

METALLURGY

CONTENTS

Particular	Page No.
Theory	01 – 24
Exercise - 1	25 – 29
Part - I : Subjective Questions	
Part - II : Only One Option Correct Type	
Part - III : Match the Columns	
Exercise - 2	29 – 34
Part - I : Only One Option Correct Type	
Part - II : Single or Double Digit Integer Type Questions	
Part - III : One or More Than One Options Correct Type	
Part – IV : Comprehensions	
Exercise - 3	35 – 39
Part - I : JEE(ADVANCED) / IIT-JEE Problems (Previous Years)	
Part - II : JEE(MAIN) / AIEEE Problems (Previous Years)	
Answers	40 – 42
Additional Problems for Self Practice (APSP)	43 – 51
Part - I : Practice Test-1 (IIT-JEE (Main Pattern))	
Part - II : National Standard Examination in Chemistry (NSEC) Stage-I	
Part - III : Additional Theory	
Part – IV : Practice Test-2 (IIT-JEE (Advanced Pattern))	
APSP Answers	52
APSP Solutions	52 – 57

JEE (Advanced) Syllabus

Extractive metallurgy: Chemical principles and reactions only (industrial details excluded); Carbon reduction method (iron and tin); Self reduction method (copper and lead); Electrolytic reduction method (magnesium and aluminium); Cyanide process (silver and gold).

JEE(Main) Syllabus

General Principles and Processes of Isolation of Metals

Modes of occurrence of elements in nature, minerals, ores; steps involved in the extraction of metals- concentration, reduction (chemical. and electrolytic methods) and refining with special reference to the extraction of Al, Cu, Zn and Fe; Thermodynamic and electrochemical principles involved in the extraction of metals.



Metallurgy

Introduction :

The compound of a metal found in nature is called a mineral. The minerals from which metal can be economically and conveniently extracted are called **ores**. An ore is usually contaminated with earthy or undesired materials known as gangue. So all minerals are not ores but all ores are minerals. Ores may be classified mainly into following four classes.

- (a) **Native ores** : They contain the metal in free state. Silver, gold, platinum etc, occur as native ores.
- (b) **Oxidised ores** : These ores consist of oxides or oxysalts (e.g. carbonates, phosphates, sulphates and silicates) of metals.
- (c) **Sulphurised ores** : These ores consist of sulphides of metals like iron, lead, zinc, mercury etc.
- (d) **Halide ores** : These ores consist of halides of metals.

Section (A) : ORES & Method of concentration

Important ore :

1. Oxide ore :

- (i) Bauxite $\rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (Major ore of Al)
- (ii) Haematite $\rightarrow \text{Fe}_2\text{O}_3$
- (iii) Zincite $= \text{ZnO}$
- *** (iv) Cassiterite or tin stone $\rightarrow \text{SnO}_2$ (Black Tin = 60 – 70% SnO_2)

2. Carbonate ore :

- (i) Lime stone $\rightarrow \text{CaCO}_3$
- (ii) Dolomite $\rightarrow \text{CaCO}_3 \cdot \text{MgCO}_3$
- (iii) Siderite $\rightarrow \text{FeCO}_3$
- (iv) Malachite $\rightarrow \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
- (v) Azurite $\rightarrow 2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
- *** (vi) Calamine $\rightarrow \text{ZnCO}_3$
- *** (vii) Cerussite $\rightarrow \text{PbCO}_3$

3. Sulphate ore : Epsom salt $\rightarrow \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

4. Silicate ore : Feldspar $\rightarrow \text{KAlSi}_3\text{O}_8$

5. Sulphurised ore : Consist of sulphides of metal like Iron, lead, zinc & mercury.

- (i) Iron pyrites $\rightarrow \text{FeS}_2$
- (ii) Copper glance $\rightarrow \text{Cu}_2\text{S}$
- (iii) Copper pyrite or chalcopyrite $\rightarrow \text{CuFeS}_2$
- (iv) Zinc Blende $\rightarrow \text{ZnS}$
- (v) Galena $\rightarrow \text{PbS}$
- (vi) Cinnabar $\rightarrow \text{HgS}$

6. Halide ore :

- (i) Cryolite $\rightarrow \text{Na}_3\text{AlF}_6$
- (ii) Sylvine $\rightarrow \text{KCl}$
- ** (iii) Carnallite $\rightarrow \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- (iv) Fluorspar $\rightarrow \text{CaF}_2$
- (v) Horn silver $\rightarrow \text{AgCl}$

Note : Mg obtained from both sea water & earth crust.

Solved Examples

Ex-1 Which metals are supposed to occur in the native state in nature ?

Sol. Elements below hydrogen in the electrochemical series like Cu, Ag, Au etc, exist native ores.

Ex-2 Match the ores listed in Column-I with their correct chemical formula listed in Column-II.

	Column I		Column II
(A)	Cassiterite	(p)	FeCO_3
(B)	Siderite	(q)	SnO_2
(C)	Cerussite	(r)	PbSO_4
(D)	Anglesite	(s)	PbCO_3

Sol. SnO_2 is called as cassiterite or tin stone, FeCO_3 is called as siderite, PbCO_3 is called as cerussite and PbSO_4 is called anglesite. So correct match is (A) \rightarrow (q), (B) \rightarrow (p), (C) \rightarrow (s) and (D) \rightarrow (r).





Metallurgy :

The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

The isolation and extraction of metals from their ores involve the following major steps:

- (A) Crushing of the ore. (B) Dressing or concentration of the ore.
(C) Isolation of the crude metal from its ore (D) Purification or refining of the metal.

Chart1:

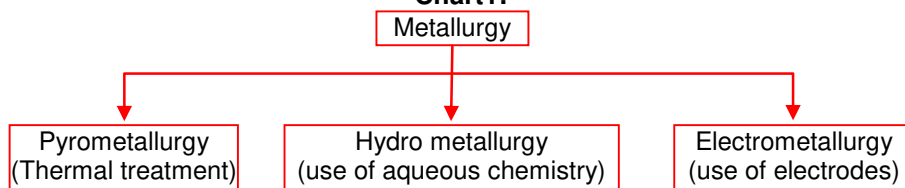
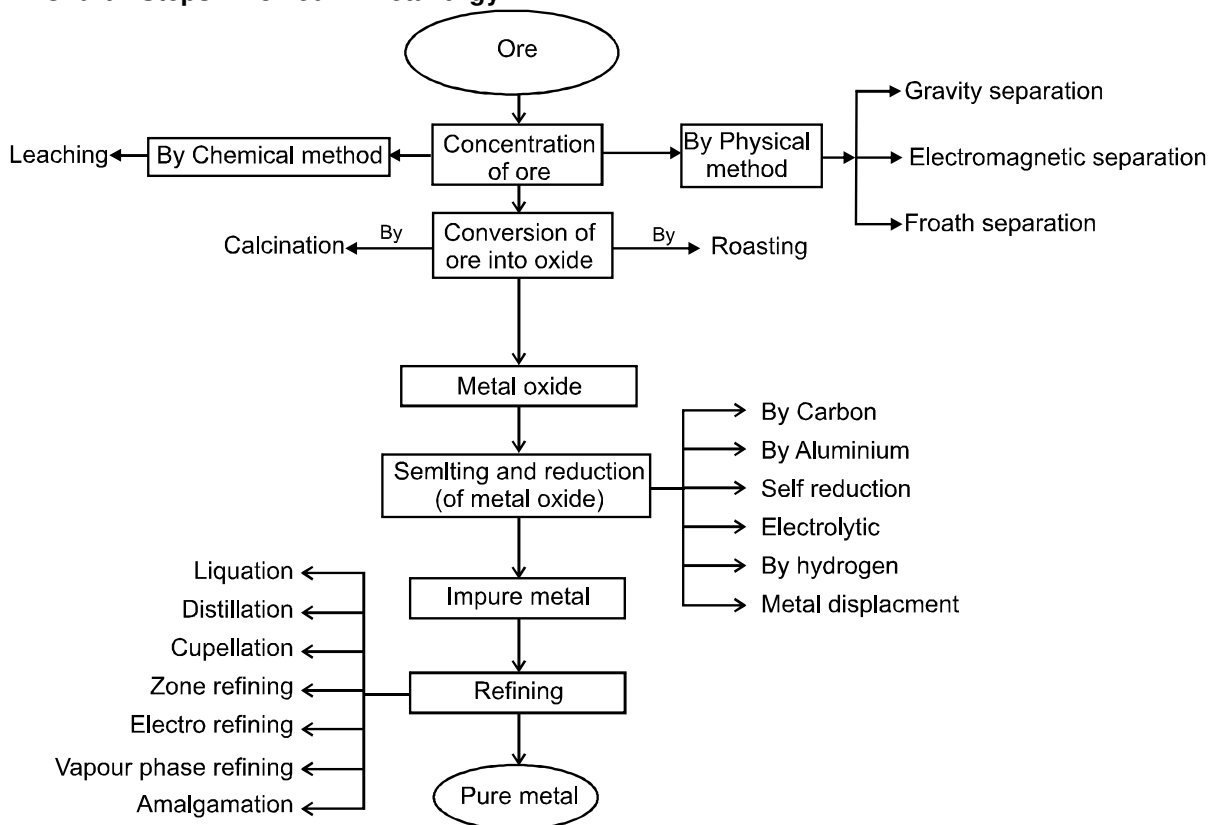


Chart2: Steps involved in metallurgy.



1. Physical Method :

(A) Crushing and Grinding : The ore is first crushed by jaw crushers and ground to a powder (pulverisation of the ore) in equipments like ball mills and stamp mills.

(B) Concentration : The removal of unwanted useless impurities from the ore is called **dressing, concentration or benefaction of ore**.

It involves several steps and selection of these steps depends upon the difference in physical properties of the compound of metal and that of gangue. Some of the important procedures are described below.

(i) Hydraulic washing or Gravity separation or Levigation method : It is based on the difference in the densities of the gangue and ore particles. In this, the powdered ore is agitated with water or washed with an upward stream of running water, the lighter particles of sand, clay etc. are washed away leaving behind heavier ore particles. For this either hydraulic classifier or Wilfley table is used. This method is generally used for the concentration of oxide and native ores.

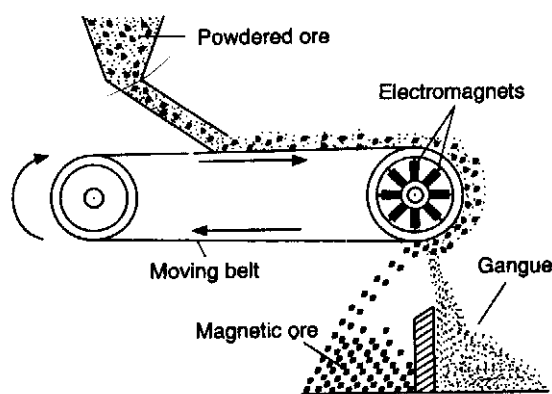
(ii) Electromagnetic separation :

It is based on differences in magnetic properties of the ore components.



It is used when either the ore or the impurities associated with it are magnetic in nature. A magnetic separator consists of a belt (of leather or brass) moving over two rollers, one of which is magnetic. When the powdered ore is dropped on the belt at the other end, magnetic component of the ore is attracted by the magnetic roller and falls nearer to the roller while the non-magnetic impurities fall away from it.

Examples : Chromite ore ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) is separated from non-magnetic silicious impurities and cassiterite ore (SnO_2) is separated from magnetic Wolframite ($\text{FeWO}_4 + \text{MnWO}_4$).



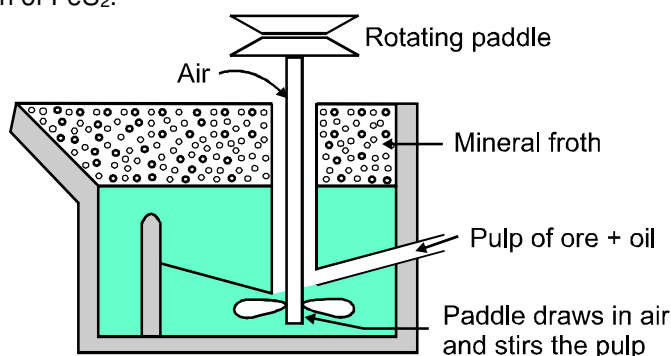
Electromagnetic separation

(iii) Froth floatation process : This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb) ; copper pyrites $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ or CuFeS_2 (ore of copper) ; zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil. In this process one or more chemical frothing agents are added.

(a) Frothers : These form stable froth which rises to the top of the flotation cell. Oils like pine oil, camphor oil etc., are used as frothers. These are added in small quantity. The stabiliser are added to the frothers so that the froth can last for longer period.

(b) Collectors : Potassium or sodium ethyl xanthate is used as a collector. These get attached with the particles of the sulphide ore and thus make them water-repellant. Consequently the ore particles pass on into the froth. Collectors are always added in small quantity.

