers, one of which is magnetic. When the powdered ore is dropped on the belt at the other end, magnetic component of the ore is attracted by the magnetic roller and falls nearer to the roller while the non-magnetic impurities fall away from it.

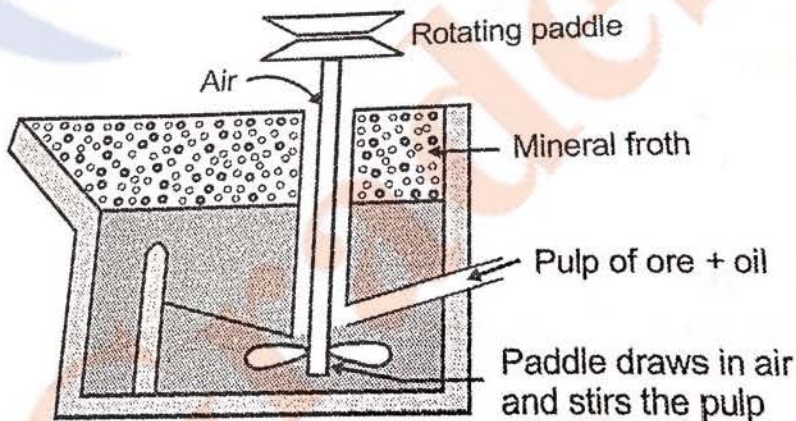
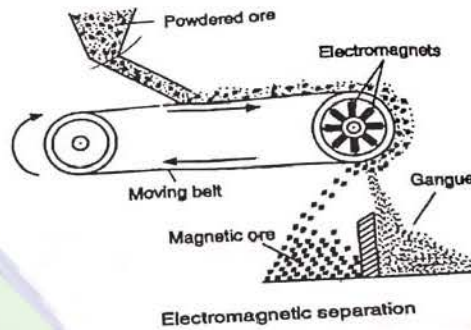
Examples : Chromite ore ($FeO \cdot Cr_2O_3$) is separated from non-magnetic silicious impurities and cassiterite ore (SnO_2) is separated from magnetic Wolframite ($FeWO_4 + MnWO_4$).

(iii) Froth floatation process : This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb) ; copper pyrites $Cu_2S \cdot Fe_2S_3$ or $CuFeS_2$ (ore of copper) ; zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil. In this process one or more chemical frothing agents are added.

(a) Frothers : These form stable froth which rises to the top of the floatation cell. Oils like pine oil, camphor oil etc., are used as frothers. These are added in small quantity. The stabiliser are added to the frothers so that the froth can last for longer period.

(b) Collectors : Potassium or sodium ethyl xanthate is used as a collector. These get attached with the particles of the sulphide ore and thus make them water-repellant. Consequently the ore particles pass on into the froth. Collectors are always added in small quantity.

(c) Activating and depressing agents : When a mineral contains other minerals as impurities. The addition of these agents activates or depresses the floatation property of other minerals present as impurities and thus helps in separating the impurities. For example galena (PbS) usually contains the minerals namely zinc blende (ZnS) and pyrites (FeS_2) as impurities. Flotation is carried out by using potassium ethyl xanthate (used as a collector) along with $NaCN$ and Na_2CO_3 (used as depressing agent). The addition of Na_2CO_3 depresses the floatation property of ZnS and FeS_2 grains, so mainly PbS passes into the froth when air is blown in. After PbS has been collected with the froth, the process is repeated by adding $CuSO_4$ (activator) which activates the floatation property of ZnS grains which are now removed with the froth. The acidification of the remaining material left in the floatation cell leads to the floatation of FeS_2 .



Froth floatation process

Example-3
Solution

Example-4
Solution

2.



Solved Examples

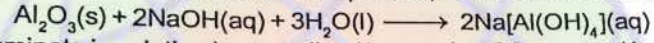
- Example-3** How does NaCN act as a depressant in preventing ZnS from forming the froth?
Solution NaCN reacts with ZnS and forms a layer of $\text{Na}_2[\text{Zn}(\text{CN})_4]$ complex on the surface of ZnS and thus prevents it from the formation of froth.
- Example-4** What is the role of stabiliser in froth floatation process?
Solution Froth can last for a longer period in presence of stabiliser.

2. Chemical Method :

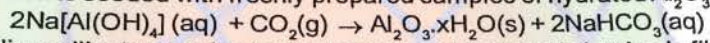
(iv) Leaching : Leaching is often used if the ore is soluble in some suitable solvent, e.g. acids, bases and suitable chemical reagents. e.g. Al ore, Ag ore, Au ore, low grade copper ore.

Leaching of alumina from bauxite :

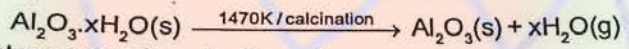
The principal ore of aluminium, bauxite, usually contains SiO_2 , iron oxide and titanium oxide (TiO_2) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473-523 K and 35-36 bar pressure. This way, Al_2O_3 is leached out as sodium aluminate (and also SiO_2 as sodium silicate) leaving behind the impurities, iron oxide and titanium oxide.



The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces the precipitation.



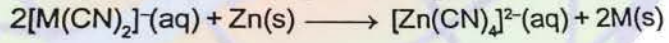
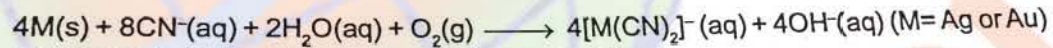
The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3 :



These steps comprises the **Bayer's process**.

