

CHEMISTRY

CHAPTER 6: ISOLATION OF ELEMENTS



ISLATION 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,
 - $\Delta G^\circ = -RT \ln K$
- If ΔG° 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:**

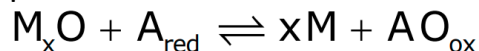
1. The graphical representation of Gibbs energy was first used by H.J.T. Ellingham.
2. This representation provides a basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham diagram.
3. Such diagrams help us in predicting the feasibility of thermal reduction of an ore.
4. Ellingham diagram normally consists of plots of $\Delta_f G^\circ$ 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 $\Delta_f G^\circ$ 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.

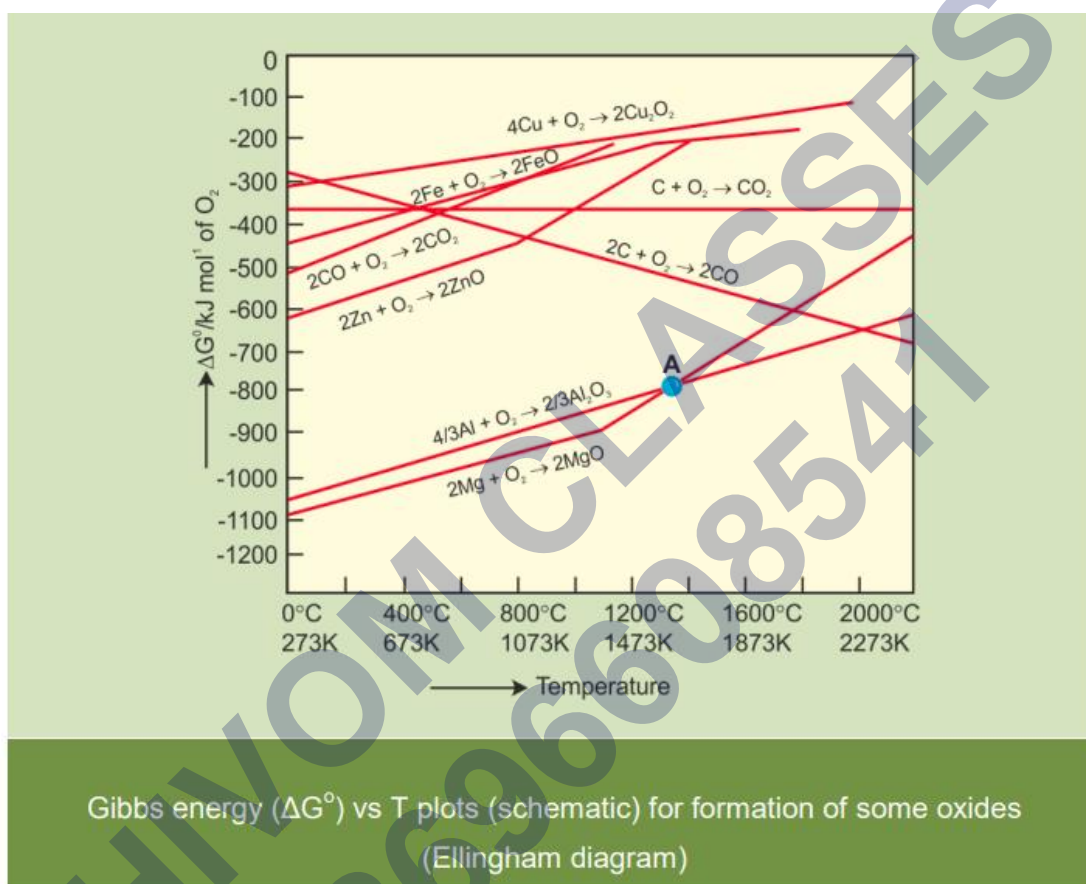
➤ **Limitations of Ellingham Diagram:**

- 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° is based upon the equilibrium constant K . Thus, it is presumed that the reactants and products are in equilibrium.



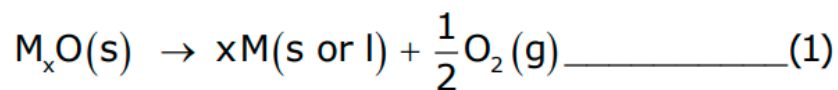
- But, this is not always true because the reactant or product may be solid.



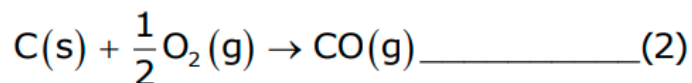
Theory of pyrometallurgy:

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**.

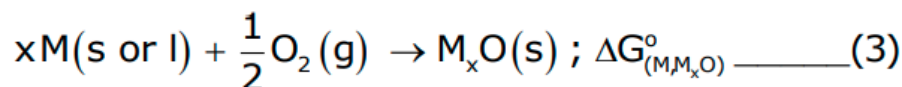
- During reduction, the oxide of the metal decompose



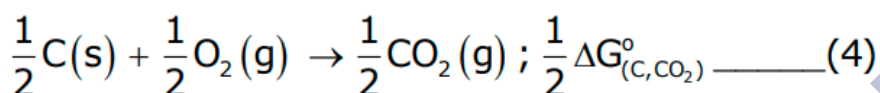
- The reducing agent takes away the oxygen given by the metal oxide.



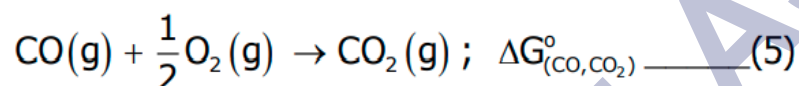
- By reversing the equation (1), we will get the oxidation reaction.



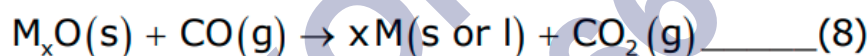
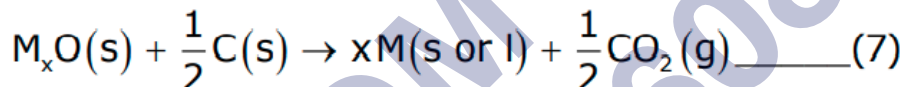
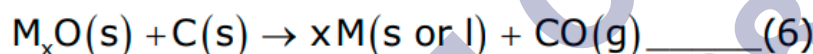
- If instead of partial oxidation of C to CO, complete oxidation of C to CO₂ occurs, then the oxidation of the reducing agent may be represented as



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



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



- 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° value. Therefore, the temperature is chosen such that the sum of Δ_rG° in the two combined redox processes is negative.
- In Δ_rG° vs T plots, this is indicated by the point of intersection of the two curves. After that point, the Δ_rG° value becomes more negative for the combined process including the reduction of M_xO.
- If the difference between two Δ_rG° values is large, then reduction is easier.

Applications of Pyrometallurgy:

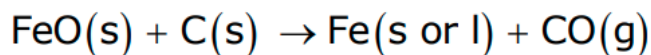
➤ **Extraction of iron from its oxides:**

▪ Theory of reduction process:

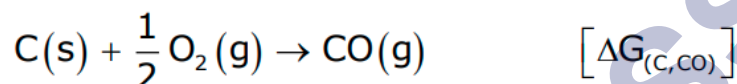
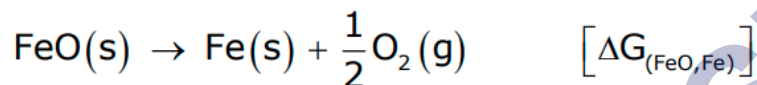
- Oxide ores of iron, after concentration through calcination/roasting, are mixed

with limestone and coke and fed into a blast furnace from its top.

- The oxide is reduced to the metal. The reduction takes place as follows



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



- The net free energy change becomes,

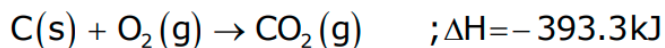
$$\Delta G_{(\text{C, CO})} + \Delta G_{(\text{FeO, Fe})} = \Delta_r G$$

- The reaction will take place only when the $\Delta_r G$ is negative.
- If we plot the graph of ΔG° 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.
- This means that the coke will reduce FeO to Fe and itself will be oxidized to CO.
- Below 1073K, the CO, CO₂ 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:*

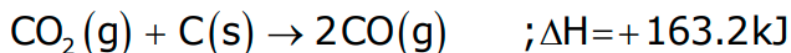
Near the tuyeres, where small pipes through which a blast of hot air is introduced, coke burns to form carbon dioxide.



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

(b) *Zone of heat absorption:*

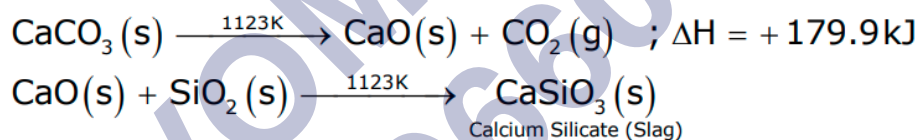
This is lower part of furnace and temperature is between 1423K–1673K. The CO_2 formed, meets the descending charge. The coke present in the charge reduces CO_2 to CO.



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

(c) *Zone of slag formation:*

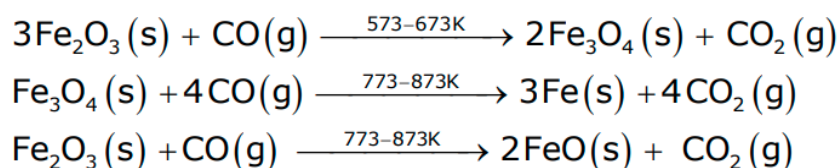
It is the middle part of the furnace. The temperature is around 1123K. In this region, limestone decomposes to form CaO and CO_2 . This CaO combines with silica to form fusible calcium silicate slag.



(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.



