General Principles and Processes of Isolation of Elements

Concentration of Ores

- Some important ores of some metals are given in the following table.

Metal	Occurrence
Aluminium	1. Bauxite, $Al_2O_3 . x\ H_2O$ 2. Cryolite, Na_3AlF_6
Iron	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4 B.
Copper	1. Copper pyrites, $CuFeS_2$ 2. Copper glance, Cu_2S 3. Malachite, $CuCO_3.Cu(OH)_2$ 4. Cuprite, Cu_2O
Zinc	1. Zinc blende or Sphalerite, ZnS 2. Calamine, $ZnCO_3$ 3. Zincite, ZnO

Some Important Terms

- **Metallurgy**: Process of extracting pure metal from their ore
- **Minerals**: Mixture of metal compounds, soil, sand, limestone and rock
- **Gangue**: Impurities present in ore like mud, silica etc.
- **Ores**: Minerals from which metals can be extracted economically at low cost and with minimum cost
- **Flux**: Substance added in furnace to remove gangue
- **Slag**: The fusible mass formed when flux combined with gangue
- **Smelting**: Process of extracting metal from their oxide ores by reducing the roasted oxides

Steps Involved in Extraction

1. Crushing and grinding ore
2. Concentration of the ore
3. Roasting and Calcination of the ore
4. Reduction of the metal oxide
5. Refining of the pure metal

Crushing and Grinding

- Crushing of the ore to fine powder with the help of big jaw crushers and ball mills
- The process is known as **pulverisation**

Concentration (or Dressing or Benefaction) of ores

- Removal of unwanted materials such as sand and clay from ores

Some Important Procedures

- **Hydraulic washing**

- Based on gravity differences between the ore and the gangue particles

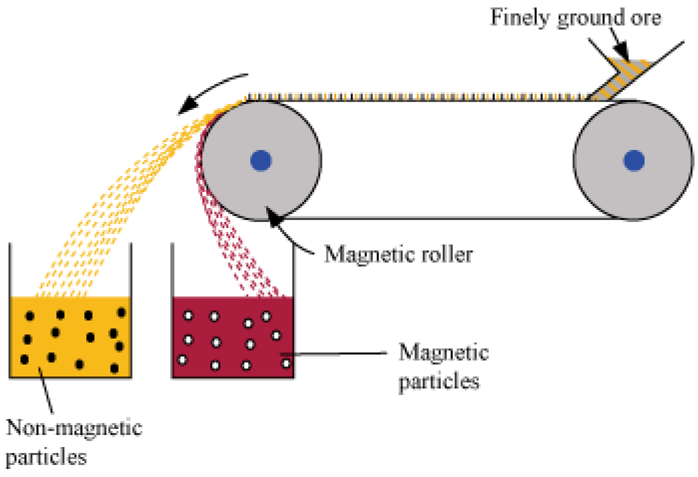
- In one such process, the lighter gangue particles are washed away by a stream of water, leaving behind the heavier ore.

- **Magnetic separation**

- Based on differences in magnetic properties between the ore and the gangue particles

- Magnetic field is applied to separate magnetically attractive particles from magnetically non-attractive particles.

- Schematic diagram of magnetic separation is as follows:



- **Froth-Floatation method**
- Applied to remove gangue from sulphide ores
- Mineral and gangue particles are separated by first wetting the mineral particles with oil, and gangue particles with water, and then the mineral particles are carried out by forming froth.
- Sometimes, depressants are used for separating two sulphide ores by selectively preventing one ore from forming froth. For example, NaCN is used as a depressant for separating two sulphide ores, ZnS and PbS.
- **Leaching**

  Used if the ore is soluble in some suitable solvent
- Leaching of alumina from bauxite:

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \xrightarrow[35-36\text{ bar}]{473-523\text{K}} 2Na\left[Al(OH)_4\right]_{(aq)}$$

$$2Na\left[Al(OH)_4\right]_{(aq)} + CO_{2(g)} \longrightarrow Al_2O_3 \cdot xH_2O_{(s)} + 2NaHCO_{3(aq)}$$

$$Al_2O_3 \cdot xH_2O_{(s)} \xrightarrow{1470\text{ K}} Al_2O_{3(s)} + xH_2O_{(g)}$$