(c) Activating and depressing agents : When a mineral contains other minerals as impurities. The addition of these agents activates or depresses the flotation property of other minerals present as impurities and thus helps in separating the impurities. For example galena (PbS) usually contains the minerals namely zinc blende (ZnS) and pyrites (FeS_2) as impurities. Flotation is carried out by using potassium ethyl xanthate (used as a collector) along with NaCN and Na_2CO_3 (used as depressing agent). The addition of NaCN and Na_2CO_3 depresses the flotation property of ZnS and FeS_2 grains, so mainly PbS passes into the froth when air is blown in. After PbS has been collected with the froth, the process is repeated by adding CuSO_4 (activator) which activates the flotation property of ZnS grains which are now removed with the froth. The acidification of the remaining material left in the flotation cell leads to the flotation of FeS_2 .



Froth floatation process

Solved Examples

Ex-3 How does NaCN act as a depressant in preventing ZnS from forming the froth?

Sol. NaCN reacts with ZnS and forms a layer of $\text{Na}_2[\text{Zn}(\text{CN})_4]$ complex on the surface of ZnS and thus prevents it from the formation of froth.

Ex-4 What is the role of stabiliser in froth floatation process ?

Sol. Froth can last for a longer period in presence of stabiliser.



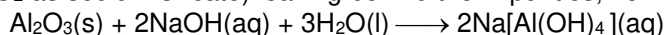


2. Chemical Method :

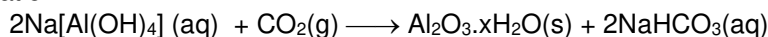
(iv) **Leaching** : Leaching is often used if the ore is soluble in some suitable solvent, e.g, acids, bases and suitable chemical reagents. e.g. Al ore, Ag ore, Au ore, low grade copper ore.

Leaching of alumina from bauxite :

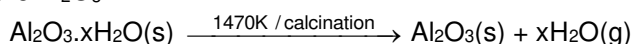
The principal ore of aluminium, bauxite, usually contains SiO_2 , iron oxide and titanium oxide (TiO_2) as impurities. Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at 473-523 K and 35-36 bar pressure. This way, Al_2O_3 is leached out as sodium aluminate (and also SiO_2 as sodium silicate) leaving behind the impurities, iron oxide and titanium oxide.



The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces the precipitation.

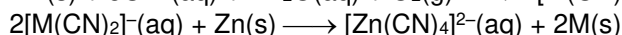
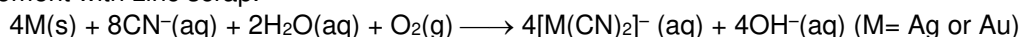


The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3 :



These steps comprises the **Bayer's process**.

Other examples : In the metallurgy of **silver** and that of **gold**, the respective metal/ore is leached with a dilute solution of NaCN or KCN in the presence of air (or O_2) from which the metal is obtained later by displacement with zinc scrap.



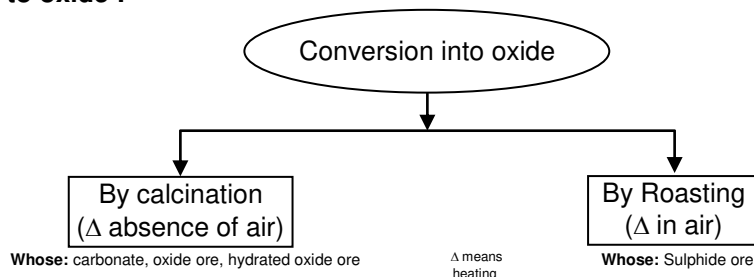
(C) Extraction of crude metal from concentrated ore :

The concentrated ore must be converted into a form which is suitable for reduction. Usually the sulphide ore is converted to oxide before reduction. Oxides are easier to reduce. Thus isolation of metals from concentrated ore involves two major steps as given below.

(i) Conversion to oxide

(ii) Reduction of the oxide to metal.

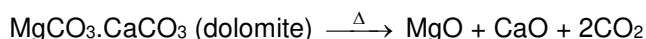
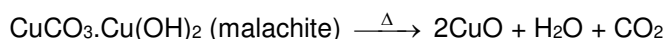
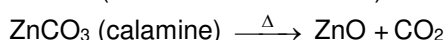
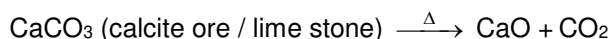
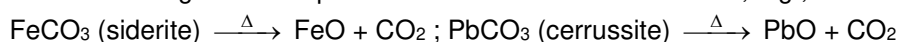
(i) Conversion to oxide :



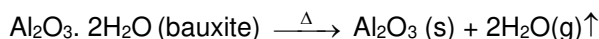
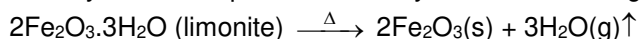
Conversion of ore into oxide is carried out in two ways depending upon the nature of ore.

Calcination. It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of calcination brings about the following changes :

(a) The carbonate ore gets decomposed to form the oxide of the metal, e.g.,



(b) Water of crystallisation present in the hydrated oxide ore gets lost as moisture, e.g.,

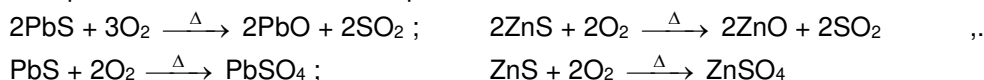


(c) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

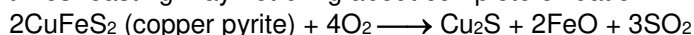


Roasting. It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or O_2 below its melting point. Roasting is an exothermic process once started it does not require additional heating. The process of roasting does the following things :

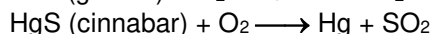
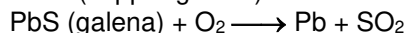
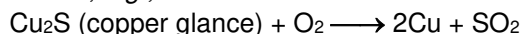
(a) Roasting at moderate temperature. Some portion of the sulphide ores like galena (PbS), Zinc blende (ZnS) is converted into metallic oxide. If the temperature is fairly low (about $500^\circ C$) and the concentration of SO_2 in the gaseous environment is more, sulphate may be produced that are stable, and high temperature is needed to decompose them.



* Some times roasting may not bring about complete oxidation.

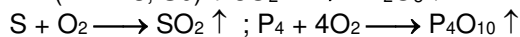
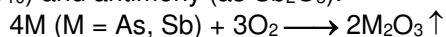


(b) Roasting at high temperature. The sulphide ores of some of the metals like Cu, Pb, Hg, Sb etc., when heated strongly in the free supply of air or O_2 are reduced directly to the metal rather than to the metallic oxides, e.g.,



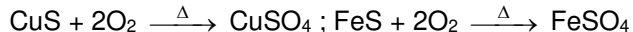
The reduction of the sulphide ore directly into metal by heating it in air or O_2 is called by various names like self-reduction, auto-reduction, air-reduction etc. The SO_2 produced is utilised for manufacturing of H_2SO_4 .

(c) It removes easily oxidisable volatile impurities like arsenic (as As_2O_3) sulphur (as SO_2), phosphorus (as P_4O_{10}) and antimony (as Sb_2O_3).



These oxides are volatile and hence escape as gases through the chimney.

(d) When the concentrated tin stone ore SnO_2 (ore of Sn) is heated strongly in a free supply of air (roasting), the impurities of CuS and FeS present in the ore are converted into $CuSO_4$ and $FeSO_4$ respectively.



Both calcination and roasting are generally carried out in a reverberatory furnace. In case of roasting, the air holes are kept open while they are partially or completely closed during calcination.

Section (B) : Thermodynamic Principles of metallurgy

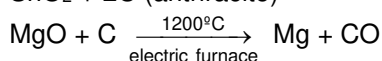
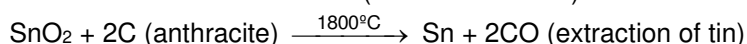
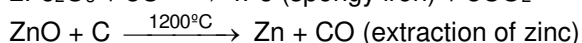
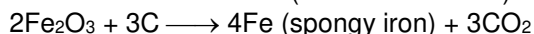
(ii) Reduction of a metal oxide :

The free metal is obtained by reduction of a compound, using either a chemical reducing agent or electrolysis.

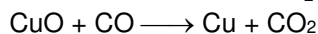
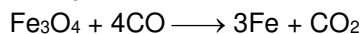
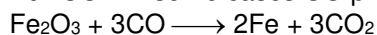
1. Chemical reduction method :

A large number of commercial processes come under this category. Carbon can be used to reduce a number of oxides and other compounds, and because of the low cost and availability of coke this method is widely used. The disadvantages are that a high temperature is needed, which is expensive and necessitates the use of blast furnace.

(A) Reduction with carbon :



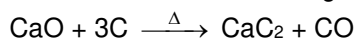
(B) Reduction with CO : In some cases CO produced in the furnace itself is used as a reducing agent.



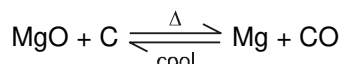


Carbon or carbon monoxide reduction process is usually carried out in blast furnace. There are some disadvantage of using carbon as reducing agents e.g.,

(a) Some metallic oxides like CaO give metallic carbides instead of metals.

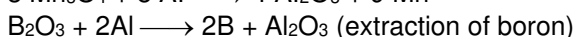
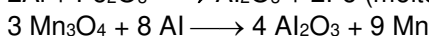
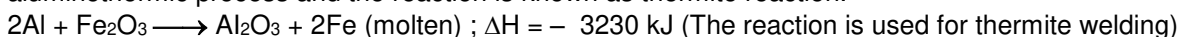


(b) During the cooling of the products, in many cases, reformation of the oxide and carbon may take place.



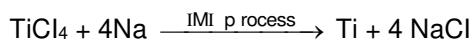
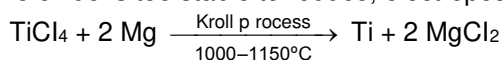
2. Reduction by other metals :

If the temperature needed for carbon to reduce an oxide is too high, for economical or practical purposes, reduction by other metals is done. Also, certain metallic oxides cannot be reduced by carbon because the affinity of oxygen for the metal is greater than its affinity for carbon. Such metallic oxides (Cr and Mn) can be reduced by a highly electropositive metal such as aluminium that liberates a large amount of energy (1675 kJ/mol) on oxidation to Al_2O_3 . The process is known as Goldschmidt or aluminothermic process and the reaction is known as thermite reaction.



As it is a strongly exothermic reaction, it proceeds with explosive violence and only initial heating is needed.

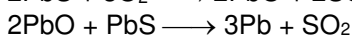
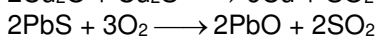
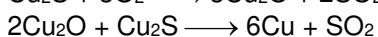
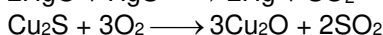
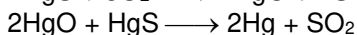
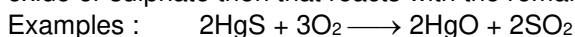
Magnesium reduction method : Magnesium is used in similar way to reduce oxides. In certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce halides.



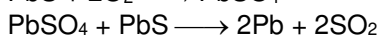
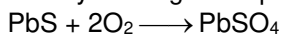
Advantages of using Na and Mg as reducing agents are the higher reducing power of the metals and solubility of their halides in water so that the reduced metals can be washed free from impurities.

3. Self-reduction method :

This method is also called auto-reduction method or air reduction method. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb, Sb, etc. are heated in air, a part of these is changed into oxide or sulphate then that reacts with the remaining part of the sulphide ore to give its metal and SO_2 .



The extraction of Pb by heating its sulphide ore (PbS) in air can also be represented as



4. Electrolytic reduction :

It presents the most powerful method of reduction and gives a very pure product. As it is an expensive method compared to chemical methods, it is used either for very reactive metals such as magnesium or aluminum or for production of samples of high purity. Electrolytic reduction of copper has the additional advantage of allowing the recover of valuable minor contaminants such as silver.

THERMODYNAMICS OF EXTRACTION : ELLINGHAM DIAGRAM OF A METAL

The standard electrode reduction potential of metal provides a very good indicator or the ease or difficulty of extracting the metal from its compounds. However, since most metals of industrial importance are obtained by chemical reduction of their oxide, the free energy changes occurring during these processes are of more fundamental importance. Despite the fact that redox reactions do not always reach equilibrium thermodynamics can at least be used to identify which reactions are feasible.

For a spontaneous reaction the change in free energy ΔG must negative, $\Delta G = \Delta H - T\Delta S$.

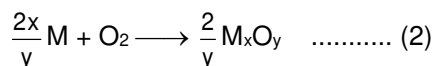
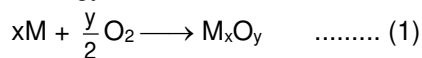
It is sufficient to consider ΔG because it is related to the equilibrium constant through, $\Delta G = - RT \ln K$.



Here a negative value of ΔG corresponds to $K > 1$ and, therefore, a favourable reaction. Reaction rates are also relevant, but at high temperature reactions are often fast and we can normally assume that any thermodynamically permissible process can occur.

The problem of extracting a metal from its ore is essentially concerned with decomposing the oxide of the metal (apart from simple binary compounds such as metal sulfides and chlorides that occur in nature). Most metal ores consist essentially of a metal oxide in association with one or more nonmetal oxides. Ores like carbonates, sulphides etc., are also converted to oxides, prior to reduction.

The free energy of formation ΔG is the standard free energy of the reaction.



