METALLURGY

NEET-JEE 2020
EXTRACTION
OF
METALS
WHAT IS METALLURGY?

- **Metallurgy** is a domain of materials science and engineering that studies the physical and chemical behaviour of metallic elements, their inter-metallic compounds, and their mixtures, which are called alloys.
INDEX

INTRODUCTION

OCCURRENCE OF METALS

THE MAJOR STEPS

METALLURGY OF IRON

USES
For obtaining a particular metal,

- We look for **minerals**, which are naturally occurring chemical substances in the earth’s crust obtained by mining.
- Out of many minerals only a few are viable to be used as sources of metals. Such minerals are called **ores**.
- Ores are usually contaminated with earthly or undesired materials known as **gangue**.
- The entire scientific and technological process used for isolation of metal from it’s ores is known as **METALLURGY**.
METALS AND THEIR ORES

- **Aluminium**
  - Bauxite
  - Kaolinite (a form of clay)
- **Iron**
  - Haematite
  - Magnetite
  - Siderite
  - Iron pyrites
- **Copper**
  - Copper pyrites
  - Malachite
  - Cuprite
  - Copper glance
- **Zinc**
  - Zinc blend/Sphalerite
  - Calamine
  - Zincite

\[\text{Al}_2 (\text{OH})_4 \text{Si}_2 \text{O}_5\]
\[\text{AlO}_x(\text{OH})_{3-2x} [\text{where } 0 < x < 1]\]
# METALS AND ITS EXTRACTING TECHNIQUES

<table>
<thead>
<tr>
<th>Metals - in decreasing order of reactivity</th>
<th>Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium, Sodium, Calcium, Magnesium, Aluminium</td>
<td>extract by <strong>electrolysis</strong></td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
</tr>
<tr>
<td>Zinc, Iron, Tin, Lead</td>
<td>extract by reaction with <strong>carbon</strong> or <strong>carbon monoxide</strong></td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
</tr>
<tr>
<td>Copper, Silver, Gold, Platinum</td>
<td>extracted by various chemical reactions</td>
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</tbody>
</table>
PYRO-METALLURGY

- **Pyro metallurgy** is a branch of extractive metallurgy.
- It consists of the thermal treatment of minerals and metallurgical ores and concentrates to bring about physical and chemical transformations in the materials to enable recovery of valuable metals.
- Pyrometallurgy is suitable for less reactive materials like iron, copper, zinc, chromium, tin, and manganese.
The 3 major steps involved in extraction and isolation of metals from ores are as follows:

- Concentration of Ores
- Extraction of Metal from Concentrated Ore
- Refining of Metal
Removal of unwanted materials from the ore is known as **concentration**.

On the basis of the type of ores, some of the important processes are given below:

- **HYDRAULIC WASHING**
- **MAGNETIC SEPARATION**
- **FROTH FLOATATION**
- **LEACHING**
Hydraulic washing is based on the differences in gravities of the ores and the gangue.

In this process an upward steam of running water is used to wash the powdered ore.

The lighter gangue particles are washed away and the heavier ores are left behind.
Magnetic separation is based on differences in magnetic properties of the ore components.

If either the ore or the gangue is capable of being attracted by a magnetic field, then such separations are carried out.

The ground ore is carried on a conveyer belt which passes over a magnetic roller.

Click here to see the animation
Magnetic separation process:
1. Powdered ore fed into the system.
2. Ore moves through magnetic rollers.
3. Magnetic ore is attracted and collected.
4. Non-magnetic impurities pass through.

Click to Start
This method is being used for removing gangue from *sulphide ores*.

In this process, a suspension of the powdered ore is made with water.

To it, *collectors* and *froth stabilizers* are added. The mineral particles become wet by oils while the gangue particles by water.

A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles.
Froth Floatation method:

- Principle: The mineral particles are wetted by oil while the gangue particles are wetted by water.
- This method has been in use for removing gangue from sulphide ores.
- In this process, a suspension of the powdered ore is made with water. To it collectors and froth stabilizers are added.
- Collectors - pine oil, fatty acids, xanthates, etc. - enhance non-wettability of the mineral particles.
- Froth stabilizers – cresols, aniline, etc. - stabilise the froth.
- The mineral particles are wetted by oil while the gangue particles are wetted by water. A rotating paddle agitates the mixture and draws air in it. As a result, the froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles.
The role of a depressant in the floatation process

- Depressant selectively prevents one of the sulphide ore coming to froth by complexation
- NaCN is used as depressant when ore containing ZnS and PbS, it selectively prevents ZnS from coming to the froth but allows PbS to come with the froth
Rotating Paddle

Pulp of ore + oil

Heavier gangue particle

Froth with mineral particles

Air

Pulp of ore + oil

Enlarged view of an air bubble showing mineral particles attached to it

Click to Start
HYDRO-METALLURGY

- **Hydrometallurgy** is a method for obtaining metals from their ores. It is a technique involving the use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual materials. Hydrometallurgy is typically divided into three general areas:
  i. Leaching
  ii. Solution concentration and purification
  iii. Metal or metal compound recovery
This method depends on the difference in some chemical property of the metal compound present in ore and gangue.