- Leaching of some other ores:

  Ores of metals like Ag and Au are leached with a dilute solution of NaCN and KCN in the presence of air.

$$4M_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(aq)} + O_{2(g)} \rightarrow 4\,[M(CN)_2]^-_{(aq)} + 4OH^-_{(aq)}$$

$$(M = Ag \text{ or } Au)$$

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

Extraction of Crude Metal from Concentrated Ore & Thermodynamic Principles of Metallurgy

Extraction of Crude Metal from Concentrated Ore

- Two steps –
- Conversion of concentrated ore into oxide
- Reduction of the oxide to metal
- Ores are converted into oxides because it is easier to reduce oxides
- Conversion into oxide
- **Calcination**

It involves the conversion of hydroxide and carbonate ores into oxides by heating the ores either in the absence or in a limited supply of air, at a temperature below the melting point of the metal.

This process causes the volatile matter to escape, thereby leaving behind the metal oxide.

$$Fe_2O_3.3H_2O_{(s)} \xrightarrow{\Delta} Fe_2O_{3(s)} + 3H_2O_{(g)}$$

Limonite

$$ZnCO_{3(s)} \xrightarrow{\Delta} ZnO_{(s)} + CO_{2(g)}$$

Calamine

$$CaMg(CO_3)_2 \xrightarrow{\Delta} CaO_{(s)} + MgO_{(s)} + 2CO_{2(g)}$$

Dolomite

- **Roasting**

It involves the conversion of sulphide ores into oxides by heating the ores in a regular supply of air, at a temperature below the melting point of the metal.

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

Zinc blende

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$$

Galena

$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$

Copper glance

If the ore contains iron, then it slags off as iron silicate.

$$FeO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

- Reduction of the oxide to metal
- It involves heating the oxide with reducing agents such as C, CO and some metals.
- $M_xO_y + yC \longrightarrow xM + yCO$
- Some metal oxides require heating as they are difficult to be reduced.

Thermodynamic Principles of Metallurgy

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

Where,

ΔG = Change in Gibbs energy

ΔH = Change in enthalpy

T = Temperature

ΔS = Change in entropy

- $\Delta G^{\theta} = -RT \ln K$

Where,

ΔG^{θ} = Change in Gibbs energy in standard condition

R = Gas constant

T = Temperature

K = Equilibrium constant

- Reaction will proceed only when ΔG = − ve, i.e., $\Delta G < 0$

When $\Delta S > 0$ and T is large, $T\Delta S > \Delta H$

And then, $\Delta H - T\Delta S < 0$

$\Rightarrow \Delta G < 0$

Ellingham Diagram

Graphical representation of Gibbs energy

Useful for predicting the feasibility of thermal reduction of ores

Limitations:

It predicts whether a reaction is feasible or not.

It does not give an idea about the kinetics of the reactions

The interpretation of ΔG^{θ} is based on ($\Delta G^{\theta} = -RT \ln K$). It is presumed that the reactants and the products are in equilibrium. But this is not always true as the reactant or the product may be solid.

- When a metal oxide is reduced, the oxygen lost by it is taken away by the reducing agent and as a result, the reducing agent gets converted into its oxide as follows:

$$M_xO_{(s)} + C_{(s)} \longrightarrow xM_{(s\,or\,l)} + CO_{(g)}$$

$$M_xO_{(s)} + CO_{(g)} \longrightarrow xM_{(s\,or\,l)} + CO_{2(g)}$$

$$M_xO_{(s)} + \frac{1}{2}C_{(s)} \longrightarrow xM_{(s\,or\,l)} + \frac{1}{2}CO_{2(g)}$$

These reactions describe the actual reduction of the metal oxide M_xO. The $\Delta_r G^{\theta}$ values for these reactions can be calculated from $\Delta_f G^{\theta}$ values, and from this, it can be predicted whether a reaction is feasible or not. A selection of suitable reducing agent and appropriate temperature is required for the reduction of a metal oxide.

