



# INDUSTRIAL METALLURGY

## BSC. (H) CHEMISTRY SEMESTER- VI

BY DR. SUNIL YADAV

EMAIL: [SUNILGAYADIN@GMAIL.COM](mailto:SUNILGAYADIN@GMAIL.COM)

# Metallurgy

Metallurgy is a subject which deals with the science and technology applied for the extraction of metals economically on a large scale from their respective ores.

**Mineral:** The compounds of a metal which are naturally available in the earth's crust and can be obtained by mining.

**Ore:** The minerals from which a metal can be extracted economically and conveniently.

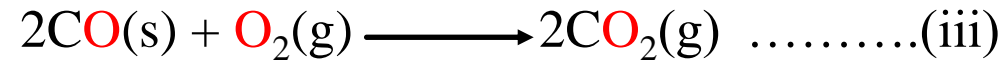
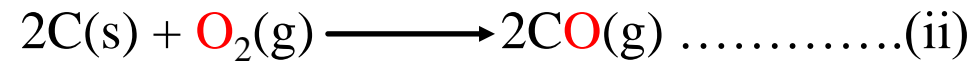
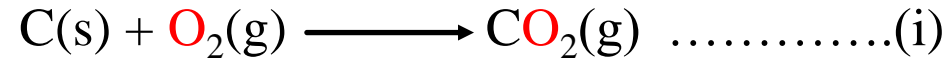
## Principal Steps Involved in the Recovery of a Metal from its Ore:

- 1. Concentration of Ore or Dressing of Ore:** Two methods. **(i) Physical:** Gravity separation or levigation, magnetic separation and froth floatation. **(ii) Chemical:** Leaching-by using chemical reagent.
- 2. Conversion of Ore into its Oxide:** Calcination (heating to high temp. in limited supply of air or in absence of air) and roasting (heating to high temp. in presence of excess air).
- 3. Production of Metals by Reduction:** Carbon reduction, self reduction ( $\text{PbS}$ ,  $\text{Cu}_2\text{S}$  and  $\text{HgS}$ ), thermite reduction (Goldschmidt-thermite process- for high m.p. metal oxides), metal replacement method (hydrometallurgy), electrolytic reduction (for strong electropositive metals) and thermal decomposition method (e.g.  $\text{Hg}$ ,  $\text{Ag}$  etc).
- 4. Purification and Refining of Metals:** The metals obtained by reduction methods from the concentrated ores are usually impure. These impure metals may be associated with small amounts of: **(i)** Unchanged ore, **(ii)** Other metals produced by the simultaneous reduction of their compounds originally present in the ore, **(iii)** Non-metals like silicon, carbon, phosphorus, etc., **(iv)** Residual slag, flux, etc. **(v)** The impure metal is thus subjected to some purifying processes known as refining in order to remove the undesired impurities.

# Reducing Nature of Carbon

❖ Carbon in the form of coke, charcoal or carbon monoxide is used as a reducing agent in *pyrometallurgical* operations. Such a reduction process used in the extraction of a metal is termed smelting.

❖ When carbon is to act as a reducing agent, the following three reactions are possible:

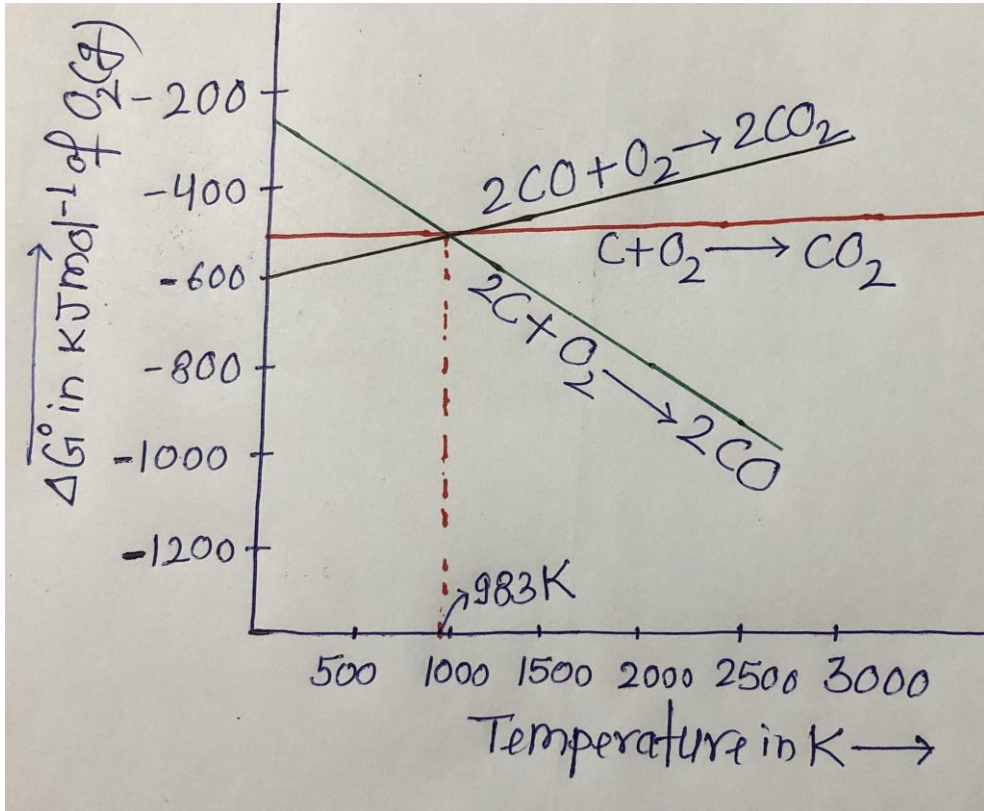


❖ In the first reaction (formation of CO<sub>2</sub>) there is hardly any change in entropy, *i.e.*,  $\Delta S^\circ = 0$  and therefore,  $\Delta G^\circ$  remains nearly the same with rise in temperature *i.e.*,  $\Delta G^\circ$  is independent of temperature.

❖ In the second reaction (formation of CO), there is increase in entropy ( $\Delta S^\circ$  is positive) and therefore,  $\Delta G^\circ$  becomes more negative with increase in temperature.

❖ However, in third reaction, there is decrease in entropy ( $\Delta S^\circ$  is negative) and therefore,  $\Delta G^\circ$  becomes less negative with increase in temperature.

# Ellingham Diagram of Carbon



**Figure: Ellingham Diagram of Carbon.**

- ❖ The three curves have been found to intersect at 983 K.
- ❖ It implies that above this temperature, the reaction (ii) is most suitable. It means that carbon can reduce any metal oxide at very high temperatures and is then itself oxidised to CO.
- ❖ However, the reduction with carbon at high temperatures is not preferred in all cases due to the following reasons:
  - ❖ It involves high cost.
  - ❖ Some metals react with carbon at high temperatures and form carbides.
  - ❖ There are many practical difficulties in the maintenance of high temperature.
  - ❖ From the plot for the reaction of carbon monoxide with oxygen, it is evident that carbon monoxide acts as a better reducing agent than carbon at temperatures below 983 K.

# Theory of Reduction of Metal Oxide with Carbon

- ❖ During reduction the metal oxide decomposes



and the carbon (reducing agent) takes away the oxygen, *i.e.* it undergoes oxidation.



- ❖ The role of the reducing agent is to provide a large negative  $\Delta G^\circ$  to make the sum of the  $\Delta_r G^\circ$  of the above two reactions, (*i.e.*, reduction of metal oxide and oxidation of carbon or carbon monoxide) negative.

Reversing the equation (i)



Subtracting equation (v) from equations (ii), (iii) and (iv) respectively, we have,



# Theory of Reduction of Metal Oxide with Carbon

- ❖ The equations (vi), (vii) and (viii) describe the reduction of the metal oxide,  $M_xO$ . The  $\Delta_r G^\circ$  values of these equations can be obtained from Ellingham diagram (Fig.).
- ❖ If  $\Delta_r G^\circ$  values are negative, the reduction is feasible otherwise not.
- ❖ Greater the difference, easier is the reduction.
- ❖ Without making any calculations for  $\Delta_r G^\circ$  the prediction about the feasibility of a reduction process can be made by looking at the Ellingham diagram.
- ❖ Metal oxide placed higher in the diagram can be reduced by the element (metal) involved in the formation of the oxide placed lower in the diagram.
- ❖ It is important to note that if a particular reduction process does not take place at a lower temperature, it may take place at a higher temperature.
- ❖ Ellingham diagram also helps in selecting such a temperature.
- ❖ The temperature is indicated by the intersection of the two curves.



# Theory of Reduction of Haematite

In the Ellingham diagram (Fig.), there are three curves which illustrate the formation of ferric oxide from iron, formation of CO from carbon and formation of CO<sub>2</sub> from CO. The curves cross each other at 1073 K.

