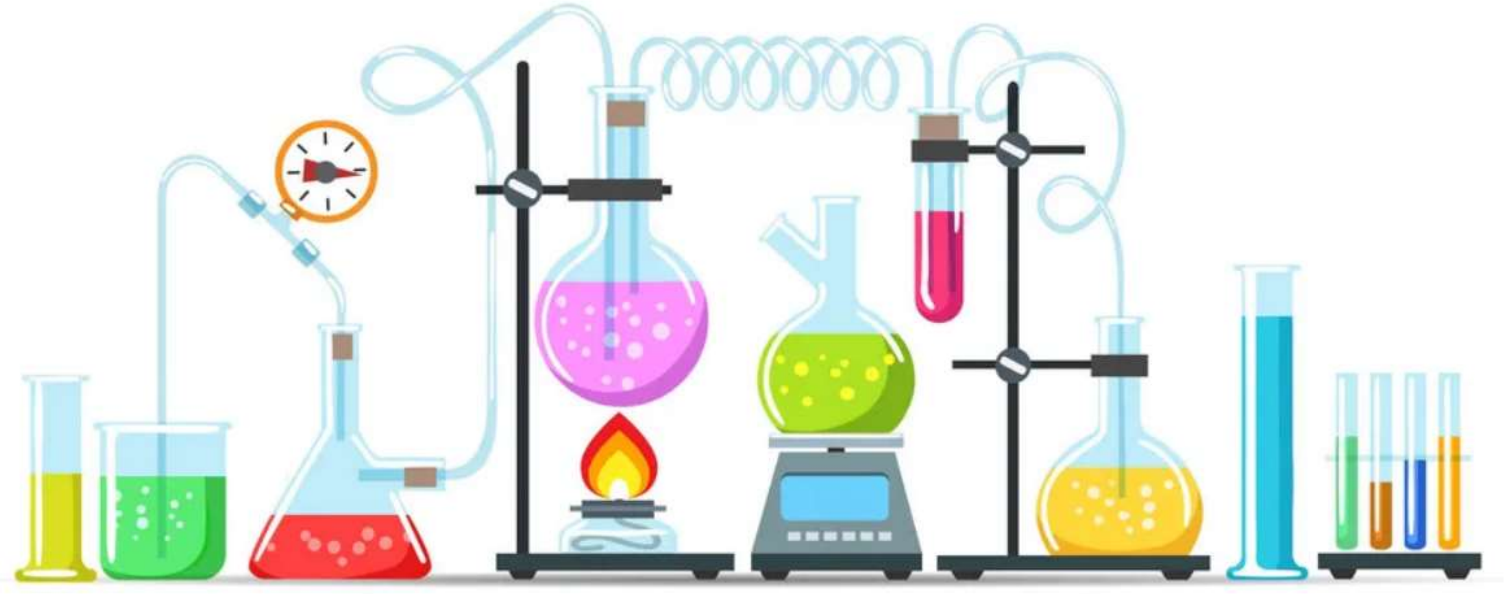
CHEMISTRY



ISOLATION OF ELEMENTS

Principles of Metallurgy

Thermodynamic Principles of Metallurgy:

- Some theories of thermodynamics help us in understanding the theory of metallurgical transformations.
- For any process, Gibbs free energy change (ΔG) is given by the equation,

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

Where,

ΔH = The enthalpy change

ΔS = Entropy change

T = Absolute temperature

- This free energy change is also related to the equilibrium constant K of the reactant product system which is given by the equation,
  - $\Delta G^{o} = -RT\ln k$
- If ΔG^{o} is negative, then K will be positive. This means that the reaction will proceed towards products. From this, we can draw the following conclusions:

When the value of ΔG is negative in equation, then the reaction will proceed. If ΔS is positive, then on increasing the temperature (T), the value of $T\Delta S$ would increase ($\Delta H < T\Delta S$) and then ΔG will become negative.

A reaction with ΔG positive can still be made to occur by coupling it with another reaction having large negative ΔG so that the net ΔG of the two reactions is negative.

Ellingham Diagram:

1. The graphical representation of Gibbs energy was first used by H.J.T. Ellingham.
2. This representation provides a basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham diagram.
3. Such diagrams help us in predicting the feasibility of thermal reduction of an ore.
4. Ellingham diagram normally consists of plots of $\Delta_f G^o$ vs T for the formation of oxides of elements. These diagrams can also be constructed for sulphides and halides of elements.
5. Consider the reaction involving formation of metal oxide.

   $$2xM(s) + O_2(g) \rightarrow 2M_xO(s)$$

6. In this reaction, oxygen gas is consumed and metal oxide is formed.
7. Because gases have higher entropy than liquids and solids ΔS becomes negative. Thus, if temperature is increased, $T\Delta S$ becomes more negative. Also, ΔG becomes less negative.
8. This means that $\Delta_f G^o$ against T lines have positive slope for the reactions of above type.
9. Each line is a straight line except some change in phase which takes place. The temperature at which such change occurs is indicated by an increase in slope on positive side.
10. For example, in the Zn-ZnO plot, at boiling point of zinc, there is an abrupt increase in the positive slope of the curve.

Limitations of Ellingham Diagram:

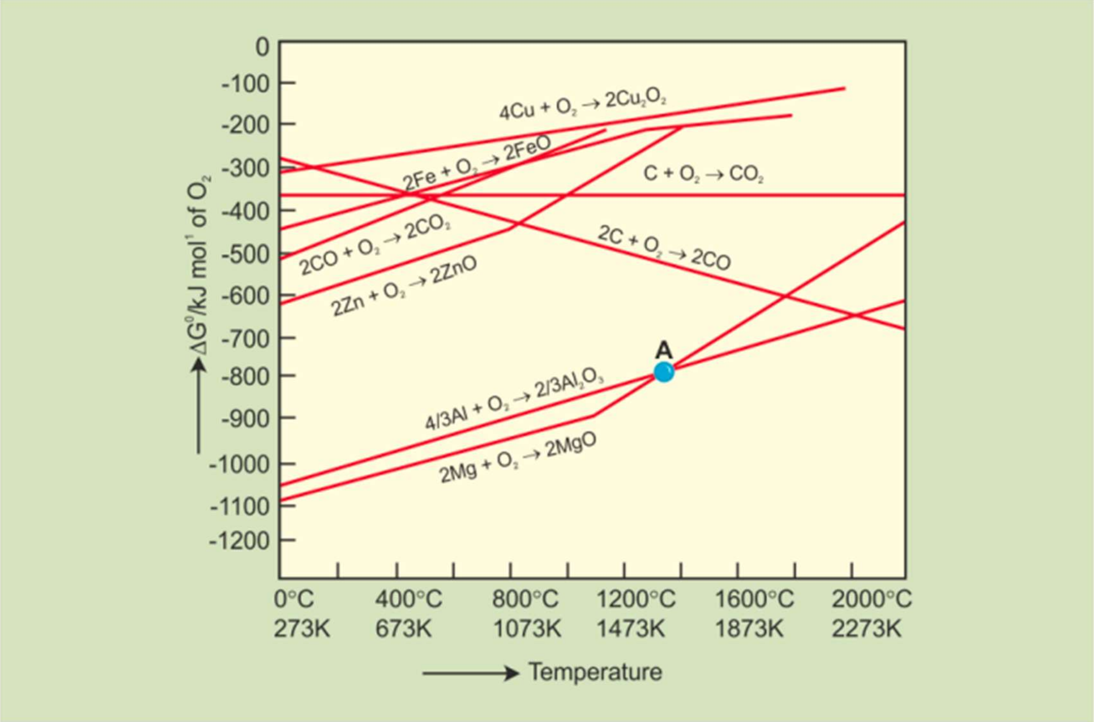
a. Kinetics of reduction:
   - Ellingham diagrams are based on thermodynamic concepts. Hence, these diagrams suggest whether the reduction of the given metal oxide with a particular reducing agent is possible or not.
   - It does not tell anything about the kinetics of the reduction process.

b. Reactant/product equilibrium:

- The interpretation of ΔG^{o} is based upon the equilibrium constant K. Thus, it is presumed that the reactants and products are in equilibrium.

$$M_xO + A_{red} \rightleftharpoons xM + AO_{ox}$$

- But, this is not always true because the reactant or product may be solid.



Gibbs energy (ΔG^{o}) vs T plots (schematic) for formation of some oxides (Ellingham diagram)

Theory of pyrometallurgy:

The process of extracting a metal by reduction of its oxide with carbon in the form of coke, charcoal or carbon monoxide is called **smelting**.

- During reduction, the oxide of the metal decompose

$$M_xO(s) \rightarrow xM(s \text{ or } l) + \frac{1}{2}O_2(g) \_\_\_\_\_\_\_\_\_\_\_\_(1)$$

- The reducing agent takes away the oxygen given by the metal oxide.

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \underline{\qquad\qquad} (2)$$

- By reversing the equation (1), we will get the oxidation reaction.

$$xM(s \text{ or } l) + \frac{1}{2}O_2(g) \rightarrow M_xO(s)\ ;\ \Delta G^o_{(M,M_xO)} \underline{\qquad} (3)$$

- If instead of partial oxidation of C to CO, complete oxidation of C to CO_2 occurs, then the oxidation of the reducing agent may be represented as

$$\frac{1}{2}C(s) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g)\ ;\ \frac{1}{2}\Delta G^o_{(C,CO_2)} \underline{\qquad} (4)$$

- If CO is used instead of C as a reducing agent, the oxidation of the reducing agent may be represented as

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)\ ;\ \Delta G^o_{(CO,CO_2)} \underline{\qquad} (5)$$

- Subtracting eq. (3) from each of the three equations, (2), (4) and (5), we have,

$$M_xO(s) + C(s) \rightarrow xM(s \text{ or } l) + CO(g) \underline{\qquad} (6)$$
$$M_xO(s) + \frac{1}{2}C(s) \rightarrow xM(s \text{ or } l) + \frac{1}{2}CO_2(g) \underline{\qquad} (7)$$
$$M_xO(s) + CO(g) \rightarrow xM(s \text{ or } l) + CO_2(g) \underline{\qquad} (8)$$

- These equations (6), (7) and (8) describe the actual reduction of the metal oxide, M_xO to the free metal, M.
- More heating gives the more negative Δ_rG^o value. Therefore, the temperature is chosen such that the sum of Δ_rG^o in the two combined redox processes is negative.
- In Δ_rG^o vs T plots, this is indicated by the point of intersection of the two curves. After that point, the Δ_rG^o value becomes more negative for the combined process including the reduction of MxO.
- If the difference between two Δ_rG^o values is large, then reduction is easier.