Applications of Thermodynamic Principles

Extraction of Iron from Its Oxide

- One of the main steps in the reduction of iron oxide is

$$\mathrm{FeO}_{(s)} + \mathrm{C}_{(s)} \longrightarrow \mathrm{Fe}_{(s/l)} + \mathrm{CO}_{(g)}$$

It is a combination of two simpler reactions.

$$\mathrm{FeO}_{(s)} \longrightarrow \mathrm{Fe}_{(s)} + \frac{1}{2}\mathrm{O}_{2(g)} \left[\Delta G_{(\mathrm{FeO,Fe})}\right]$$

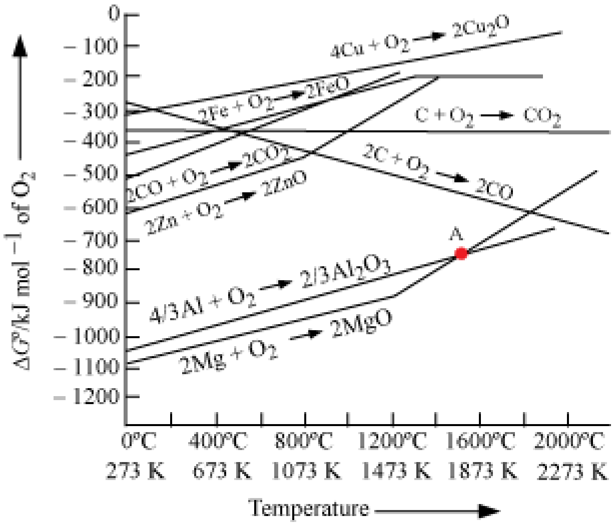
$$\mathrm{C}_{(s)} + \frac{1}{2}\mathrm{O}_{2(g)} \longrightarrow \mathrm{CO}_{(g)} \left[\Delta G_{(\mathrm{C,CO})}\right]$$

Net Gibbs energy change

$$\Delta G_{(\mathrm{C,CO})} + \Delta G_{(\mathrm{FeO,Fe})} = \Delta_r G$$

The result reaction will take place when $\Delta_r G$ is negative.

- The following figure is a plot of Gibbs energy $\left(\Delta G^{\theta}\right)$ vs *T* for the formation of some oxides (Ellingham diagram).



- An element can reduce the oxide of another element if the standard free energy of formation $\left(\Delta_f G^{\theta}\right)$ of the oxide of the former is more negative than the latter.
- It can be observed from the given graph that above 1073 K (approx.), $\Delta G_{(\mathrm{C,CO})} < \Delta G_{(\mathrm{Fe,FeO})}$. So, coke will reduce FeO, and will itself be oxidised to CO.
- During the extraction of iron, the reduction of iron oxides takes place in a blast furnace. In this process, hot air is blown from the bottom of the furnace and coke is burnt to raise the temperature

up to 2200 K in the lower portion itself. The temperature is lower in the upper part. Thus, it is the lower part where the reduction of iron oxides (Fe_2O_3 and Fe_3O_4) takes place.

- The reactions taking place in the lower temperature range (500 – 800 K) are:

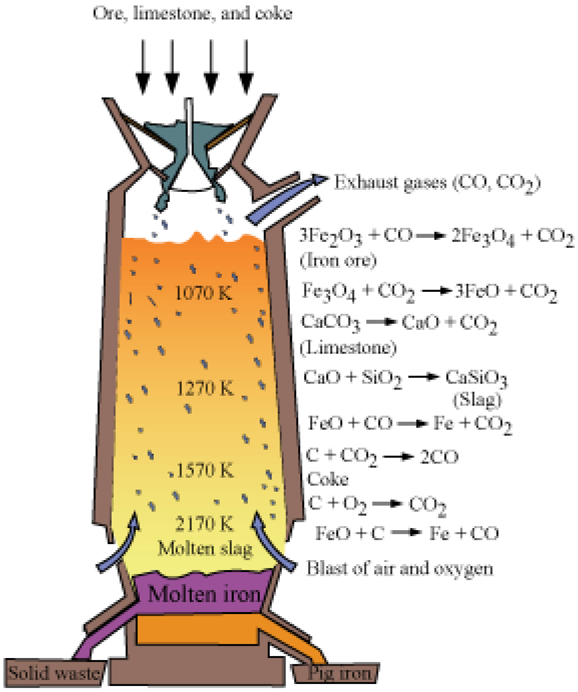
$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$
$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

- The reactions taking place in the higher temperature range (900 – 1500 K) are:

$$C + CO_2 \longrightarrow 2CO$$
$$FeO + CO \longrightarrow Fe + CO_2$$

- The silicate impurity of the ore is removed as slag by calcium oxide (CaO), which is formed by the decomposition of limestone ($CaCO_3$).