FOR EXAMPLE:

Bauxite ore is impure aluminum oxide ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) containing $\text{Fe}_2\text{O}_3$ and $\text{SiO}_2$ as the gangue. The bauxite ore is treated with hot sodium hydroxide solution.

$$\text{Al}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}$$

The iron oxide and sand present in bauxite ore do not dissolve in sodium hydroxide solution, so they are separated by filtration.
SOLUTION CONCENTRATION AND PURIFICATION

• After leaching, the leach liquor must normally undergo concentration of the metal ions that are to be recovered. Additionally, undesirable metal ions sometimes require removal.
• Two major types are: i) Solvent extraction ii) Ion Exchange
METAL RECOVERY

- Sometimes, however, further refining is required if ultra-high purity metals are to be produced.
- The primary types of metal recovery processes are i) electrolysis, ii) gaseous reduction, and iii) precipitation.
- For example, a major target of hydrometallurgy is copper, which is conveniently obtained by electrolysis. Cu$^{2+}$ ions reduce at mild potentials, leaving behind other contaminating metals such as Fe$^{2+}$ and Zn$^{2+}$. 
Leaching Gold and Silver

- In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (for O₂) from which the metal is obtained later by replacement:

(Mac Arthur Forest Cyanide Process)

\[ 4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq) \quad (M=\text{Ag or Au}) \]

\[ 2[M(CN)_2]^-(aq) + Zn(s) \rightarrow [Zn(CN)_4]^{2-} (aq) + 2M(s) \]

The role of NaCN in gold extraction

- In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN
EXTRACTION OF 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:

- **CONVERSION TO OXIDE**
- **REDUCTION OF OXIDE TO METAL**
Before reduction can be done the ore must be converted into metal oxide which can then be reduced. The concentrated ore can be converted into metal oxide by following two processes:

- **CALCINATION**
- **ROASTING**
CALCINATION

- Calcination is heating to high temperatures in the absence of air or oxygen.
- The main purpose of calcination of ores are to convert carbonates and hydroxides ores into oxides.
- $\text{ZnCO}_3 \rightarrow \text{ZnO} + \text{CO}_2$
- $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
- $2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$
• Purpose of calcination
  i. Remove the volatile impurities
  ii. To remove moisture
  iii. Make the mass porous
ROASTING

• The processing of strong heating of the ore in presence of excess amount of air below its melting point.

• Purpose of roasting:

  i. To convert the sulphide into oxide and sulphate
  ii. To remove impurities like S, As, Sb.
  iii. To remove moisture
  iv. To Oxidise easily oxidisable substances
• It is mainly used for sulphide ores
• it converts the sulphides into oxides

\[ 2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + \text{SO}_2 \]

\[ 4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2 \]
**CALCINATION VS ROASTING**

<table>
<thead>
<tr>
<th>CALCINATION</th>
<th>ROASTING</th>
</tr>
</thead>
<tbody>
<tr>
<td>It is the process of heating in absence of air</td>
<td>It is the process of heating in presence of air to oxidise the impurities</td>
</tr>
<tr>
<td>It is employed for carbonate ores</td>
<td>It is employed for sulphide ores</td>
</tr>
<tr>
<td>Calcination produces carbon dioxide along with metal oxide</td>
<td>Roasting produces sulphur dioxide along with metal oxide</td>
</tr>
</tbody>
</table>

**SIMILARITIES**

- Both are processes of heating the ore below its melting point.
- Both aim at removal of impurities in the ore.
The conversion of metal oxide into metal is called reduction. Depending on the nature of the metal to be extracted, the following 3 methods are used for reduction:

- Reduction by heat alone
- Chemical Reduction
- Electrolytic Reduction
The process of purifying impure metal is called refining of metals.

For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below:

- DISTILLATION
- LIQUATION
- ELECTROLYTIC REFINING
- ZONE REFINING
- VAPOUR PHASE REFINING
- CHROMATOGRAPHIC METHODS
This method is used for the purification of volatile metals like zinc, cadmium and mercury (which forms vapours easily).

In this method, the impure metal is heated in a vessel and its vapours are condensed separately in a receiver to get pure metal.