ΔG is the free energy of formation per mole of O_2 consumed.

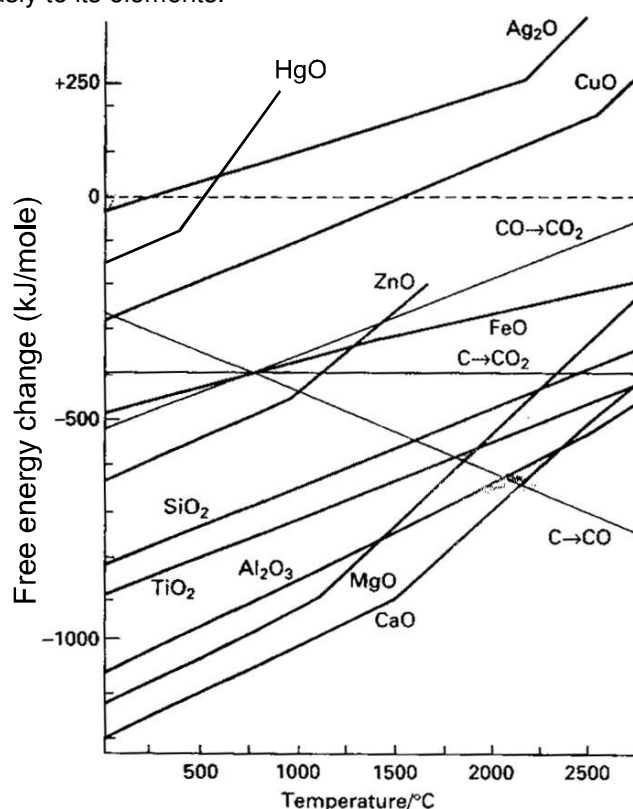
If the standard free energy of formation ΔG has a negative sign at a given temperature, then the oxide can be expected to form spontaneously from the metal plus oxygen. If ΔG has a positive sign, the oxide will be expected to decompose spontaneously to its elements.

The free energy of formation of an oxide can now be determined, provided we know the entropy of formation.

$$\Delta G = \Delta H - T\Delta S \quad \dots\dots\dots (3)$$

In reaction (2) oxygen is used up in the course of reaction. Gases have a more random structure (less ordered) than liquid or solids. In this reaction the entropy or randomness decreases, and hence ΔS is negative (provided that neither the metal nor its oxide M_xO_y are vaporized). Thus, if the temperature is raised then $T\Delta S$ becomes more negative. Since $T\Delta S$ is subtracted in equation (3), ΔG then becomes less negative. Thus, the change in free energy decreases with increase in temperature.

The free energy change that occurs when 1 mol of common reactant (in this case O_2) is used may be plotted graphically against temperature for a number of reaction of metals to their oxides. This graph is shown in following figure and is called an Ellingham diagram for oxides. Similar diagrams can be produced for 1 mol of S, giving Ellingham diagram for sulphides and similarly for halides using 1 mol of halogen.



This figure shows a number of oxide plots with slopes defined by $\Delta G / T = -\Delta S$. It is noted that the entropy change in reaction (2) is roughly the same for all metal oxides provided that the boiling point of neither the metal nor oxide is exceeded. Thus, below the boiling point of metal the slope of all the graphs are roughly the same, since $T\Delta S$ factor is same whatever be the metal. When the temperature is raised a point will be reached where the graph crossed the $\Delta G = 0$ line. Below this temperature the free energy of formation of oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of the oxide is positive, and the oxide becomes unstable and should decompose into metal and oxygen. This explains why HgO , for instance, decomposes spontaneously into its elements when heated. Theoretically, all oxides can be decomposed to give metal and oxygen if a sufficiently high temperature can be attained. In practice, that are easily attainable and these metals can be extracted by thermal decomposition of their oxides. The diagram predicts that MgO and ZnO ought to decompose if heated strongly enough, but it does not hold out much hope for obtaining say pure Mg by straight forward heating of the oxide to a high temperature where the boiling point of the metal is exceeded. However the slope increases since the reaction is now involving a larger entropy change as the randomness increases in reactants. For example, $2Mg(g) + O_2(g) \longrightarrow 2MgO(s)$

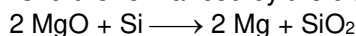


Here, three moles of gas phases are converted into solid phase in the reaction. This takes place above 1120°C , which is the boiling point of Mg.

Similarly Hg–HgO line changes slope at 365°C . Several of the plots show abrupt changes in the slopes. These breaks occur at temperature at which the metal undergoes a phase transition. A smaller effect is seen at the melting point. If, however the oxide undergoes a phase change, there will be an increase in the entropy of the oxide, and at such a point the curve becomes less steep. For example in the case of Pb, the oxide (PbO) boils while lead is liquid. In these instances the entropy change becomes positive for the reaction and hence the slope $\Delta G/T$ changes sign, the situation reverting to normal once the boiling point of Pb is reached.

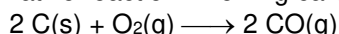
In principle, when the plot of one metal lies below that of another, the first metal is capable of reducing the oxide of the second. A vertical line drawn on the Ellingham plot of the metal oxides at any T gives the sequence of the stabilities of metal oxides. A metal forming a more stable oxide (higher $-\Delta G$) will be potential reducing agent for a less stable oxide. If the two lines intersect, the free energy change for the reduction will be zero at that temperature and equilibrium results, but a change of temperature will make the reaction proceed provided no kinetic barriers (activation energy) exist. Thus, Mg metal will reduce CuO and FeO but not CaO. Also, it is seen that at room temperature (27°C) the order of reducing ability approximates that of standard electrode potential.

Although the SiO_2 line is above the MgO line, Si can successfully reduce MgO to free metal. Up to 1100°C , the normal boiling point of Mg, the ΔG plot for formation of SiO_2 and MgO are parallel. However, above 1100°C the plot for MgO changes slope owing to the increased entropy effect, and above 1700°C the reaction between Si and MgO proceeds with decrease in free energy. In practice, the reaction is further enhanced by the distillation of Mg metal from the reaction mixture.



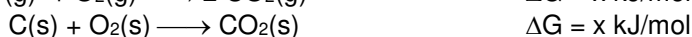
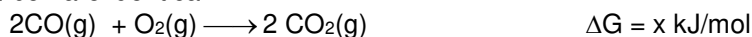
Carbon or carbon monoxide as reducing agent.

In figure the plot corresponding to the change $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ is shown by a horizontal line. For this reaction ΔS is relatively small because in this case one mole of gaseous product is formed while one mole of gaseous reactant is used up. ΔG for this reaction is almost independent of temperature. The plot for CO_2 is relatively high in the figure, and at low temperature C will reduce only a few of metal oxides shown. However, the slopes of the plots for several of the metals are such that they cross the CO_2 plot; hence theoretically these metals can be reduced by C at elevated temperature. An alternative reaction involving carbon and oxygen is the formation of CO.



Since two of gaseous product is formed from one mole of gaseous reactant, this process is accompanied by an increase in entropy. Hence, the slope of the corresponding line is negative as shown by the downward sloping line in the figure. If the temperature is high enough, C should reduce all the metal oxides, being converted into CO. The plot for the reaction of CO with oxygen is also shown.

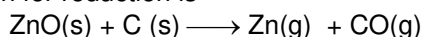
There are three curves for carbon, corresponding to complete oxidation of C to CO_2 , partial oxidation to carbon monoxide, and oxidation of CO to carbon dioxide. The three curves pass through a common point at 710°C . Thus, the free energies of formation of CO_2 from carbon monoxide and carbon dioxide from carbon are identical.

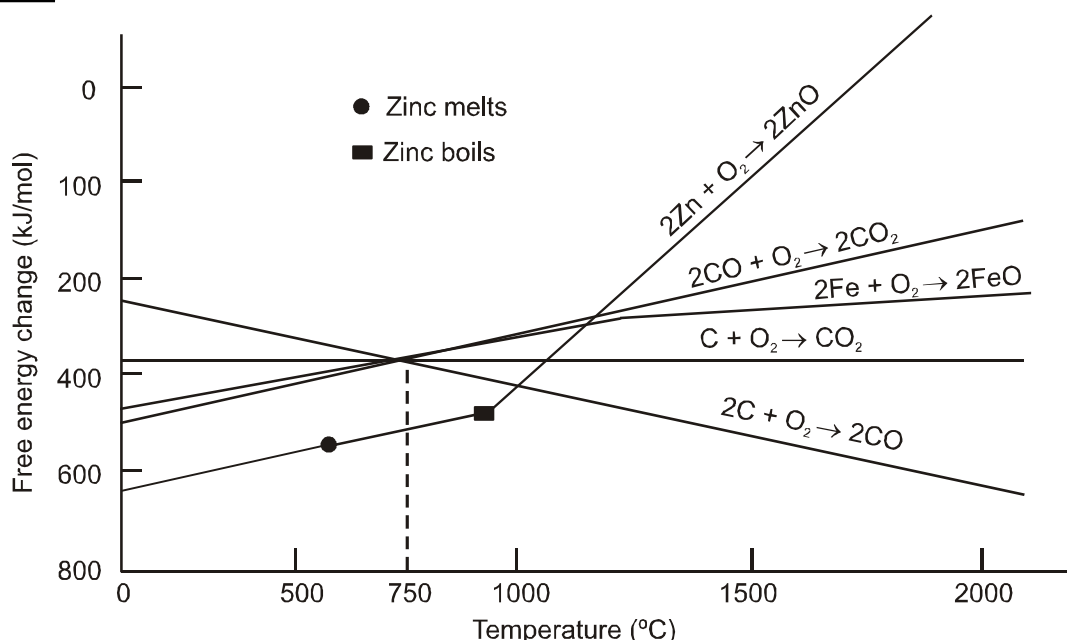


Subtracting one equation from the other and rearranging, the following is obtained :



That is, an equilibrium is set. It is clear below a temperature of 710°C , CO is a more effective reducing agent than carbon, but above this temperature the reverse is true. All three oxidation curves for the carbon system lie above that for oxidation of zinc, until a temperature of approximately 1000°C is reached. At this point, carbon is thermodynamically capable of reducing ZnO to Zn. Since this temperature is greater than the boiling point of Zn (907°C), it will be formed as a vapour. The overall equation for reduction is





It is interesting to note that the value of carbon as reducing agent is due to marked increase in disorder that takes place when carbon (an ordered solid) reacts with one mole of oxygen to give two moles of CO. The net effect is an extra mole of gas and hence an increase in disorder (an increase in entropy). It is a fact that in the region of 2000°C, carbon is thermodynamically capable of reducing most metal oxides to metal.

Thus, for most metal oxides, a reducing agent is required and we should consider the overall reaction obtained by subtracting the metal oxidation from one of carbon oxidation as

$$\Delta G_{\text{Overall}} = \Delta G_{(\text{C})} - \Delta G_{(\text{M})}$$

Metals as reducing agents :

Metal oxide reduction is thermodynamically favourable for temperatures at which the line for the metal oxide is above any one of the lines for carbon oxidation, for the ΔG for metal oxide reduction by carbon is negative.

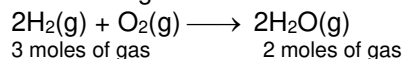
Note : The Gibb's energies of formation of most sulphides are greater than that for CS_2 . In fact, CS_2 is an endothermic compound. There, the $\Delta_f G^\circ$ of M_xS is not compensated. So reduction of M_xS is difficult. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.

Similar principles apply to other types of reduction. For instances if the plot of $\Delta G_{(\text{M})}$ lies above $\Delta G_{(\text{M}')} from M' is now taking the place of C. When $\Delta G = \Delta G_{(\text{M}')} - \Delta G_{(\text{M})}$ is negative, the reaction, $\text{MO} + \text{M}' \longrightarrow \text{M} + \text{M}'\text{O}$ is feasible.$

Hydrogen as a reducing agent :

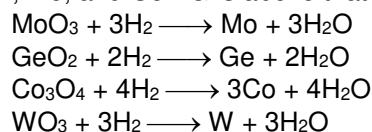
Hydrogen is not very effective reducing agent for obtaining metals from their oxides.

The reason is that ΔS is negative for the reaction :



as the products are less disordered. The plot of ΔG against T therefore rises with temperature, meaning that not many metal oxide plots are intersected. H_2 will therefore reduces oxides such as Cu(I) oxide and Cu(II) oxide, but not the oxides of Al , Mg , and Ca . Oxides of iron are reduced only with difficulty. In the case of magnetic iron oxide Fe_3O_4 an equilibrium composition is readily established.

In the case of W , Mo , and Co ΔG is above that of H_2O so H_2 can be reduce these oxides.



This method is not widely used because many metals react with H_2 at elevated temperature forming hydride. There is also a risk of explosion for H_2 and oxygen in the air.



Solved Examples

- Ex-5** The reaction $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$ ($\Delta G^\circ = -421 \text{ kJ}$) is thermodynamically feasible as is apparent from the Gibb's energy value. Why does it not take place at room temperature ?
- Sol.** Certain amount of activation energy is essential even for such reactions which are thermodynamically feasible, therefore heating is required.
- Ex-6** Is it true that under certain conditions, Mg can reduce Al_2O_3 and Al can reduce MgO? What are those conditions ?
- Sol.** Below 1350°C Mg can reduce Al_2O_3 and above 1350°C , Al can reduce MgO as evident from the Ellingham diagram.