Other examples :

In the metallurgy of **silver** and that of **gold**, the respective metal/ore is leached with a dilute solution of NaCN or KCN in the presence of air (or O_2) from which the metal is obtained later by displacement with zinc scrap.

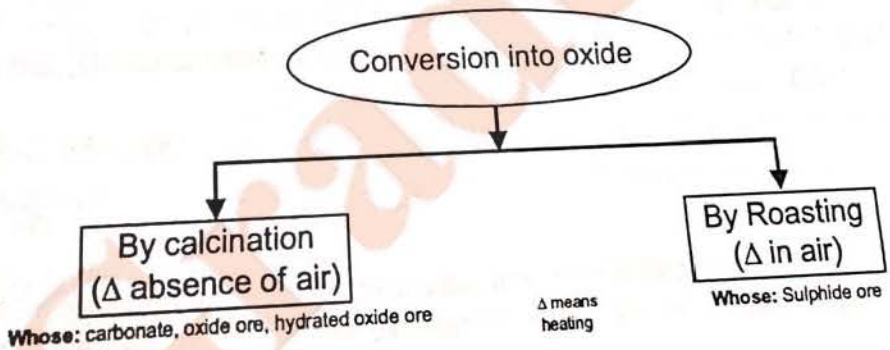


(C) Extraction of crude metal from concentrated ore :

The concentrated ore must be converted into a form which is suitable for reduction. Usually the sulphide ore is converted to oxide before reduction. Oxides are easier to reduce. Thus isolation of metals from concentrated ore involves two major steps as given below.

- (i) Conversion to oxide
- (ii) Reduction of the oxide to metal.

(i) Conversion to oxide :



Conversion of ore into oxide is carried out in two ways depending upon the nature of ore.

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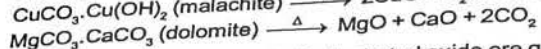
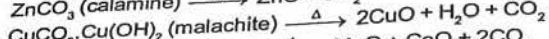
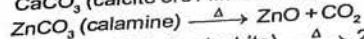
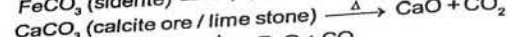
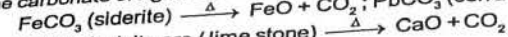
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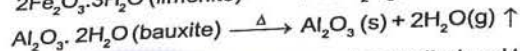
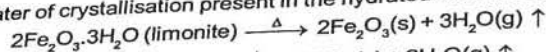
**Metallurgy**

Calcination. It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of calcination brings about the following changes :

(a) The carbonate ore gets decomposed to form the oxide of the metal, e.g.,



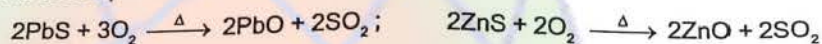
(b) Water of crystallisation present in the hydrated oxide ore gets lost as moisture, e.g.,



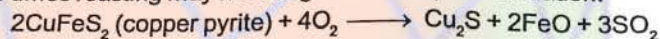
(c) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

Roasting. It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or O_2 below its melting point. Roasting is an exothermic process once started it does not require additional heating. The process of roasting does the following things :

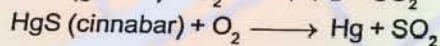
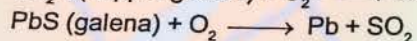
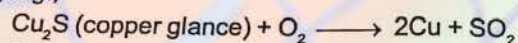
(a) Roasting at moderate temperature. Some portion of the sulphide ores like galena (PbS), Zinc blende (ZnS) is converted into metallic oxide. If the temperature is fairly low (about 500°C) and the concentration of SO_2 in the gaseous environment is more, sulphate may be produced that are stable, and high temperature is needed to decompose them.



* Some times roasting may not bring about complete oxidation.

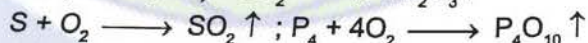
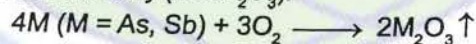


(b) Roasting at high temperature. The sulphide ores of some of the metals like Cu, Pb, Hg, Sb etc., when heated strongly in the free supply of air or O_2 are reduced directly to the metal rather than to the metallic oxides, e.g.,



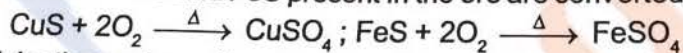
The reduction of the sulphide ore directly into metal by heating it in air or O_2 is called by various names like self-reduction, auto-reduction, air-reduction etc. The SO_2 produced is utilised for manufacturing of H_2SO_4 .

(c) It removes easily oxidisable volatile impurities like arsenic (as As_2O_3), sulphur (as SO_2), phosphorus (as P_4O_{10}) and antimony (as Sb_2O_3).



These oxides are volatile and hence escape as gases through the chimney.

(d) When the concentrated tin stone ore SnO_2 (ore of Sn) is heated strongly in a free supply of air (roasting), the impurities of CuS and FeS present in the ore are converted into CuSO_4 and FeSO_4 respectively.



Both calcination and roasting are generally carried out in a reverberatory furnace. In case of roasting, the air holes are kept open while they are partially or completely closed during calcination.

Smelting :

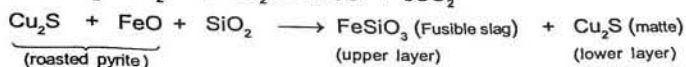
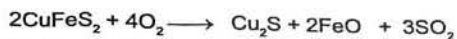
Slag formation : In many extraction processes, an oxide is added deliberately to combine with other impurities and form a stable molten phase immiscible with molten metal called a slag. The process is termed smelting.