Applications of Pyrometallurgy:

➢ *Extraction of iron from its oxides:*

- Theory of reduction process:

1. Oxide ores of iron, after concentration through calcination/roasting, are mixed with limestone and coke and fed into a blast furnace from its top.
2. The oxide is reduced to the metal. The reduction takes place as follows

$$FeO(s) + C(s) \rightarrow Fe(s\text{ or }l) + CO(g)$$

3. Here, we can see two different reactions, one is reduction of FeO and other is oxidation of C to CO,

$$FeO(s) \rightarrow Fe(s) + \frac{1}{2}O_2(g) \qquad [\Delta G_{(FeO, Fe)}]$$
$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad [\Delta G_{(C, CO)}]$$

4. The net free energy change becomes,

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

5. The reaction will take place only when the $\Delta_r G$ is negative.
6. If we plot the graph of ΔG^o against T for the given reaction, then we can observe that at 1073K or above, the C, CO line is much below the Fe, FeO line.
7. This means that the coke will reduce FeO to Fe and itself will be oxidized to CO.
8. Below 1073K, the CO, CO_2 line lies below Fe, FeO line. Hence, in this region, CO reduces the oxides of iron.

- Reactions taking place in furnace:

(a) Zone of combustion:

Near the tuyeres, where small pipes through which a blast of hot air is introduced, coke burns to form carbon dioxide.

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad ;\Delta H = -393.3\,kJ$$

Because the reaction is exothermic, lot of heat is produced and temperature is around 2170K.

(b) Zone of heat absorption:

This is lower part of furnace and temperature is between 1423K–1673K. The CO_2 formed, meets the descending charge. The coke present in the charge reduces CO_2 to CO.

$$CO_2(g) + C(s) \rightarrow 2CO(g) \qquad ;\Delta H = +163.2\,kJ$$

This reaction is endothermic. Therefore, the temperature gradually falls to 1423K.

(c) Zone of slag formation:

It is the middle part of the furnace. The temperature is around 1123K. In this region, limestone decomposes to form CaO and CO_2. This CaO combines with silica to form fusible calcium silicate slag.

$$CaCO_3(s) \xrightarrow{1123K} CaO(s) + CO_2(g) \quad ;\ \Delta H = +179.9\,kJ$$

$$CaO(s) + SiO_2(s) \xrightarrow{1123K} \underset{\text{Calcium Silicate (Slag)}}{CaSiO_3(s)}$$

(d) Zone of reduction:

This is the upper part of the furnace. The temperature is between 500K-900K.

Here, ores are reduced to Fe by CO.

$$3Fe_2O_3(s) + CO(g) \xrightarrow{573-673K} 2Fe_3O_4(s) + CO_2(g)$$
$$Fe_3O_4(s) + 4CO(g) \xrightarrow{773-873K} 3Fe(s) + 4CO_2(g)$$
$$Fe_2O_3(s) + CO(g) \xrightarrow{773-873K} 2FeO(s) + CO_2(g)$$

In the middle part of furnace, the temperature is 900-1500K. At a temperature above 1073K, FeO reduces to Fe by carbon.

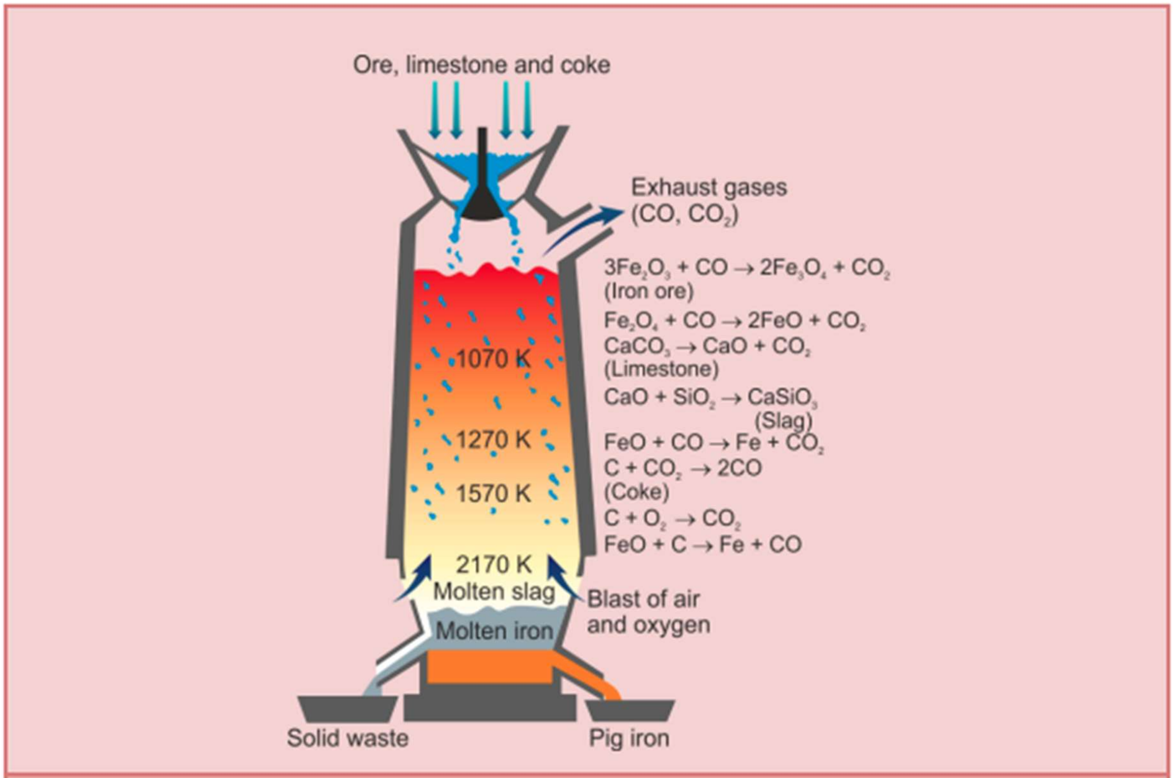
$$FeO(s) + C(s) \xrightarrow{>1073K} Fe(s \text{ or } l) + CO(g)$$

Finally, the direct reduction of iron ore takes place completely to iron by carbon above 1073K.

$$Fe_2O_3(s) + 3C(s) \xrightarrow{>1073K} 2\,Fe(s \text{ or } l) + 3CO(g)$$

(e) Zone of fusion:

1. This is the lower part of furnace.
2. Temperature here is between 1423K-1673K. In this region, spongy iron with impurities and $CaSiO_3$ slag melts.
3. Both molten iron and molten slag forms two separate layers.
4. The molten slag is lighter. Hence, it forms upper layer while molten iron is heavier and forms lower layer.
5. The iron obtained from this furnace contains 4% carbon and many impurities in small amount. This is called pig iron.



Blast furnace

- ***Extraction of copper from cuprous oxide [copper(I) oxide]:***

1. In the Ellingham diagram of formation of Cu_2O from Cu, it can be seen that the (Cu, Cu_2O) curve is at the top, while (C, CO) and (CO, CO_2) lines lie below in the temperature range of 500K-600K. Hence, it is very easy to reduce cuprous oxide to metallic copper.
2. But most of the ores of copper are sulphides. Therefore, the sulphide ores are first roasted in the reverberatory furnace to convert them into oxides.

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

3. These oxides can then be reduced to metallic copper using coke as a reducing agent.

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

4. In the actual process, the sulphide ore is roasted in the reverberatory furnace

where the copper pyrites is converted into a mixture of FeS and Cu_2S.

$$\underset{\text{Copper pyrites}}{2CuFeS_2} + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$
$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

5. Iron is more reactive than copper. Hence, FeS is preferentially oxidized to FeO than Cu_2S to Cu_2O. The Cu_2O is then combined with FeS and converted back to Cu_2S.

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

6. Therefore, the roasted ore mainly contains Cu_2S and FeO along with some unreacted FeS.
7. The roasted ore is then mixed with silica and some powdered coke and heated strongly in a blast furnace. During this, FeO combines with silica to form fusible ferrous silicate slag.

$$FeO + \underset{\text{Silica}}{SiO_2} \rightarrow \underset{\text{Ferrous silicate(slag)}}{FeSiO_3}$$

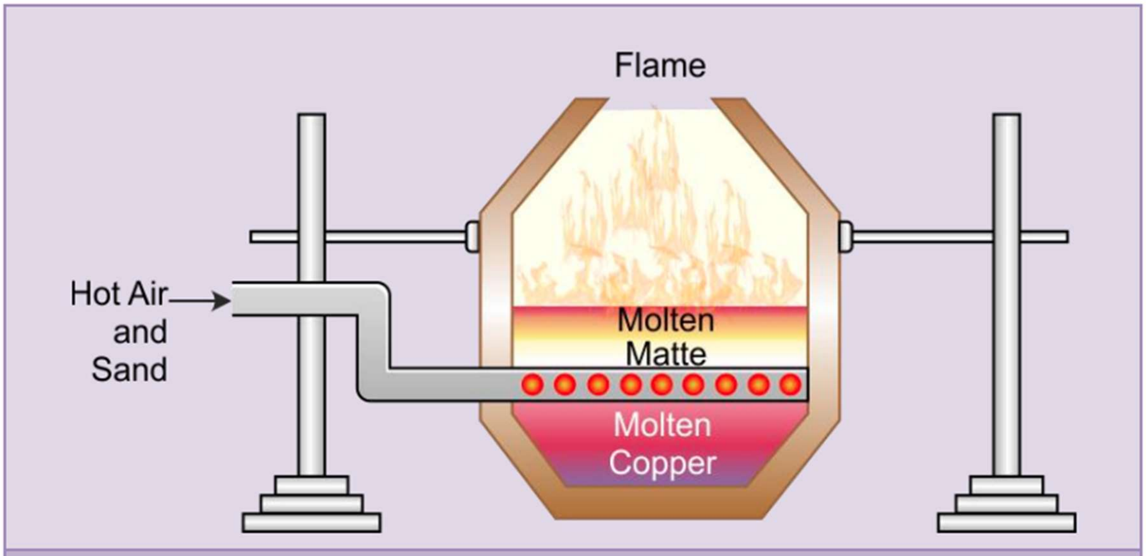
8. At the furnace's temperature, the entire solid melts and two layers of molten solids are formed. The slag, being lighter, forms upper layer and can be withdrawn from slag hole time to time.
9. The lower molten layer is called copper matte. It consists of Cu_2S and FeS.
10. This copper matte is then transferred to the Bessemer converter where the impurities such as As, S and Sb escape as their respective volatile oxide. Also the Fes is oxidized to FeO which combines with silica to form $FeSiO_3$ slag.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \rightarrow FeSiO_3\,(\text{slag})$$

11. That slag melts and floats on the top of the molten mass from where it is removed. When the whole iron is removed as a slag, some of the cuprous sulphide undergoes oxidation to form cuprous oxide which then reacts with cuprous sulphide to form copper metal.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

12. The copper metal formed is then cooled so as to remove SO_2. Some gas bubbles are trapped during this solidification giving blister like appearance to the metal, Hence, they are called as blister copper.
13. The blister copper is finally purified by electrolytic refining or poling.