Section (C) : Metallurgy of some useful metals

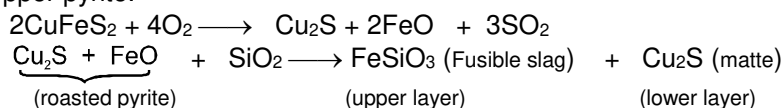
Smelting :

Slag formation : In many extraction processes, an oxide is added deliberately to combine with other impurities and form a stable molten phase immiscible with molten metal called a slag. The process is termed smelting.

The principle of slag formation is essentially the following:

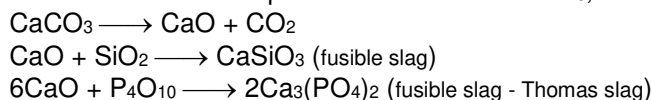
Nonmetal oxide (acidic oxide) + Metal oxide (basic oxide) \longrightarrow Fusible (easily melted) slag

Removal of unwanted basic and acidic oxides: For example, FeO is the impurity in extraction of Cu from copper pyrite.



Matte also contains a very small amount of iron(II) sulphide.

To remove unwanted acidic impurities like sand and P_4O_{10} , smelting is done in the presence of limestone.



Properties of a slag :

- Slag is a fusible mass.
- It has low melting point.
- It is lighter than and immiscible with the molten metal. It is due to these impurities that the slag floats as a separate layer on the molten metal and can thus be easily separated from the metal. The layer of the slag on the molten metal prevents the metal from being oxidised.

Type of flux : Fluxes are of two types viz., acidic flux and basic flux.

(a) Acidic flux : It is an acidic oxide (oxide of a non-metal) like SiO_2 , P_2O_5 , B_2O_3 (from borax). It is used to remove the basic impurity like CaO, FeO, MgO etc. The acidic flux combines with the basic impurity and forms a slag.

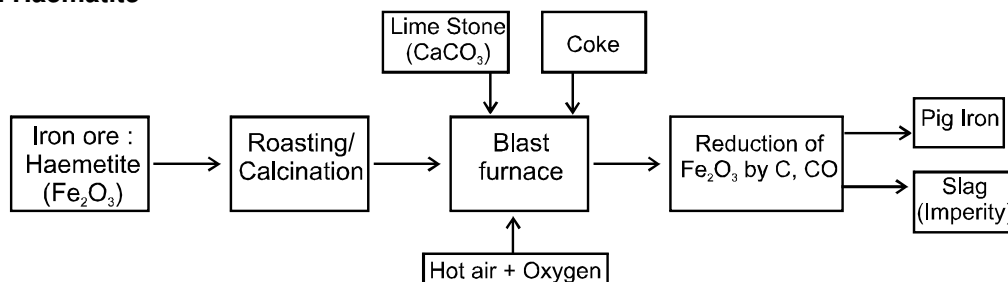
(b) Basic flux : It is a basic oxide (i.e., oxide of a metal) like CaO (obtained from lime stone, CaCO_3), MgO (from magnesite, MgCO_3), haematite (Fe_2O_3) etc. It is used to remove the acidic impurity like SiO_2 , P_2O_5 etc. The basic flux combines with the acidic impurity and forms a slag.

Thus, slag can be defined as a fusible mass, which is obtained when a flux reacts with an infusible acidic or basic impurity present in the oxide ore.

Metallurgy of Some Important Metals

1. Extraction of iron (Fe)

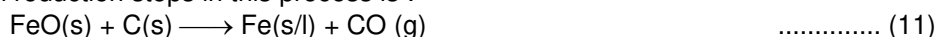
Ore: Haemetite



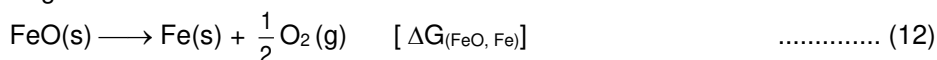


Oxide ores of iron, after concentration through calcination/roasting in reverberatory furnace (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with lime stone and coke and fed into a Blast furnace from its top with the help of a cup and cone arrangement. Here, the oxide is reduced to the metal.

Thermodynamics helps us to understand how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process is :



It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO :

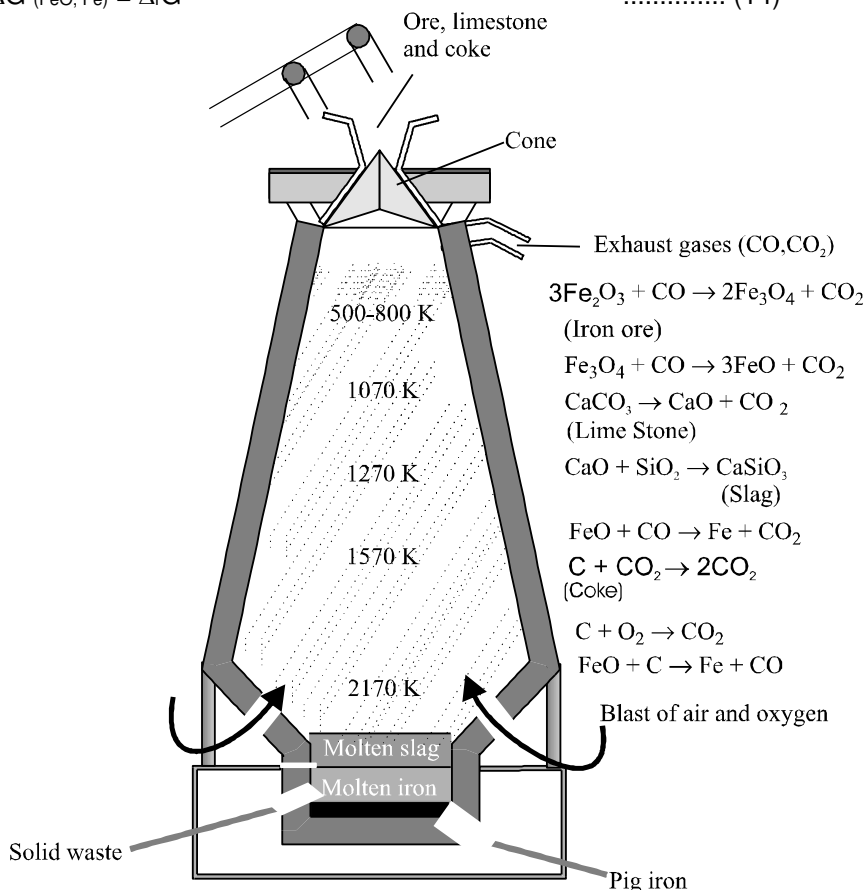


When both the reactions take place to yield the equation (10), the net Gibbs energy change becomes:



Naturally, the resultant reaction will take place when the right hand side in equation (14) is negative. In ΔG° vs T plot representing reaction (12), the plot goes upward and that representing the change C, CO (C, CO) goes downward.

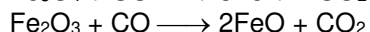
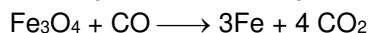
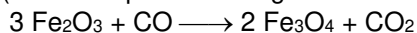
At temperatures above 1073K (approx.), the C, CO line comes below the Fe, FeO line [$\Delta G_{(\text{C}, \text{CO})} < \Delta G_{(\text{Fe}, \text{FeO})}$]. So in this range, coke will be reducing the FeO and will itself be oxidised to CO. In a similar way the reduction of Fe_3O_4 and Fe_2O_3 at relatively lower temperatures by CO can be explained on the basis of lower lying points of intersection of their curves with the CO, CO_2 curve in the given figure.



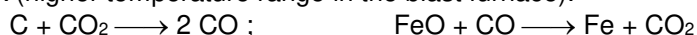
In the Blast furnace, reduction of iron oxides takes place in different temperature ranges. Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto about 2200K in the lower portion itself. The burning of coke therefore supplies most of the heat required in the process. The CO and heat moves to upper part of the furnace. In upper part, the temperature is lower and the iron oxides (Fe_2O_3 and Fe_3O_4) coming from the top are reduced in steps to FeO.

Reactions involved : The reactions proceed in several stages at different temperatures. Since the air passes through in a few seconds, the individual reactions does not reach equilibrium.

At 500 – 800 K (lower temperature range in the blast furnace)



At 900 – 1500 K (higher temperature range in the blast furnace):



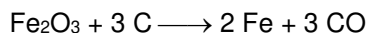


Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.



The iron obtained from blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn). This is known as pig iron and cast into variety of shapes. Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Further Reductions : Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon to carbon monoxide:



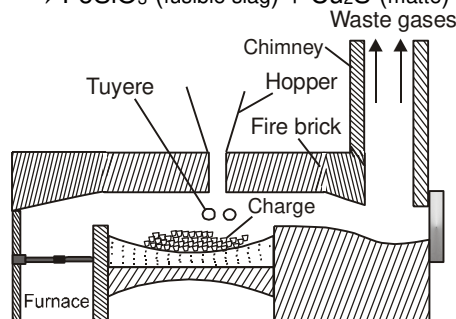
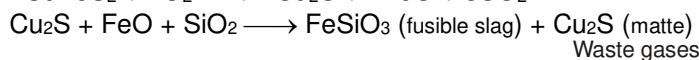
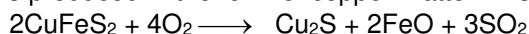
Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag. The metal is removed and freed from the slag by passing through rollers.

2. Extraction of copper :

(a) From cuprous oxide [Copper(I) oxide] : In the graph of $\Delta_r G^\circ$ vs T for formation of oxides the Cu_2O line is almost at the top. So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C, CO_2 are at much lower positions in the graph particularly after 500-600K). However most of the ores are sulphide and some may also contain iron. The sulphide ores are roasted/smelted to give oxides : $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$

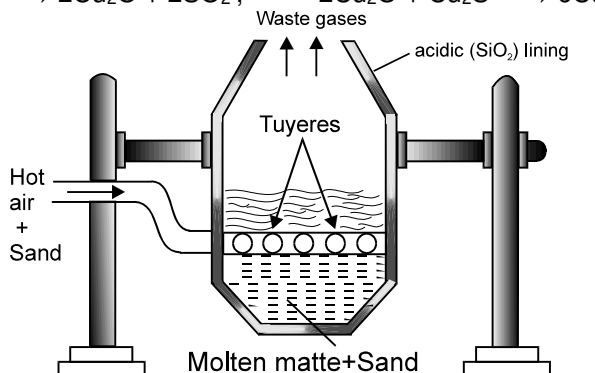
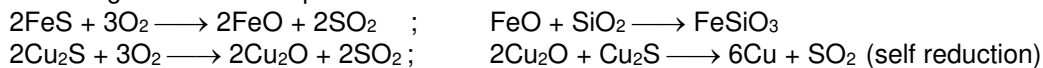
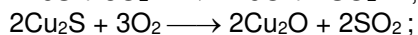
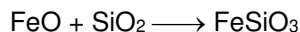
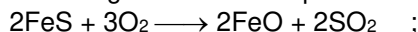
The oxide can then be easily reduced to metallic copper using coke: $\text{Cu}_2\text{O} + \text{C} \longrightarrow 2\text{Cu} + \text{CO}$

(b) From copper glance / copper pyrite (self reduction) : In actual process the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags off' as iron silicate and copper is produced in the form of copper matte. This contains mostly Cu_2S and some FeS .



Reverberatory furnace

Copper matte is then charged into silica lined converter (Bessemer converter). Some silica is also added and hot air blast is blown to convert the remaining FeS_2 , FeO and $\text{Cu}_2\text{S}/\text{Cu}_2\text{O}$ to the metallic copper. Following reactions take place:

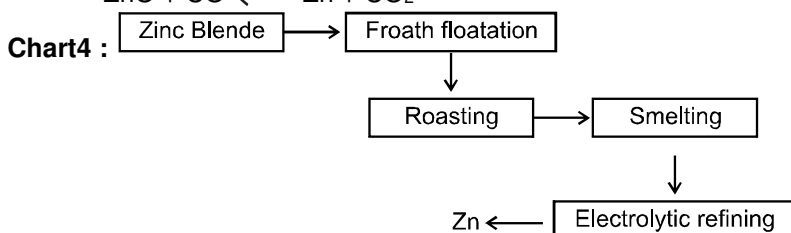


Bessemer converter

The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called blister copper.



gaseous. If the gaseous mixture of Zn and CO_2 was simply removed from the furnace and cooled, then reoxidation of Zn would occur. Thus the zinc powder obtained would contain large amounts of ZnO.