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

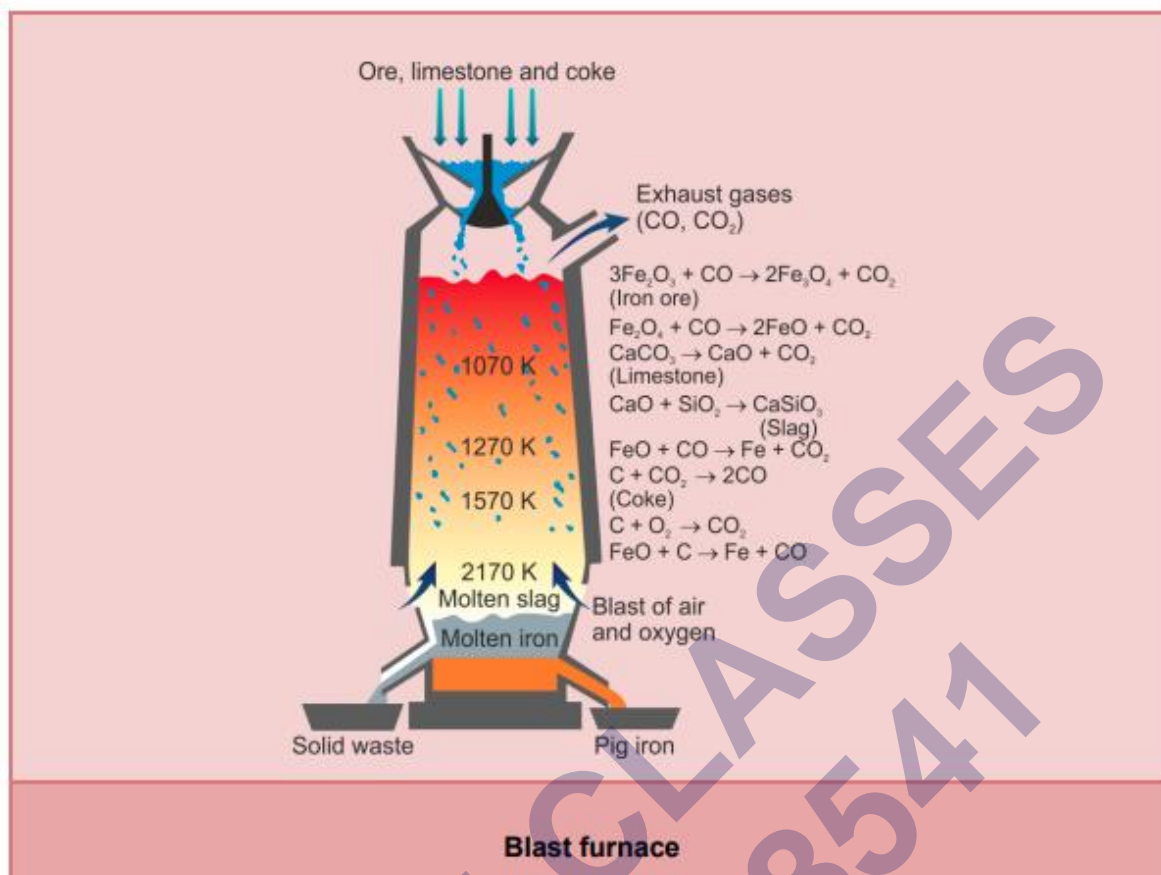


Finally, the direct reduction of iron ore takes place completely to iron by carbon above 1073K.



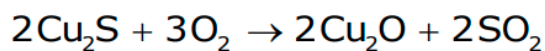
(e) *Zone of fusion:*

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.

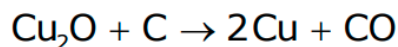


➤ **Extraction of copper from cuprous oxide [copper(I) oxide]:**

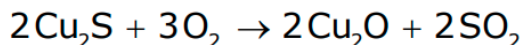
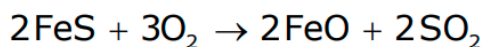
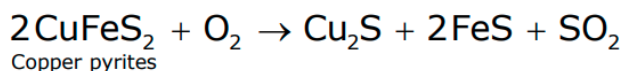
1. In the Ellingham diagram of formation of Cu_2O from Cu , it can be seen that the $(\text{Cu}, \text{Cu}_2\text{O})$ curve is at the top, while (C, CO) and (CO, CO_2) lines lie below in the temperature range of 500K-600K. Hence, it is very easy to reduce cuprous oxide to metallic copper.
2. But most of the ores of copper are sulphides. Therefore, the sulphide ores are first roasted in the reverberatory furnace to convert them into oxides.



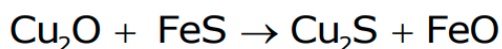
3. These oxides can then be reduced to metallic copper using coke as a reducing agent.



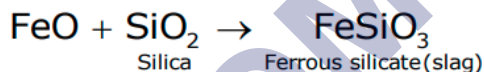
4. In the actual process, the sulphide ore is roasted in the reverberatory furnace where the copper pyrites is converted into a mixture of FeS and Cu_2S .



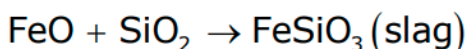
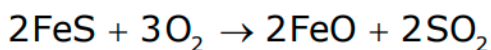
5. Iron is more reactive than copper. Hence, FeS is preferentially oxidized to FeO than Cu₂S to Cu₂O. The Cu₂O is then combined with FeS and converted back to Cu₂S.



6. Therefore, the roasted ore mainly contains Cu₂S 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.

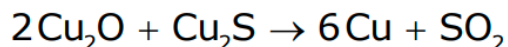
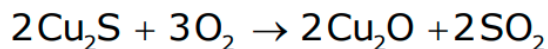


8. At the furnace's temperature, the entire solid melts and two layers of molten solids are formed. The slag, being lighter, forms upper layer and can be withdrawn from slag hole time to time.
9. The lower molten layer is called copper matte. It consists of Cu₂S and FeS.
10. This copper matte is then 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 FeSiO₃ slag.

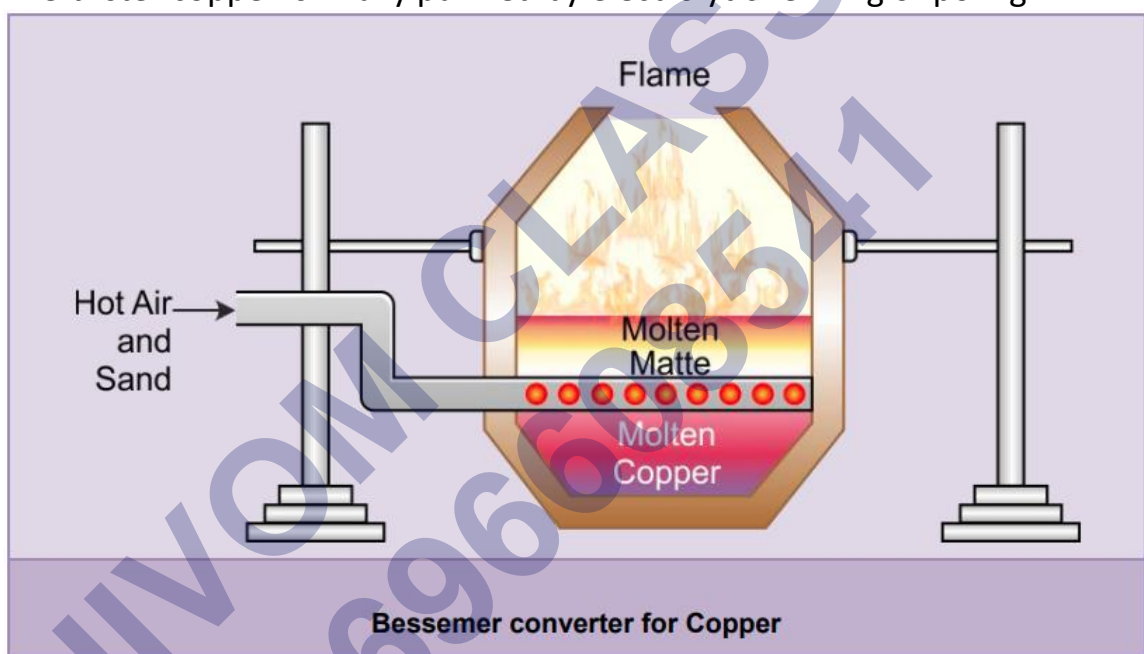


11. That slag melts and floats on the top of the molten mass from where it is removed. When the whole iron is removed as a slag, some of the cuprous

sulphide undergoes oxidation to form cuprous oxide which then reacts with cuprous sulphide to form copper metal.



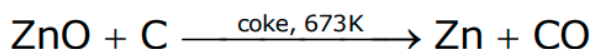
12. The copper metal formed is then cooled so as to remove SO_2 . Some gas bubbles are trapped during this solidification giving blister like appearance to the metal, Hence, they are called as blister copper.
13. The blister copper is finally purified by electrolytic refining or poling.



➤ **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 $(\text{Cu}, \text{Cu}_2\text{O})$ 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 , $\Delta_f G^\circ$ for ZnO is higher than that of CO_2 and CO . Hence, above this temperature, $\Delta_f G^\circ$ 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.



- It is noted that the $\Delta_f G^\circ$ of CO_2 from CO is always higher than that of ZnO . Hence, CO cannot be used for reduction of ZnO to Zn .
- 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,

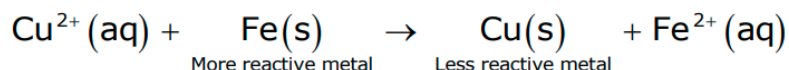
$$\Delta G^\circ = -nFE^\circ$$

Where,

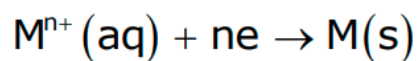
n = Number of electrons involved in the reduction process

E° = 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.



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



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

Applications of Electrolysis to Metallurgy:

➤ *Extraction of Aluminium from Alumina:*

- 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

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

1140K.

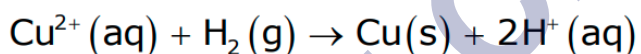
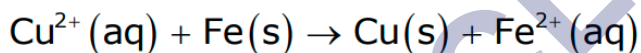
- The electrolysis of the molten mass is carried out in an electrolytic tank made of iron using carbon electrode.
- The molten electrolyte is covered with a layer of powdered coke to prevent oxidation and loss of heat due to radiation. The temperature of tank is maintained at about 1173k.
- The reactions taking place during electrolysis are
 Cathode : $Al^{3+} (melt) + 3e^- \rightarrow Al(l)$
 Anode : $C(s) + O^{2-} (melt) \rightarrow CO(g) + 2e^-$
 $C(s) + 2O^{2-} (melt) \rightarrow CO_2(g) + 4e^-$
- 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.