The principle of slag formation is essentially the following :

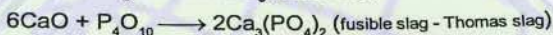
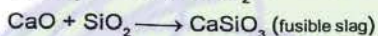
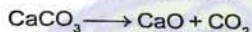
Nonmetal oxide (acidic oxide) + Metal oxide (basic oxide) \longrightarrow Fusible (easily melted) slag

Removal of unwanted basic and acidic oxides: For example, FeO is the impurity in extraction of Cu from copper pyrite.



Matte also contains a very small amount of iron(II) sulphide.

To remove unwanted acidic impurities like sand and P_4O_{10} , smelting is done in the presence of limestone.



Properties of a slag :

- (i) Slag is a fusible mass.
- (ii) It has low melting point.
- (iii) It is lighter than and immiscible with the molten metal. It is due to these impurities that the slag floats as a separate layer on the molten metal and can thus be easily separated from the metal. The layer of the slag on the molten metal prevents the metal from being oxidised.

Type of flux : Fluxes are of two types viz., acidic flux and basic flux.

(a) Acidic flux : It is an acidic oxide (oxide of a non-metal) like SiO_2 , P_2O_5 , B_2O_3 (from borax). It is used to remove the basic impurity like CaO, FeO, MgO etc. The acidic flux combines with the basic impurity and forms a slag.

(b) Basic flux : It is a basic oxide (i.e., oxide of a metal) like CaO (obtained from lime stone, CaCO_3), MgO (from magnesite, MgCO_3), haematite (Fe_2O_3) etc. It is used to remove the acidic impurity like SiO_2 , P_2O_5 etc.

The basic flux combines with the acidic impurity and forms a slag. Thus, slag can be defined as a fusible mass, which is obtained when a flux reacts with an infusible acidic or basic impurity present in the oxide ore.

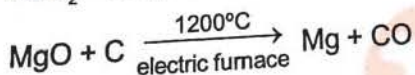
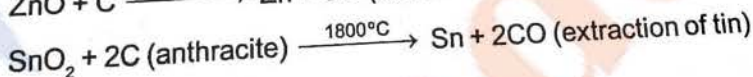
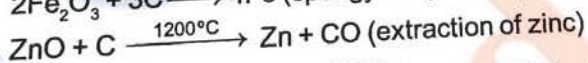
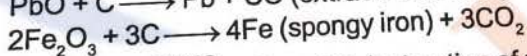
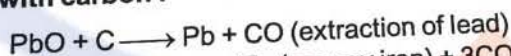
(ii) Reduction of a metal oxide :

The free metal is obtained by reduction of a compound, using either a chemical reducing agent or electrolysis.

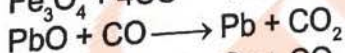
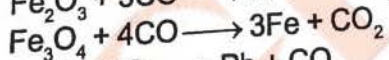
1. Chemical reduction method :

A large number of commercial processes come under this category. Carbon can be used to reduce a number of oxides and other compounds, and because of the low cost and availability of coke this method is widely used. The disadvantages are that a high temperature is needed, which is expensive and necessitates the use of blast furnace.

(A) Reduction with carbon :

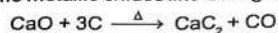


(B) Reduction with CO : In some cases CO produced in the furnace itself is used as a reducing agent.

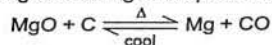


Metallurgy

Carbon or carbon monoxide reduction process is usually carried out in blast furnace. There are some disadvantages of using carbon as reducing agents e.g.,
 (a) Some metallic oxides like CaO give metallic carbides instead of metals.

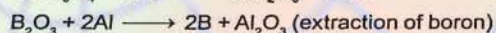
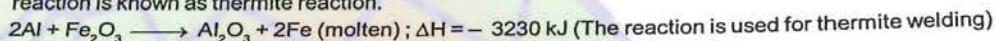


(b) During the cooling of the products, in many cases, reformation of the oxide and carbon may take place.

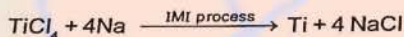


2. Reduction by other metals :

If the temperature needed for carbon to reduce an oxide is too high, for economical or practical purposes, the reduction by other metals is done. Also, certain metallic oxides cannot be reduced by carbon because the affinity of oxygen for the metal is greater than its affinity for carbon. Such metallic oxides (Cr and Mn) can be reduced by a highly electropositive metal such as aluminium that liberates a large amount of energy (1675 kJ/mol) on oxidation to Al_2O_3 . The process is known as Goldschmidt or aluminothermic process and the reaction is known as thermite reaction.



As it is a strongly exothermic reaction, it proceeds with explosive violence and only initial heating is needed.
Magnesium reduction method : Magnesium is used in similar way to reduce oxides. In certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce halides.



Advantages of using Na and Mg as reducing agents are the higher reducing power of the metals and solubility of their halides in water so that the reduced metals can be washed free from impurities.

3. Self-reduction method :

This method is also called auto-reduction method or air reduction method. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb, Sb, etc. are heated in air, a part of these is changed into oxide or sulphate then that reacts with the remaining part of the sulphide ore to give its metal and SO_2 .

Examples :



The extraction of Pb by heating its sulphide ore (PbS) in air can also be represented as



4. Electrolytic reduction :

It presents the most powerful method of reduction and gives a very pure product. As it is an expensive method compared to chemical methods, it is used either for very reactive metals such as magnesium or aluminum or for production of samples of high purity. Electrolytic reduction of copper has the additional advantage of allowing the recover of valuable minor contaminants such as silver.