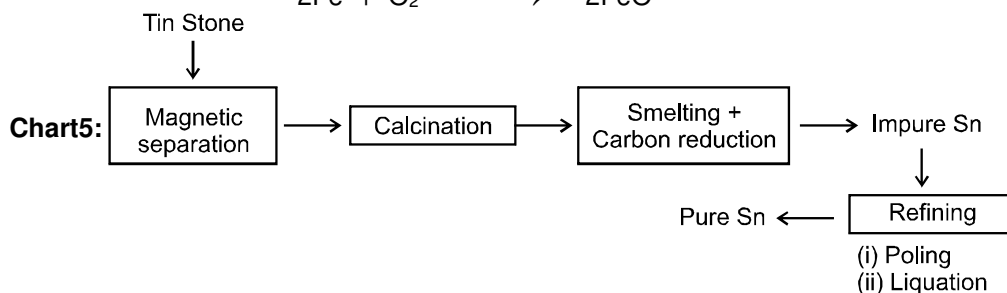
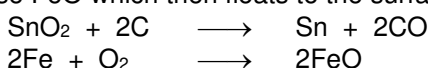
5. **Extraction of tin from cassiterite (SnO_2) :** It involves following steps.

(A) **Purification :**

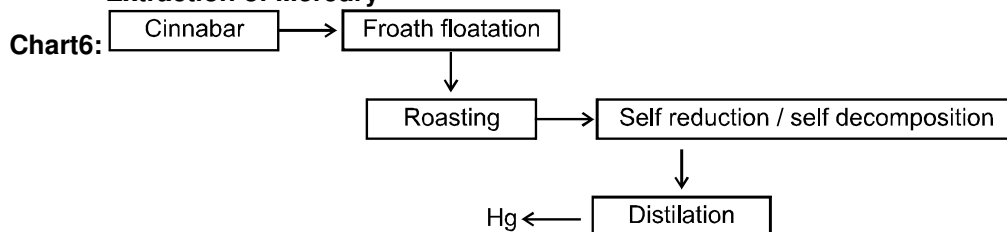
- Crushing and concentration :** The ore is crushed and washed with a stream of running water to remove the lighter earthy and silicious impurities.
- Electromagnetic separation :** The concentrated ore is subjected to the electromagnetic separation to remove magnetic impurity of Wolframite.
- Roasting:** The ore is then heated in presence of air, when volatile impurities (S as SO_2 , As as As_2O_3 and Sb as Sb_2O_3) are removed. The impurities of pyrites of copper and iron are converted into their respective oxides and sulphates

$$\text{CuS} + 2\text{O}_2 \rightarrow \text{CuSO}_4 ; \text{FeS} + 2\text{O}_2 \rightarrow \text{FeSO}_4$$
- Leaching :** Sulphates of copper and iron are dissolved in water.
- Washing :** The ore is washed with running water to remove the finer iron oxide produced in roasting. The ore thus obtained contains 60–70% SnO_2 and is called as black tin.

(B) **Smelting :** SnO_2 is reduced to metal using carbon at $1200\text{--}1300^\circ\text{C}$ in an electric furnace. The product often contains traces of Fe, which is removed by blowing air through the molten mixture to oxidise FeO which then floats to the surface.



Extraction of Mercury



Section (D) : Electrochemical principles of metallurgy

Medium :

- In aqueous solution :** Electrolysis can be carried out conveniently and cheaply in aqueous solution that the products do not react with water. Copper and zinc are obtained by electrolysis of aqueous solution of their sulphates.
- In other solvents :** Electrolysis can be carried out in solvents other than water. Fluorine reacts violently with water and it is produced by electrolysis of KHF_2 dissolved in anhydrous HF.
- In fused melts :** Elements that react with water are often extracted from fused melts of their ionic salts. Aluminum is obtained by electrolysis of a fused mixture of Al_2O_3 and cryolite $\text{Na}_3[\text{AlF}_6]$. Both sodium and chlorine are obtained from the electrolysis of fused NaCl. In this case upto two-third by weight of CaCl_2 is added as an impurity to lower the melting point from 803 to 505°C .



Electrochemical principles of metallurgy : Electrolytic reduction can be regarded as a technique for driving a reduction by coupling it through electrodes and external circuit to a reactive or a physical process with a more negative ΔG . The free energy available from the external source can be assessed from the potential it produces across the electrodes using the thermodynamic relation :

$$\Delta G = -nFE \quad \dots\dots\dots(i)$$

where n is the number of electrons transferred, F is Faraday's constant ($F = 96.5 \text{ kJ/mol}$) and E° is electrode potential of the redox coupled formed in the system.

Hence, the total Gibb's energy of the coupled internal and external process is

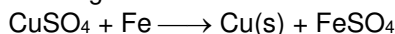
$$\Delta G + \Delta G (\text{external}) = \Delta G - nFE_{\text{ext}}$$

If the potential difference of the external source exceeds, $E_{\text{ext}} = -\frac{\Delta G}{nF}$

The reduction is thermodynamically feasible; thus, the overall process occurs with a decrease in free energy. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two E° values corresponds to a positive E° and consequently negative ΔG° in equation (i), then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g., $\text{Cu}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \longrightarrow \text{Cu}(\text{s}) + \text{Fe}^{2+}(\text{aq})$

In simple electrolysis, the M^{n+} ions are discharged at negative electrodes (cathodes) and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added for making the molten mass more conducting.

Hydrometallurgy : The processing of ores and minerals as well as metals and their compounds at relatively low, often ambient temperatures employing aqueous solution is known as hydrometallurgy. Occasionally, organic reagents are also used. This method of extraction is generally used for low grade ores. Copper is extracted by hydrometallurgy from low grade ore it is leached out using acid and bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2 .

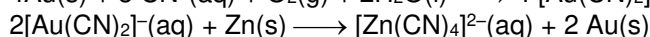
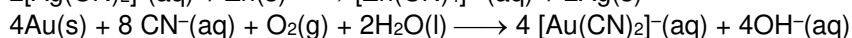
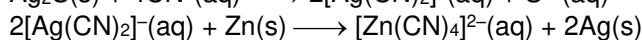
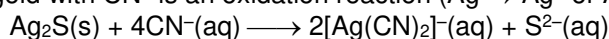


A hydrometallurgical process for the extraction of metals from ores, concentrates, or secondary materials essentially contains three basic steps-dissolution of the valuable metal in the aqueous solution (leaching) purification of leach solution and subsequent recovery of metal from the purified solutions either by electrolysis or by adding some electropositive metal to it.

Some of the metals obtained by hydrometallurgy are as follows :

(A) Extraction of Ag and Au : Metals like Au and Ag can be precipitated for their salt solution by electropositive metals for example, Zn.

Metallic Ag is dissolved from its ore in dilute NaCN solution, and the solute so obtained is treated with scrap Zn when Ag is precipitated. Air is blown into the solution oxidize Na_2S . Leaching the metals like silver, gold with CN^- is an oxidation reaction ($\text{Ag} \rightarrow \text{Ag}^+$ or $\text{Au} \rightarrow \text{Au}^+$)



Here Zn acts as reducing agent.

(B) Extraction of Aluminium : It involves the following processes

(a) Purification of bauxite :

(i) Bayer's Method	(ii) Hall's Method	(iii) Serpeck's Method
(used for red bauxite containing Fe_2O_3 and silicates as impurities)	(used for red bauxite containing Fe_2O_3 and silicates as impurities)	(used for white bauxite containing silica as impurities)
$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \xrightarrow[8 \text{ atm}]{190^\circ\text{C}}$	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \xrightarrow{\text{Fuse}}$	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 3\text{C} + \text{N}_2 \xrightarrow[1800^\circ\text{C}]{\text{Electric furnace}}$
$2\text{NaAlO}_2(\text{soluble}) + 3\text{H}_2\text{O}$	$2\text{NaAlO}_2(\text{soluble}) + \text{CO}_2 + 2\text{H}_2\text{O}$	$2\text{AlN} + 3\text{CO} + 2\text{H}_2\text{O}$
Fe_2O_3 (insoluble) separated as red mud by filtration solution is diluted with water and seeded with freshly prepared $\text{Al}(\text{OH})_3$. It induces the precipitation of $\text{Al}(\text{OH})_3$. $\text{Al}(\text{OH})_3$ is filtered leaving behind silicates in solution.	$2\text{NaAlO}_2 + 3\text{H}_2\text{O} + \text{CO}_2 \xrightarrow{60^\circ\text{C}}$	$2\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3\downarrow + \text{NH}_3$
$\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{NaOH} + \text{Al}(\text{OH})_3\downarrow$	$2\text{Al}(\text{OH})_3\downarrow + \text{Na}_2\text{CO}_3$	$\text{SiO}_2 + 2\text{CO} \rightarrow 2\text{CO}_2 + \text{Si}$
$2\text{Al}(\text{OH})_3 \xrightarrow{1473 \text{ K } \Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$	$2\text{Al}(\text{OH})_3 \xrightarrow{1473 \text{ K } \Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$	Silicone volatilises at this temp.
		$2\text{Al}(\text{OH})_3 \xrightarrow{1473 \text{ K } \Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$

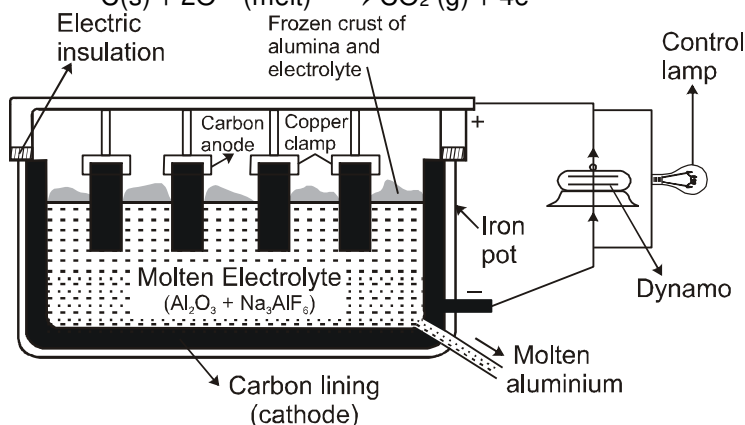
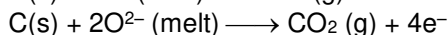
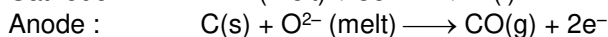
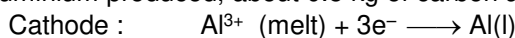


**(b) Electrolytic reduction (Hall-Heroult process) :**

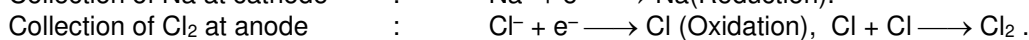
The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar) which lowers the melting point of the mixture and brings conductivity. The fused matrix is electrolysed. Steel cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal. The overall reaction may be taken as :



The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2 . This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away. The electrolytic reactions are :



Extraction of Na: The fused mixture of NaCl and CaCl_2 is taken in Down's cell which consists of circular iron cathode and carbon anode. On passing the electric current the following reactions take place :



Na can also be obtained by electrolysis of molten NaOH in Castner's cell.

Solved Examples

Ex-9 Common impurities present in Bauxite are :

- (A) CuO (B) ZnO (C) Fe_2O_3 (D) SiO_2

Sol. (C) Red Bauxite contains Fe_2O_3 as impurity. (D) white Bauxite contains SiO_2 as impurity. Therefore, (C) and (D) are correct options.

Ex-10 Which metals are generally extracted by the electrolytic reduction and why ?

Sol. Sodium, aluminium, magnesium etc. are extracted by the electrolytic reduction of their fused salts because being more reactive and electropositive elements they themselves acts as strong reducing agents. Hence they can not be extracted by any of the chemical methods.

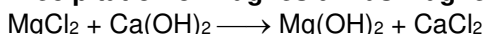
6. Extraction of Magnesium :

(i) **From Carnallite :** The ore is dehydrated in a current of hydrogen chloride and the mixture of fused chlorides is electrolysed.

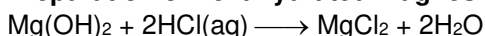
(ii) **From Sea water (Dow's process) :**

Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

(a) **Precipitation of magnesium as magnesium hydroxide by slaked lime :**

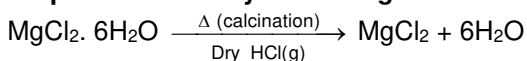


(b) **Preparation of hexahydrated magnesium chloride :**

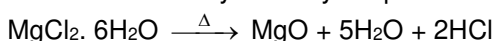


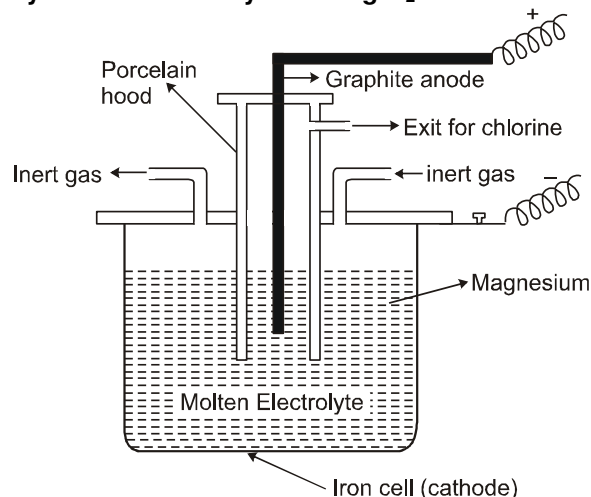
The solution on concentration and crystallisation gives the crystals of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

(c) **Preparation of anhydrous magnesium chloride :**

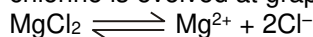


It is not made anhydrous by simple heating because it gets hydrolysed



(d) **Electrolysis of fused anhydrous MgCl_2 :**

Magnesium chloride obtained by any of the above methods is fused and mixed with sodium chloride and calcium chloride in the temperature range of 973–1023 K. The molten mixture is electrolysed. Magnesium is liberated at the cathode (iron pot) and chlorine is evolved at graphite anode.