Above 1073 K,  $\Delta G^\circ$  for the formation of Fe<sub>2</sub>O<sub>3</sub> is less negative than  $\Delta G^\circ$  for the formation of carbon monoxide from carbon. Thus, above 1073 K, carbon (coke) can reduce Fe<sub>2</sub>O<sub>3</sub>, i.e.,  $\Delta_r G^\circ$  for the reaction, is negative (T greater than 1073 K).

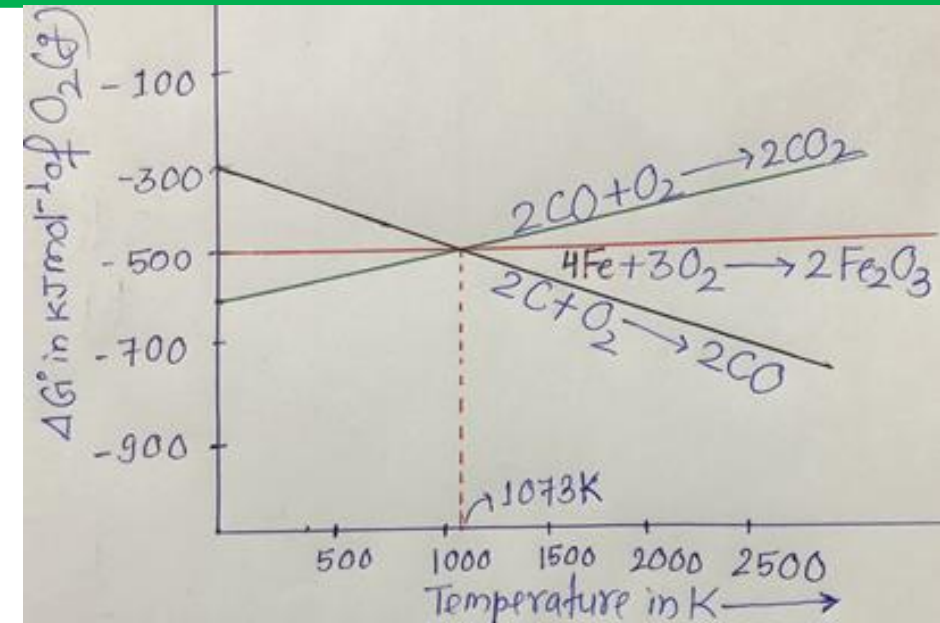
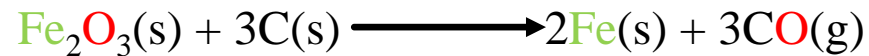


Figure: Ellingham diagram for the reduction of haematite.

Below 1073 K,  $\Delta G^\circ$  for formation of CO from carbon is less negative than  $\Delta G^\circ$  for the formation of Fe<sub>2</sub>O<sub>3</sub>.  $\Delta_r G^\circ$  for the reduction of Fe<sub>2</sub>O<sub>3</sub> with carbon will be positive and hence, reduction- is not possible. However, it is observed from the diagram that  $\Delta G^\circ$  formation of CO<sub>2</sub> from CO is more negative than  $\Delta G^\circ$  of formation of Fe<sub>2</sub>O<sub>3</sub>. This means that Fe<sub>2</sub>O<sub>3</sub> can be reduced by CO below 1073 K, i.e.,  $\Delta_r G^\circ$  for the reaction, is negative