- The aluminium metal liberated at cathode melts at high temperature of the tank.
- 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.
- The metal obtained from this process is 99.95% pure.

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

- Copper is extracted by hydrometallurgy from low grade ores.
- The low grade ores are leached by treating with an acid when copper metal goes into a solution as Cu^{2+} ions.
- The solution containing Cu^{2+} ions is then treated with scrap iron or H_2 gas.



- Because E° 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:

- Non metals occur in a combined state in its reduced form. Therefore, they are generally extracted or isolated by oxidation of their compounds.

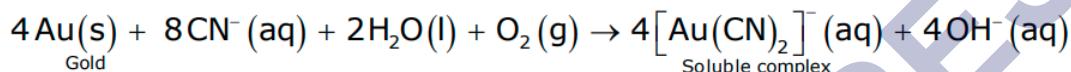
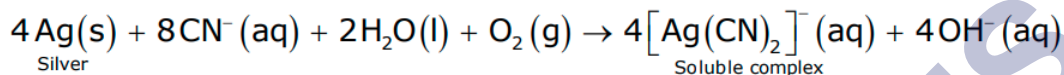
- Consider an isolation of chlorine from brine.



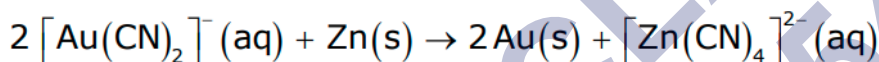
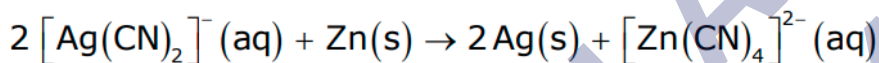
- Because oxidation cannot be carried out by ordinary chemical methods, it is accomplished by electrolysis.
- During electrolysis, Cl_2 is liberated at anode and H_2 at the cathode while NaOH is obtained in the solution.
- Electrolysis of molten NaCl can be carried out but here Na metal is liberated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



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



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.

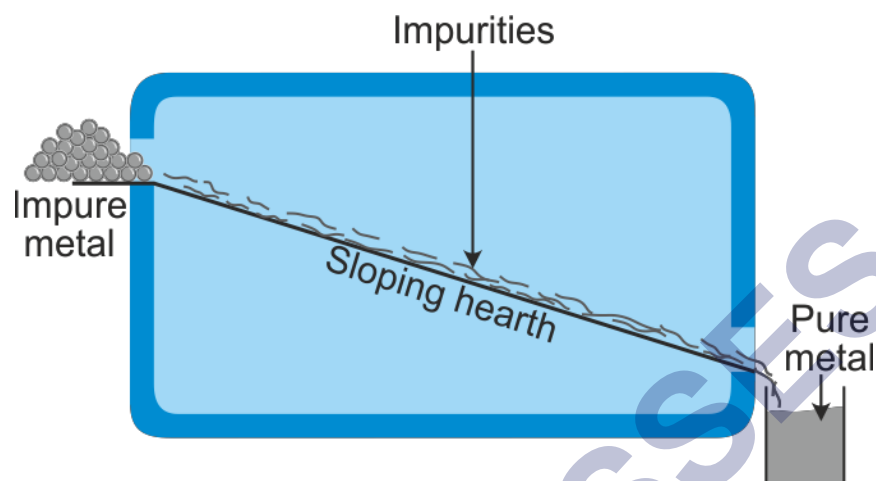
Unreacted oxides and sulphides of the metals

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**.

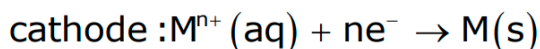
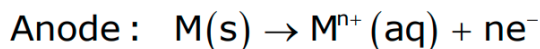
- The common methods used for refining of metals are
 - **Distillation process:**
 1. This method is employed for purification of volatile methods such as zinc, mercury and cadmium.
 2. The impure metal is heated in an iron retort and the vapours are condensed in a separate receiver.
 3. The pure metal 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.



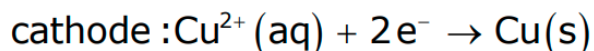
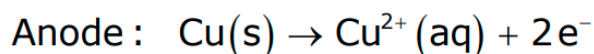
Liquation process

➤ **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.

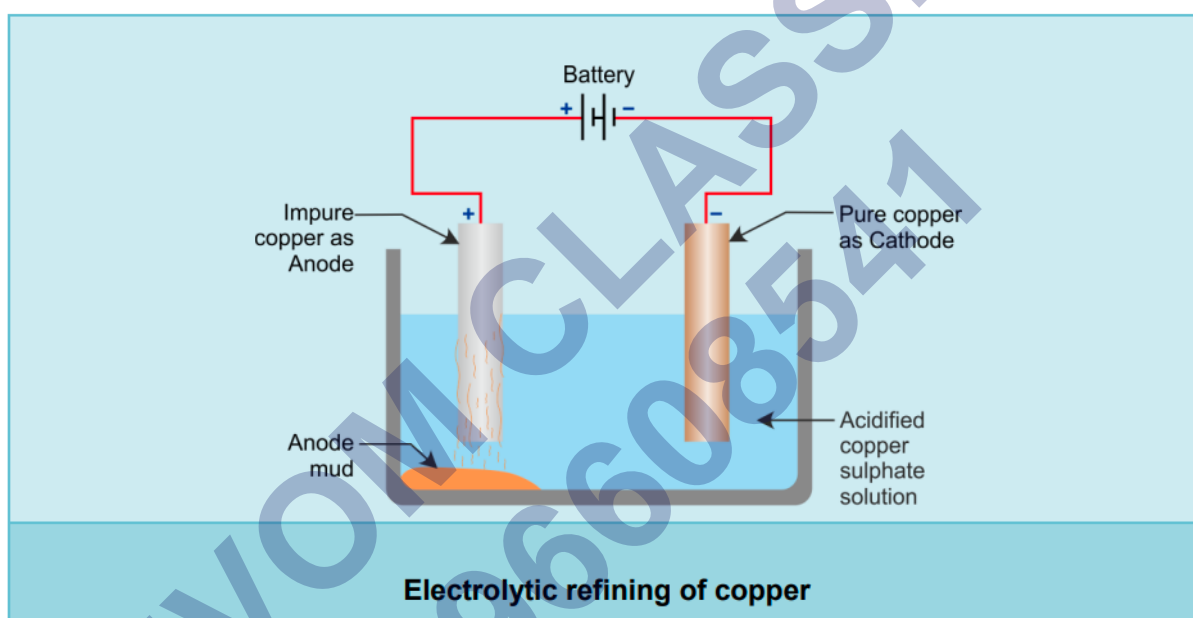


5. In case of electrolytic refining of copper, crude copper metal acts as an



anode while thin sheet of pure copper acts as a cathode. An electrolyte takes in the copper sulphate solution acidified with sulphuric acid.

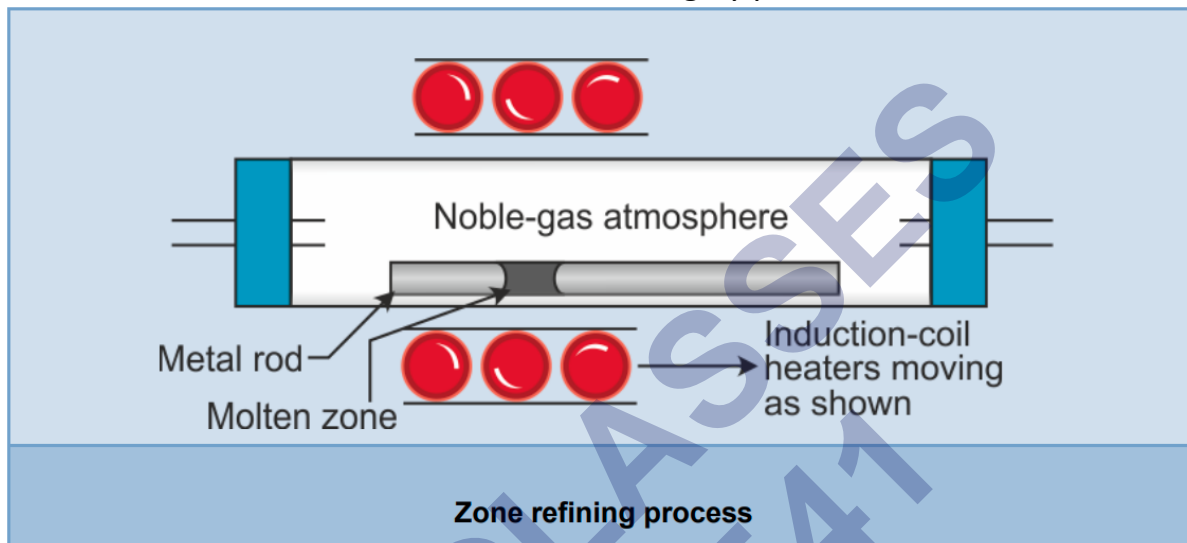
6. The impurities of iron, nickel, zinc and cobalt present in copper are passed into the solution as soluble sulphates.
7. The other impurities such as antimony, tellurium, selenium, gold and silver are less electropositive, and hence they do not get affected by the electrolytic solution and settle down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



➤ **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.



➤ **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:

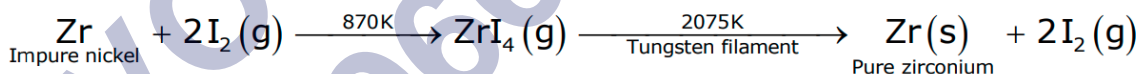
(a) Mond Process:

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.