At cathode : $\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg (99\% pure)}$;

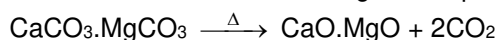
At anode : $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$



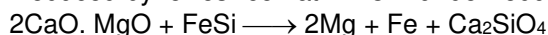
A stream of coal gas is passed through the pot to prevent oxidation of magnesium metal. The magnesium obtained in liquid state is purified by distillation under reduced pressure. (1 mm of Hg at 873 K).

(iii) **From dolomite :**

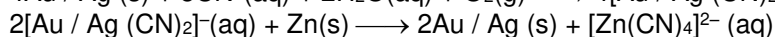
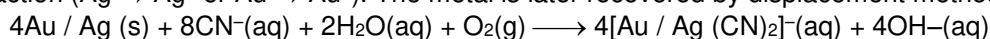
The concentrated ore is calcined at higher temperature



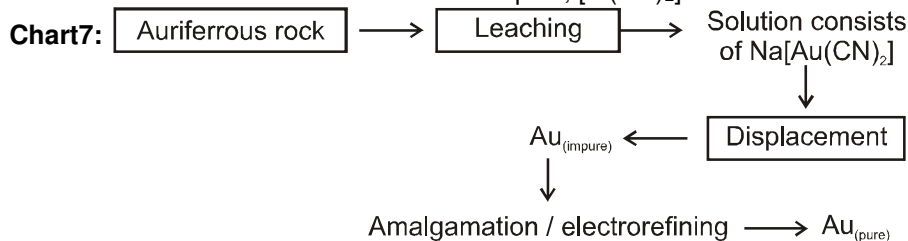
It is then reduced by ferrosilicon at 1273 K under reduced pressure.

7. **Extraction of gold and silver (MacArthur-Forrest cyanide process) :**

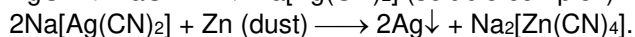
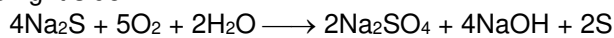
(a) From native ores : Extraction of gold and silver involves leaching the metal with CN^- . This is also an oxidation reaction ($\text{Ag} \rightarrow \text{Ag}^+$ or $\text{Au} \rightarrow \text{Au}^+$). The metal is later recovered by displacement method.

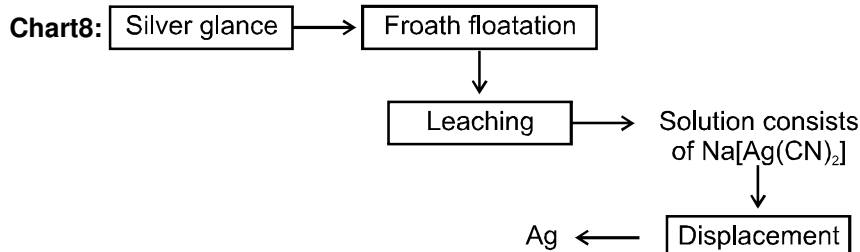


Note : The leaching is carried out in presence of air or oxygen to oxidise metal, M (Ag / Au) to M^+ which then react with CN^- to form soluble complex, $[\text{M}(\text{CN})_2]^-$.

**(b) From argentite ore :**

Ag_2S and AgCN are in equilibrium so Na_2S is oxidised by air in to Na_2SO_4 . Hence equilibrium shifts towards right side.





Section (E) : Purification or Refining of Impure Metals

(D) Purification or Refining of metals :

Metals obtained by reduction processes still contain some objectionable impurities and have to be refined. Refining techniques vary widely from metal to metal and also depend on the use to which a metal has to be put. Sometimes during refining some substances may have to be added to impart some desirable characteristic to the metal. In some cases a metal is refined to recover some valuable by-products, for example, Ag, Au, Pt etc., may be present as impurities. Numerous techniques are available, including the following :

Physical methods : These methods include the following processes :

(I) Liquation process : This process is used for the purification of the metal, which itself is readily fusible, but the impurities present in it are not, i.e., the impurities are infusible. In other words, we can say that the melting point of the metal to be purified should be lower than that of each of the impurities associated with the metal. This process is used for the purification of Sn and Zn, and for removing Pb from Zn-Ag alloy, which is obtained at the end of Parke's process and contains Pb as impurity.

Examples :

Purification of impure tin metal : The impure tin metal contains Cu, Fe, W etc. as impurities. This metal is placed on the slopping heat of a reverberatory furnace and gently heated. When the temperature of the furnace reaches the melting point of tin metal, this metal, on account of its lower melting point melts earlier than the impurities and hence flows down the inclined hearth and the solid infusible (non-fusible) impurities (called dross) are left behind on the hearth. The pure tin metal is collected in a cast iron vessel in the molten state. The metal obtained in this manner is called **pig tin**.

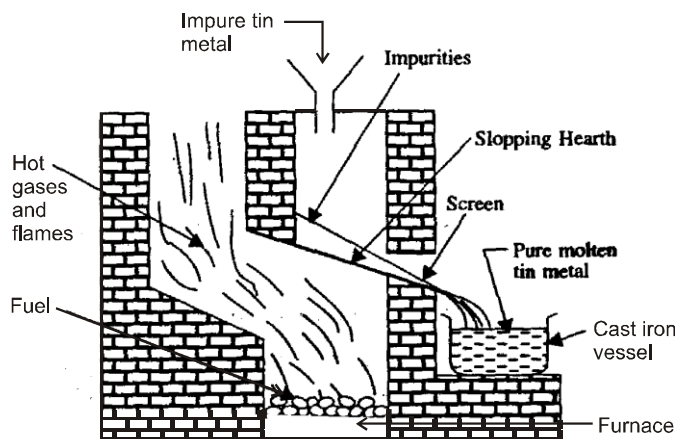


Fig. Purification of tin metal by liquation process.

Purification of crude zinc : The crude zinc or the spelter is melted on the slopping hearth of a reverberatory furnace. Molten zinc flows down while the non-fusible impurities are left on the hearth.

(II) Fractional distillation process: This process is used to purify those metals which themselves are volatile and the impurities in them are nonvolatile and vice-versa. Zn, Cd and Hg are purified by this process.

(III) Zone refining method (Fractional crystallisation method) :

This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.

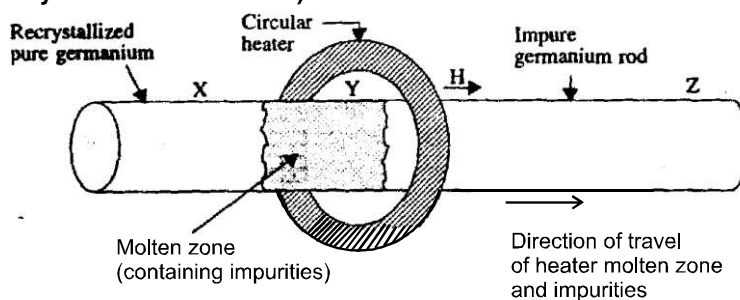


Fig. Zone refining of germanium metal



Germanium metal, which is used in semiconductor devices, is refined (purified) by the zone refining method. The impure germanium metal to be refined is taken in the form of a rod. A circular heater H is fitted around this rod and this heater is slowly moved along the length of the rod. When the heater is at the extreme left end of the impure germanium rod, it melts a narrow zone (narrow region) of the germanium rod at that place. Now, when the heater moves on a little to the right side, then the molten metal at the previous position cools down and crystallizes to give pure metal at region X of the rod. The impurities, which were initially present in region X of germanium rod, now pass on to the region Y in the adjacent molten zone. Now, as the heater is shifted more and more to the right side on the germanium rod, the impurities also keep on shifting to the right side in to the newer and newer molten zones. Ultimately, the impurities reach the extreme right end Z of the germanium rod. This end Z of the germanium rod containing all the impurities is then discarded. The remaining rod is now of highly pure germanium metal. In addition to germanium, silicon and gallium used as semiconductors are also refined by the zone refining method.

(IV) Chromatographic methods :

This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent. Different components are adsorbed at different levels on the column. Later the adsorbed components are removed (eluted) by using suitable solvent (eluant). Depending upon the physical state of the moving medium and the adsorbent material and also on the process of passage of the moving medium, the chromatographic method is given the name. In one such method the column of Al_2O_3 is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form. This is an example of column chromatography. This is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified. There are several chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc. Procedures followed in column chromatography have been depicted in the following figures.

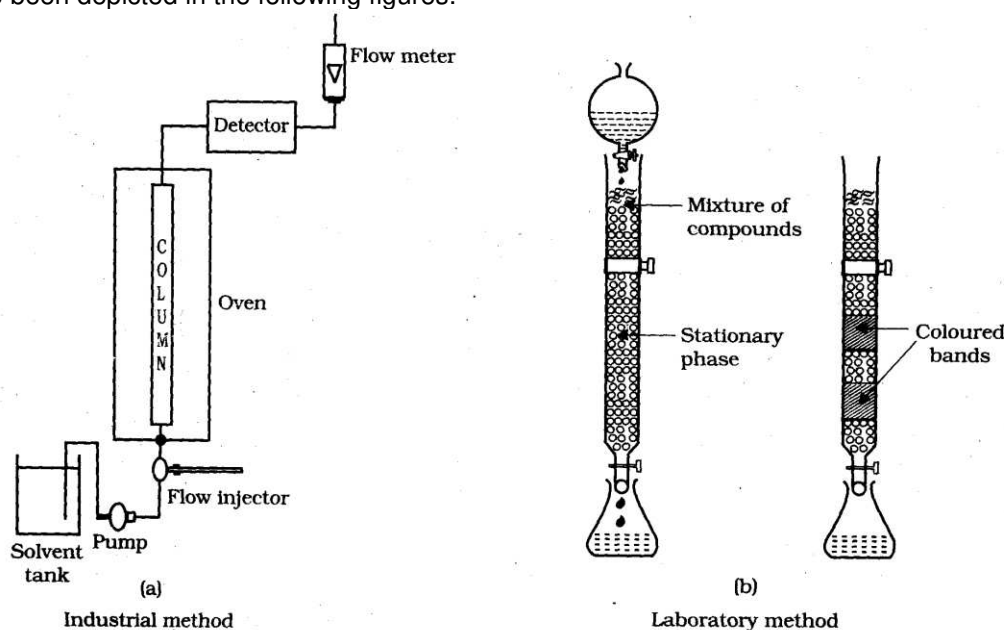


Fig. Schematic diagrams showing column chromatography

Chemical methods : These methods include the following methods :

(I) OXIDATIVE REFINING :

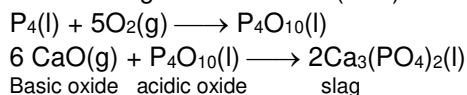
The method is used when the impurities present in the metal have a greater affinity for oxygen and are more readily oxidized than the metal. Then these oxides may be removed as follows :

- These oxide may form a scum on the surface of the metal. This scum can easily be removed by skimming.
- If the oxides are volatile, they escape from the mouth of the furnace.
- The oxides may form a slag with the lining on the inside surface of the furnace and may thus be removed. In the formation of the slag, the lining acts as a flux.

This method is usually employed for refining metals like **Pb, Ag, Cu, Fe**, etc. In this method the molten impure metal is subjected to oxidation by various ways.

(i) **Bessemerisation (Purification of iron) :**

The **iron** obtained from a blast furnace is a brittle material called cast iron or pig iron. It contains about 4% elemental C and smaller amounts of other impurities such as elemental Si, P, S and Mn that are formed from their compounds in the reducing atmosphere of the furnace. The most important of several methods for purifying the iron and converting it to steel is the basic oxygen process or oxidative refining. Molten iron from blast furnace is exposed to a jet of pure O₂ gas for about 20 minutes in a furnace that is lined with basic oxide such as CaO. The impurities in the iron are oxidized and the acidic oxides that form react with basic CaO to yield a molten slag that can be poured off. Phosphorous, for example, is oxidized to P₄O₁₀, which then reacts with CaO to give molten Ca₃(PO₄)₂.

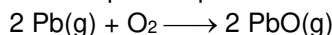


Mn also passes into the slag because its oxide is basic and reacts with SiO₂ yielding molten manganese silicate.

This process produces steel that contains about 1% carbon but only very small amount of P and S. Usually the composition of liquid steel is monitored by chemical analysis and the amount of oxygen and impure iron used are adjusted to achieve the desired concentration of carbon and other impurities.

(ii) **Cupellation (removal of lead) :**

In this process the molten impure metal is heated in a cupel, which is boat-shaped dish made of bone ash or cement, and a blast of air is passed over the molten metal. The impurities are oxidized and the volatile oxides thus produced escape with the blast of air. The pure metal remains behind in the cupel. Pb present in silver is removed by cupellation process.