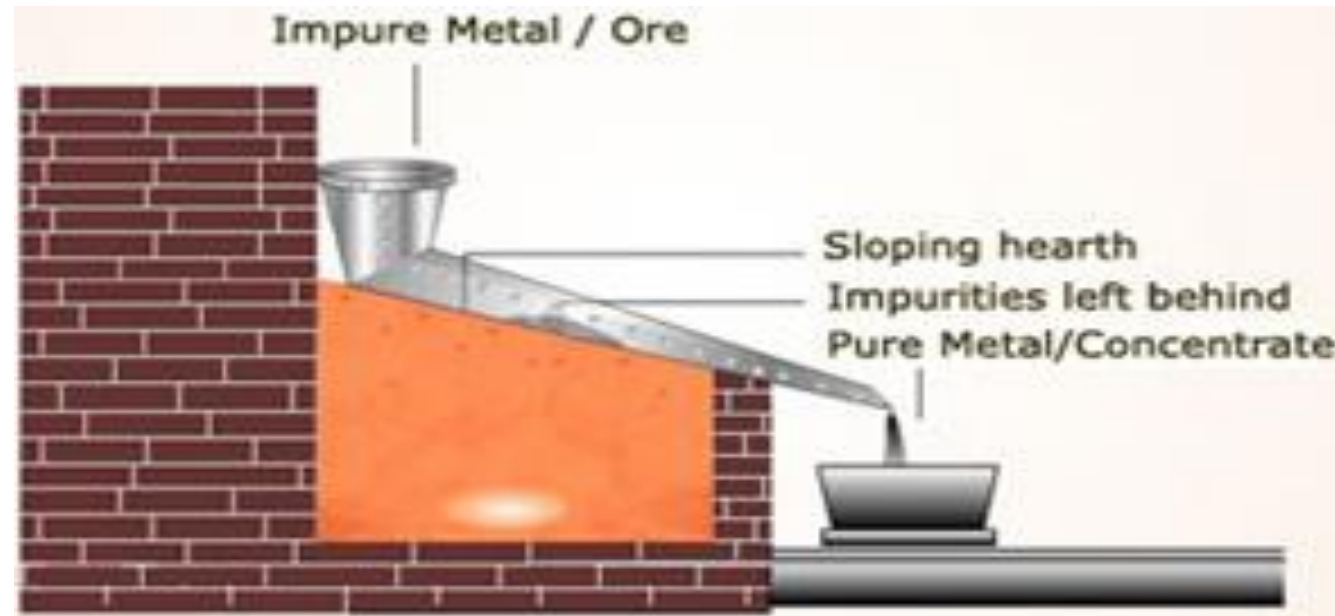


Thus, in the blast furnace, reduction of Fe<sub>2</sub>O<sub>3</sub> occurs in different temperature ranges either below 1073 K by carbon monoxide or above 1073 K by carbon (coke).

# Refining or Purification or Preparation of Ultrapure Metals

- ❖ The following refining processes may be applied depending upon the nature of the metal under treatment and the nature of the impurities.

**1. Liquation process:** This process is based on the difference in fusibility of the metal and impurities. When the impurities are less fusible than the metal itself, this process is employed. The impure metal is placed on the sloping hearth of a furnace and gently heated. The metal melts and flows down leaving behind the impurities on the hearth. This method is used to purify the metals like Bi, Sn, Pb, Hg, etc.



**Figure: Diagrammatic representation of liquation.**

<https://ask.learncbse.in/t/what-is-liquation-method-explain-briefly-with-proper-diagram-and-also-tell-where-it-is-used/67255>



# Refining or Purification or Preparation of Ultrapure Metals

**2. Distillation:** This process is used for those metals which are easily volatile. The impure metal is heated in a retort and its vapours are separately condensed in a receiver. The non-volatile impurities are left-behind in the retort. This is used for the purification of Zn, Cd, Hg, etc.

**3. Pyrometallurgical oxidation process:** This process is used when the impurities have a greater affinity for oxygen than the metal itself. This method is usually employed for refining the metals like Fe, Cu, Ag, etc. The oxidation is done by various ways:

(i) **Cupellation**: The impure metal is heated in a cupel or oval shaped crucible made of bone ash or cement and a blast of air is passed over the molten mass. The impurities get oxidised and removed with the blast of air. For example the impurity of lead present in silver is removed by cupellation process.

(ii) **Bessemerisation**: The impure metal is heated in a furnace and a blast of compressed air is blown through the molten mass. The impurities get oxidised. For example, the molten pig iron is taken in a Bessemer converter and compressed air is passed which oxidises the impurities.



(iii) **Poling**: The impure metal containing oxides as impurity can be purified by this method. The molten impure metal is stirred with green poles of wood. The green poles of wood release the hydrocarbon gases which reduce the oxide impurities. This method is especially used in the purification of copper (old method).