The non volatile impurities are left behind.
The easily fusible metals like tin, lead and bismuth are refined by the process called liquration.

Liquration process is used where the metal to be refined is easily fusible but the impurities do not fuse easily.

In liquration process of refining metals, the block of impure metal is placed on the top side of a sloping hearth of a furnace and heated gradually.

Under these conditions, the pure metal melts and flows down to the container. The infusible impurities are left behind on the hearth.
The metal melts inside the inert atmosphere of CO on the sloping hearth of the furnace.

Infusible impurities are left behind on the hearth.

Sloping Hearth

The metal melts inside the inert atmosphere of CO on the sloping hearth of the furnace.

Pure metal in liquid form

LIQUATION PROCESS
ELECTRO-METALLURGY

- **Electrometallurgy** is the field concerned with the processes of metal electrodeposition. There are four categories of these processes:
  - Electrowinning
  - Electrorefining
  - Electroplating
  - Electroforming
  - Electropolishing
- Electrowinning, the extraction of metal from ores.
- Electrorefining, the purification of metals.
- Metal powder production by electrodeposition is included in this category, or sometimes electrowinning, or a separate category depending on application.
Refining

- **Primary Refining**: Refining consists of purifying an impure metal. It is to be distinguished from other processes like smelting and calcining in that those two involve a chemical change to the raw material, whereas in refining, the final material is identical chemically to the original one, only it is purer.

- **Electro Refining**: It is the process of using electrolysis to increase the purity of a metal extracted from its ore (compound or mixture of compounds from which a metal can be extracted commercially).
Refining (contd...)  

- To use grey pig iron, a preliminary refining process was necessary to remove silicon. The pig iron was melted in a *running out furnace* and then run out into a trough. This process oxidised the silicon to form a slag, which floated on the iron and was removed by lowering a dam at the end of the trough. The product of this process was a white metal, known as *finers metal* or *refined iron*. 
Secondary Refining

• The purposes of secondary refining are many: temperature homogenization or adjustment; chemical adjustments for carbon, sulphur, phosphorus, oxygen and precise alloying; inclusion control; degassing, and others. The equipment and processes are equally varied.
Electro-slag refining (ESR)

• The process of electro-slag refining (ESR) is well known for production of high cleanliness steels. It involves melting of an electrode by resistive heating through a slag pool, and solidification of the droplets at the bottom of the Pool.

• Steel of the desired overall chemical composition is prepared before-hand and shaped in the form of an electrode. This requires addition of the necessary ferro-alloys to the liquid steel in order to attain the aimed concentration of alloying elements.
Electrolytic refining means refining by electrolysis.

Many metals like Cu, Zn, Ni, Ag and Au are refined by this process.

**For refining an impure metal by electrolysis:**

- A thick block of impure metal is made anode.
- A thin strip of the pure metal is made cathode.
- A water soluble salt (of the metal to be refined) is taken as electrolyte.
- On passing the electric current, impure metal dissolves from cathode and goes into electrolyte solution and pure metal from the electrolyte deposits on the cathode.
- The impurities are left behind in the solution, below the anode.

[Click here to see ANIMATION]
Zone refining is based on the principle that the impurities are more soluble in melt than in the solid state of the metal.

- A circular mobile heater is fixed at one end of a rod of the impure metal.
- The molten zone moves along with the heater which is moved forward.
- As the heater moves forward, the pure metal crystallizes out of the melt and the impurities pass on into the adjacent molten zone.
- At one end the impurities get concentrated. This end is cut off.

Click here to see ANIMATION
Moving heaters

Noble gas Atmosphere

IMPURE METAL

Crystallized pure metal

Molten Zone Containing Impurities

Metal Rod

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In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal.

The two requirements are:

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

Click here for an example
**Example:**

**Mond process for refining nickel**

In this process, nickel is heated in a stream of CO forming a volatile complex, nickel tetra carbonyl

\[
\text{Ni} + 4\text{CO} \xrightarrow{330-350 \text{ K}} \text{Ni} + 4\text{Ni(CO)}_4
\]

The carbonyl is subjected to higher temperature so that it is decomposed to give pure metal.

\[
\text{Ni(CO)}_4 \xrightarrow{450-470 \text{ K}} \text{Ni} + 4\text{CO}
\]
Vapour phase refining:

**van- Arkel method:** It is used to get ultra pure metals. Zr and Ti are purified by this process. Zr or Ti are heated in iodine vapours at about 870 K to form volatile ZrI$_4$ or TiI$_4$ which are heated over tungsten filament at 1800K to give pure Zr or Ti.