(II) **PARTING PROCESS :**

Crude gold obtained by MacArthur-Forrest cyanide and chlorination process contains **Ag, Cu, Zn, and sometimes Pb as impurity**. Zn and Pb are removed by cupellation process. Cu and Ag are removed by parting process.

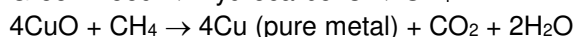
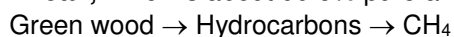
(i) **Parting with sulfuric acid or nitric acid:** Gold is not attacked by these acids while Cu and Ag dissolve. If, however, the Au content in an impure sample is more than 30%, the Cu and Ag are also not attacked by the acid of any strength. Hence, before the acid treatment, the impure sample is melted with necessary amount of Ag to reduce its gold content to about 25% (quartation). The resulting alloy, after being granulated in water, is boiled with H₂SO₄ or nitric acid when Cu and Ag pass into solution, leaving Au undissolved. Au is separated and fused again with borax and nitre when 100% Au is obtained.

(ii) **Parting with Cl₂:** Sometimes chlorine is used for the purification of Au. The impure sample of Au is fused with borax and Cl₂ gas is forced through it. The base metals are converted into chlorides that pass out as fumes at this high temperature, and AgCl forms a separate layer between the fused layer of Au and borax, which is skimmed off and the Au left behind cast into ingots.

(III) **POLING PROCESS :**

This process is used for the purification of **copper and tin**.

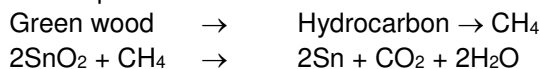
(i) **Purification of impure copper :** Impure copper is remelted in a reverberatory furnace lined with SiO₂ and a blast of O₂ is blown into the furnace. O₂ oxidises S, Sb and As to their respective oxides which, being, volatile, get volatilised and are thus removed. Fe is oxidised to FeO which forms a slag of FeSiO₃ with SiO₂ lining of the furnace. Molten copper left behind contains CuO as impurity. This molten copper is treated with powdered anthracite and then stirred with a pole of green wood. **Green wood, at high temperature, liberates hydrocarbon gases, which are converted into methane (CH₄). Methane thus obtained reduces CuO to free Cu-metal**, which is about 99.5% pure and is called tough pitch copper.



(ii) **Purification of impure tin :** Impure tin metal contains the impurities of Cu, Fe, W and SnO₂. The impurity of SnO₂ is due to the incomplete reduction of tin stone ore (SnO₂) during smelting.

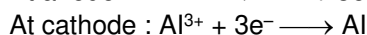
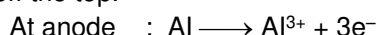


In order to remove these impurities, the impure molten tin metal is taken in a big pot and stirred with a pole of green wood. **Green wood, at high temperature liberates hydrocarbon gases, which are converted into methane CH_4 . Methane thus obtained reduces SnO_2 to pure metal while the impurities of Cu, Fe, W etc. come up to the surface**, where they come in contact with air and are oxidised to their respective oxides. The oxides form a scum on the surface of pure tin metal. This scum is removed from the surface. Tin metal obtained by this method is 99% pure.



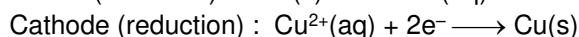
(IV) ELECTROLYTIC REFINING :

Some metals such as **Cu, Ni, and Al** are refined electrolytically. The Hooper process is a process for the electrolytic refining of aluminum. Impure Al forms the anode and pure Al forms the cathode of the Hooper's cell which contains three liquid layers. The bottom layer is molten impure Al, the middle is a fused salt layer containing aluminum fluoride, and the top layer is pure Al. At the anode (bottom layer), Al passes with solution as aluminum ion (Al^{3+}), and at the cathode (top layer), these ions are reduced to the pure metal. In operation, molten metal is added to the bottom of the cell and pure aluminum is drawn off the top.



Copper obtained from the reduction of ores must be purified for use in making electrical wiring because impurities increase its electrical resistance. The method used is electro-refining.

Impure Cu obtained from ores is converted to pure Cu in an electrolyte cell that the impure copper as the anode and pure copper as the cathode. The electrolyte is an aqueous solution of CuSO_4 . At the impure Cu anode, Cu is oxidized along with the more easily oxidized metallic impurities such as Zn and Fe. The less easily oxidized impurities such as Ag, Au, and Pt fall to the bottom of the cell as anode mud, which is reprocessed to recover the precious metals. At the pure Cu cathode, Cu^{2+} ions get reduced to pure copper metal, but the less easily reduced metal ions (Zn^{2+} , Fe^{2+} and so forth) remain in the solution.



Thus, the net cell reaction simply involves transfer of Cu metal from the impure anode to the pure cathode, Cu obtained by this process is 99.95% pure.

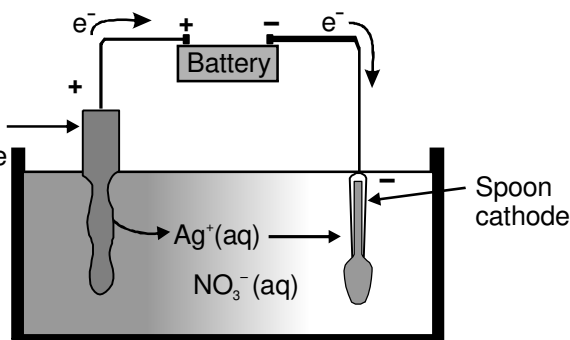
Solved Examples

Ex-11 Sketch an electrolytic cell suitable for electroplating a silver spoon. Describe the electrode and the electrolyte. Label the anode and cathode, and indicate the direction of electron and Silver ion flow. Write balanced equations for the anode and cathode half reaction.

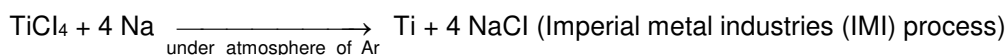
Sol. Anode : $\text{Ag(s)} \longrightarrow \text{Ag}^+(\text{aq}) + \text{e}^-$

Cathode : $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag(s)}$

The overall reaction is transfer of Ag metal from silver anode to the silver spoon.



(V) KROLL'S PROCESS :

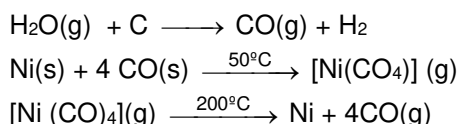


NaCl is leached with H_2O . Ti is in the form of small granules. These can be fabricated into metal parts using "powder forming" techniques and sintering in an inert atmosphere. Zr is also produced by Kroll's process.

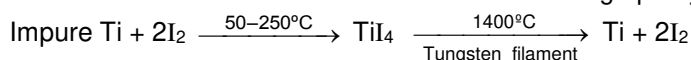
**(VI) VAPOR PHASE REFINING :****(i) Extraction of Nickel (Mond's process) :**

Nickel is extracted from sulfide ore by roasting followed by reduction with carbon, but the process is complicated by the fact that nickel is found in association with other metals. The refining is rather unusual, for nickel forms a complex with carbon monoxide tetracarbonylnickel (O) $[\text{Ni}(\text{CO})_4]$. This substance is molecular in molecular in structure and readily volatilized (boiling point 43°C). It is made by heating nickel powder to 50°C , in a stream of CO and then decomposed at 200°C . Any impurity in the nickel sample remains in the solid state and the gas is heated to 230°C , when it decomposes, giving pure metal and CO, which is recycled. $\text{Ni}(\text{CO})_4$ is gaseous and may be produced by warming nickel with CO at 50°C .

The sequence of reaction is

**(ii) Van Arkel-De Boer process :**

Small amounts of very pure metals (**Ti, Zr, or Bi**) can be produced by this method. This process is based on the fact that iodides are the least stable of the halides. The impure element is heated with iodine, producing a volatile iodide, TiI_4 , ZrI_4 or BiI_3 . These are decomposed by passing the gas over an electrically heated filament of tungsten or tantalum that is white hot. The element is deposited on the filament and the iodine is recycled. As more metal is deposited on the filament, it conducts electricity better. Thus, more electric current must be passed to keep it white hot. Thus the filament grows fatter and eventually the metal is recovered. The tungsten core is distilled out of the center and a small amount of high purity metal is obtained.



The method is very expensive and is employed for the preparation of very pure metal for specific use.

(VII) PARKE'S PROCESS :

The removal of the impurities of Ag from the commercial **lead** is called desilverisation of lead and is done by **Parke's process**. Thus, Parke's process is the desilverisation of lead.

In Parke's process, the commercial lead, which contains Ag as impurities, is melted in iron pots and 1% of Zn is added to it. The molten mass is thoroughly agitated. Since Ag is about 300 times more soluble in Zn than in Pb, most of the Ag present in the commercial lead as impurity mixes with Zn, to form Zn-Ag alloy. When the whole is cooled, two layers are obtained. The upper layer contains Zn-Ag alloy in the solid state, while the lower layer has lead in the molten state. This lead contains only 0.0004% of Ag and hence is almost pure. Lead obtained after removing most of Ag from it (desilverisation of lead) by Parke's process, is called desilverised lead. This lead contains the impurities of metals like Zn, Au, Sb etc. These metal impurities are removed from desilverised lead by **Bett's electrolytic process**.

Zn-Ag alloy, formed in the upper layer, is skimmed off from the surface of the molten lead by perforate ladles. This alloy contains lead as impurity. This impurity of Pb is removed from the alloy by **liquation process**, in which Zn-Ag alloy is heated in a slopping furnace, when the impurity of Pb melts and hence drains away from the solid alloy. Thus purified Zn-Ag is obtained. Now Ag can be obtained from this purified Zn-Ag alloy by **distillation process**, in which the alloy is heated strongly in presence of little carbon in a fire-clay retort. Zn, being more volatile, distills off while Ag remains in the retort, carbon used in the process reuses the oxide of Zn, if formed. Ag obtained from Zn-Ag alloy is contaminated with a little of Pb as impurity. This impurity of Pb placed in a cupel (cupel is a boat-shaped) dish made of bone ash which is porous in nature) in a reverberatory furnace and heated in the presence of air. By doing so, lead (impurity) is oxidised to PbO (litharge) which volatilises and pure Ag is left behind in the cupel. Last traces of PbO are absorbed by the porous mass of the cupel.

(VIII) Pudding process : This process is used for the manufacture of wrought iron from cast iron. We know that cast iron contains the impurities of C, S, Si, Mn and P. When these impurities are removed from cast iron, we get wrought iron. In this process the impurities are oxidised to their oxides not by blast of air but by the haematite (Fe_2O_3) lining of the furnace.



MISCELLANEOUS SOLVED PROBLEMS (MSPs)

- At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why?
Sol. Since zinc lies above iron in electrochemical series, it is more reactive than iron. As a result, if zinc scraps are used the reduction will be faster. However, zinc is a costlier metal than iron. Therefore, it will be advisable and advantageous to use iron scraps.
- A metal is extracted from its sulphide ore and the process of extraction involves the following steps.
Metal sulphide $\xrightarrow{(A)}$ Concentrated ore $\xrightarrow{(B)}$ Matte $\xrightarrow{(C)}$ Impure metal $\xrightarrow{(D)}$ Pure metal
Identify the steps (A), (B), (C) and (D).
Sol. (A) Froth floatation process. Sulphide ores are concentrated by froth-floatation process.
(B) Roasting. Metal sulphides are roasted to convert into metal oxide and to remove impurities.
In roasting ; $2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2$
 $2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2$
 $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$
 $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$
(C) Bessemerisation/self reduction. Reduction of metal oxide by its sulphide takes place in Bessemer converter.
In Bessemerisation ; $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$ (self - reduction)
(D) Electro-refining. Pure metal is obtained at cathode ; $\text{M}^{n+} + n\text{e}^- \longrightarrow \text{m}$
- Write chemical equations for metallurgical processes to represent :
(i) roasting of galena (PbS) in limited supply of air at moderate temperature.
(ii) reduction of Cu_2O using coke as a reducing agent.
(iii) deposition of pure silver from an aqueous solution of Ag^+ .
Sol. (i) $2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$; $\text{PbS} + 2\text{O}_2 \longrightarrow \text{PbSO}_4$
(ii) $\text{Cu}_2\text{O} + \text{C} \longrightarrow 2\text{Cu} + \text{CO}$
(iii) $\text{Ag}^+ + \text{e}^- \xrightarrow{\text{(Electrolysis)}} \text{Ag} \downarrow$ (at cathode)
- Using data given below, predict whether the reduction of MgO with C is spontaneous or not at 1500°C .
 $2\text{C} + \text{O}_2 \longrightarrow 2\text{CO} \quad \Delta G^\circ \approx -530 \text{ kJ}$
 $2\text{MgO} \longrightarrow 2\text{Mg} + \text{O}_2 \quad \Delta G^\circ \approx +730 \text{ kJ}$
Sol. The positive value of ΔG° indicates that the reduction of MgO with C does not occur to a significant extent at 1500°C .
 $2\text{C} + \text{O}_2 \longrightarrow 2\text{CO} \quad \Delta G^\circ \approx -530 \text{ kJ}$
 $2\text{MgO} \longrightarrow 2\text{Mg} + \text{O}_2 \quad \Delta G^\circ \approx +730 \text{ kJ}$
 $\hline 2\text{MgO} + 2\text{C} \longrightarrow 2\text{Mg} + 2\text{CO}$
or $\text{MgO} + \text{C} \longrightarrow \text{Mg} + \text{CO} \quad \Delta G^\circ \text{ positive value.}$
- Sea water $\xrightarrow{(A)} \text{Mg}(\text{OH})_2 \xrightarrow{(B)} \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{(C)} \text{MgCl}_2 \xrightarrow{(D)} \text{Mg} + \text{Cl}_2 \uparrow$
Identify the reagents and processes (A) to (D) and give the name of this process.
Sol. MgCl_2 (from sea water) + $\text{Ca}(\text{OH})_2$ (A) $\rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaCl}_2$;
 $\text{Mg}(\text{OH})_2 + 2\text{HCl}$ (B) $\rightarrow \text{MgCl}_2 (\text{aq.}) + 2\text{H}_2\text{O}$
Crystallisation of $\text{MgCl}_2(\text{aq})$ yields $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow[\Delta \text{ Dry HCl}]{\text{Calcination (C)}} \text{MgCl}_2 + 6\text{H}_2\text{O}$
 $\text{MgCl}_2(\ell) \xrightarrow{\text{Electrolysis(D)}} \text{Mg}^{2+} + 2\text{Cl}^-$
 $\downarrow + 2\text{e}^- \quad \downarrow \text{Cl}_2$
 $\text{Mg} \quad \text{Cl}_2$
(cathode) (anode)
Name of the process is Dow's process.
- Convert magnesite into anhydrous MgCl_2 .
Sol. $\text{MgCO}_3 \xrightarrow{\Delta} \text{MgO} + \text{CO}_2$; $\text{MgO} + \text{C} + \text{Cl}_2 \longrightarrow \text{MgCl}_2 + \text{CO}$