Bessemer converter for Copper

- ***Extraction of zinc from zinc oxide:***

1. From the Ellingham diagram of formation of ZnO from Zn, we can see that the intersection of (Zn, ZnO) and (C, CO) curves lies at a higher temperature than that of (Cu, Cu_2O) and (C, CO) curves. Therefore, reduction of ZnO with coke is carried out at a higher temperature than that of Cu_2O.

2. Above 1270K, $\Delta_f G^o$ for ZnO is higher than that of CO_2 and CO. Hence, above this temperature, $\Delta_f G^o$ for reduction of ZnO by carbon is negative, and therefore ZnO is easily reduced by coke.
3. For the purpose of heating, the oxide is made into briquettes with coke and clay and heated above 1270K.

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

4. It is noted that the $\Delta_f G^o$ of CO2 from CO is always higher than that of ZnO. Hence, CO cannot be used for reduction of ZnO to Zn.
5. Because the boiling point of Zn is low (1180K), the metal is distilled off and collected by rapid chilling.

Electrochemical Principles of Metallurgy:

- The principles of thermodynamics can also be applied in the reduction of metal ions in the solutions or molten state. These reductions are usually carried out either by electrolysis or by adding some suitable reducing agent.
- In the reduction of a molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation,

$$\Delta G^o = -nFE^o$$

Where,

n = Number of electrons involved in the reduction process

E^O = Standard electrode potential of redox couple (M/M^{n+}) present in the system

- Highly reactive metals have large negative values of electrode potential. So, their reduction is difficult.

- If the difference of two E° values corresponds to a positive E° and consequently a negative ΔG° , then the less reactive metal will come out from the solution and more reactive metal will go into the solution.

$$Cu^{2+}(aq) + \underset{\text{More reactive metal}}{Fe(s)} \rightarrow \underset{\text{Less reactive metal}}{Cu(s)} + Fe^{2+}(aq)$$

- In simple electrolysis, the M^{n+} ions are discharged at the cathode and deposited there.

$$M^{n+}(aq) + ne \rightarrow M(s)$$

- Depending upon the reactivity of the metal produced, the materials of the electrode are selected. Sometimes, a flux is added for making the molten mass more conducting.

A substance which chemically combines with the gangue which may still be present in the roasted or the calcined ore to form an easily fusible material called the slag is known as the **flux**.

Applications of Electrolysis to Metallurgy:

The process of extraction of metals by electrolysis of their fused salts is called as
electrometallurgy.

➢ *Extraction of Aluminium from Alumina:*

1. Fused alumina (Al_2O_3) is a bad conductor of electricity. Therefore, Cryolite (Na_3AlF_6) and Fluorspar (CaF_2) are added to alumina which makes the alumina, a good conductor of electricity and also reduces the melting point of mixture around 1140K.

The process of obtaining aluminium by electrolysis of a mixture of purified alumina and cryolite is called **Hall and Heroult process**.

2. The electrolysis of the molten mass is carried out in an electrolytic tank made of iron using carbon electrode.
3. The molten electrolyte is covered with a layer of powdered coke to prevent oxidation and loss of heat due to radiation. The temperature of tank is maintained at about 1173k.
4. The reactions taking place during electrolysis are

$$\begin{aligned}&\text{Cathode}: Al^{3+}(melt) + 3e^{-} \rightarrow Al(l)\\&\text{Anode}: \quad C(s) + O^{2-}(melt) \rightarrow CO(g) + 2e^{-}\\&\qquad\qquad C(s) + 2O^{2-}(melt) \rightarrow CO_2(g) + 4e^{-}\end{aligned}$$

5. For each kg of aluminium produced, 0.5 kg of carbon anode is burnt away. Because of this, the anodes have to be replaced time to time.
6. The aluminium metal liberated at cathode melts at high temperature of the tank.
7. The molten aluminium is heavier than the molten electrolyte and hence it sinks to the bottom of the tank from where it is withdrawn time to time through the tapping hole.
8. The metal obtained from this process is 99.95% pure.

- ***Copper from Low Grade Ores and Scraps:***

1. Copper is extracted by hydrometallurgy from low grade ores.
2. The low grade ores are leached by treating with an acid when copper metal goes into a solution as Cu^{2+} ions.

3. The solution containing Cu^{2+} ions is then treated with scrap iron or H_2 gas.

$$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$$
$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^{+}(aq)$$

4. Because E^o of Fe^{2+}/Fe (-0.44V) or that of H^+/H_2 (0.0V) redox couple is lower than that of Cu^{2+}/Cu (+0.34V), Fe and H_2 can displace Cu from Cu^{2+} ions.

Extraction of Non-Metals by Oxidation:

1. Non metals occur in a combined state in its reduced form. Therefore, they are generally extracted or isolated by oxidation of their compounds.
2. Consider an isolation of chlorine from brine.

$$2Cl^{-}(aq) + 2H_2O(l) \rightarrow 2OH^{-}(aq) + H_2(g) + Cl_2(g)$$

3. Because oxidation cannot be carried out by ordinary chemical methods, it is accomplished by electrolysis.
4. During electrolysis, Cl_2 is liberated at anode and H_2 at the cathode while NaOH is obtained in the solution.
5. Electrolysis of molten NaCl can be carried out but here Na metal is liberated at cathode and Cl_2 at anode.

Extraction of Metals by Oxidation and Reduction:

1. Extraction of gold and silver involves leaching of the metals. This is an oxidation reaction because during leaching process, Ag is oxidized to Ag^+ and Au to Au^+ which are then combined with CN^- ions to form their respective soluble complexes.

$$\underset{\text{Silver}}{4\,Ag(s)} + 8CN^-(aq) + 2H_2O(l) + O_2(g) \rightarrow 4\underset{\text{Soluble complex}}{\left[Ag(CN)_2\right]^-}(aq) + 4OH^-(aq)$$
$$\underset{\text{Gold}}{4\,Au(s)} + 8CN^-(aq) + 2H_2O(l) + O_2(g) \rightarrow 4\underset{\text{Soluble complex}}{\left[Au(CN)_2\right]^-}(aq) + 4OH^-(aq)$$

2. The metals are then recovered from these complexes by reduction or displacement methods using more electropositive zinc metal.

$$2\left[Ag(CN)_2\right]^-(aq) + Zn(s) \rightarrow 2Ag(s) + \left[Zn(CN)_4\right]^{2-}(aq)$$
$$2\left[Au(CN)_2\right]^-(aq) + Zn(s) \rightarrow 2Au(s) + \left[Zn(CN)_4\right]^{2-}(aq)$$

   In these above displacement reactions, zinc acts as a reducing agent.

3. From the above theory, we can conclude that the extraction of gold and silver occurs by hydrometallurgy.

The process of extraction of metals by dissolving the ore in a suitable reagent followed by precipitation or displacement of the metal by a more reactive or a more electropositive metal is called **hydrometallurgy**.

Refining:

- Metals which even after extraction method contain some impurities are called crude metals. The impurities present in crude metals are

The impurities present in other metals are produced by simultaneous reduction of their respective oxides originally present in the ore.

Impurities in non-metals such as silicon and phosphorous are formed by reduction in furnace.

Unreacted oxides and sulphides of the metals

Substances takes up in the furnace. For e.g. residual slag and flux

- The crude metals are, therefore, purified or refined. The method used for purification of metals depends upon the nature of metal and the nature of the impurities to be removed.

The process of purifying the crude metal is called **refining**.

- The common methods used for refining of metals are

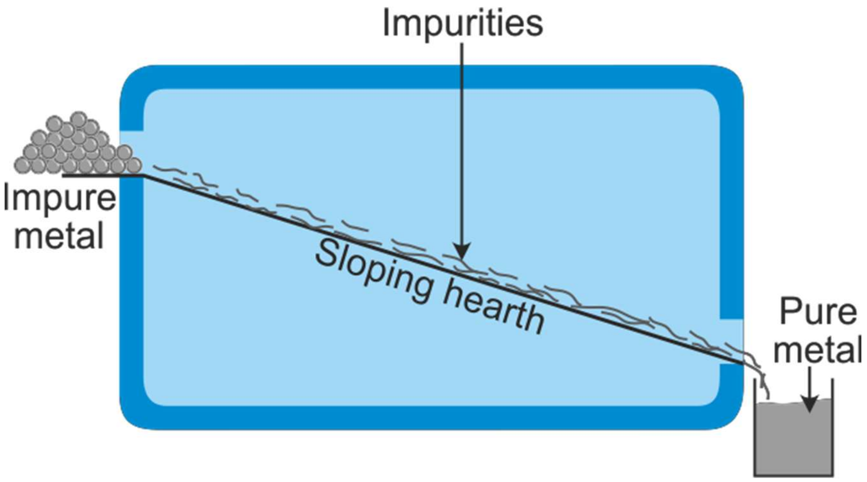
➢ *Distillation process:*

1. This method is employed for purification of volatile methods such as zinc, mercury and cadmium.
2. The impure metal is heated in an iron retort and the vapours are condensed in a separate receiver.

3. The pure metal distils over, leaving behind the non-volatile impurities in retort.

Liquation process:

1. This method is used for purification of metals whose melting point is lower than those of impurities present in it.
2. In this process, a crude metal is heated in an inert atmosphere of carbon monoxide on the sloping hearth of a reverberatory furnace.
3. The metal melts and flows down into the receiver leaving behind the impurities on the hearth.
4. Metals such as tin and lead are purified by this method.