Metallurgy

- Medium :**
 In aqueo products sulphate
 1. In other water a
 2. In fuse Alumir chlorir adder
 3. Elec Elec and for the

wi p f

Metallurgy

- Medium :**
- In aqueous solution :** Electrolysis can be carried out conveniently and cheaply in aqueous solution that the products do not react with water. Copper and zinc are obtained by electrolysis of aqueous solution of their sulphates.
 - In other solvents :** Electrolysis can be carried out in solvents other than water. Fluorine reacts violently with water and it is produced by electrolysis of KHF_2 dissolved in anhydrous HF.
 - In fused melts :** Elements that react with water are often extracted from fused melts of their ionic salts. Aluminum is obtained by electrolysis of a fused mixture of Al_2O_3 and cryolite $Na_3[AlF_6]$. Both sodium and chlorine are obtained from the electrolysis of fused NaCl. In this case upto two-third by weight of $CaCl_2$ is added as an impurity to lower the melting point from 803 to 505°C.

Electrochemical principles of metallurgy :

Electrolytic reduction can be regarded as a technique for driving a reduction by coupling it through electrodes and external circuit to a reactive or a physical process with a more negative ΔG . The free energy available from the external source can be assessed from the potential it produces across the electrodes using the thermodynamic relation :

$$\Delta G = -nFE \dots\dots\dots(i)$$

where n is the number of electrons transferred, F is Faraday's constant ($F = 96.5 \text{ kJ/mol}$) and E^0 is electrode potential of the redox coupled in the system.

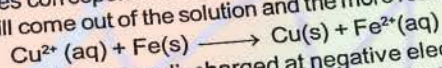
Hence, the total Gibb's energy of the coupled internal and external process is

$$\Delta G + \Delta G(\text{external}) = \Delta G - nFE_{\text{ext}}$$

If the potential difference of the external source exceeds

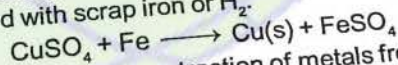
$$E_{\text{ext}} = -\frac{\Delta G}{nF}$$

the reduction is thermodynamically feasible; thus, the overall process occurs with a decrease in free energy. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two E^0 values corresponds to a positive E^0 and consequently negative ΔG^0 in equation (i), then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g.,



In simple electrolysis, the M^{n+} ions are discharged at negative electrodes (cathodes) and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added for making the molten mass more conducting.

Hydrometallurgy : The processing of ores and minerals as well as metals and their compounds at relatively low, often ambient temperatures employing aqueous solution is known as hydrometallurgy. Occasionally, organic reagents are also used. This method of extraction is generally used for low grade ores. Copper is extracted by hydrometallurgy from low grade ore it is leached out using acid and bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2 .

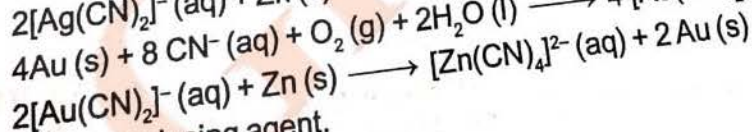
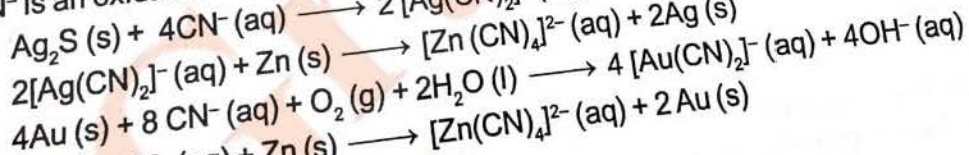
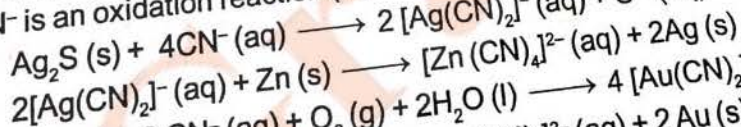
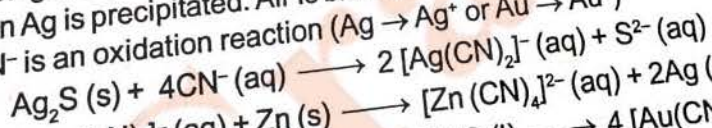


A hydrometallurgical process for the extraction of metals from ores, concentrates, or secondary materials essentially contains three basic steps—dissolution of the valuable metal in the aqueous solution (leaching) purification of leach solution and subsequent recovery of metal from the purified solutions either by electrolysis or by adding some electropositive metal to it.

Some of the metals obtained by hydrometallurgy are as follows :

(A) Extraction of Ag and Au : Metals like Au and Ag can be precipitated for their salt solution by electropositive metals for example, Zn.

Metallic Ag is dissolved from its ore in dilute NaCN solution, and the solute so obtained is treated with scrap Zn when Ag is precipitated. Air is blown into the solution oxidize Na_2S . Leaching the metals like silver, gold with CN^- is an oxidation reaction ($Ag \rightarrow Ag^+$ or $Au \rightarrow Au^+$)



Here Zn acts as reducing agent.