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$CaO + SiO_2 \longrightarrow \underset{\substack{\text{Calcium silicate} \\ \text{(Slag)}}}{CaSiO_3}$$



Extraction of Copper from Cuprous Oxide (Cu_2O)

- Coke will reduce Cu_2O as $\Delta G_{(C,CO)} < \Delta G_{(Cu,Cu_2O)}$

  (From Ellingham diagram)

- The sulphide ores are roasted/smelted to give oxides

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

- Then, coke can be used for reducing the oxide metallic copper

  $$Cu_2O + C \longrightarrow 2Cu + CO$$

- In the actual process, the ore is mixed with silica and heated in a reverberatory furnace.

- In the furnace, iron slags off as iron silicate, and copper is formed as copper matte (containing Cu_2S and FeS).

  $$FeO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

- Copper matte is put in a silica-lined convertor to remove the remaining FeO and FeS present in the matte as slag ($FeSiO_3$). Also, the same silica is added to the silica-lined convertor. Then, a hot air blast is blown. As a result, the remaining FeS and FeO are converted into iron silicate ($FeSiO_3$), and Cu_2S is converted into metallic copper.

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

- Copper is obtained as blister copper.

Extraction of Zinc from Zinc Oxide

- Coke is used for reducing zinc oxide.

  $$ZnO + C \xrightarrow{\text{coke, 673 K}} Zn + CO$$

- The obtained metal is distilled off and collected by rapid chilling.

Electrochemical Principles of Metallurgy

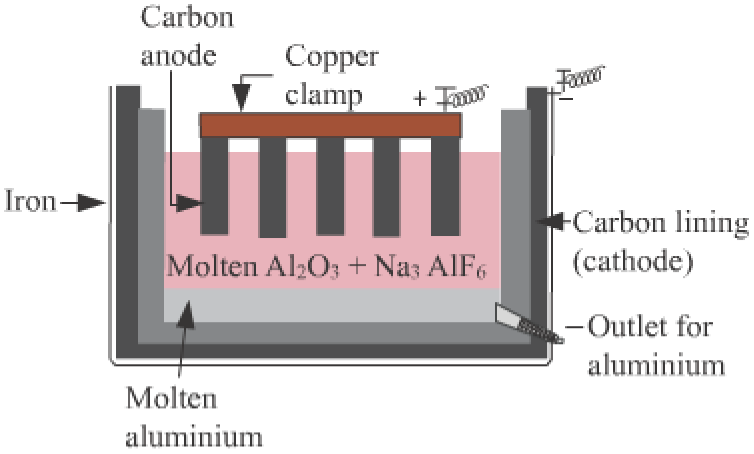
- Metals can be obtained by the reduction of metal ions in solution or molten state.
- The reduction can be carried out by electrolysis, in which, the metal is reduced by a more reactive metal.

$$Cu^{2+}_{(aq)} + Fe_{(s)} \longrightarrow Cu_{(s)} + Fe^{2+}_{(aq)}$$

- Highly reactive metals such as Na and K are difficult to reduce by this method.
- During electrolysis, the M^{n+} ions are discharged at the cathode and get deposited there.
- For the electrodes, suitable materials are selected, considering the reactivity of the metal produced.
- Sometimes, a flux is added to the electrolyte for making the molar mass more conducting.