Liquation process

Electrolytic Refining:

1. A large number of metals such as copper, silver, gold, lead, nickel, chromium and zinc are refined by this method.

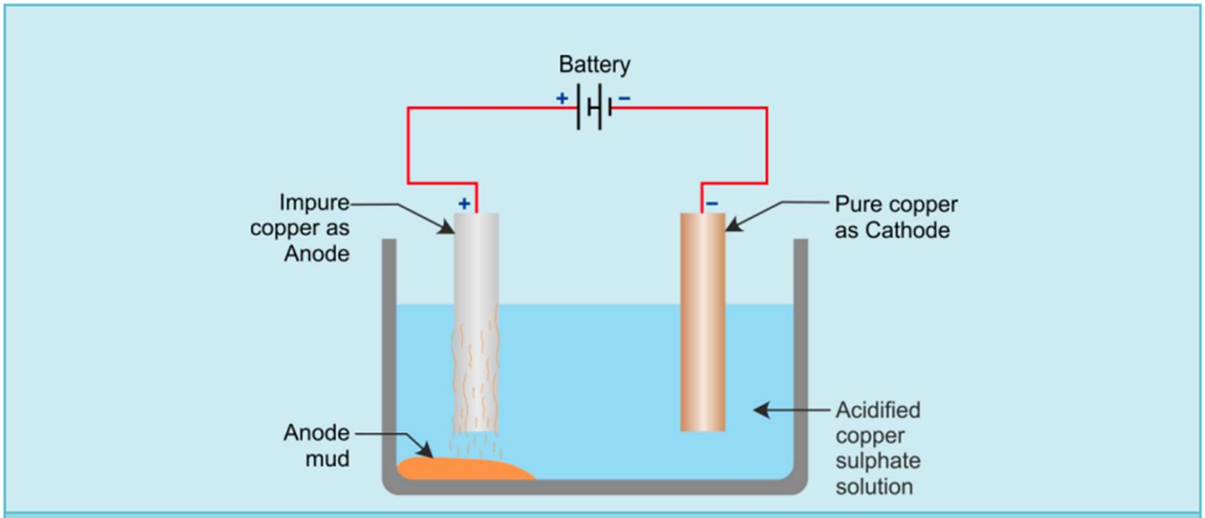
2. In this method, the impure metal is converted into a block which acts as an anode while cathode is made by a pure strip of the same metal.
3. These electrodes are dipped into the solution of double salt of metal.
4. When an electric current is passed, metal ions from electrolyte are deposited at cathode in the form of pure metal while metal from the anode goes into the electrolyte solution as metal ions.

$$\text{Anode}: \quad M(s) \rightarrow M^{n+}(aq) + ne^-$$
$$\text{cathode}: M^{n+}(aq) + ne^- \rightarrow M(s)$$

5. In case of electrolytic refining of copper, crude copper metal acts as an anode while thin sheet of pure copper acts as a cathode. An electrolyte takes in the copper sulphate solution acidified with sulphuric acid.

$$\text{Anode}: \quad Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$
$$\text{cathode}: Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

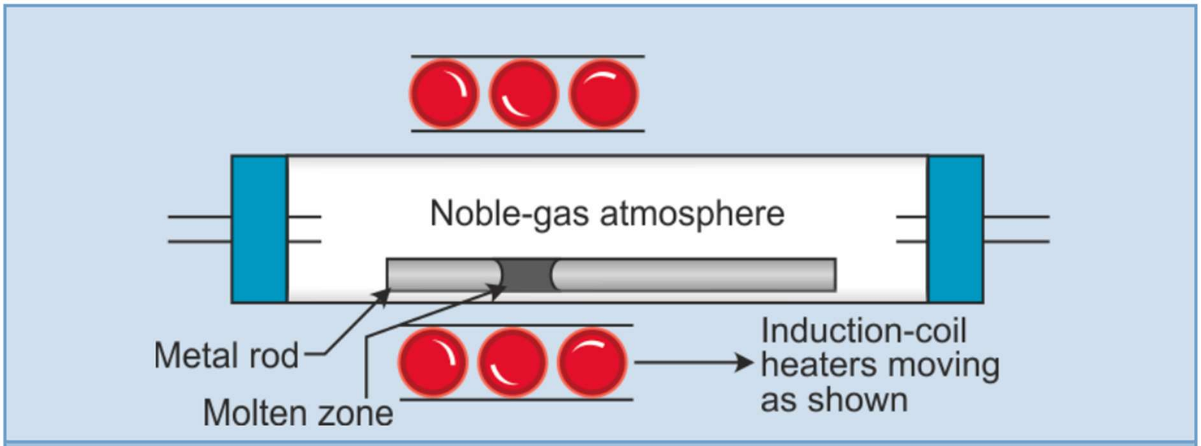
6. The impurities of iron, nickel, zinc and cobalt present in copper are passed into the solution as soluble sulphates.
7. The other impurities such as antimony, tellurium, selenium, gold and silver are less electropositive, and hence they do not get affected by the electrolytic solution and settle down under the anode as anode mud or anode sludge.
8. The copper obtained from this method is 99.95% pure.



Electrolytic refining of copper

➢ *Zone Refining:*

1. This method is very useful for obtaining metals of high purity. For e.g. germanium, silicon, gallium and boron.
2. This method is based upon the principle that the impurities are more soluble in the molten state than in the solid state of the metal.
3. In this method, an impure metal is converted into a bar which is heated at one end with a moving circular heater, so that it forms a molten zone.
4. Because of the slow moving heater along the length of the rod, the pure metal crystallizes out of the melt, whereas the impurities pass into the adjacent molten zone.
5. This process is repeated a number of times till the impurities are completely removed.
6. This process is usually carried out in an inert atmosphere to avoid oxidation of metal.
7. The metals obtained from this method are highly pure.

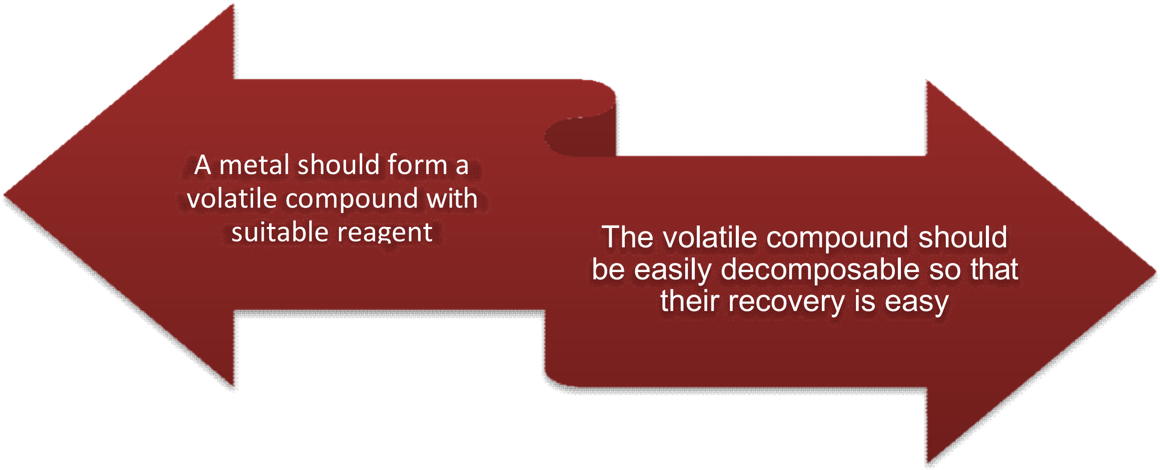


Zone refining process

- ***Vapour-phase Refining:***

In this method, a crude metal is separated from impurities by first converting it into a suitable volatile compound by heating it with a specific reagent at a low temperature and then decomposing the volatile compound at some higher temperature to get a pure metal.

Thus, the two requirements are



A metal should form a volatile compound with suitable reagent

The volatile compound should be easily decomposable so that their recovery is easy

This method is described by the following two processes:

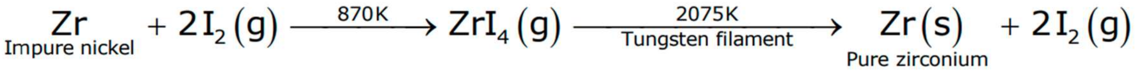
(a) Mond Process:

1. It is used for refining of nickel.
2. When impure nickel is heated in a presence of CO at 330K-350K, it forms volatile nickel tetracarbonyl complex leaving behind the impurities.
3. The nickel tetracarbonyl is then heated to a higher temperature and undergoes thermal decomposition giving pure nickel.

$$\underset{\text{Impure nickel}}{Ni} + 4CO \xrightarrow{330-350K} \underset{\text{Nickel tetracarbonyl}}{Ni(CO)_4} \xrightarrow{450-470K} \underset{\text{Pure nickel}}{Ni} + 4CO$$

(b) Van Arkel Method:

1. This method is very useful for preparing ultra-pure metal by removing all oxygen and nitrogen impurities from metals such as zirconium and titanium.
2. In this method, crude zirconium is heated in an evacuated vessel with iodine at 870K to form zirconium tetraiodide.
3. It is then separated and decomposed by heating over a tungsten filament at 2075K to get pure zirconium



$$\underset{\text{Impure nickel}}{Zr} + 2I_2(g) \xrightarrow{870K} ZrI_4(g) \xrightarrow[\text{Tungsten filament}]{2075K} \underset{\text{Pure zirconium}}{Zr(s)} + 2I_2(g)$$

- ***Chromatographic methods:***

1. Chromatography is the most versatile and modern method for separation, purification and testing the purity of elements and their compounds.
2. This method is based upon the principle that different components of mixture are adsorbed to different extent on an adsorbent.
3. It consists of two phases, stationary phase and mobile phase. The stationary phase can be either solid or liquid on solid support while the mobile phase

can be a liquid, gas or super critical fluid such as CO_2.