Metallurgy

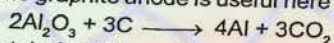
(B) Extraction of Aluminium : It involves the following processes

(a) Purification of bauxite :

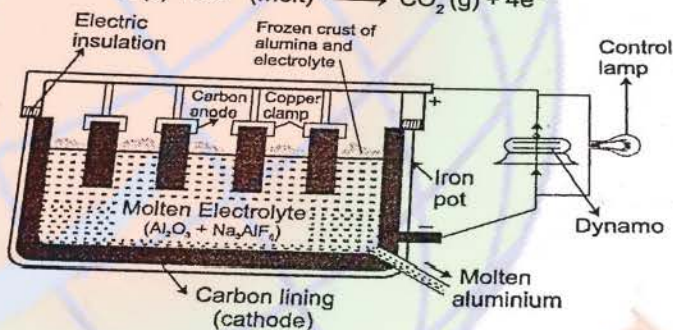
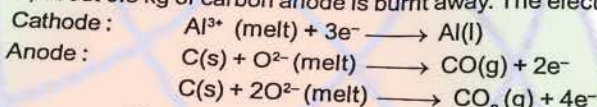
<p>(I) Bayer's Method (used for red bauxite containing Fe_2O_3 and silicates as impurities) $Al_2O_3 \cdot 2H_2O + 2NaOH \xrightarrow[8 \text{ atm}]{190^\circ C}$ $2NaAlO_2 \text{ (soluble)} + 3H_2O$ $Fe_2O_3 \text{ (insoluble)}$ separated as red mud by filtration solution is diluted with water and seeded with freshly prepared $Al(OH)_3$. It induces the precipitation of $Al(OH)_3$. $Al(OH)_3$ is filtered leaving behind silicates in solution. $NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3 \downarrow$ $2Al(OH)_3 \xrightarrow{1473K \Delta} Al_2O_3 + 3H_2O$</p>	<p>(II) Hall's Method (used for red bauxite containing Fe_2O_3 and silicates as impurities) $Al_2O_3 \cdot 2H_2O + Na_2CO_3 \xrightarrow{\text{Fuse}}$ $2NaAlO_2 \text{ (soluble)} + CO_2 + 2H_2O$ $2NaAlO_2 + 3H_2O + CO_2 \xrightarrow{60^\circ C}$ $2Al(OH)_3 \downarrow + Na_2CO_3$ $2Al(OH)_3 \xrightarrow{1473K \Delta} Al_2O_3 + 3H_2O$</p>	<p>(III) Serpeck's Method (used for white bauxite containing silica as impurities) $Al_2O_3 \cdot 2H_2O + 3C + N_2 \xrightarrow[Electric \text{ furnace}]{1800^\circ C}$ $2AlN + 3CO + 2H_2O$ $2AlN + 3H_2O \rightarrow Al(OH)_3 \downarrow + NH_3$ $SiO_2 + 2CO \rightarrow 2CO_2 + Si$ Silicone volatilises at this temp. $2Al(OH)_3 \xrightarrow{1473K \Delta} Al_2O_3 + 3H_2O$</p>
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(b) Electrolytic reduction (Hall-Heroult process) :

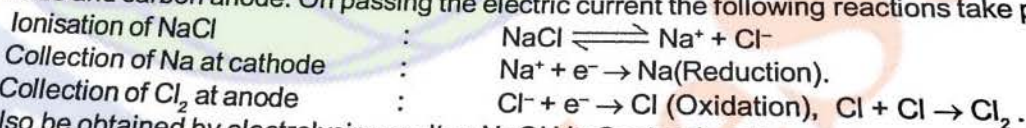
The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar) which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal. The overall reaction may be taken as :



The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2 . This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are :



Extraction of Na : The fused mixture of $NaCl$ and $CaCl_2$ is taken in Down's cell which consists of circular iron cathode and carbon anode. On passing the electric current the following reactions take place :



Na can also be obtained by electrolysis of molten $NaOH$ in Castner's cell.

Solved Examples

Example-5 Common impurities present in Bauxite are :

- (1) CuO (2) ZnO (3) Fe_2O_3 (4) SiO_2

Solution (3) Red Bauxite contains Fe_2O_3 as impurity. (4) white Bauxite contains SiO_2 as impurity. Therefore, (3) and (4) are correct options.

Example-6 **Question** Which metals are generally extracted by the electrolytic reduction and why ?
Solution Sodium, aluminium, magnesium etc. are extracted by the electrolytic reduction of their fused salts because being more reactive and electropositive elements they themselves acts as strong reducing agents. Hence they can not be extracted by any of the chemical methods.

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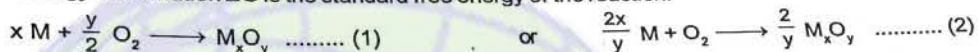
THERMODYNAMICS OF EXTRACTION : ELLINGHAM DIAGRAM OF A METAL

The standard electrode reduction potential of metal provides a very good indicator of the ease or difficulty of extracting the metal from its compounds. However, since most metals of industrial importance are obtained by chemical reduction of their oxide, the free energy changes occurring during these processes are of more fundamental importance. Despite the fact that redox reactions do not always reach equilibrium thermodynamics can at least be used to identify which reactions are feasible. For a spontaneous reaction the change in free energy ΔG must be negative, $\Delta G = \Delta H - T\Delta S$.

It is sufficient to consider ΔG because it is related to the equilibrium constant through, $\Delta G = -RT \ln K$. Here a negative value of ΔG corresponds to $K > 1$ and, therefore, a favourable reaction. Reaction rates are also relevant, but at high temperature reactions are often fast and we can normally assume that any thermodynamically permissible process can occur.