(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



➤ **Chromatographic methods:**

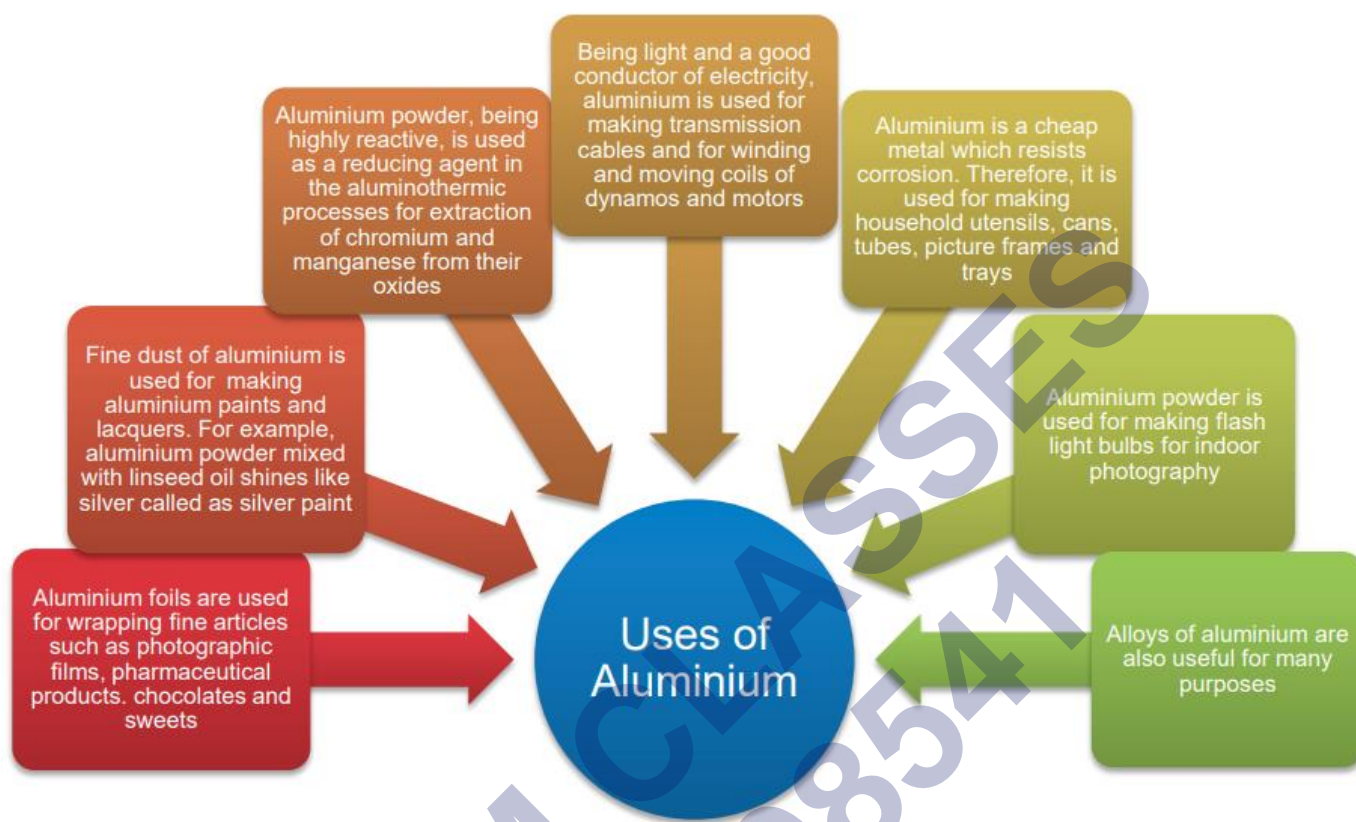
1. Chromatography is the most versatile and modern method for separation, purification and testing the purity of elements and their compounds.
2. This method is based upon the principle that different components of mixture are adsorbed to different extent on an adsorbent.
3. It consists of two phases, 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 CO₂.
4. There are several types of chromatography depending upon the physical

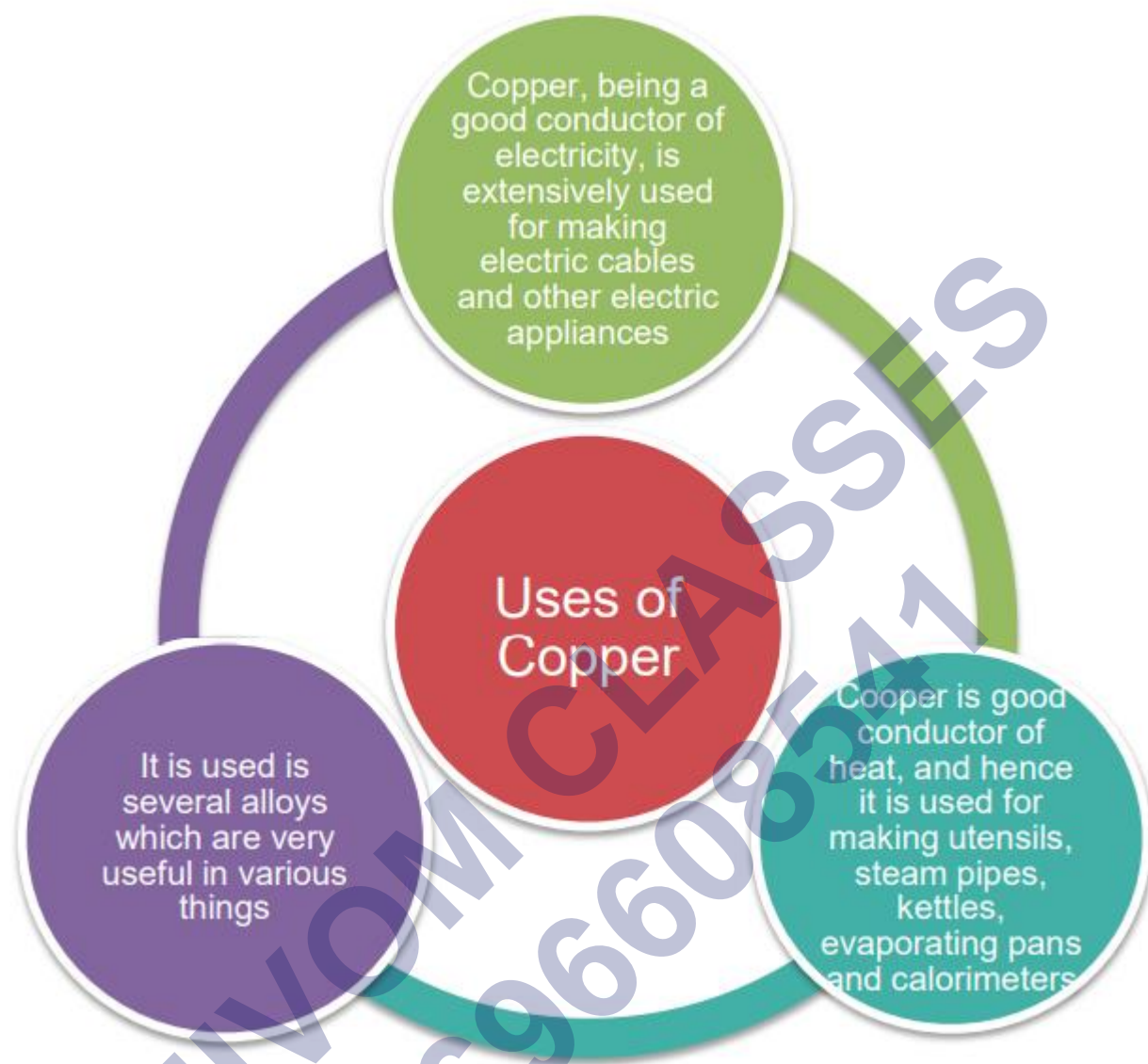
state of the stationary phase and mobile phase. Let us discuss one of the many, column chromatography.

➤ **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 give 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:







Modes of Occurrence of Elements and Metals

Modes of Occurrence of Elements

The elements generally occur in the free state (called native state) or in the combined state. This is mainly because of different chemical reactivities of elements.

1) Native State

The elements which have very low reactivity and are not attacked by oxygen or air, moisture, carbon dioxide or other non-metals occur in the free state, called native state.

For example: carbon, sulphur, nitrogen, noble gases, metals like gold, silver, platinum, etc.

occur in nature in the native state.

Therefore, these elements are also called native elements.

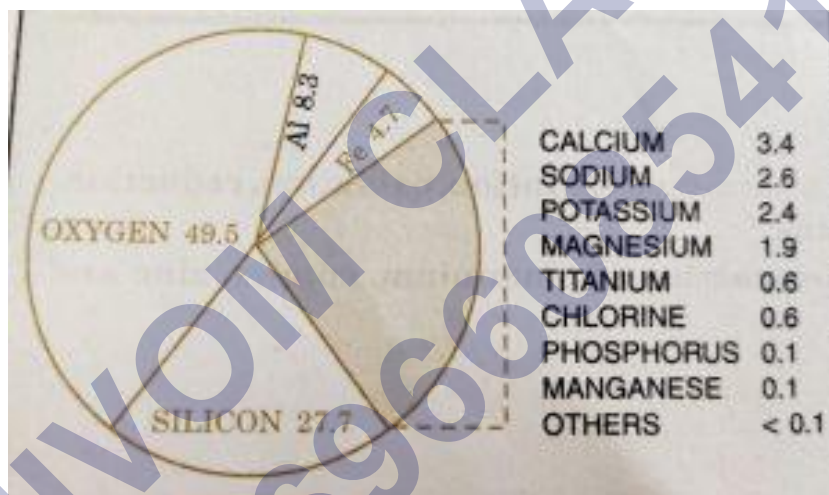
2) Combined State

The elements which are reactive and have a tendency to combine with oxygen or air, moisture, carbon dioxide and non-metals like carbon, nitrogen, sulphur, phosphorus, arsenic, halogen, etc. occur in the combined state.

These elements occur in the crust of the earth in the form of their compounds. In the combined state the non-metals are usually found in the reduced form and the metals in the oxidised form.