\[
\text{Ti} + 2\text{I}_2 \rightarrow \text{TiI}_4 \rightarrow \text{Ti} + 2\text{I}_2
\]

Impure \hspace{2cm} pure

\[
\text{Zr} + 2\text{I}_2 \rightarrow \text{ZrI}_4 \rightarrow \text{Zr} + 2\text{I}_2
\]

Impure \hspace{2cm} pure
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 on a gaseous medium which is moved through the adsorbent.
- Different components are adsorbed at different levels on the column.
- Later the adsorbed components are removed by using suitable solvent.
Solvent + Mixture of compounds (A + B + Sand) i.e. mobile phase

Absorbent (Stationary Phase)

Sand

A

B

Glass Wool

Click to Start
Thermodynamic aspect of metallurgy:

- $\Delta_r H$ & $\Delta_r S$ can not decide the feasibility of a reaction separately at constant Temperature (T) & Pressure (P)
- Ellingham Diagram decides the better reducing agent for metallurgy at different temperature
- $\Delta_r G$ decides the spontaneity of a reaction.
- $\Delta_r G < 0$ or negative for a spontaneous of feasible process
\( \Delta G = \Delta H - T \Delta S \)

- \( \Delta G < 0 \) or -ve means the reaction is spontaneous.
- \( \Delta G > 0 \) or +ve means the reaction is non-spontaneous.
- \( \Delta G = 0 \) means the reaction is at equilibrium.
- \( \Delta H \) is -ve for oxidation with \( O_2 \).
- For \( \Delta S \) +ve at high temperature, \( T \Delta S \) value increases,
- So, -\( T \Delta S \) in eqn. (1) becomes more -ve.
- \( \Delta G \) value becomes more –ve. The reaction becomes spontaneous & vice versa.
(ii) $\Delta_r^0 G = -RT \ln K = -2.303RT \log K$

- For a reaction: Reactants $\rightleftharpoons$ Products
  - If equilibrium constant value, $K$ is large &
  - $T$ increases, $\Delta_r^0 G$ values become more $-ve$ with increase in temperature & reaction becomes spontaneous.

(iii) $\Delta G^0 = -nF E^\theta_{cell}$

If $E^\theta_{cell}$ is positive, $\Delta_r^0 G$ values become $-ve$ & reaction becomes spontaneous.
For a coupled reaction:

(1) \( A \rightarrow B, \Delta G_1 > 0 \) or +ve means non spontaneous reaction.
(2) \( C \rightarrow D, \Delta G_2 < 0 \) or -ve means spontaneous reaction.
Reactions (1) & (2) are coupled i.e.
\[ A + C \rightarrow B + D \]
If \( \Delta G_1 + \Delta G_2 < 0 \) or –ve
Both the reaction becomes spontaneous.

Example: (1) \( \text{2FeO} \rightarrow \text{2Fe} + \text{O}_2, \quad \Delta G_1 > 0 \approx \text{Non-spontaneous.} \)
(2) \( \text{C} + \text{O}_2 \rightarrow \text{CO}_2, \quad \Delta G_2 < 0 \approx \text{Highly Spontaneous} \)
(1) + (2) : \( \text{2FeO + C + O}_2 \rightarrow \text{2Fe + CO}_2 + \text{O}_2 \)

**Overall reaction:** \( \text{2FeO + C} \rightarrow \text{Fe + CO}_2 \)
Here if \( \Delta G_1 + \Delta G_2 < 0 \) or –ve, so the reaction is spontaneous.
This is the basis of metallurgy from Ellingham diagram.
Ellingham Diagrams:
Plots of $\Delta G^\circ$ values for 1 mole of a common reactant like $O_2$, sulphur or halogen versus temperature for a number of metal & non metal to their oxide, sulphide or chloride reactions are known as *Ellingham diagram*.

If $\Delta G^\circ$ is $-$ve, the thermal reduction of an ore is feasible.
$\Delta G = \Delta H - T \Delta S$ can be compared with straight line equation: 

$$y = c + (-m) x$$

i.e. a slope is $-m$ (negative slope).

If the entropy change ($\Delta S$) is negative (non spontaneous) & with the increase in temperature, $-T \Delta S$ value becomes less negative or more positive, the slope of straight line becomes more, & the straight line graph rises up.
(a) \(2\text{CO}_\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}\) Here \(\Delta H = -\text{ve}, \Delta S = -\text{ve}\), as the temperature increases, \(\Delta G\) becomes less negative or more positive, so the plot of straight line rises up.

(b) \(2\text{C}_\text{(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_\text{(g)}\), Here \(\Delta H = -\text{ve}, \Delta S = +\text{ve}\), as the temperature increases, \(\Delta G\) becomes more negative or less positive, so the plot of straight line lowers down.