Metallurgy of Aluminium

- Electrolytic cell for the extraction of aluminium



- Na_3AlF_6 or CaF_2 is added to alumina to lower the melting point, and to increase the conductivity of the electrolyte.
- The overall reaction is

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

- This electrolytic process is known as Hall−Heroult process.
- The oxygen liberated at the anode reacts with the carbon of the anode to produce CO and CO_2.
- The cell reactions are

At Cathode: $\mathrm{Al^{3+}_{(melt)} + 3e^- \longrightarrow Al_{(l)}}$

At Anode:

$$\mathrm{C_{(s)} + O^{2-}_{(melt)} \longrightarrow CO_{(g)} + 2e^-}$$
$$\mathrm{C_{(s)} + 2O^{2-}_{(melt)} \longrightarrow CO_{2(g)} + 4e^-}$$

Extraction of Copper from Low-grade Ores and Scraps

- From low-grade ores, copper is extracted by hydrometallurgy.
- The ore is leached out using acid or bacteria.
- Then, Cu^{2+} ion is reduced by treating Cu^{2+} solution with scrap iron or H_2.

$$\mathrm{Cu^{2+}{}_{(aq)} + H_{2(g)} \longrightarrow Cu_{(s)} + 2H^+{}_{(aq)}}$$

Oxidation - Reduction

Extraction of Chlorine from Brine

- Involves oxidation reaction

$$\mathrm{2NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)} + Cl_{2(g)}}$$

- For this reaction, $\Delta G^0 = -422\ \mathrm{kJ}$
- Applying the relation $\Delta G^0 = -nE^0\mathrm{F}$, we have $E^0 = 2.2$ V
- This reaction naturally requires an external emf greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions.
- Electrolysis of molten NaCl is also carried out, which produces Na metal in the place of NaOH.

Extraction of Gold and Silver

- In the extraction of gold and silver, the metal is leached with NaCN or KCN, which is an oxidation reaction.
- During the process, Ag is oxidised to Ag^+ and Au is oxidised to Au^+

$$4M_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(aq)} + O_{2(g)} \longrightarrow 4\left[M(CN)_2\right]^-_{(aq)} + 4OH^-_{(aq)}$$

$$(M = Ag \text{ or } Au)$$

$$2\left[M(CN)_2\right]^-_{(aq)} + Zn_{(s)} \longrightarrow \left[Zn(CN)_4\right]^{2-}_{(aq)} + 2M_{(s)}$$

Refining

Distillation

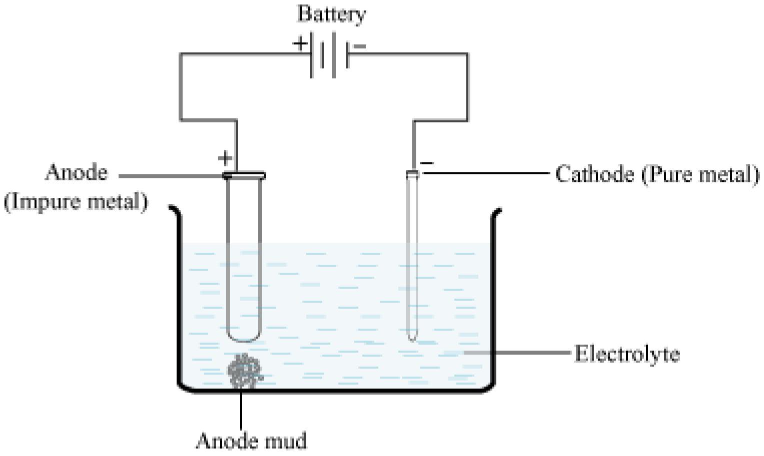
- Involves evaporation of impure metal
- Used for metals having low boiling points, such as Zn, Hg

Liquation

- Involves flowing of low melting metal like tin on a sloping surface so that higher melting impurities are left behind

Electrolytic Refining

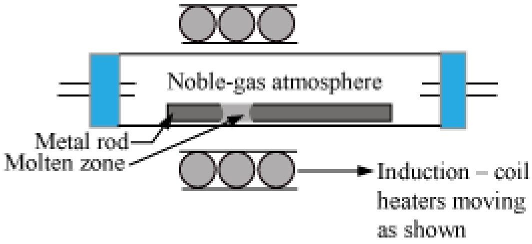
- Impure metal is refined using electricity.
- The impure metal is made the anode, and a strip of pure metal is made the cathode.
- A solution of a soluble salt of the same metal is taken as the electrolyte.
- Impurities get collected below the anode and are known as anode mud.
- At anode: $M \longrightarrow M^{n+} + ne^-$
- At cathode: $M^{n+} + ne^- \longrightarrow M$



- Anode mud of blister copper contains antimony, selenium, tellurium, silver, gold and platinum.