Among the metals, only a few metals, such as silver, gold, platinum, etc. occur in native state. Non-metals such as carbon and sulphur also occur in native state as well as in combined state.

Abundance of Elements



Most metals occur in the combined states. The most common forms of metals in the combined state are oxides, carbonates, sulphides, silicates, halides, sulphates, arsenides, phosphate, etc.

Among metals, aluminium is the most abundant. It is the third most abundant element in earth's crust (8.31% by wt). It occurs widely as a constituent of rocks and soils. It is a major component of many igneous minerals including mica and clay.

Iron is the second most abundant metal in earth's crust. It forms a variety of compounds which have various important uses. This makes iron a very important element. Iron is also one of the essential elements in biological systems.

Mineral and Ores

Most of the metals have a tendency to react with moisture, oxygen, sulphur, halogens, etc. and therefore, occur in the crust of the earth in the form of their compounds such as oxides, sulphides, halides, silicates, carbonates, nitrates, phosphates, etc.

The naturally occurring chemical substances in which metals occur in the earth's crust are called minerals. The mineral, from which the metal can be economically and conveniently extracted, is called an ore.

The type of mineral from which the metal can be extracted is decided on the basis of profitability.

For example: Metals are not generally extracted from silicate minerals because of the difficulties during extraction.

2) Aluminium occurs in the earth's crust in the form of two minerals, bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) and clay ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). Aluminium can be conveniently and economically extracted from bauxite, while it has not been possible to extract aluminium from clay by some easy and cheap method.

3) The main minerals of copper are copper glance (Cu_2S), cuprite (Cu_2O), copper pyrites (CuFeS_2), malachite [$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$], etc. but copper can be conveniently extracted from copper pyrites. Therefore, the ore of copper is copper pyrites.

Metal	Name	Composition
Aluminium	Bauxite	$\text{AlO}_x(\text{OH})_{3-2x}$
	Feldspar	KAlSiO_8
	Cryolite	Na_3AlF_6
	Kaolinite	$\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$
	Iron	Haematite
Magnetite		Fe_3O_4
Siderite		FeCO_3
Iron Pyrites		FeS_2
Limonite		$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Copper	Copper glance	Cu_2S
	Copper pyrite	CuFeS_2
	Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	Cuprite	Cu_2O
	Azurite	$2 \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
Zinc	Zinc blende	ZnS

	Calamine	Zn_2SiO_4
	Zincite	$ZnO.Fe_2O_3$
	Willemite	$ZnO.Fe_2O_3$
Manganese	Pyrolusite	MnO_2
	Braunite	Mn_2O_3
Calcium	Limestone	$CaCO_3$
	Gypsum	$CaSO_4.2H_2O$
Magnesium	Magnesite	$MgCO_3$
	Dolomite	$CaCO_3.MgCO_3$
Lead	Galena	PbS
	Cerrusite	$PbCO_3$
Mercury	Cinnabar	HgS

Extraction of Copper and Zinc

Occurrence and Extraction of Copper

Occurrence of Copper

It occurs as native copper as well as in combined state. The main ores of copper are:

- Copper glance Cu_2S
- Copper pyrites $CuFeS_2$
- Malachite $Cu(OH)_2CuCO_3$
- Cuprite or (Rubby copper) Cu_2O
- Azurite $2CuCO_3.Cu(OH)_2$

Extraction of Copper

It is mainly extracted from copper pyrites ($CuFeS_2$). The sulphide ore is usually of very low grade and contains iron sulphide, gangue and smaller quantities of arsenic, antimony, selenium tellurium, silver, gold and platinum.

The various steps involved in the extraction are:

1) Crushing and concentration

The ore is crushed in jaw crushers and then finally powdered.

It is concentrated by froth floatation process.

In this process, the finely powdered ore is mixed with water and some pine oil in a tank.

The mixture is agitated by blowing compressed air into it.

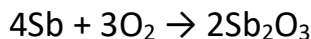
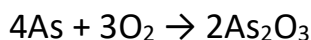
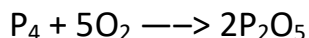
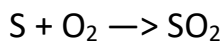
The particles are preferentially wetted by oil and rise to the surface of the tank in the form of a froth (a foam) from where these are skimmed off.

The silicious and earthy impurities are preferentially wetted by water and sink to the bottom of the tank.

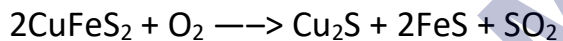
2) Roasting

The concentrated ore is roasted i.e., heated strongly in the presence of excess air in a reverberatory furnace. During roasting the following changes occur:

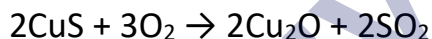
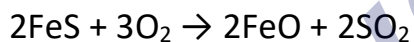
- Moisture is removed from the ore and it becomes dry.
- The impurities of sulphur, arsenic, antimony and phosphorus are removed as their volatile oxides.



(iii) Copper pyrites is converted to ferrous sulphide (FeS), cuprous sulphide (Cu₂S) which are partially oxidised



Copper pyrites



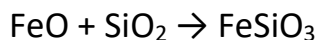
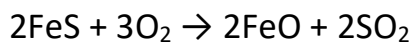
3) Smelting

The roasted ore is mixed with some powdered coke and sand and is heated strongly in a blast furnace.

The blast furnace is made up of steel and is lined inside with fire bricks. A blast of hot air is introduced at the lower part of the furnace.

The following changes occur during smelting :

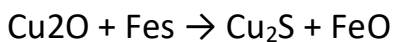
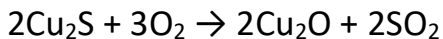
(a) Most of the ferrous sulphide gets oxidised to ferrous oxide which combines with silica (flux) to form fusible slag.



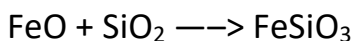
Ferrous silicate (slag)

The slag being lighter floats and forms the upper layer. It is removed through the slag hole from time to time.

(b) During roasting or in the blast furnace if any oxide of copper is formed, it combines with FeS and is changed back into its sulphide.

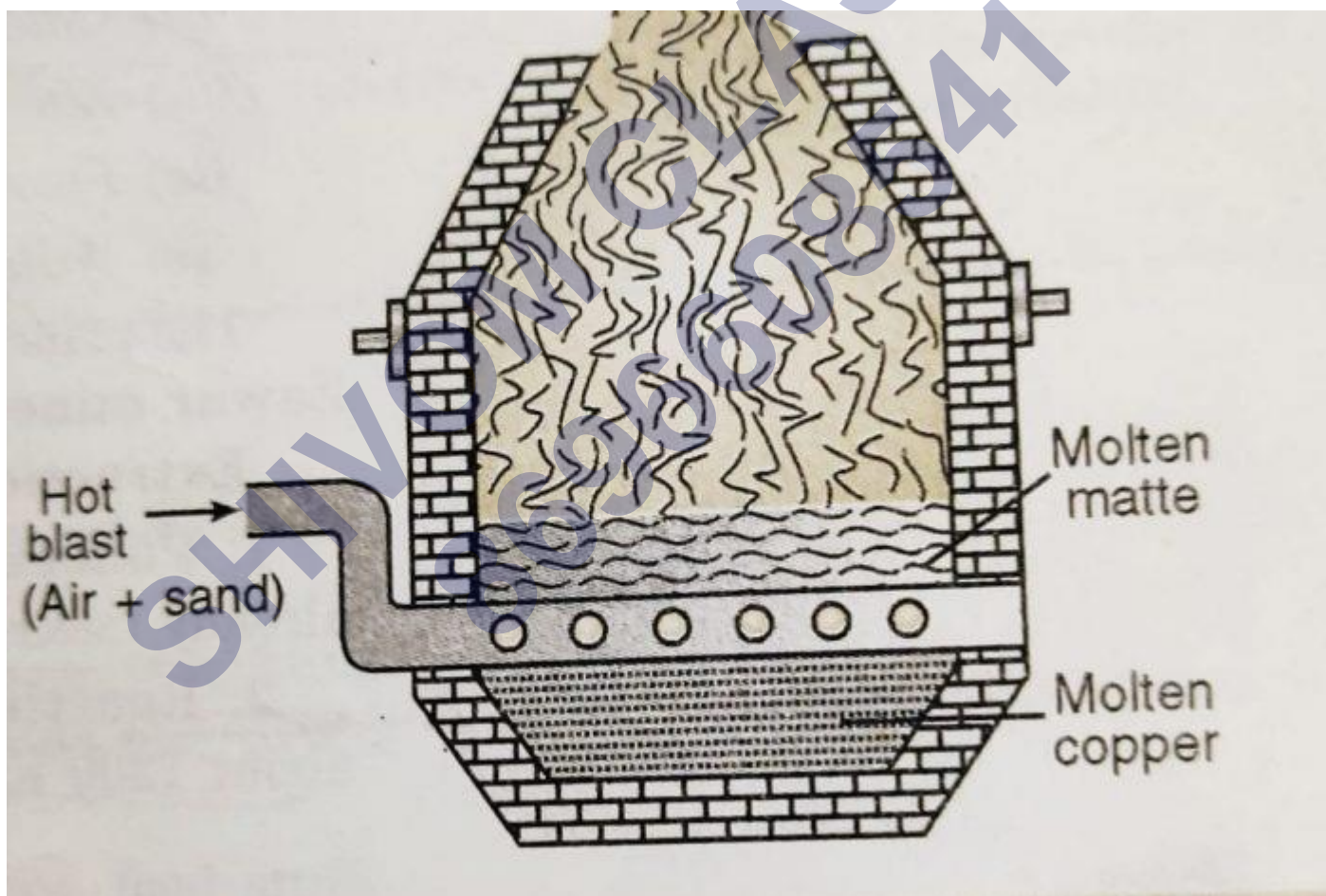


Ferrous oxide thus formed again combines with silica to form more slag.



As a result of smelting, two separate layers are formed at the bottom of the furnace. The upper layer consists of slag and is removed as a waste. The lower layer of molten mass contains mostly cuprous sulphide and some traces of ferrous sulphide. It is called matte and is taken out from the tapping hole at the bottom.