The problem of extracting a metal from its ore is essentially concerned with decomposing the oxide of the metal (apart from simple binary compounds such as metal sulfides and chlorides that occur in nature). Most metal ores consist essentially of a metal oxide in association with one or more nonmetal oxides. Ores like carbonates, sulphides etc., are also converted to oxides, prior to reduction.

The free energy of formation ΔG is the standard free energy of the reaction.



ΔG is the free energy of formation per mole of O_2 consumed.

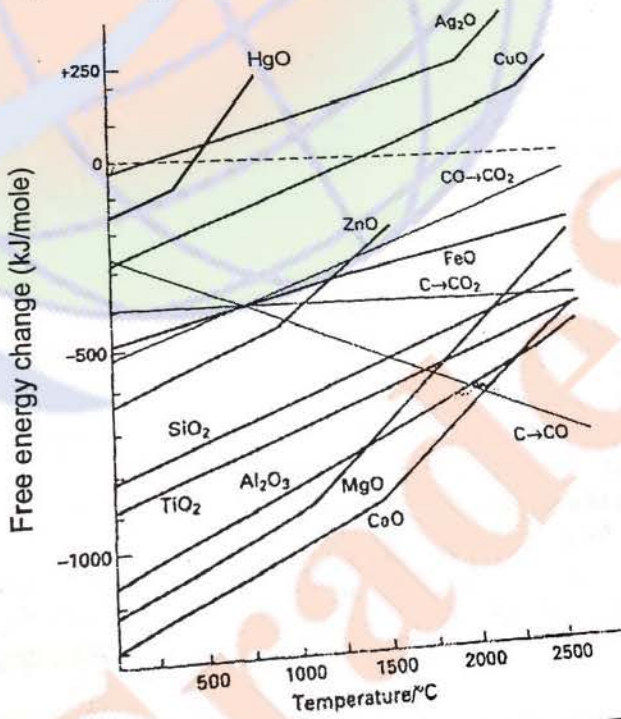
If the standard free energy of formation ΔG has a negative sign at a given temperature, then the oxide can be expected to form spontaneously from the metal plus oxygen. If ΔG has a positive sign, the oxide will be expected to decompose spontaneously to its elements.

The free energy of formation of an oxide can now be determined, provided we know the entropy of formation.

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots (3)$$

In reaction (2) oxygen is used up in the course of reaction. Gases have a more random structure (less ordered) than liquid or solids. In this reaction the entropy or randomness decreases, and hence ΔS is negative (provided that neither the metal nor its oxide M_xO_y are vaporized). Thus, if the temperature is raised then $T\Delta S$ becomes more negative. Since $T\Delta S$ is subtracted in equation (3), ΔG then becomes less negative. Thus, the change in free energy decreases with increase in temperature.

The free energy change that occurs when 1 mol of common reactant (in this case O_2) is used may be plotted graphically against temperature for a number of reaction of metals to their oxides. This graph is shown in following figure and is called an Ellingham diagram for oxides. Similar diagrams can be produced for 1 mol of S, giving Ellingham diagram for sulphides and similarly for halides using 1 mol of halogen.

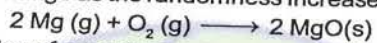


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This figure shows a number of oxide plots with slopes defined by $\Delta G / T = -\Delta S$. It is noted that the entropy change in reaction (2) is roughly the same for all metal oxides provided that the boiling point of neither the metal nor oxide is exceeded. Thus, below the boiling point of metal the slope of all the graphs are roughly the same, since $T\Delta S$ factor is same whatever be the metal. When the temperature is raised a point will be reached where the graph crossed the $\Delta G = 0$ line. Below this temperature the free energy of formation of the oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of the oxide is positive, and the oxide becomes unstable and should decompose into metal and oxygen. This explains why HgO, for instance, decomposes spontaneously into its elements when heated. Theoretically, all oxides can be decomposed to give metal and oxygen if a sufficiently high temperature can be attained. In practice, that are easily attainable and these metals can be extracted by thermal decomposition of their oxides. The diagram predicts that MgO and ZnO ought to decompose if heated strongly enough, but it does not hold out much hope for obtaining say pure Mg by straight forward heating of the oxide to a high temperature where the boiling point of the metal is exceeded. However the slope increases since the reaction is now involving a larger entropy change as the randomness increases in reactants. For example,



Here, three moles of gas phases are converted into solid phase in the reaction. This takes place above 1120°C, which is the boiling point of Mg.

Similarly Hg—HgO line changes slope at 365°C. Several of the plots show abrupt changes in the slopes. These breaks occur at temperature at which the metal undergoes a phase transition. A smaller effect is seen at the melting point. If, however the oxide undergoes a phase change, there will be an increase in the entropy of the oxide, and at such a point the curve becomes less steep. For example in the case of Pb, the oxide (PbO) boils while lead is liquid. In these instances the entropy change becomes positive for the reaction and hence the slope $\Delta G/T$ changes sign, the situation reverting to normal once the boiling point of Pb is reached.

In principle, when the plot of one metal lies below that of another, the first metal is capable of reducing the oxide of the second. A vertical line drawn on the Ellingham plot of the metal oxides at any T gives the sequence of the stabilities of metal oxides. A metal forming a more stable oxide (higher $-\Delta G$) will be potential reducing agent for a less stable oxide. If the two lines intersect, the free energy change for the reduction will be zero at that temperature and equilibrium results, but a change of temperature will make the reaction proceed provided no kinetic barriers (activation energy) exist. Thus, Mg metal will reduce CuO and FeO but not CaO. Also, it is seen that at room temperature (27°C) the order of reducing ability approximates that of standard electrode potential.