(c) \(\text{C}_\text{(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}\), Here \(\Delta H = -\text{ve}, \Delta S \approx 0\), as the temperature increases, \(\Delta G \approx \Delta H\) so, \(\Delta G\) practically remains constant & the plot of straight line is parallel to temperature axis.

(d) \(2\text{M}_\text{(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MO}_\text{(s)}\), Here \(\Delta H = -\text{ve}, \Delta S = -\text{ve}\), as the temperature increases, \(\Delta G\) becomes less negative or more positive, so the plot of straight line rises up.
In case of reaction: \(2\text{Mg(s)} + \text{O}_2(g) \rightarrow 2\text{MgO(s)}\), the straight line bends at a point B with more slope in straight line. This is because at the temperature corresponding to point B, the metal Mg melts, so \(\Delta H\) remaining nearly same, \(\Delta S\) becomes more \(-\)ve than Mg in solid state.

So, \(-T\Delta S\) becomes more \(+\)ve and \(\Delta G\) becomes more positive. The slope of the straight rises up further with more slope from B to C.
This graph shows that at low temperature below 462K, the $\Delta G^\theta$ value is negative ($< 0$), so formation of $\text{Ag}_2\text{O} \,(s)$ is spontaneous & $\text{Ag}_2\text{O}(s)$ is stable.

Above 462K, the $\Delta G^\theta$ value is positive ($> 0$), so formation of $\text{Ag}_2\text{O} \,(s)$ is non-spontaneous & $\text{Ag}_2\text{O}(s)$ is unstable so $\text{Ag}(s)$ is stable at high temperature.
For reaction:  \(2\text{Mg}_s + \text{CuO}_g \rightarrow \text{MgO}_s + \text{Cu}_s\), \(\Delta_r G^\theta = -700 - (-200) = -500\text{KJ}\), i.e. \(\Delta_r G^\theta < 0\), so the above reaction is feasible, Hence, Mg can reduce CuO.

The conclusion is: \textbf{Mg is a reducing agent} (the graph lies below in Elling. Diag.) & it can reduce CuO (The graph lying above in Elling. Diagram, backward reaction)

The substance (metal, Non metal or lower oxide) whose graph is \textbf{below} in Elling. Diagram is a \textbf{better} reducing agent having \textbf{lower} \(\Delta_r G^\theta\) value.)
Try 1:
Qu. Out of C & CO which is a better reducing agent for FeO?

(i) In the lower part of blast furnace (higher temperature)?
(ii) In the upper part of blast furnace (lower temperature)?
(iii) Can MO be reduced by C or CO or both? Explain.
Qu. Out of C & CO which is a better reducing agent for ZnO?

OR

Qu. Why is Zn not extracted from ZnO through reduction using CO?
Qu. Suggest a condition under which Mg can reduce Al\(_2\)O\(_3\) & Al can reduce MgO?
Qu. Though thermodynamically feasible, Mg can reduce Al\(_2\)O\(_3\), yet we do not prefer this method?
Reactions in a Blast furnace for Iron extraction

- Ore, limestone, and coke
- Exhaust gases (CO, CO₂)
- 3Fe₂O₃ + CO → 2Fe₃O₄ + CO₂ (Iron ore)
- Fe₃O₄ + CO₂ → 3FeO + CO₂
- CaCO₃ → CaO + CO₂ (Limestone)
- CaO + SiO₂ → CaSiO₃ (Slag)
- FeO + CO → Fe + CO₂
- C + CO₂ → 2CO
- Coke
- C + O₂ → CO₂
- FeO + C → Fe + CO
- Molten slag
- Solid waste
- Molten iron
- Pig iron
- Blast of air and oxygen
Aid to memory for the reactions taking in a blast furnace:

Charge: Fe₂O₃ (iron ore) + C (coke) + CaCO₃ (Limestone)

(a) CaCO₃ + heat (1070K) → CaO + CO₂
   C + O₂ (1070 K) → CO₂ + heat

(b) C + CO₂ (2070K) → 2CO + heat

(c) With CO₉(g)
   Temperature change: 1070K → 1270K → 1470K
   Fe₂O₃ (1070K) → Fe₃O₄ (1270K) → FeO (1470 K) → Fe

(d) With C (coke): FeO (2070K) → Fe

(e) Slag formation:
   CaO (flux) + SiO₂ (gangue) (1270K) → CaSiO₃ (Slag)
Limitations of Ellingham Diagram

(1) It does not tell anything about the kinetics of the reduction process.

(2) The concept is based on $\Delta G^\circ$ whose value is calculated from ‘$K$’ from the relation: $\Delta G^\circ = -RT \ln K$

It has presumed that all reactants & products are in equilibrium.