# 3. Electrolytic Refining of Metals

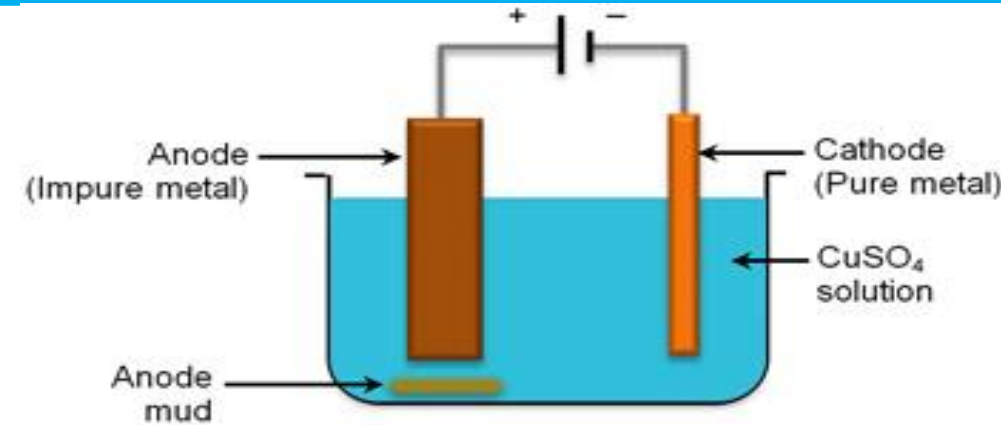
- ❖ Many of the metals such as copper, silver, gold, aluminium, lead, etc. are purified by this method. This is perhaps the most important method.
- ❖ The impure metal is made anode while a thin sheet of pure metal acts as a cathode.
- ❖ The electrolytic solution consists of generally an aqueous solution of a salt or a complex of the metal. On passing the current, the pure metal is deposited on the cathode and equivalent amount of the metal gets dissolved from the anode.
- ❖ Thus, the metal is transferred from anode to cathode through solution.
- ❖ The soluble impurities pass into the solution while the insoluble one, especially less electropositive impurities collect below the anode as anodic mud or anode sludge.

## (i) Purification of Copper:

Impure metal: **Anode**

Thin sheets of copper: **Cathode**

Electrolyte-An aqueous solution of copper sulphate containing  $\text{H}_2\text{SO}_4$ . A current of 1.3 volt is used. Anodic mud contains Ag, Au, Pt, Pd, etc. and impurities like Fe, Zn, Ni, etc. pass into the solution. 99.9% pure copper is obtained.



**Figure: Diagrammatic representation of electrorefining**

<https://etn-socrates.eu/the-unsung-heroes-of-copper-electro-refinery>

## (ii) Purification of Silver:

Impure metal-**Anode**

A thin sheet of pure silver-**Cathode**

Electrolyte-An aqueous solution of  $\text{AgNO}_3$  containing  $\text{HNO}_3$ .

## (iii) Purification of Lead:

Impure metal-**Anode**

A sheet of pure lead-**Cathode**

Electrolyte-A solution of lead silico fluoride  $\text{PbSiF}_6$  containing 8-10% of  $\text{H}_2\text{SiF}_6$ .

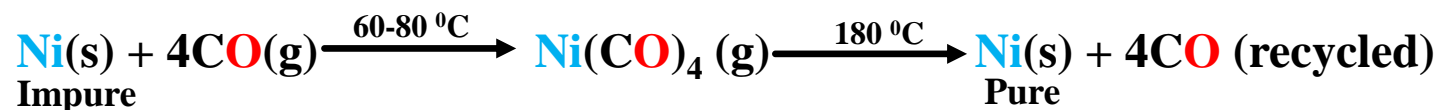
## 4. Special Methods

1. **Vapour Phase Refining:** The two essential criteria for vapour phase refining are:

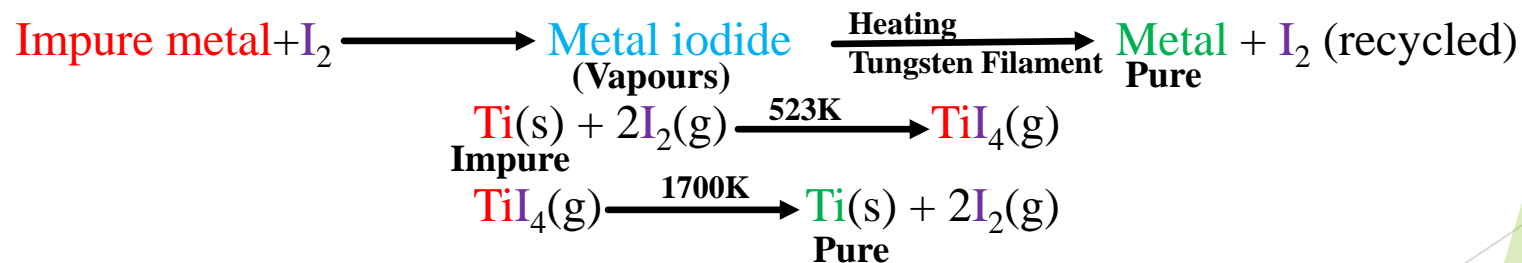
- ❖ The intermediate compound formed has to be volatile.
- ❖ The intermediate compound formed has to be unstable, *i.e.* it should decompose on heating at practically achievable temperature.