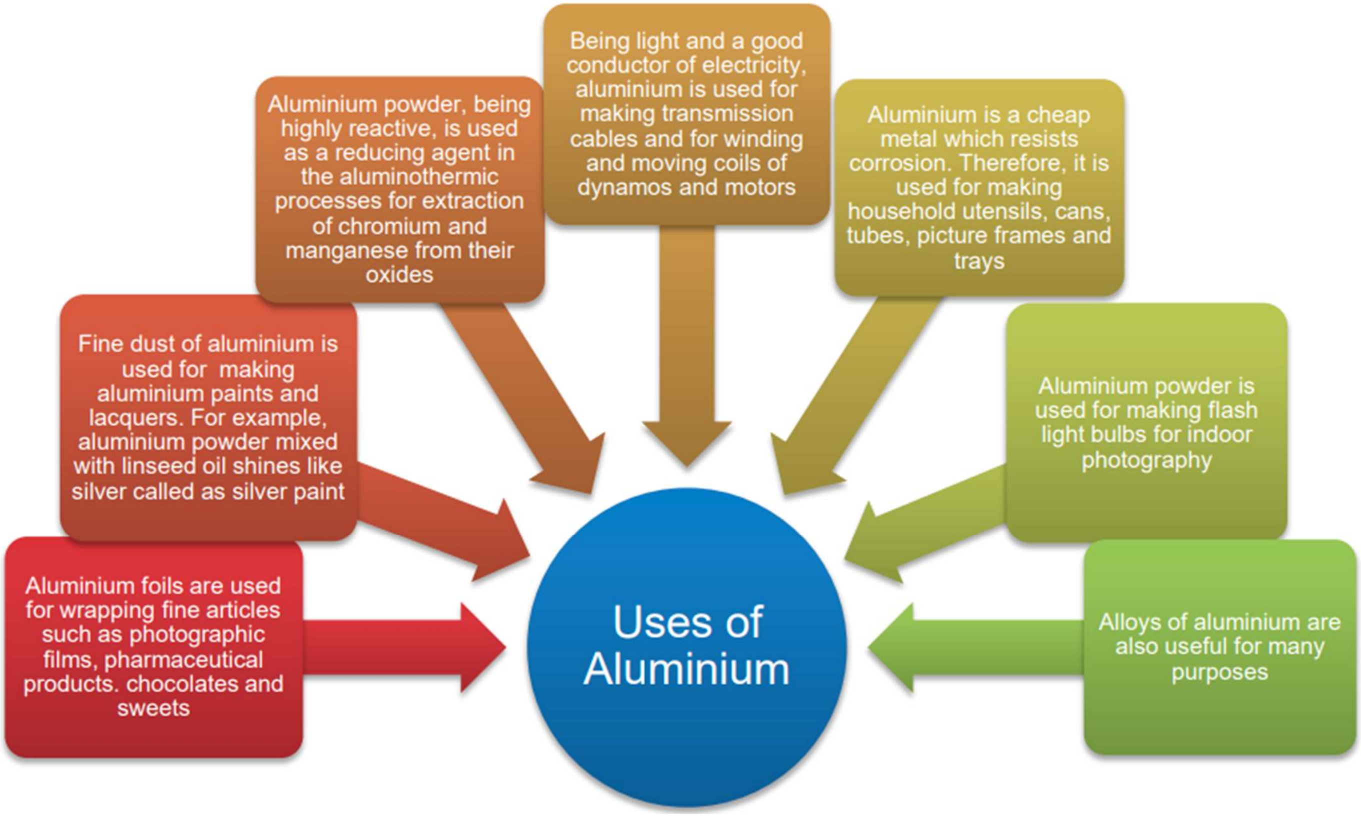
4. There are several types of chromatography depending upon the physical state of the stationary phase and mobile phase. Let us discuss one of the many, column chromatography.

- ***Column Chromatography:***

1. It is a widely used technique.
2. In this, an adsorbent such as alumina or silica gel is packed in a column. This forms a stationary phase.
3. The mixture to be separated is dissolved in a suitable solvent and applied to the top of the column. This forms a mobile phase.
4. Suppose a mixture of three different components say A, B and C is applied to the column for separation. Also, suppose that the component A is more strongly adsorbed, B is moderately adsorbed and C is weakly adsorbed.
5. While elution, three different components began to separate and form three different coloured bands, if the mixture is coloured.
6. The C is weakly adsorbed, and hence moves faster down the column, followed by B and A which moves slowly down the column.
7. These are collected in different flasks. Evaporation of solvent will gives us the desired component.
8. If the mixture is colourless, a column is extracted with suitable solvent and collected in different flasks. The suitable chemical and physical methods are used to get the desired component.
9. This technique is especially suitable for those elements which are available in very minute quantities and the impurities are not very much different in chemical properties from the elements to be purified.

10. Lanthanides are purified by this technique using ion-exchange as adsorbent.

Uses of Aluminium, Copper, Zinc and Iron:



Uses of Aluminium

Aluminium foils are used for wrapping fine articles such as photographic films, pharmaceutical products. chocolates and sweets

Fine dust of aluminium is used for making aluminium paints and lacquers. For example, aluminium powder mixed with linseed oil shines like silver called as silver paint

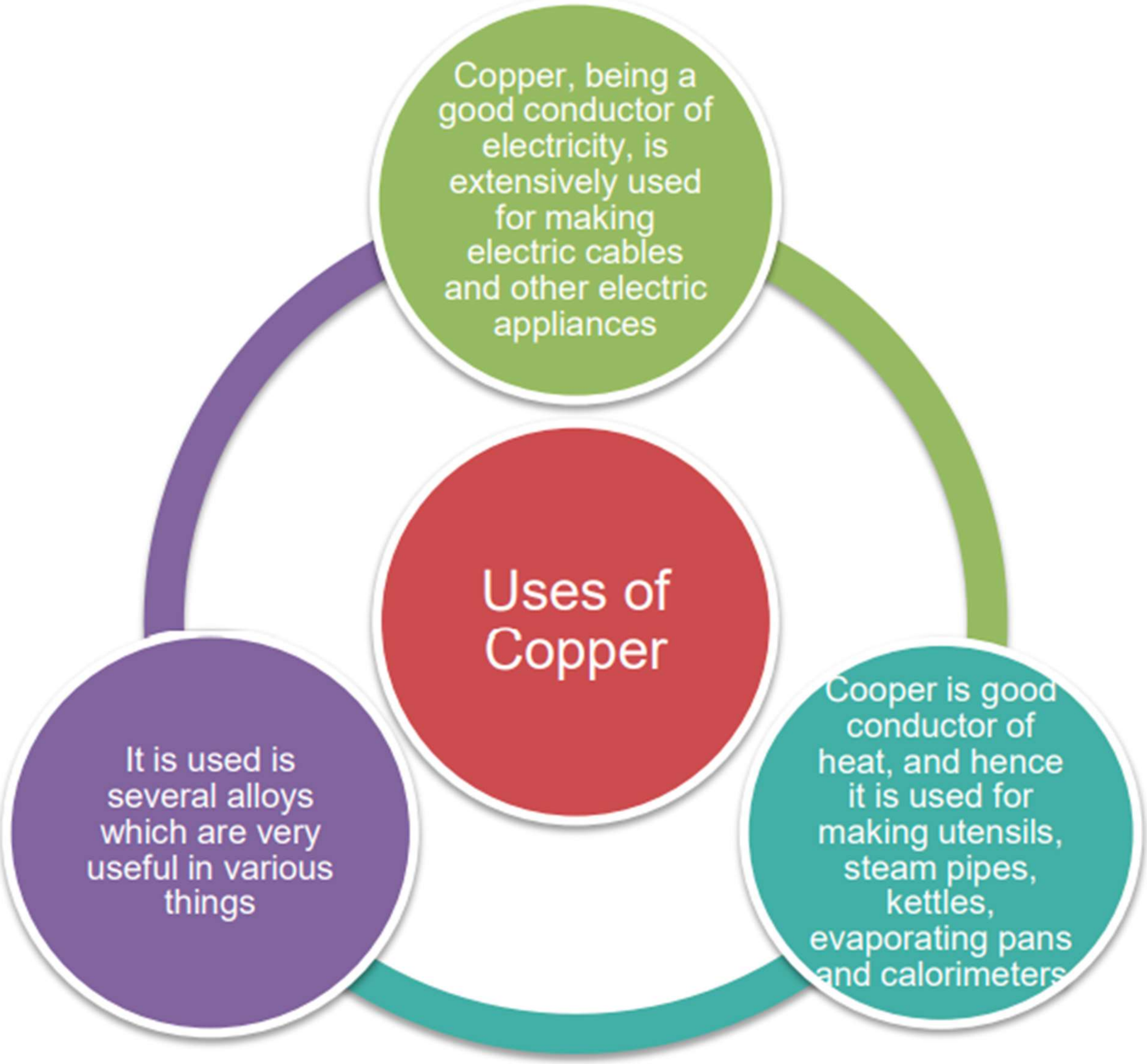
Aluminium powder, being highly reactive, is used as a reducing agent in the aluminothermic processes for extraction of chromium and manganese from their oxides

Being light and a good conductor of electricity, aluminium is used for making transmission cables and for winding and moving coils of dynamos and motors

Aluminium is a cheap metal which resists corrosion. Therefore, it is used for making household utensils, cans, tubes, picture frames and trays

Aluminium powder is used for making flash light bulbs for indoor photography

Alloys of aluminium are also useful for many purposes

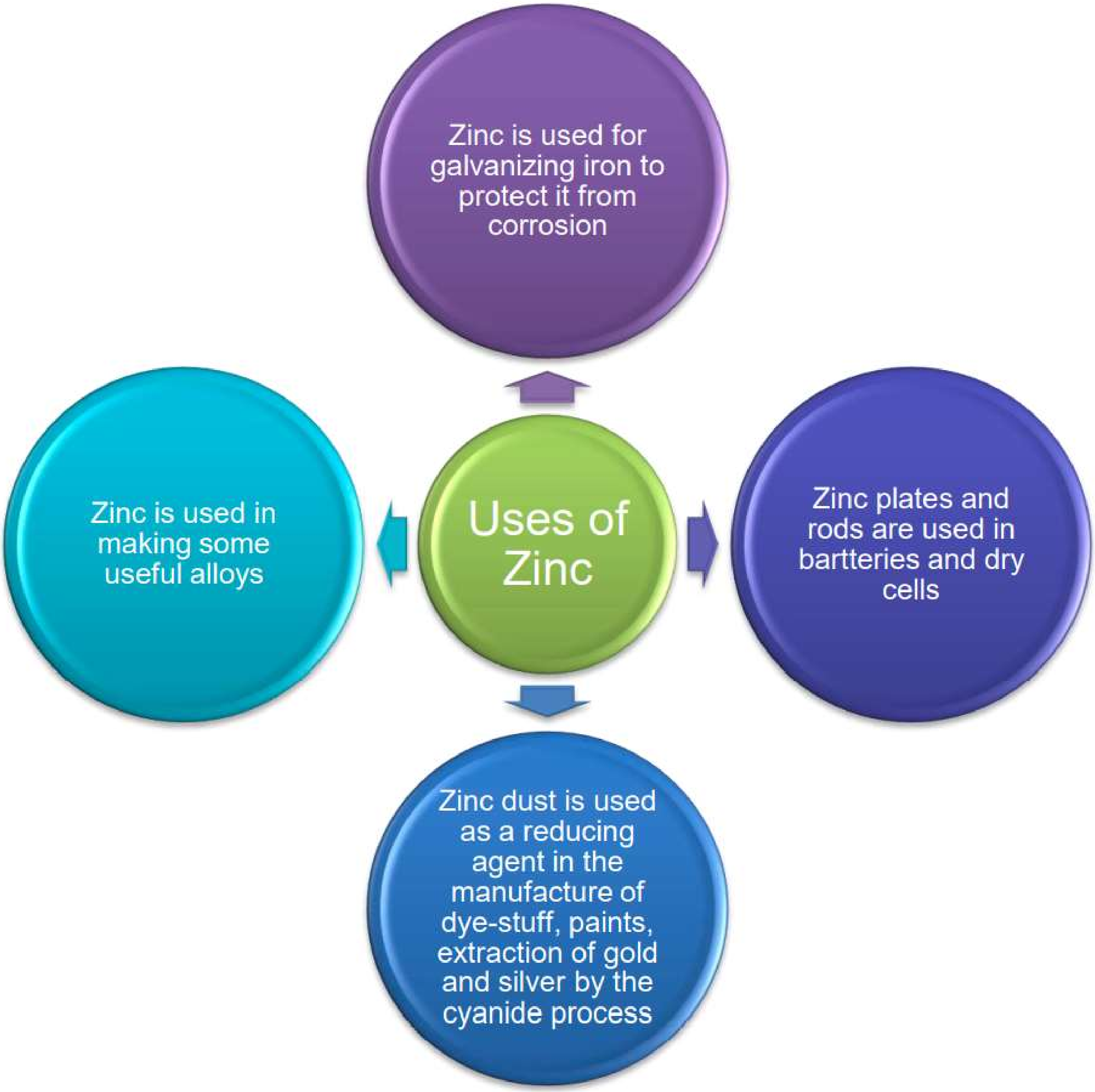


Uses of Copper

Copper, being a good conductor of electricity, is extensively used for making electric cables and other electric appliances