But this is not always true.

(3) The reactants / products may be solid. So at room temperature activation energy of reaction is high & reaction may not occur even if $\Delta G^\circ$ is negative.
Metallurgy Of Iron

The Blast Furnace:
What is a Blast Furnace?

• The purpose of a blast furnace is to reduce and convert iron oxides into liquid iron called "hot metal".

• The blast furnace is a huge, steel stack lined with refractory brick.

• Iron ore, coke and limestone are put into the top, and preheated air is blown into the bottom.
Why does iron have to be extracted in a blast furnace??

• Iron can be extracted by the blast furnace because it can be displaced by carbon.

• This is more efficient method than electrolysis because it is more cost effective.
The Method

Three substances are needed to enable the extraction of iron from its ore. The combined mixture is called the charge:

Iron ore, haematite - often contains sand with iron oxide, Fe₂O₃.

Limestone (calcium carbonate).

Coke - mainly carbon

The charge is placed in a giant chimney called a blast furnace. The blast furnace is around 30 metres high and lined with fireproof bricks. Hot air is blasted through the bottom.
Several reactions take place before the iron is finally produced...

- Oxygen in the air reacts with coke to give carbon dioxide:

\[ C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \]

- The limestone breaks down to form carbon dioxide:

\[ CaCO_{3(s)} \rightarrow CO_{2(g)} + CaO_{(s)} \]

- Carbon dioxide produced in 1 + 2 react with more coke to produce carbon monoxide:

\[ CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \]
• The carbon monoxide reduces the iron in the ore to give molten iron:

\[ 3\text{CO}_{(g)} + \text{Fe}_2\text{O}_3(s) \rightarrow 2\text{Fe}_{(l)} + 3\text{CO}_{2(g)} \]

• The limestone from 2, reacts with the sand to form slag (calcium silicate):

\[ \text{CaO}_{(s)} + \text{SiO}_{(s)} \rightarrow \text{CaSiO}_3_{(l)} \]
• Both the slag and iron are drained from the bottom of the furnace.

• The slag is mainly used to build roads.

• The iron whilst molten is poured into moulds and left to solidify - this is called cast iron and is used to make railings and storage tanks.

• The rest of the iron is used to make steel.
Cast iron is used for casting stoves, railway sleepers, gutter pipes etc.

Aluminium foils are used as wrappers for chocolates.

The fine dust of the aluminium metal is used in paints.
Chalcopyrite
Open Pit mining
Wrought Iron

- **Wrought iron**: The product of the blast furnace is pig iron, which contains 4–5% carbon and usually some silicon. To produce a forgeable product a further process was needed, usually described as *fining*, rather than *refining*. At the end of the 18th century, this began to be replaced by puddling (in a puddling furnace).
Refined iron

- **Refined iron**: To use grey pig iron, a preliminary refining process was necessary to remove silicon. The pig iron was melted in a *running out furnace* and then run out into a trough. This process oxidised the silicon to form a slag, which floated on the iron and was removed by lowering a dam at the end of the trough. The product of this process was a white metal, known as *finers metal* or *refined iron*. 
Purpose of alloying

- Strengthening of the ferrite
- Improved corrosion resistance
- Better hardenability
- Grain size control
- Improved mechanical properties like ductility, strength, toughness, etc.
- Improved Cutting ability
- Better wear resistance
Major alloying elements

- Carbon:
  Imparts hardness  Tensile strength
  Machinability  Melting point
- Nickel:
  Increases toughness and resistance to impact.
  Lessens distortion in quenching
  Strengthens steel
• Chromium:
  Joins with carbon to form chromium carbide, thus adds to depth hardenability with improved resistance to abrasion and wear. Improves corrosion resistance.

• Silicon:
  Improves oxidation resistance
  Strengthens low alloy steels
  Acts as deoxidisers
SOME ALLOY STEELS

• Nickel steels
• Chrome steels
• Chrome – Nickel steels
• Chrome – Vanadium steels
• Manganese steel
• Silicon steels
CARBON STEEL

• LOW CARBON STEELS:
  Carbon %------ 0.05 to 0.30%
  APPLICATIONS: Connecting rods, valves, gears, crankshafts.