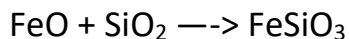
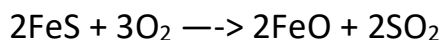
4) Bessemerisation



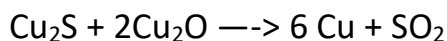
The molten matte from the blast furnace is transferred into a Bessemer converter.

The vessel is made of steel and is lined inside with lime or magnesium oxide. A hot blast of air mixed with sand is blown into the molten matte. During this process :

(i) traces of ferrous sulphide present in the matte is oxidised to FeO which combines with silica to form slag.



(ii) copper sulphide is partially oxidised to cuprous oxide which further reacts with remaining copper sulphide to form copper and sulphur dioxide.



After the reaction has been completed, the converter is tilted and the molten copper is poured into sand moulds. On cooling, sulphur dioxide, nitrogen and oxygen escape from the metal. The copper thus, obtained is about 99% pure and is known as blister copper. The name blister comes from the fact that as the metal solidifies, the dissolved SO_2 , escapes producing blisters on the metal surface.

5) Refining

a) Poling: The blister copper is purified by heating it strongly in a reverberatory furnace in the presence of excess of air. The impurities are either removed as volatile oxides or converted into slag.

Some of the copper also changes to cuprous oxide. This is reduced back to copper by stirring the molten metal with green poles of wood. The hydrocarbons present in these freshly cut poles reduce cuprous oxide to copper which is about 99.5% pure.

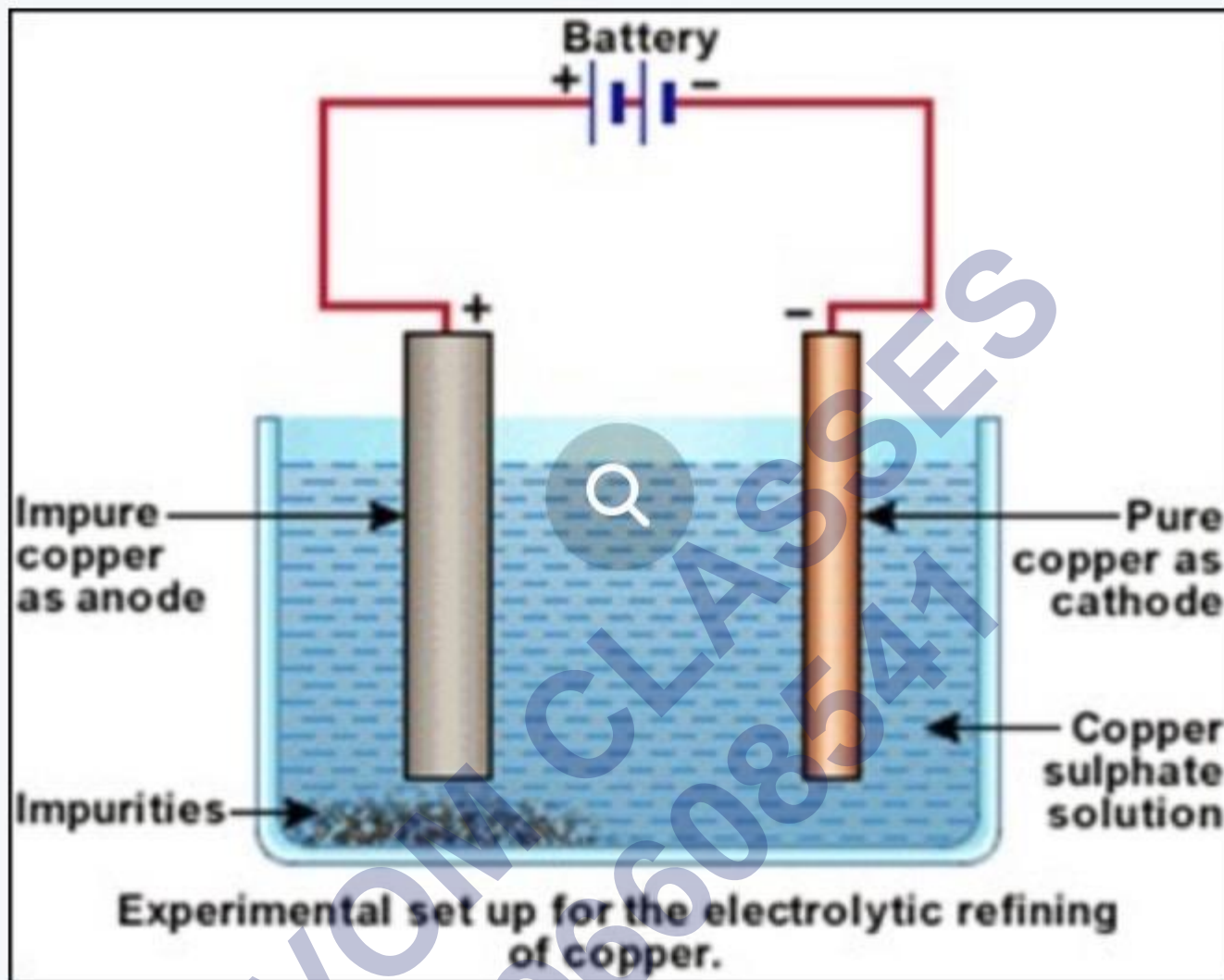
b) Electrolytic refining: In this method, a thin sheet of metal is made as cathode and the block of crude metal is made as anode.

Both the electrodes are placed in an acidified copper sulphate solution. When electric current is passed through the solution impure copper from anode goes into the solution and pure copper from the solution gets deposited on the cathode.



The impurities of zinc, nickel, iron, etc. get collected below the anode as anode mud.

Prolonged exposure of copper pyrites to air and rain leads to the formation of dilute solution of copper sulphate. Copper can be precipitated from this solution by the addition of scrap iron. It is then refined electrolytically.



Occurrence and Extraction of Zinc

Zinc does not occur in native form because it is a reactive metal. The main ores of zinc are:

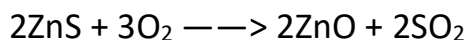
- Zinc blende ZnS
- Calamine $ZnCO_3$
- Zincite ZnO
- Franklinite $ZnO \cdot Fe_2O_3$
- Willemite Zn_2SiO_4

The principal ore of zinc is zinc blende.

Extraction: Zinc can be extracted from zinc blende by the following steps:

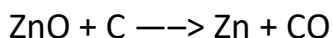
1) Concentration: The ore is concentrated by froth floatation process.

2) Roasting: Concentrated ore is roasted in the presence of excess of air at about 1200 K to convert zinc sulphide into zinc oxide.



Sulphur dioxide gas evolved in this process may be used in the manufacture of sulphuric acid.

3) Reduction: Zinc oxide is reduced to zinc by heating with crushed coke at 673 K in vertical fire clay retorts.



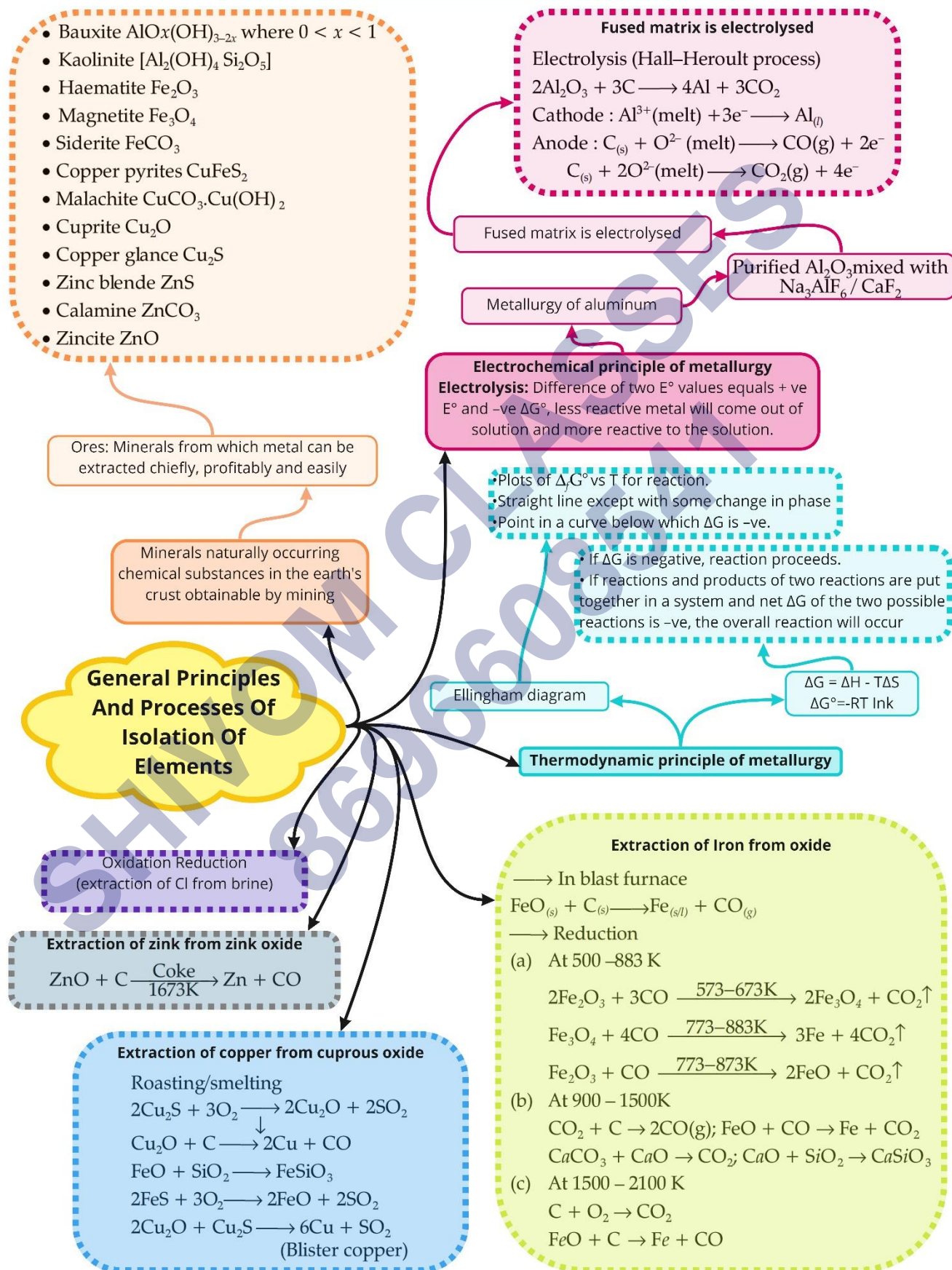
The vapours of zinc formed are collected and condensed.