Cooper is good conductor of heat, and hence it is used for making utensils, steam pipes, kettles, evaporating pans and calorimeters

It is used is several alloys which are very useful in various things



Uses of Zinc

Zinc is used for galvanizing iron to protect it from corrosion

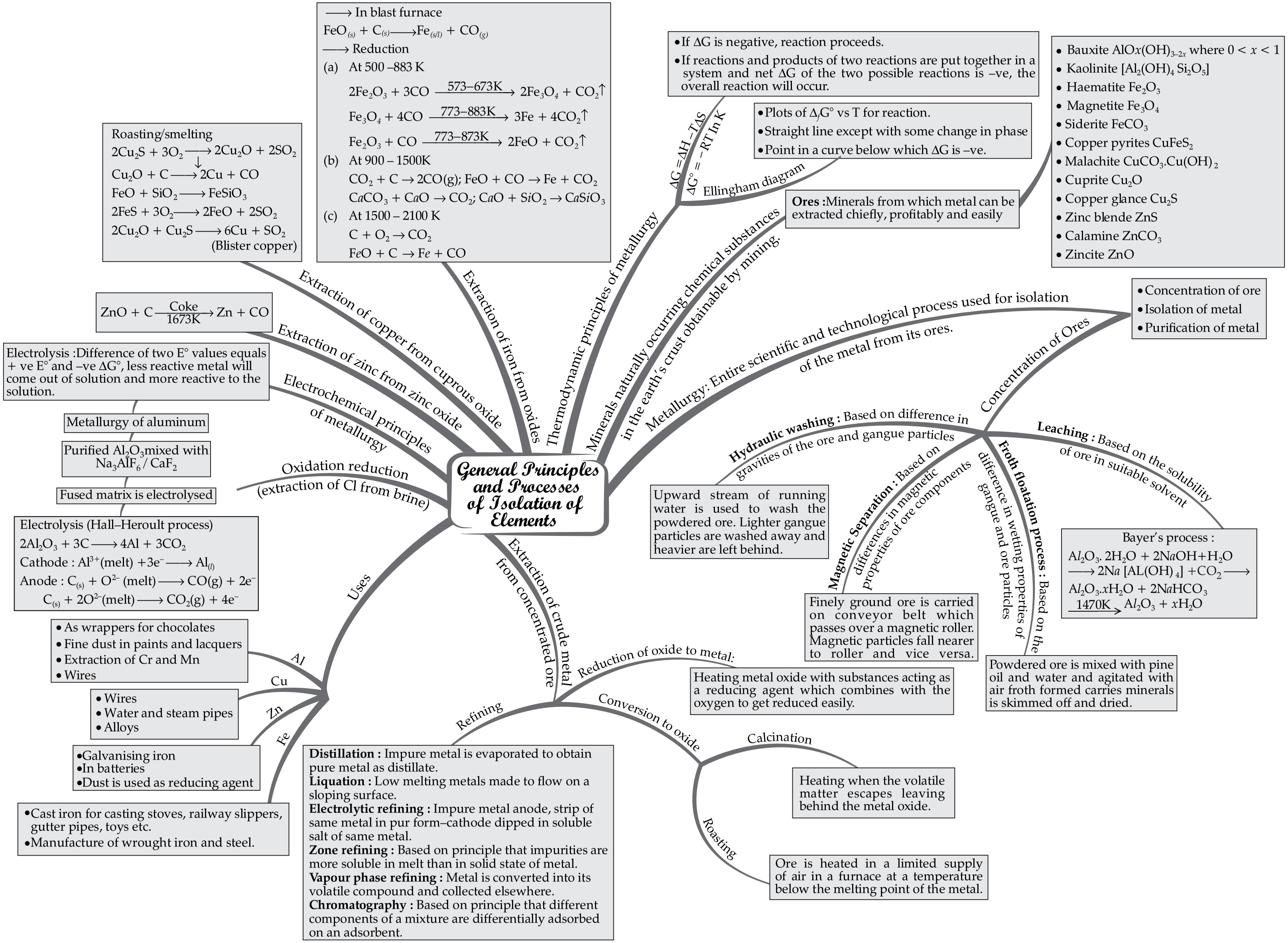
Zinc plates and rods are used in bartteries and dry cells

Zinc dust is used as a reducing agent in the manufacture of dye-stuff, paints, extraction of gold and silver by the cyanide process

Zinc is used in making some useful alloys

MIND MAP : LEARNING MADE SIMPLE

CHAPTER - 6



General Principles and Processes of Isolation of Elements

- Thermodynamic principles of metallurgy
  - $\Delta G = \Delta H - T\Delta S$
    - If ΔG is negative, reaction proceeds.
    - If reactions and products of two reactions are put together in a system and net ΔG of the two possible reactions is –ve, the overall reaction will occur.
  - $\Delta G° = -RT \ln K$
  - Ellingham diagram
    - Plots of $\Delta_f G°$ vs T for reaction.
    - Straight line except with some change in phase
    - Point in a curve below which ΔG is –ve.
- Minerals naturally occurring chemical substances in the earth's crust obtainable by mining.
  - **Ores :** Minerals from which metal can be extracted chiefly, profitably and easily
    - Bauxite $AlO_x(OH)_{3-2x}$ where $0 < x < 1$
    - Kaolinite $[Al_2(OH)_4 Si_2O_5]$
    - Haematite Fe_2O_3
    - Magnetite Fe_3O_4
    - Siderite $FeCO_3$
    - Copper pyrites $CuFeS_2$
    - Malachite $CuCO_3.Cu(OH)_2$
    - Cuprite Cu_2O
    - Copper glance Cu_2S
    - Zinc blende ZnS
    - Calamine $ZnCO_3$
    - Zincite ZnO
- Metallurgy: Entire scientific and technological process used for isolation of the metal from its ores.
  - Concentration of ore
  - Isolation of metal
  - Purification of metal
- Concentration of Ores
  - **Hydraulic washing :** Based on difference in gravities of the ore and gangue particles
    - Upward stream of running water is used to wash the powdered ore. Lighter gangue particles are washed away and heavier are left behind.
  - **Magnetic Separation :** Based on differences in magnetic properties of ore components
    - Finely ground ore is carried on conveyor belt which passes over a magnetic roller. Magnetic particles fall nearer to roller and vice versa.
  - **Froth floatation process :** Based on the difference in wetting properties of gangue and ore particles
    - Powdered ore is mixed with pine oil and water and agitated with air froth formed carries minerals is skimmed off and dried.
  - **Leaching :** Based on the solubility of ore in suitable solvent
    - Bayer's process :
      $Al_2O_3.\,2H_2O + 2NaOH + H_2O \longrightarrow 2Na\,[AL(OH)_4] + CO_2 \longrightarrow$
      $Al_2O_3.xH_2O + 2NaHCO_3 \xrightarrow{1470K} Al_2O_3 + xH_2O$
- Extraction of crude metal from concentrated ore
  - Reduction of oxide to metal:
    - Heating metal oxide with substances acting as a reducing agent which combines with the oxygen to get reduced easily.
  - Conversion to oxide
    - Calcination
      - Heating when the volatile matter escapes leaving behind the metal oxide.
    - Roasting
      - Ore is heated in a limited supply of air in a furnace at a temperature below the melting point of the metal.
  - Refining
    - **Distillation :** Impure metal is evaporated to obtain pure metal as distillate.
    - **Liquation :** Low melting metals made to flow on a sloping surface.
    - **Electrolytic refining :** Impure metal anode, strip of same metal in pur form–cathode dipped in soluble salt of same metal.
    - **Zone refining :** Based on principle that impurities are more soluble in melt than in solid state of metal.
    - **Vapour phase refining :** Metal is converted into its volatile compound and collected elsewhere.
    - **Chromatography :** Based on principle that different components of a mixture are differentially adsorbed on an adsorbent.
- Uses
  - Al
    - As wrappers for chocolates
    - Fine dust in paints and lacquers
    - Extraction of Cr and Mn
    - Wires
  - Cu
    - Wires
    - Water and steam pipes
    - Alloys
  - Zn
    - Galvanising iron
    - In batteries
    - Dust is used as reducing agent
  - Fe
    - Cast iron for casting stoves, railway slippers, gutter pipes, toys etc.
    - Manufacture of wrought iron and steel.
- Oxidation reduction (extraction of Cl from brine)
- Electrochemical principles of metallurgy
  - Electrolysis :Difference of two E° values equals + ve E° and –ve ΔG°, less reactive metal will come out of solution and more reactive to the solution.
  - Metallurgy of aluminum
    - Purified Al_2O_3 mixed with Na_3AlF_6 / CaF_2
    - Fused matrix is electrolysed
    - Electrolysis (Hall–Heroult process)
      - $2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$
      - Cathode : $Al^{3+}(melt) + 3e^- \longrightarrow Al_{(l)}$
      - Anode : $C_{(s)} + O^{2-}\,(melt) \longrightarrow CO(g) + 2e^-$
      - $C_{(s)} + 2O^{2-}(melt) \longrightarrow CO_2(g) + 4e^-$
- Extraction of zinc from zinc oxide
  - $ZnO + C \xrightarrow[1673K]{Coke} Zn + CO$
- Extraction of copper from cuprous oxide
  - Roasting/smelting
  - $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$
  - $Cu_2O + C \longrightarrow 2Cu + CO$
  - $FeO + SiO_2 \longrightarrow FeSiO_3$
  - $2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$
  - $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$ (Blister copper)
- Extraction of iron from oxides
  - ⟶ In blast furnace
  - $FeO_{(s)} + C_{(s)} \longrightarrow Fe_{(s/l)} + CO_{(g)}$
  - ⟶ Reduction
  - (a) At 500 –883 K
    - $2Fe_2O_3 + 3CO \xrightarrow{573-673K} 2Fe_3O_4 + CO_2\uparrow$
    - $Fe_3O_4 + 4CO \xrightarrow{773-883K} 3Fe + 4CO_2\uparrow$
    - $Fe_2O_3 + CO \xrightarrow{773-873K} 2FeO + CO_2\uparrow$
  - (b) At 900 – 1500K
    - $CO_2 + C \rightarrow 2CO(g)$; $FeO + CO \rightarrow Fe + CO_2$
    - $CaCO_3 + CaO \rightarrow CO_2$; $CaO + SiO_2 \rightarrow CaSiO_3$
  - (c) At 1500 – 2100 K
    - $C + O_2 \rightarrow CO_2$
    - $FeO + C \rightarrow Fe + CO$

Important Questions

Multiple Choice questions-

1. The electrolytic reduction technique is used in the extraction of
(a) Highly electronegative elements.
(b) Highly electropostive elements.
(c) Metalloids.
(d) Transition metals.