• MEDIUM CARBON STEELS:
  Carbon %------ 0.3 to 0.7%
  APPLICATIONS: Die blocks, Clutch discs, Drop forging dies.
# Plain Carbon Steel

<table>
<thead>
<tr>
<th>Low carbon</th>
<th>Medium carbon</th>
<th>High carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good formability and weldability</td>
<td>Can be quenched to form martensite or bainite</td>
<td>Low toughness and formability</td>
</tr>
<tr>
<td>Strengthening by coldwork</td>
<td>Compromising structure between ductility and strength</td>
<td>Good hardness and wear resistance</td>
</tr>
<tr>
<td>Structure usually pearlite and ferrite</td>
<td></td>
<td>Can form martensite by quenching but risk of cracking</td>
</tr>
</tbody>
</table>

**Compare to other engineering materials**

- High strength and stiffness, reasonable toughness, easy to recycle and low cost
- Rust easily, require surface protection
CHROME STEELS

• Composition:
  • Carbon- 0.15 to 0.5%
  • Chromium- 0.7 to 11%
Mostly widely used in chemical industries because of its resistance to corrosion.
Very good strength. High resistance to wear. Cr increases tensile strength and corrosion resistance.
NICKEL STEELS

- Composition:
  - Carbon --- 0.35%
  - Nickel----- 3.5%
- Addition of nickel increases strength without a proportionality great decrease of ductility.
- Applications:
  - Storage cylinder for liquefied gases and for low temperature applications.
  - Turbine blades, highly stressed screws
CHROME- NICKEL ALLOYS

- Composition:
- Carbon - 0.35%
- Nickel – 1.25%
- Chromium – 0.6%
- Chrome-nickel steel will have, after heat treatment, almost the same strength and ductility as 3.5% Nickel steel which has also been treated.
• Nickel – increases the toughness and ductility
• Chromium- improves hardenability and wear resistance.
MANGANESE STEELS

- Composition:
  - Carbon – 0.18 to 0.48%
  - Manganese – 1.6 to 1.9%
  - Silicon – 0.2 to 0.35%
  - Manganese increases hardness and tensile strength.
  - Increased resistance to abrasion and shock
  - Applications: Grinding crushing machinery, railway tracks, etc.
CHROME VANADIUM STEELS

• Composition:
  • C - 0.26%, Cr- 0.92%, V – 0.2%
  • Chromium and vanadium increases hardenability and impart a finer grain structure.

• Applications:
  • Shafts of automobiles, aeroplanes, locomotives.
SILICON STEELS

- Composition:
  - C – 0.1%, Mn- 0.6%, Si -1%
  - Silicon imparts Strength and fatigue resistance and improves electrical properties of steel.
  - Many bridges are constructed with Silicon Structural steel which is stronger than carbon steel of equal ductility.
  - Silicon steels with greater than 4%silicon called electrical steels.
METALLURGY OF COPPER

Metallurgy of copper means

EXTRACTION OF COPPER

From its ore.
OCCURRENCE OF METAL

- NATIVE OR FREE STATE
- MINERAL
- ORES
GENERAL METHODS FOR EXTRACTION

• CRUSHING AND GRINDING
• CONCENTRATION

(1) LEVIGATION
(2) FROTH FLOATATION
(3) MAGNETIC SEPARATION
(4) LEACHING
EXTRACTION OF METAL FROM ORE

1. CONVERSION OF ORE IN METAL OXIDE (ROASTING, CALCINATION)

2. CONVERSION OF OXIDE IN METAL
   (1) SMELTING
   (2) REDUCTION BY HYDROGEN OR ALUMINIUM
   (3) ELECTROLYTIC REDUCTION
   (4) AUTO REDUCTION
• PURIFICATION

• LIQUATION

• DISTILLATION

• POLING

• CUPELLATION

• ELECTRO REFINING

• ZONE REFINING
OCCURRENCE OF COPPER

- Copper pyrite or chalcopyrite (CuFeS$_2$).
- Chalocite (Cu$_2$S) or copper glance.
- Malachite green [CuCO$_3$.Cu(OH)$_2$]
- Azurite blue [2CuCO$_3$.Cu(OH)$_2$].
- Bornite (3Cu$_2$S.Fe$_2$S$_3$) or peacock ore.
- Melaconite (CuO) etc.
STEPS INVOLVED IN EXTRACTION

- CONCENTRATION
- ROASTING
- SMELTING
- BESSEMERIZATION
- REFINING
CONCENTRATION OF ORE

The finely crushed ore is concentrated by Froth-Floatation process. The finely crushed ore is suspended in water containing a little amount of pine oil. A blast of air is passed through the suspension. The particles get wetted by the oil and float as a froth which is skimmed. The gangue sinks to the bottom.
CONCENTRATION OF ORE

- FROTH FLOATATION PROCESS

Ore & Foam

Air

Oil & Water

Powdered Ore

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The following reaction takes place.