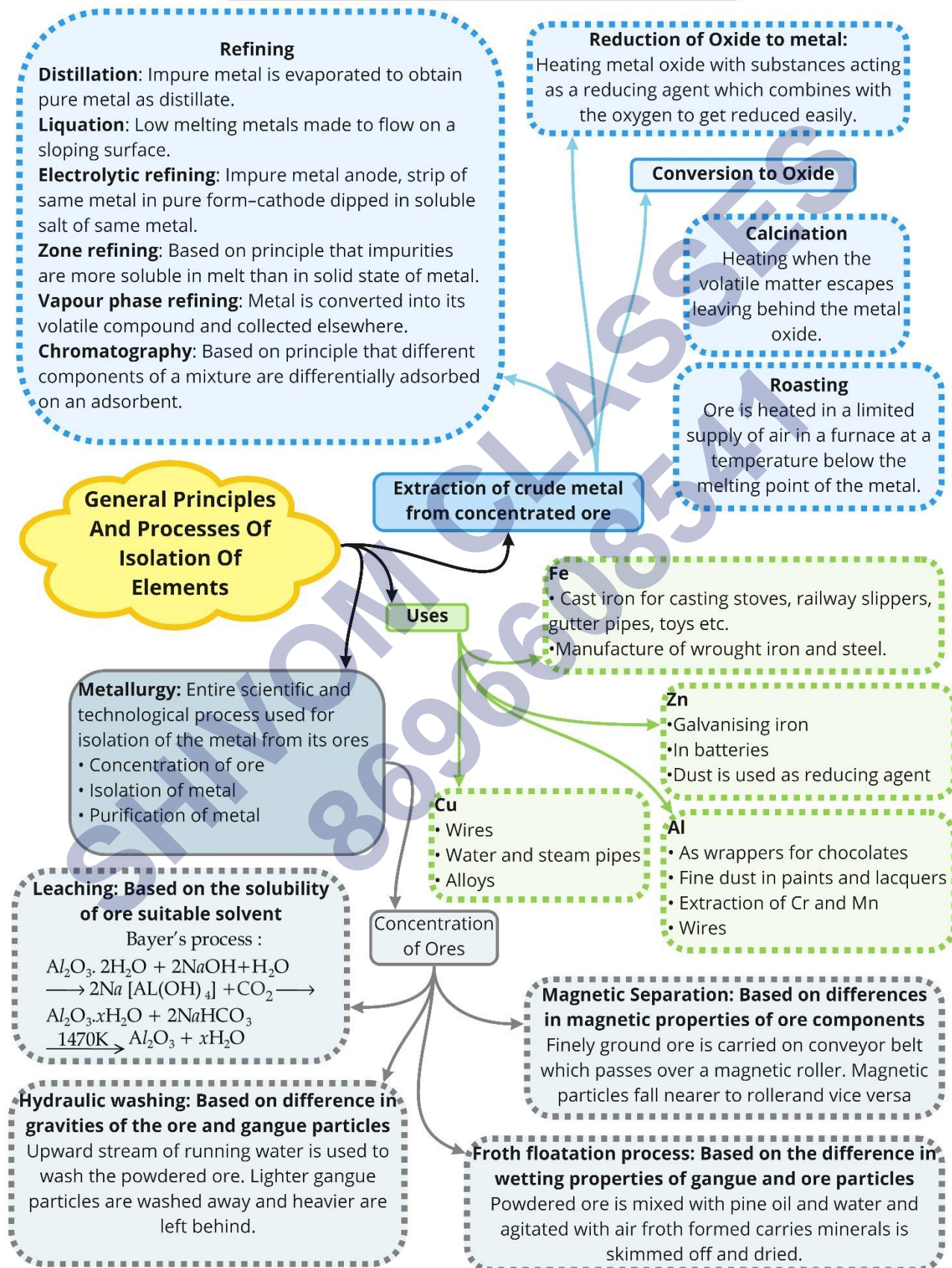
4) Refining: The impure metal is refined by fractional distillation or by electrolytic method.

(i) By fractional distillation: Impure zinc contains impurities of cadmium (b.p. = 1073 K), lead (b.p. 2024 K) and iron (b.p. 3273 K). The boiling point of zinc is 1183 K. The impure metal is distilled when zinc and cadmium with low boiling points distil over leaving behind lead and iron.

The boiling points of zinc and cadmium are also different and therefore, the mixture of zinc and cadmium is again subjected to fractional distillation when low boiling cadmium distils leaving behind zinc metal in the distillation flask.

(ii) By electrolytic refining: In this process, the impure zinc is made anode while a plate of pure zinc is made the cathode. The electrolyte is zinc sulphate containing a small amount of dilute sulphuric acid. On passing current, zinc from the electrolyte is deposited at the cathode while an equivalent amount of zinc from anode goes into the electrolyte. Therefore, pure zinc is obtained on cathode.





Important Questions

Multiple Choice questions-

- The electrolytic reduction technique is used in the extraction of
 - Highly electronegative elements.
 - Highly electropositive elements.
 - Metalloids.
 - Transition metals.
- In the commercial electrochemical process for aluminium extraction, electrolyte used is
 - Al(OH)_3 in NaOH solution.
 - An aqueous solution of $\text{Al}_2(\text{SO}_4)_3$.
 - A molten mixture of Al_2O_3 and Na_3AlF_6 .
 - A molten mixture of Al_2O_3 and Al(OH)_3 .
- Which ore can be best concentrated by froth floatation process?
 - Malachite
 - Cassiterite
 - Galena
 - Magnetite
- Electrolytic reduction of Al_2O_3 to Al by Hall- Herault process is carried out
 - in presence of NaCl.
 - in presence of fluorite.
 - in presence of cryolite which forms a melt with lower melting point.
 - in presence of cryolite which forms a melt with high melting point.
- The chemical composition of 'slag' formed during the melting process in the extraction of copper is
 - $\text{Cu}_2\text{O} + \text{FeS}$
 - FeSiO_3
 - CuFeS_2
 - $\text{Cu}_2\text{S} + \text{FeO}$
- Bessemer converter is used in the manufacture of
 - Pig iron
 - Steel
 - Wrought iron
 - Cast iron

7. The method of zone refining of metals is based on the principle of
- greater mobility of the pure metal than that of the impurity.
 - higher melting point of the impurity than that of the pure metal.
 - greater noble character of the solid metal than that of impurity.
 - 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
- The reaction between Ag_2S and NaCN is reversible.
 - to oxidise Na_2S formed in the reaction to Na_2SO_4 .
 - to oxidise Ag_2S to Ag_2O .
 - Both (a) and (b).
9. Purest form of iron is
- Cast iron
 - Hard Steel
 - Stainless steel
 - Wrought iron
10. Consider the following reaction at 1000°C
- A. $\text{Zn(s)} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{ZnO(s)}$
 $\Delta G^\circ = -360 \text{ kJ mol}^{-1}$
- B. $\text{C(gr)} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO(g)}$
 $\Delta G^\circ = -460 \text{ kJ mol}^{-1}$
- Choose the correct statement at 1000°C
- Zinc can be oxidised by carbon monoxide.
 - Zinc oxide can be reduced by graphite.
 - Both statements (a) and (b) are correct.
 - Both statements (a) and (b) are false.

Very Short Questions-

- What is pig iron?
- What is cast iron?
- What is wrought iron?
- What is added as flux in extraction of iron?
- What is Blister copper?
- Write the equation for reduction of zinc oxide?
- Why is cryolite used during extraction of Aluminium?
- 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.

- Assertion and reason both are correct statements and reason is correct explanation for assertion.
- Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- Assertion is correct statement but reason is wrong statement.
- 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-

- Answer: b
- Answer: c
- Answer: c
- Answer: c
- Answer: b
- Answer: b
- Answer: d
- Answer: d
- Answer: d
- Answer: b

Very Short Answers-

- 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.
- Ans.** Iron obtained by melting pig iron with scrap iron and coke using hot air blast is cast iron.
- Ans.** Wrought iron and malleable iron is the purest form of commercial iron which is

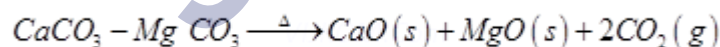
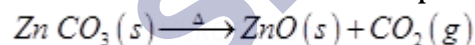
prepared from cast iron by oxidizing impurities in a reverberatory furnace lined with hematite.

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

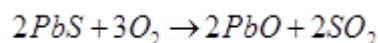
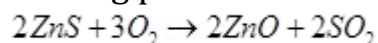
Short Answers-

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.



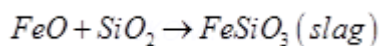
Roasting: - Here ore is heated in a regular supply of air at a temperature below the melting point of metal e.g.



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

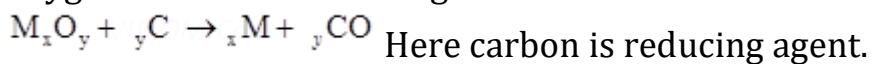
Flux + Impurity \rightarrow Slag.

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



Impurity flux

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



Ans 5. When ΔS is entropy change, ΔH is enthalpy change, then at temperature T, the change in Gibbs free energy is given by

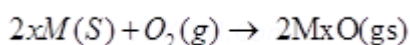
$$\Delta G = \Delta H - T\Delta S.$$

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 $T\Delta S$ 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



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.

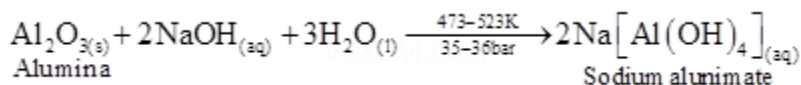
Ans 10. If the ore or the gangue can be attracted by the magnetic field, then the ore can be concentrated by the process of magnetic separation. Among the ores

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.