2. In the commercial electrochemical process for aluminium extraction, electrolyte used is
(a) $Al(OH)_3$ is NaOH solution.
(b) An aqueous solution of $Al_2 (SO_4)_3$.
(c) A molten mixture of Al_2O_3 and Na_3AlF_6.
(d) A molten mixture of Al_2O_3 and $Al(OH)_3$.

3. Which ore can be best concentrated by froth floatation process?
(a) Malachite
(b) Cassiterite
(c) Galena
(d) Magnetite

4. Electrolytic reduction of Al_2O_3 to Al by Hall- Herault process is carried out
(a) in presence of NaCl.
(b) in presence of fluorite.
(c) in presence of cryolite which forms a melt with lower melting point.
(d) in presence of cryolite which forms a melt with high melting point.

5. The chemical composition of ‘slag’ formed during the melting process in the extraction of copper is
(a) $Cu_2O + FeS$
(b) $FeSiO_3$
(c) $CuFeS_2$
(d) $Cu_2S + FeO$

6. Bessemer converter is used in the manufacture of
(a) Pig iron
(b) Steel
(c) Wrought iron
(d) Cast iron

7. The method of zone refining of metals is based on the principle of
(a) greater mobility of the pure metal than that of the impurity.
(b) higher melting point of the impurity than that of the pure metal.
(c) greater noble character of the solid metal than that of impurity.
(d) greater solubility of the impurity in the molten state than in the solid.

8. In the leaching of Ag_2S with NaCN, a stream of air is also passed. It is because
(a) The reaction between Ag_2S and NaCN is reversible.
(b) to oxidise Na_2S formed in the reaction to Na_2SO_4.
(c) to oxidise Ag_2S to Ag_2O.
(d) Both (a) and (b).

9. Purest form of iron is
(a) Cast iron
(b) Hard Steel
(c) Stainless steel
(d) Wrought iron

10. Consider the following reaction at 1000° C

A. $Zn(s) + \frac{1}{2}O_2(g) \longrightarrow ZnO(s)$

$$\Delta G^\circ = -360 \text{ kJ mol}^{-1}$$

B. $C(gr) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

$$\Delta G^\circ = -460 \text{ kJ mol}^{-1}$$

Choose the correct statement at 1000°C
(a) Zinc can be oxidised by carbon monoxide.
(b) Zinc oxide can be reduced by graphite.
(c) Both statements (a) and (b) are correct.
(d) Both statements (a) and (b) are false.

Very Short Questions-

1. What is pig iron?
2. What is cast iron?
3. What is wrought iron?
4. What is added as flux in extraction of iron?
5. What is Blister copper?
6. Write the equation for reduction of zinc oxide?
7. Why is cryolite used during extraction of Aluminium?
8. How is copper extracted from low grade ores?
9. State one limitation of Ellingham diagrams.

10. Give an example of extraction based on oxidation reduction.

Short Questions-

1. Sulphide and carbonate ores are converted to oxide before reduction. Why?
2. What is calcinations and roasting? Give one example of each?
3. What is slag? Give an example.
4. How does a reducing agent helps in reduction?
5. Write the relationship between Gibbs free energy, enthalpy change and change in entropy?
6. What is the condition for a reduction reaction to occur in terms of free energy change? How can it be achieved?
7. What are Ellingham diagrams?
8. Give the requirements for vapour phase refining?
9. What is the basis of reduction of a molten metal salt? Explain
10. Which of the ores mentioned in Table 6.1 can be concentrated by magnetic separation method?

Long Questions-

1. What is the significance of leaching in the extraction of aluminium?
2. Explain: (i) Zone refining (ii) Column chromatography.
3. Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.
4. Write chemical reactions taking place in the extraction of zinc from zinc blende.
5. How can you separate alumina from silica in bauxite ore associated with silica? Give equations, if any.
6. Giving examples, differentiate between 'roasting' and 'calcination'.
7. The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with two examples.
8. Name the processes from which chlorine is obtained as a by-product. What will happen if an aqueous solution of NaCl is subjected to electrolysis?

Assertion and Reason Questions:

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Coke and flux are used in smelting.

Reason: The phenomenon in which ore is mixed with suitable flux and coke is heated to fusion is known as smelting.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Leaching is a process of reduction.

Reason: Leaching involves treatment of the ore with a suitable reagent so as to make it soluble while impurities remains insoluble.

MCQ Answers-

1. Answer: b
2. Answer: c
3. Answer: c
4. Answer: c
5. Answer: b
6. Answer: b
7. Answer: d
8. Answer: d
9. Answer: d
10. Answer: b

Very Short Answers-

1. **Ans.** The iron which is obtained from blast furnace and contains about 4% carbon and many other impurities in smaller amounts like S, P, Si, Mn etc, is called pig iron.

2. **Ans.** Iron obtained by melting pig iron with scrap iron and coke using hot air blast is cast iron.
3. **Ans.** Wrought iron and malleable iron is the purest form of commercial iron which is prepared from cast iron by oxidizing impurities in a reverberatory furnace lined with hematite.

4. **Ans.** Limestone is used as flux in extraction of iron.

5. **Ans.** The solidified copper obtained after extraction has blistered appearance due to evolution of SO_2 is called blister copper.

6. **Ans.** The reduction of zinc-oxide is done using coke. $ZnO + C \xrightarrow{COKE, 673\,K} Zn + CO$

7. **Ans.** Cryolite is used to lower the melting point of alumina and increase conductivity.

8. **Ans.** Copper is extracted by hydrometallurgy from low grade ores. It is leached out using acid or bacteria.

9. **Ans.** Ellingham diagrams only tell us about the feasibility of a reaction. They do not tell anything about the reaction kinetics.

10. **Ans.** An example based on extraction by oxidation is extraction of chlorine from brine.

Short Answers-

Ans 1. Since the reduction of oxide ores involves a decrease in Gibb's free energy making ΔG value more negative, it is easier to reduce oxides therefore sulphide and carbonate ores are converted to oxides before reduction.

Ans 2. Calcination: - It is the process of heating carbonate ore in the absence of air when volatile matter escape leaving behind metal oxide. e.g.

$$Zn\,CO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$

$$CaCO_3 - Mg\,CO_3 \xrightarrow{\Delta} CaO(s) + MgO(s) + 2CO_2(g)$$

Roasting: - Here ore is heated in a regular supply of air at a temperature below the melting point of metal e.g.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

Ans 3. Slag is the substance obtained after flux reacts with impurity.

Flux + Impurity → Slag.

For example silica is added as flux to remove iron oxide during extraction of copper as ferrous silicate.

$$FeO + SiO_2 \rightarrow FeSiO_3\,(slag)$$

Impurity flux

Ans 4. During the reduction of the metal oxide, the reducing agent combines with oxygen of metal oxide and gets itself oxidized.

$M_xO_y + {}_yC \rightarrow {}_xM + {}_yCO$ Here carbon is reducing agent.

Ans 5. When ΔS is entropy change, ΔH is enthalpy change, then at temperature T, the change in Gibbs free energy is given by
$\Delta G = \Delta H - T\Delta S$.

Ans 6. When the value of ΔG is negative, the reduction reaction is said to be spontaneous
1) If ΔS is positive, on increasing the temperature, the value of TΔS would increase & ΔG will become negative.
2) For a process which is otherwise having ΔG positive & is non- spontaneous, it can be coupled with a reaction having highly negative ΔG value so that the overall ΔG is negative and the process can take place.

Ans 7. Ellingham diagrams are graphical representation of variation of ΔG vs T for the formation of oxides of elements i.e., for the reaction
$2xM(S) + O_2(g) \rightarrow 2MxO(gs)$

Ans 8. The two requirements of vapour phase refining are: -
1) The metal should form a volatile compound with an available reagent,
2) The volatile compound should be easily decomposable so that recovery is easy.

Ans 9. In the reduction of molten metal salt, electrolysis is done which is based on electrochemical principles following equation $\Delta G = -nFE^0$
Here n is the number of electrons and E^0 is the electrode potential of redox couple. More reactive metals have large negative values of the electrode potential and are difficult to reduce.

Ans 10. If the ore or the gangue can be attracted by the magnetic field, then the ore can be concentrated by the process of magnetic separation. Among the ores mentioned in table 6.1, the ores of iron such as haematite (Fe_2O_3), magnetite (Fe_3O_4), siderite $(FeCO_3)$ and iron pyrites (FeS_2) can be separated by the process of magnetic separation.

Long Answers-

Ans 1. In the extraction of aluminium, the significance of leaching is to concentrate pure alumina (Al_2O_3) from bauxite ore.
Bauxite usually contains silica, iron oxide, and titanium oxide as impurities. In the process of leaching, alumina is concentrated by digesting the powdered ore with a concentrated solution of NaOH at 473-523 K and 35-36 bar. Under these conditions, alumina (Al_2O_3) dissolves as sodium meta-aluminate and silica (SiO_2) dissolves as sodium silicate leaving the impurities behind.