\[
2\text{CuFeS}_2 + O_2 \rightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2
\]

\[
\text{S} + O_2 \rightarrow \text{SO}_2
\]

\[
4\text{As} + 3O_2 \rightarrow 2\text{As}_2\text{O}_3
\]

\[
4\text{Sb} + 3O_2 \rightarrow 2\text{Sb}_2\text{O}_3
\]

Cuprous sulphide and ferrous sulphide are further oxidized into their oxides.

\[
2\text{Cu}_2\text{S} + 3O_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2
\]

\[
2\text{FeS} + 3O_2 \rightarrow 2\text{FeO} + 2\text{SO}_2
\]
SMELTING PROCESS (REDUCTION BY CARBON)

- SMELTING IS CARRIED OUT IN BLAST FURNACE
  1. HOT AIR BLAST
  2. MELTING ZONE
  3, 4. REDUCTION ZONE
  5. PREHEATING ZONE
  6. ORE, SILICA, COKE
  7. EXHAUST GASES
  8. COLUMN OF ORE, SILICA, COKE
  9. REMOVAL OF SLAG
  10. MOLTEN MATTER
  11. COLLECTION OF WASTE GASES
The roasted ore is mixed with coke and silica (sand) SiO$_2$ and is introduced into a blast furnace. The hot air is blasted and FeO is converted into ferrous silicate FeSiO$_3$.
BESSEMERIZATION

Copper metal is extracted from molten matte through bessemerization. The matte is introduced into a Bessemer converter which is held in place by tuyers. The air is blown through the molten matte. Blast of air converts \( \text{Cu}_2\text{S} \) partly into \( \text{Cu}_2\text{O} \) which reacts with the remaining \( \text{Cu}_2\text{S} \) to give molten copper.
The roasted ore is mixed with coke and silica (sand) $\text{SiO}_2$ and is introduced into a blast furnace. The hot air is blasted and FeO is converted into ferrous silicate ($\text{FeSiO}_3$).

$$\text{FeO} + \text{SiO}_2 \rightarrow \text{FeSiO}_3$$

$$\text{Cu}_2\text{O} + \text{FeS} \rightarrow \text{Cu}_2\text{S} + \text{FeO}$$

$\text{FeSiO}_3$ (slag) floats over the molten matte of copper.
BESSEMERIZATION

• $2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$
• $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$
Blister copper is refined by electrolysis. Blocks of blister copper are used as anodes and thin sheets of pure copper act as cathodes. The cathode plates are coated with graphite in order to remove depositing copper. The electrolyte is copper sulphate (CuSO$_4$) mixed with a little amount of H$_2$SO$_4$ to increase the electrical conductivity. Optimum potential difference is 1.3 volt for this electrolytic process.
During electrolysis, pure copper is deposited on the cathode plates and impurities which are soluble and fall to the bottom of the cell as anode mud or sludge.
REFINING OF COPPER

- \( \text{Cu} \rightarrow \text{Cu}^{+2} + 2e^- \) (at the anode)
- \( \text{Cu}^{+2} + 2e^- \rightarrow \text{Cu} \) (at the cathode)

This electrically refined copper is 100% pure
<table>
<thead>
<tr>
<th>Metal</th>
<th>Main Occurrence</th>
<th>Main method of Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>Common Salt,</td>
<td>Electrolysis of fused with</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Carnallite, Magnesite</td>
<td>Electrolysis of fused with</td>
</tr>
<tr>
<td>Calcium</td>
<td>Lime stone, Gypsum,</td>
<td>Electrolysis of fused and</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Bauxite,</td>
<td>Electrolysis of in molten (cryolite)</td>
</tr>
<tr>
<td>Copper</td>
<td>Bauxite,</td>
<td>Partial oxidation of sulphide ore</td>
</tr>
<tr>
<td>Silver</td>
<td>Argentite, Native silver</td>
<td>Hydrometallurgy</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zinc Blende, Calamine,</td>
<td>Reduction of with carbon or electrolysis of</td>
</tr>
<tr>
<td>Lead</td>
<td>Galena,</td>
<td>Reduction of with carbon</td>
</tr>
<tr>
<td>Tin</td>
<td>Cassiterite,</td>
<td>Reduction of with carbon</td>
</tr>
<tr>
<td>Iron</td>
<td>Haematite, Magnetite,</td>
<td>Reduction of oxide with carbon monoxide</td>
</tr>
<tr>
<td>Chromium</td>
<td>Chromite,</td>
<td>Reduction of with</td>
</tr>
<tr>
<td>Nickel</td>
<td>Millerite,</td>
<td>Reduction of with</td>
</tr>
<tr>
<td>Mercury</td>
<td>Cinnabar,</td>
<td>Direct reduction of HgS by heat alone</td>
</tr>
</tbody>
</table>