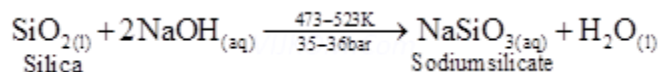
Long Answers-

Ans 1. In the extraction of aluminium, the significance of leaching is to concentrate pure alumina (Al_2O_3) from bauxite ore.

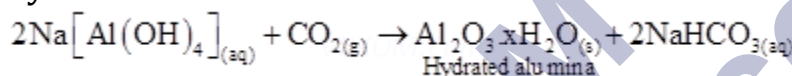
Bauxite usually contains silica, iron oxide, and titanium oxide as impurities. In the process of leaching, alumina is concentrated by digesting the powdered ore with a concentrated solution of NaOH at 473-523 K and 35-36 bar. Under these conditions, alumina (Al_2O_3) dissolves as sodium meta-aluminate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



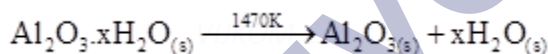
Alumina



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).

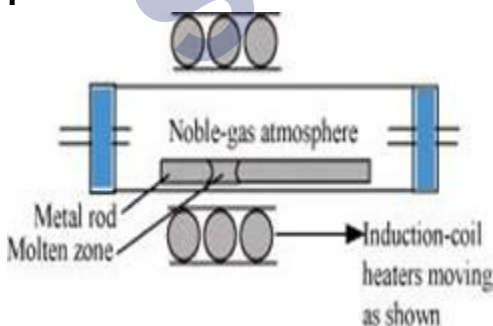


Hydrated alumina thus obtained is filtered, dried, and heated to give back pure alumina (Al_2O_3).



Ans 2. (i)

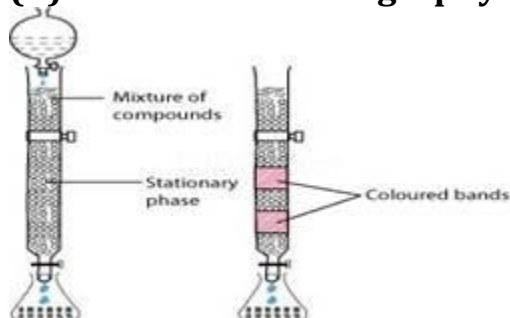
:



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

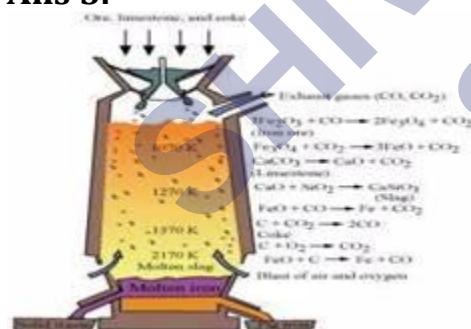
leads to the segregation of impurities at one end of the rod. Then, the end with the impurities is cut off. Silicon, boron, gallium, indium etc. can be purified by this process.

(ii) Column chromatography:



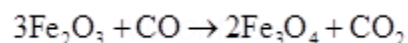
Column chromatography is a technique used to separate different components of a mixture. It is a very useful technique used for the purification of elements available in minute quantities. It is also used to remove the impurities that are not very different in chemical properties from the element to 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).

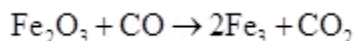
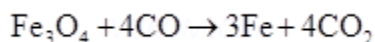
Ans 3.



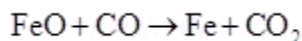
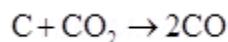
During the extraction of iron, the reduction of iron oxides takes place in the blast furnace. In this process, hot air is blown from the bottom of the furnace and coke is burnt to raise the temperature up to 2200 K in the lower portion itself. The temperature is lower in the upper part. Thus, it is the 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:

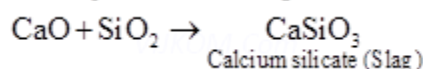
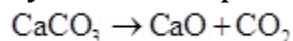




The reaction taking place in the higher temperature range (900 – 1500 K) in the blast furnace are:



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



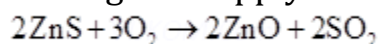
Ans 4. The different steps involved in the extraction of zinc from zinc blende (ZnS) are given below:

(i) Concentration of ore

First, the gangue from zinc blende is removed by the froth floatation method.

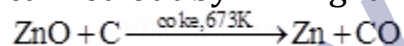
(ii) Conversion to oxide (Roasting)

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.



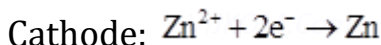
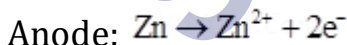
(iii) Extraction of zinc from zinc oxide (Reduction)

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.

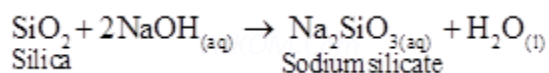
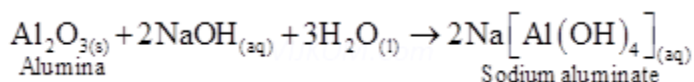


(iv) Electrolytic Refining

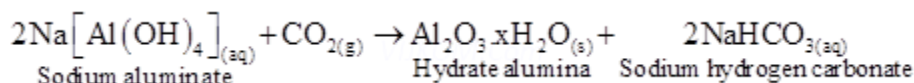
Zinc can be refined by the process of electrolytic refining. In this process, impure zinc is made the anode while a pure copper strip is made the cathode. The electrolyte used is an acidified solution of zinc sulphate (ZnSO_4). Electrolysis results in the transfer of zinc in pure from the anode to the cathode.



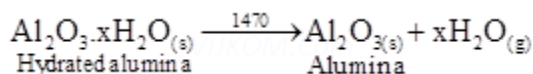
Ans 5. To separate alumina from silica in bauxite ore associated with silica, first the powdered ore is digested with a concentrated NaOH solution at 473 – 523 K and 35 – 36 bar pressure. This results in the leaching out of alumina (Al_2O_3) as sodium aluminate and silica (SiO_2) as sodium silicate leaving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



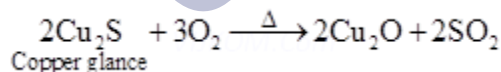
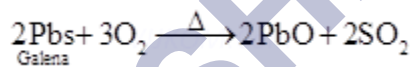
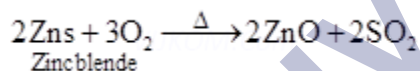
Then, CO_2 gas is passed through the resulting solution to neutralize the aluminate in the solution, which results in the precipitation of hydrated alumina. To induce precipitation, the solution is seeded with freshly prepared samples of hydrated alumina.



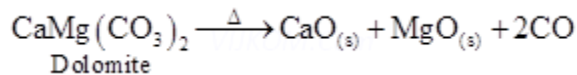
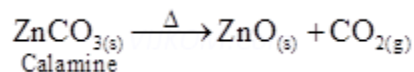
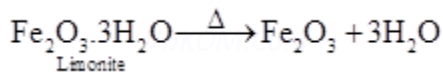
During this process, sodium silicate remains in the solution. The obtained hydrated alumina is filtered, dried, and heated to get back pure alumina.



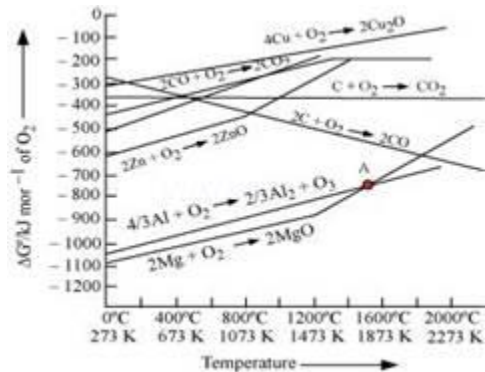
Ans 6. Roasting is the process of converting sulphide ores to oxides by heating the ores in a regular supply of air at a temperature below the melting point of the metal. For example, sulphide ores of Zn, Pb, and Cu are converted to their respective oxides by this process.



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.

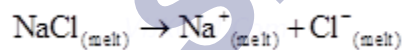


Ans 7.

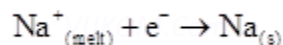


The above figure is a plot of Gibbs energy ΔG^\ominus vs. T for formation of some oxides. It can be observed from the above graph that a metal can reduce the oxide of other metals if the standard free energy of formation $\Delta_f G^\ominus$ of the oxide of the former is more negative than the latter. For example, since $\Delta_f G^\ominus_{(\text{Al}, \text{Al}_2\text{O}_3)}$ is more negative than $\Delta_f G^\ominus_{(\text{Cu}, \text{Cu}_2\text{O})}$, 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 $\Delta_f G^\ominus_{(\text{Mg}, \text{MgO})}$ is more negative than $\Delta_f G^\ominus_{(\text{Zn}, \text{ZnO})}$.

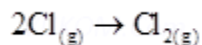
Ans 8. In the electrolysis of molten NaCl, Cl_2 is obtained at the anode as a by-product.



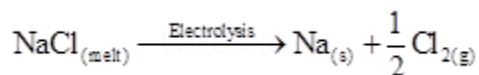
At cathode:



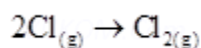
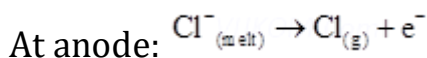
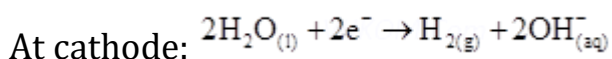
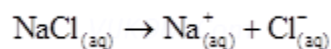
At anode: $\text{Cl}^-_{(\text{melt})} \rightarrow \text{Cl}_{(g)} + e^-$



The overall reaction is as follows:



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 $E^\circ = -2.71\text{V}$ is more negative than that of H_2O ($E^\circ = -0.83\text{V}$). Hence, H_2O will get preference to get reduced at the cathode and as a result, H_2 is evolved.



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.