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

Alumina

$$\underset{\text{Silica}}{SiO_{2(l)}} + 2NaOH_{(aq)} \xrightarrow[35-36bar]{473-523K} \underset{\text{Sodium silicate}}{NaSiO_{3(aq)}} + H_2O_{(l)}$$

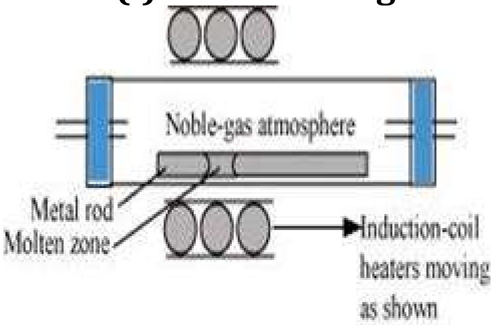
The impurities are then filtered, and the solution is neutralized by passing CO_2 gas. In this process, hydrated (Al_2O_3) gets precipitated and sodium silicate remains in the solution. Precipitation is induced by seeding the solution with freshly prepared samples of hydrated (Al_2O_3).

$$2Na\left[Al(OH)_4\right]_{(aq)} + CO_{2(g)} \rightarrow \underset{\text{Hydrated alu mina}}{Al_2O_3.xH_2O_{(s)}} + 2NaHCO_{3(aq)}$$

Hydrated alumina thus obtained is filtered, dried, and heated to give back pure alumina (Al_2O_3).

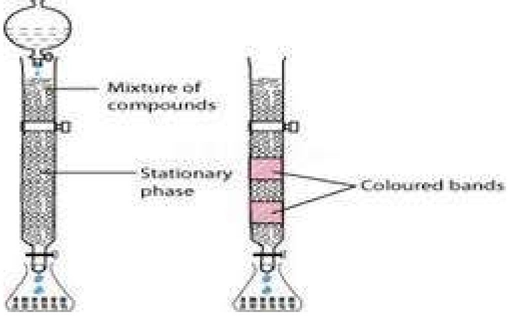
$$Al_2O_3.xH_2O_{(s)} \xrightarrow{1470K} Al_2O_{3(s)} + xH_2O_{(s)}$$

Ans 2. (i) Zone refining:



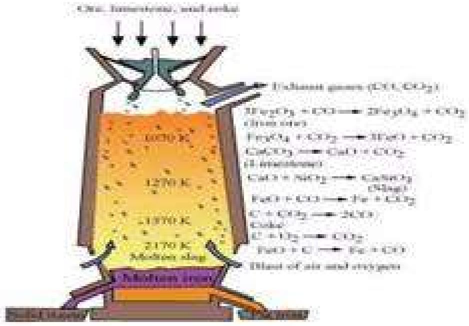
This method is based on the principle that impurities are more soluble in the molten state of metal (the melt) than in the solid state. In the process of zone refining, a circular mobile heater is fixed at one end of a rod of impure metal. As the heater moves, the molten zone of the rod also moves with it. As a result, pure metal crystallizes out of the melt and the impurities pass onto 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. Silicon, boron, gallium, indium etc. can be purified by this process.

(ii) Column chromatography:



Column chromatography is a technique used to separate different components of a mixture. It is a very useful technique used for the purification of elements available in minute quantities. It is also used to remove the impurities that are not very different in chemical properties from the element to be purified. Chromatography is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. In chromatography, there are two phases: mobile phase and stationary phase. The stationary phase is immobile and immiscible. Al_2O_3 column is usually used as the stationary phase in column chromatography. The mobile phase may be a gas, liquid, or supercritical fluid in which the sample extract is dissolved. Then, the mobile phase is forced to move through the stationary phase. The component that is more strongly adsorbed on the column takes a longer time to travel through it than the component that is weakly adsorbed. The adsorbed components are then removed (eluted) using a suitable solvent (eluant).

Ans 3.



During the extraction of iron, the reduction of iron oxides takes place in the 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) in the blast furnace are:

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$

$Fe_2O_3 + CO \rightarrow 2Fe_3 + CO_2$

The reaction taking place in the higher temperature range (900 – 1500 K) in the blast furnace are:

$C + CO_2 \rightarrow 2CO$

$FeO + CO \rightarrow Fe + CO_2$

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

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + SiO_2 \rightarrow \underset{\text{Calcium silicate (Slag)}}{CaSiO_3}$

Ans 4. The different steps involved in the extraction of zinc from zinc blende (ZnS) are given below:

(i) Concentration of ore
First, the gangue from zinc blende is removed by the froth floatation method.

(ii) Conversion to oxide (Roasting)
Sulphide ore is converted into oxide by the process of roasting. In this process, ZnS is heated in a regular supply of air in a furnace at a temperature, which is below the melting point of Zn.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

(iii) Extraction of zinc from zinc oxide (Reduction)
Zinc is extracted from zinc oxide by the process of reduction. The reduction of zinc oxide is carried out by mixing it with powdered coke and then, heating it at 673 K.

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

(iv) Electrolytic Refining
Zinc can be refined by the process of electrolytic refining. In this process, impure zinc is made the anode while a pure copper strip is made the cathode. The electrolyte used is an acidified solution of zinc sulphate (ZnSO4). Electrolysis results in the transfer of zinc in pure from the anode to the cathode.

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

Cathode: $Zn^{2+} + 2e^- \rightarrow Zn$

Ans 5. To separate alumina from silica in bauxite ore associated with silica, first the powdered ore is digested with a concentrated NaOH solution at 473 – 523 K and 35 – 36 bar pressure. This results in the leaching out of alumina (Al_2O_3) as sodium aluminate and silica (SiO_2) as sodium silicate leaving the impurities behind.

$$\underset{\text{Alumina}}{Al_2O_{3(s)}} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow \underset{\text{Sodium aluminate}}{2Na\left[Al(OH)_4\right]_{(aq)}}$$

$$\underset{\text{Silica}}{SiO_2} + 2NaOH_{(aq)} \rightarrow \underset{\text{Sodium silicate}}{Na_2SiO_{3(aq)}} + H_2O_{(l)}$$

Then, CO_2 gas is passed through the resulting solution to neutralize the aluminate in the solution, which results in the precipitation of hydrated alumina. To induce precipitation, the solution is seeded with freshly prepared samples of hydrated alumina.

$$\underset{\text{Sodium aluminate}}{2Na\left[Al(OH)_4\right]_{(aq)}} + CO_{2(g)} \rightarrow \underset{\text{Hydrate alumina}}{Al_2O_3 . xH_2O_{(s)}} + \underset{\text{Sodium hydrogen carbonate}}{2NaHCO_{3(aq)}}$$

During this process, sodium silicate remains in the solution. The obtained hydrated alumina is filtered, dried, and heated to get back pure alumina.

$$\underset{\text{Hydrated alumina}}{Al_2O_3.xH_2O_{(s)}} \xrightarrow{1470} \underset{\text{Alumina}}{Al_2O_{3(s)}} + xH_2O_{(g)}$$

Ans 6. Roasting is the process of converting sulphide ores to oxides by heating the ores in a regular supply of air at a temperature below the melting point of the metal. For example, sulphide ores of Zn, Pb, and Cu are converted to their respective oxides by this process.

$$\underset{\text{Zincblende}}{2Zns} + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

$$\underset{\text{Galena}}{2Pbs} + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$$

$$\underset{\text{Copper glance}}{2Cu_2S} + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$

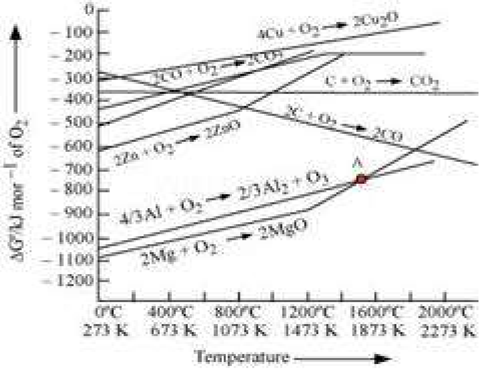
On the other hand, calcination is the process of converting hydroxide and carbonate ores to oxides by heating the ores either in the absence or in a limited supply of air at a temperature below the melting point of the metal. This process causes the escaping of volatile matter leaving behind the metal oxide. For example, hydroxide of Fe, carbonates of Zn, Ca, Mg are converted to their respective oxides by this process.

$$\underset{\text{Limonite}}{Fe_2O_3.3H_2O} \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$$

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

$$\underset{\text{Dolomite}}{CaMg(CO_3)_2} \xrightarrow{\Delta} CaO_{(s)} + MgO_{(s)} + 2CO$$

Ans 7.



The above figure is a plot of Gibbs energy $\Delta G^{\ominus}$ vs. T for formation of some oxides. It can be observed from the above graph that a metal can reduce the oxide of other metals if the standard free energy of formation $\Delta_f G^{\ominus}$ of the oxide of the former is more negative than the latter. For example, since $\Delta_f G^{\ominus}_{(Al,Al_2O_3)}$ is more negative than $\Delta_f G^{\ominus}_{(Cu,Cu_2O)}$, Al can reduce Cu_2O to Cu, but Cu cannot reduce Al_2O_3. Similarly, Mg can reduce ZnO to Zn, but Zn cannot reduce MgO because $\Delta_f G^{\ominus}_{(Mg,MgO)}$ is more negative than $\Delta_f G^{\ominus}_{(Zn,ZnO)}$.

Ans 8. In the electrolysis of molten NaCl, Cl_2 is obtained at the anode as a by-product.

$$NaCl_{(melt)} \rightarrow Na^{+}_{(melt)} + Cl^{-}_{(melt)}$$

At cathode:

$$Na^{+}_{(melt)} + e^{-} \rightarrow Na_{(s)}$$

At anode: $Cl^{-}_{(melt)} \rightarrow Cl_{(g)} + e^{-}$

$$2Cl_{(g)} \rightarrow Cl_{2(g)}$$

The overall reaction is as follows:

$$NaCl_{(melt)} \xrightarrow{Electrolysis} Na_{(s)} + \frac{1}{2}Cl_{2(g)}$$

If an aqueous solution of NaCl is electrolyzed, Cl_2 will be obtained at the anode but at the cathode, H_2 will be obtained (instead of Na). This is because the standard reduction potential of Na $E^{\circ} = -2.71V$ is more negative than that of H_2O ($E^{\circ} = -0.83V$). Hence, H_2O will get preference to get reduced at the cathode and as a result, H_2 is evolved.

$$NaCl_{(aq)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

At cathode: $2H_2O_{(l)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)}$

At anode: $Cl^{-}_{(melt)} \rightarrow Cl_{(g)} + e^{-}$

$$2Cl_{(g)} \rightarrow Cl_{2(g)}$$

Assertion and Reason Answers:

1. (b) Both assertion and reason are true but reason is not the correct explanation of assertion.

Explanation:

Non fusible mass present in ore in mixing with suitable flux are fused which are then reduced by coke to give free metal.

2. (d) Assertion is false but reason is true.

Explanation:

Leaching is a process of concentration.