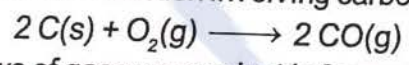
Although the SiO₂ line is above the MgO line, Si can successfully reduce MgO to free metal. Upto 1100°C, the normal boiling point of Mg, the ΔG plot for formation of SiO₂ and MgO are parallel. However, above 1100°C the plot for MgO changes slope owing to the increased entropy effect, and above 1700°C the reaction between Si and MgO proceeds with decrease in free energy. In practice, the reaction is further enhanced by the distillation of Mg metal from the reaction mixture.



Carbon or carbon monoxide as reducing agent.

In figure the plot corresponding to the change $\text{C (s)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$ is shown by a horizontal line. For this reaction ΔS is relatively small because in this case one mole of gaseous product is formed while one mole of gaseous reactant is used up. ΔG for this reaction is almost independent of temperature. The plot for CO₂ is relatively high in the figure, and at low temperature C will reduce only a few of metal oxides shown. However, the slopes of the plots for several of the metals are such that they cross the CO₂ plot; hence theoretically these metals can be reduced by C at elevated temperature.

An alternative reaction involving carbon and oxygen is the formation of CO.



Since two of gaseous product is formed from one mole of gaseous reactant, this process is accompanied by an increase in entropy. Hence, the slope of the corresponding line is negative as shown by the downward sloping line in the figure. If the temperature is high enough, C should reduce all the metal oxides, being converted into CO. The plot for the reaction of CO with oxygen is also shown.

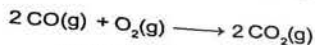
There are three curves for carbon, corresponding to complete oxidation of C to CO₂, partial oxidation to carbon monoxide, and oxidation of CO to carbon dioxide. The three curves pass through a common point at 700°C. Thus, the free energies of formation of CO₂ from carbon monoxide and carbon dioxide from carbon are equal.

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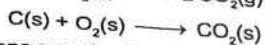
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Metallurgy

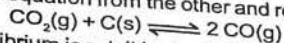


$$\Delta G = x \text{ kJ/mol}$$



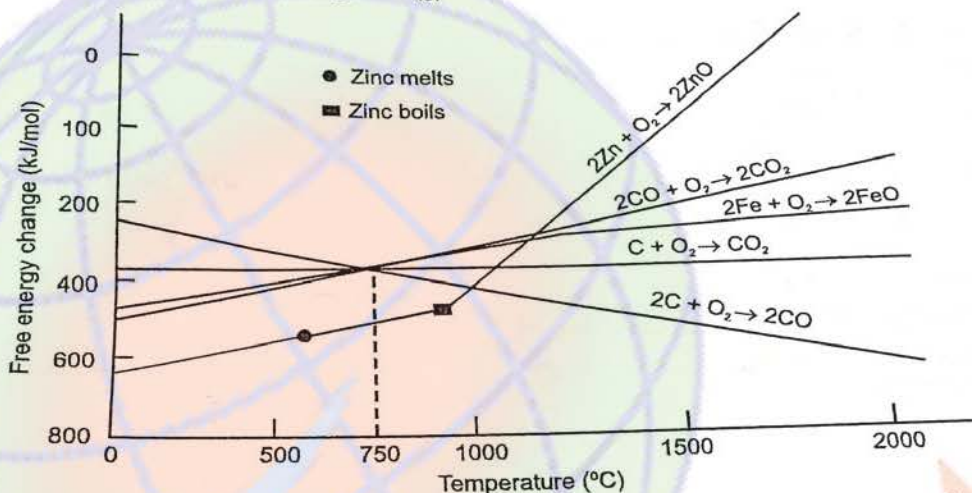
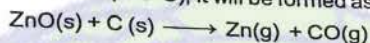
$$\Delta G = x \text{ kJ/mol}$$

Subtracting one equation from the other and rearranging, the following is obtained:



$$\Delta G = 0$$

That is, an equilibrium is set. It is clear below a temperature of 710°C, CO is a more effective reducing agent than carbon, but above this temperature the reverse is true. All three oxidation curves for the carbon system lie above that for oxidation of zinc, until a temperature of approximately 1000°C is reached. At this point, carbon is thermodynamically capable of reducing ZnO to Zn. Since this temperature is greater than the boiling point of Zn (907°C), it will be formed as a vapour. The overall equation for reduction is



It is interesting to note that the value of carbon as reducing agent is due to marked increase in disorder that takes place when carbon (an ordered solid) reacts with one mole of oxygen to give two moles of CO. The net effect is an extra mole of gas and hence an increase in disorder (an increase in entropy). It is a fact that in the region of 2000°C, carbon is thermodynamically capable of reducing most metal oxides to metal. Thus, for most metal oxides, a reducing agent is required and we should consider the overall reaction obtained by subtracting the metal oxidation from one of carbon oxidation as

$$\Delta G_{\text{overall}} = \Delta G_{\text{(C)}} - \Delta G_{\text{(M)}}$$

Metals as reducing agents :

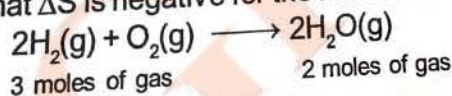
Metal oxide reduction is thermodynamically favourable for temperatures at which the line for the metal oxide is above any one of the lines for carbon oxidation, for the ΔG for metal oxide reduction by carbon is negative.