Zone Refining

- Principle − Impurities are more soluble in the molten state of metal (the melt) than in the solid state.
- In this process, a circular heater is fixed at one end of a rod of impure metal.



- As the heater moves, the molten zone of the rod also moves along with it.
- As a result, pure metal crystallises out of the melt, and the impurities pass to the adjacent molten zone.
- This process is repeated several times, which leads to the segregation of impurities at one end of the rod. Then, the end with the impurities is cut off.

Vapour Phase Refining

- In this process, the impure metal is converted into its volatile compound, which is decomposed to obtain the pure metal.
- To carry out this process −
- The metal should form a volatile compound with an available reagent

- The volatile compound should be easily decomposable so that the metal can be easily recovered
- Nickel, zirconium and titanium are refined using this process
- **Mond process for refining nickel**

$$Ni + 4CO \xrightarrow{330-350\ K} \underset{\text{(volatile complex)}}{Ni(CO)_4} \xrightarrow[\text{(Decomposition)}]{450-470\ K} Ni + 4CO$$

- **van Arkel Method for refining zirconium or titanium**
- All the oxygen and nitrogen present as impurity are removed.
- Crude metal is heated with iodine in an evacuated vessel.

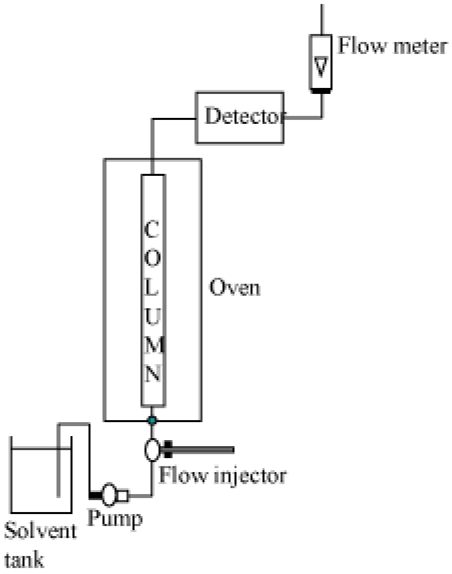
$$Zr + 2I_2 \longrightarrow ZrI_4$$

- Metal iodide is decomposed on a tungsten filament, electrically heated to about 1800 K to give the pure metal.

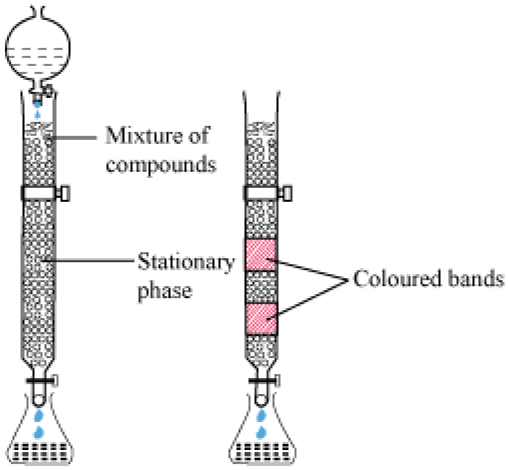
$$ZrI_4 \longrightarrow Zr + 2I_2$$

Chromatographic Methods

- Principle – Different components of a mixture are differently adsorbed on an adsorbent.
- Some chromatographic techniques are –
- Column chromatography
- Paper chromatography
- Gas chromatography
- There are two phases in chromatography: mobile phase and stationary phase.
- Column chromatography is useful for the purification of elements available in minute quantities. It is also used for removing the impurities that are not very different in chemical properties from the element to be purified.
- Adsorbed components are removed (eluted) using suitable solvents (eluents).
- Schematic diagrams of column chromatography in industrial and laboratory methods are as follows:



Industrial method



Laboratory method