This refining technique is used in the following purification processes:

(i) **Mond's Process:** Nickel is purified by this method. Impure nickel is treated with carbon monoxide at 60-80°C when volatile compound, nickel carbonyl, is formed. Nickel carbonyl decomposes at 180°C to form pure nickel and carbon monoxide which can again be used.

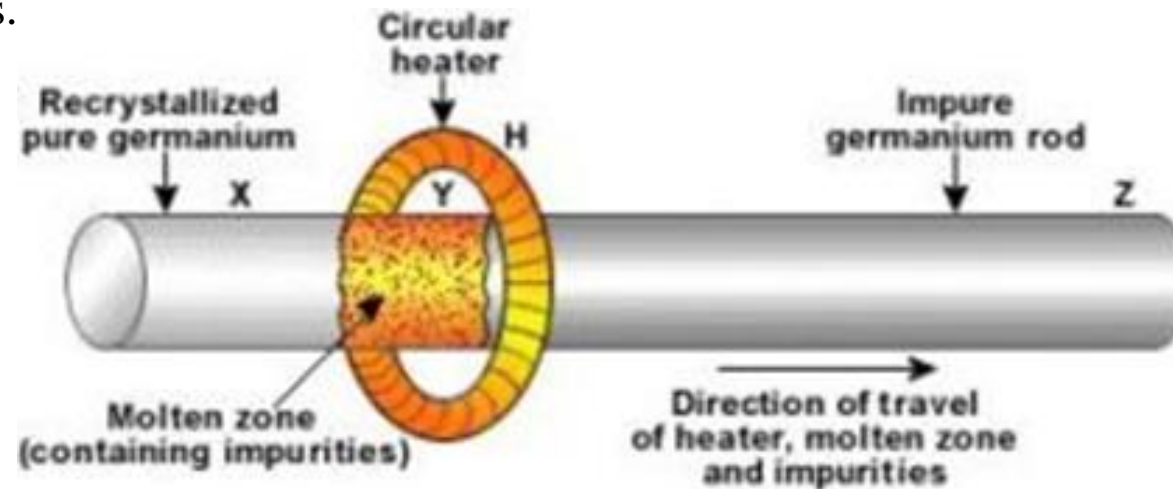


(ii) **Van-Arkel-de Boer Process:** This method is generally applied for obtaining ultrapure metals. The impure metal is converted into a volatile compound while the impurities are not affected. The volatile compound is then decomposed electrically to get the pure metal. Ti, Zr, Hf, Si, etc., have been refined by this method.



## 5. Zone refining or Fractional crystallisation

- ❖ Metals like Si, Ge and Ga of high purity (which are used in **semiconductors**) are purified by this method. This process is known as **ultrapurification** because it results in impurity level decreasing to **ppm** level.
- ❖ Zone refining is based upon fractional crystallization as the impurity prefers to stay in the melt and on solidification only the pure metal solidifies on the top surface of the melt. In this process, a ring furnace is heated to a suitable temperature for melting the metal rod and producing a thin zone throughout the cross-sectional area.
- ❖ It is desirable that the diameter of the rod,  $d$  is small enough to give a uniform melt. When the melted zone in the metal rod is ready, the furnace is allowed to move downwards very slowly together with the melted zone. The furnace is then switched off, cooled down and taken to the top again for repetition of the process. Almost all impurity sweeps out to the bottom after several repetitions of the process.



Zone refining of germanium metal.

**Figure: Diagrammatic representation of zone refining**

<https://www.velelectronics.com/zone-refining-in-india>

# References

- 1. Concise Inorganic Chemistry 5<sup>th</sup> Edition, Blackwell Science by J.D. Lee**
- 2. Shriver & Atkins' Inorganic Chemistry 5<sup>th</sup> Edition, W. H. Freeman and Company, New York**
- 3. Principles of Inorganic Chemistry 31<sup>st</sup> Edition, Milestone Publishers and Distributers, Delhi by Puri, Sharma and Kalia**
- 4. Inorganic Chemistry, G.R. Bathla Publications by O.P. Tandon**





**Thank You**