Note : The Gibb's energies of formation of most sulphides are greater than that for CS_2 . In fact, CS_2 is an endothermic compound. There, the $\Delta_f G^\circ$ of M_xS is not compensated. So reduction of M_xS is difficult. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.

Similar principles apply to other types of reduction. For instances if the plot of $\Delta G_{\text{(M)}}$ lies above $\Delta G_{\text{(C)}}$ from M' is now taking the place of C. When $\Delta G = \Delta G_{\text{(M')}} - \Delta G_{\text{(M)}}$ is negative, the reaction, $\text{MO} + \text{M}' \longrightarrow \text{M} + \text{M}'\text{O}$ is feasible.

Hydrogen as a reducing agent :

Hydrogen is not very effective reducing agent for obtaining metals from their oxides. The reason is that ΔS is negative for the reaction :



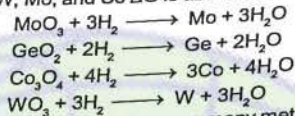
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Metallurgy

as the products are less disordered. The plot of ΔG against T therefore rises with temperature, meaning that not many metal oxide plots are intersected. H_2 will therefore reduce oxides such as $Cu(I)$ oxide and $Cu(II)$ oxide, but not the oxides of Al , Mg , and Ca . Oxides of iron are reduced only with difficulty. In the case of magnetic iron oxide Fe_3O_4 , an equilibrium composition is readily established.

In the case of W , Mo , and Co ΔG is above that of H_2O so H_2 can reduce these oxides.



This method is not widely used because many metals react with H_2 at elevated temperature forming hydrides. There is also a risk of explosion for H_2 and oxygen in the air.

Metallurgy

Naturally, the result vs T plot representation goes downward. At $[\Delta G_{(C,CO)} < \Delta G_{(Fe,Fe)}]$ a similar way the re the basis of lower T in the Blast furnace from the bottom c itself. The burnir moves to upper Fe_3O_4 coming f

Solved Examples

Example-7 The reaction $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$ ($\Delta G^\circ = -421 \text{ kJ}$) is thermodynamically feasible as is apparent from the Gibb's energy value. Why does it not take place at room temperature?

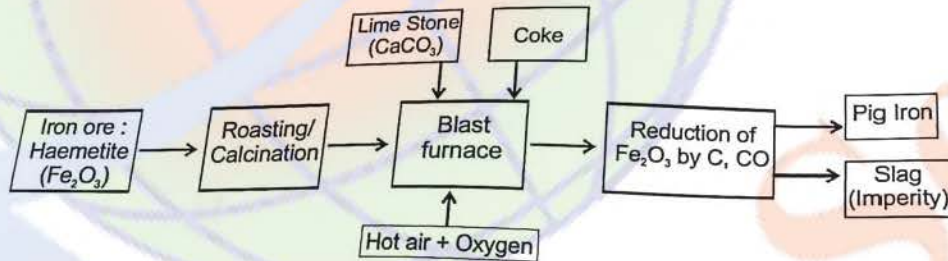
Solution Certain amount of activation energy is essential even for such reactions which are thermodynamically feasible, therefore heating is required.

Example-8 Is it true that under certain conditions, Mg can reduce Al_2O_3 and Al can reduce MgO ? What are those conditions?

Solution Below $1350^\circ C$ Mg can reduce Al_2O_3 and above $1350^\circ C$. Al can reduce MgO as evident from the Ellingham diagram.

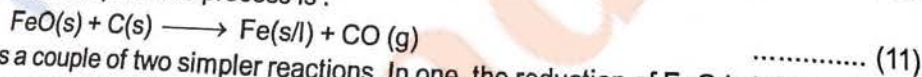
Metallurgy of Some Important Metals

- Extraction of iron (Fe)**
Ore: Haematite

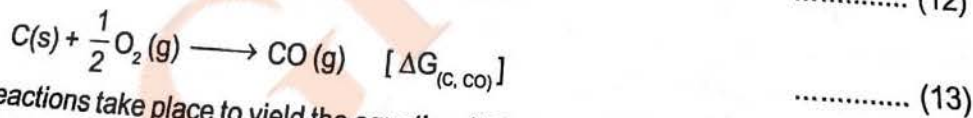
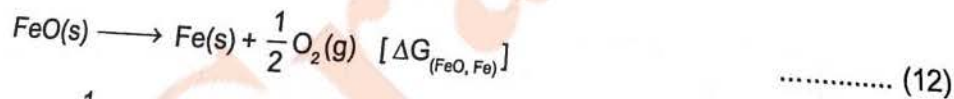


Oxide ores of iron, after concentration through calcination / roasting in reverberatory furnace (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with lime stone and coke and fed into a Blast furnace from its top with the help of a cup and cone arrangement. Here, the oxide is reduced to the metal.

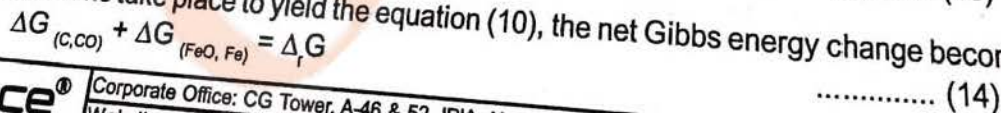
Thermodynamics helps us to understand how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process is :



It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO :



When both the reactions take place to yield the equation (10), the net Gibbs energy change becomes:



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