7. Which is not the correct process-mineral matching in metallurgical extraction.
 (A) Leaching : silver (B) Zone refining : lead.
 (C) Liquefaction : tin (D) Van Arkel : Zr
- Sol.** Lead is purified by Electro-refining. Zone refining is used for the purification of Si and Ge. Therefore, (B) option is correct.
8. Tin stone, an oxide of tin is amphoteric in nature. Explain.
- Sol.** Tin stone is cassiterite i.e. SnO_2 . SnO_2 dissolves in acid and alkali both, hence amphoteric oxide.

$$\text{SnO}_2 + 4\text{HCl} \longrightarrow \text{SnCl}_4 + 2\text{H}_2\text{O} \quad ; \quad \text{SnO}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{SnO}_3 + \text{H}_2\text{O}$$
9. Select the incorrect statement.
 (A) In the Bayer's Al_2O_3 goes in to solution as soluble $[\text{Al}(\text{OH})_4]^-$ while other basic oxides as TiO_2 and Fe_2O_3 remain insoluble
 (B) Extraction of zinc from zinc blende is achieved by roasting followed by reduction with carbon.
 (C) The methods chiefly used for the extraction of lead and tin are respectively carbon reduction and electrolytic reduction.
 (D) Extractive metallurgy of magnesium involves fused salt electrolysis.
- Sol.** Lead \rightarrow self reduction; $2\text{PbO} + \text{PbS} \longrightarrow 3\text{Pb} + \text{SO}_2$
 Tin \rightarrow carbon reduction, $\text{SnO}_2 + 2\text{C} \longrightarrow \text{Sn} + 2\text{CO}$
 Therefore, (C) option is correct.
10. Which of the following is not an ore of iron ?
 (A) limonite (B) cassiterite (C) magnetite (D) none of these
- Sol.** SnO_2 , cassiterite is an ore of tin.
 Therefore, (B) option is correct.
11. In the extraction of copper from sulphide ore the metal is formed by reduction of Cu_2O with :
 (A) FeS (B) CO (C) Cu_2S (D) SO_2
- Sol.** $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \xrightarrow{\Delta} 6\text{Cu} + \text{SO}_2$
 Therefore, (C) option is correct.
12. Which of the following is a carbonate ore ?
 (A) pyrolusite (B) malachite (C) diasporite (D) cassiterite
- Sol.** $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \rightleftharpoons \text{Malachite}$.
 Therefore, (B) option is correct.
13. Column-I and column-II contains four entries each. Entries of column-I are to be matched with some entries of column-II. Each entry of column-I may have the matching with one or more than one entries of column-II.

	Column-I		Column-II
(A)	Pb	(p)	Bessemerisation
(B)	Cu	(q)	Roasting
(C)	Zn	(r)	Pyrometallurgy
(D)	Fe (pig iron)	(s)	Self-reduction method

Ans. (A) q, r, s; (B) p, q, r, s; (C) q, r; (D) r;

Sol. (A) $2\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$ (Roasting)

$\text{PbS} + \text{PbO}_2 \xrightarrow{\Delta} 2\text{Pb} + \text{SO}_2$ (Self-reduction method)

(B) $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$ (Roasting)

$\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \xrightarrow{\Delta} 6\text{Cu} + \text{SO}_2$ (Self-reduction takes place in Bessemer converter)

(C) $2\text{ZnS} + 3\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2$ (Roasting)

$\text{ZnO} + \text{C} \xrightarrow{\Delta} \text{Zn} + \text{CO}$ (Carbon reduction)

(D) Haematite ore is calcined.

$3\text{Fe}_2\text{O}_3 + \text{CO} \xrightarrow{\Delta} 2\text{Fe}_3\text{O}_4 + \text{CO}_2$

$\text{Fe}_3\text{O}_4 + \text{CO} \xrightarrow{\Delta} 3\text{FeO} + \text{CO}_2$

$\text{FeO} + \text{CO} \xrightarrow{\Delta} \text{Fe} + \text{CO}_2$



Exercise-1

Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : ORES & Method of concentration

- A-1. Name three ores which are concentrated by froth-floatation process.
- A-2. What is meant by a depressant ?
- A-3. Which concentration method is used for separating tungsten ore particles from cassiterite ore (SnO_2) ?
- A-4. Which metals are obtained by self reduction of their ores ?
- A-5. How carnallite ore is made anhydrous ?
- A-6. What is the role of a stabiliser in froth-floatation process ?

Section (B) : Thermodynamic Principles of metallurgy

- B-1. Out of C and CO, which is a better reducing agent for ZnO ?
- B-2. Why the HgO decomposes into its constituent elements on heating ?
- B-3. CuO is less reduced by carbon but more reduced by H_2 . Explain in terms of thermodynamics, given:
 ΔG_f° for CuO = $-129.7 \text{ kJ mol}^{-1}$, CO = $-137.2 \text{ kJ mole}^{-1}$, H_2O = $-237.2 \text{ kJ mol}^{-1}$

Section (C) : Metallurgy of some useful metals

- C-1. Cinnabar (HgS) and galena (PbS) on roasting often give their respective metals but zinc blende (ZnS) does not. explain.
- C-2. Magnesium oxide is often used as the lining in steel making furnace, Explain.
- C-3. In the extraction of tin from tin stone addition of excess lime stone should be avoided. Why ?
- C-4. In the extraction of lead from galena lime stone is added, why ?
- C-5. Why excess of carbon is added in the zinc metallurgy ?
- C-6. In the extractive metallurgy of iron from haematite ore, lime stone is added during smelting. Explain why.
- C-7. State the role of silica in the metallurgy of copper.

Section (D) : Electrochemical principles of metallurgy

- D-1. Why air is continuously passed through the suspension of the concentrated ore of silver, the argentite during leaching with the aqueous solution of sodium cyanide ?
- D-2. Alkali metals and alkaline earth metals can only be extracted by electrolytic reduction of their fused salts, why ?
- D-3. What is the role of cryolite in the metallurgy of aluminium?

Section (E) : Purification or Refining of Impure Metals

- E-1. Name the physical processes which are used for the purification of impure metals ?
- E-2. Which impure metals are purified by Poling process ?
- E-3. Give the name of the metals which are purified using vapour phase thermal decomposition method.

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : ORES & Method of Concentration

- A-1. Calamine is an ore of :
 (A) Zn (B) Mg (C) Ca (D) Pb



- A-2.** Which of the following is not the ore of aluminium ?
 (A) Bauxite (B) Corundum (C) Langbeinite (D) Kaolinite
- A-3.** Which of the following is not an ore ?
 (A) Malachite (B) Calamine (C) Salt cake (D) Cerussite
- A-4.** Which of the following set of metals mostly found as sulphide ores :
 (A) Zn, Cu, Mg (B) Zn, Cu, Pb (C) Fe, Al, Ti (D) Cu, Ag, Au
- A-5.** The formula of carnallite is :
 (A) $\text{LiAl}(\text{Si}_2\text{O}_5)_2$ (B) $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
 (C) $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (D) $\text{KCl} \cdot \text{MgCl}_2 \cdot 2\text{H}_2\text{O}$
- A-6.** Magnetic separation process may be used for the concentration of :
 (A) chalcopyrite (B) bauxite (C) haematite (D) calamine
- A-7.** Which mineral has been named incorrectly ?
 (A) Bauxite : $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (B) Corundum : Al_2O_3
 (C) Cryolite : $3\text{NaF} \cdot \text{AlF}_3$ (D) Feldspar : $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
- A-8.** Black tin is
 (A) an alloy of Sn (B) an allotrope of Sn
 (C) 60-70 percent SnO_2 (D) 100 percent SnO_2
- A-9.** NaCN is sometimes added in the froth flotation process as a depressant when ZnS and PbS minerals are expected because :
 (A) $\text{Pb}(\text{CN})_2$ is precipitated while no effect on ZnS.
 (B) ZnS forms soluble complex $\text{Na}_2[\text{Zn}(\text{CN})_4]$ while PbS forms froth
 (C) PbS forms soluble complex $\text{Na}_2[\text{Pb}(\text{CN})_4]$ while ZnS forms froth.
 (D) NaCN is never added in froth floatation process.
- A-10.** Which one of the following reactions represents a calcination reaction?
 (A) $\text{HgS} + \text{O}_2 \rightarrow \text{Hg} + \text{SO}_2$
 (B) $\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{NaNO}_3$
 (C) $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \rightarrow \text{CuO} + \text{CO}_2 + \text{H}_2\text{O}$
 (D) $\text{Al}_2\text{O}_3 + \text{NaOH} \rightarrow \text{NaAlO}_2 + \text{H}_2\text{O}$

Section (B) : Thermodynamic Principles of Metallurgy

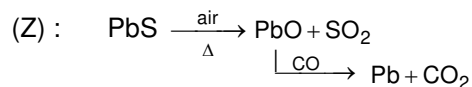
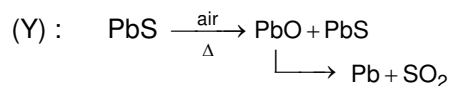
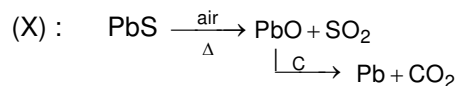
- B-1.** Selection of temperature to carry out a reduction process depends so as to make :
 (A) ΔG negative (B) ΔG positive (C) ΔH negative (D) ΔH positive
- B-2.** Ellingham diagram represents :
 (A) change of ΔG with temperature.
 (B) change of ΔH with temperature.
 (C) change of ΔG with pressure.
 (D) change of $(\Delta G - T\Delta S)$ with temperature.
- B-3.** Which of the following represents the thermite reaction?
 (A) $3\text{Mn}_3\text{O}_4 + 8\text{Al} \rightarrow 9\text{Mn} + 4\text{Al}_2\text{O}_3$ (B) $\text{MgCO}_3 + \text{SiO}_2 \rightarrow \text{MgSiO}_3 + \text{CO}_2$
 (C) $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$ (D) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$

Section (C) : Metallurgy of some useful metals

- C-1.** Self-reduction of Cu_2S to Cu can be carried out in.
 (A) bessemer convertor (B) blast furnace
 (C) both (A) and (B) (D) none of these
- C-2.** Blister copper is :
 (A) impure copper.
 (B) obtained in self reduction process during bessemerisation.
 (C) both (A) and (B) are correct.
 (D) none is correct.



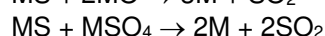
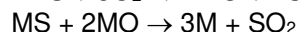
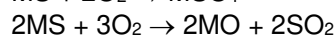
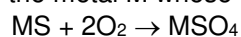
C-3. Main source of lead is PbS. It is converted to Pb by :



Self-reduction process is :

- (A) X (B) Y (C) Z (D) none

C-4. Identify the metal M whose extraction is based on the following reactions :



- (A) magnesium (B) aluminium (C) lead (D) tin

C-5. Which of the following reactions represents the self-reduction process?

- (A) $\begin{cases} \text{HgS} + \text{O}_2 \rightarrow \text{HgO} + \text{SO}_2 \\ \text{HgO} + \text{HgS} \rightarrow \text{Hg} + \text{SO}_2 \end{cases}$ (B) $\begin{cases} \text{Cu}_2\text{S} + \text{O}_2 \rightarrow \text{Cu}_2\text{O} + \text{SO}_2 \\ \text{Cu}_2\text{S} + \text{Cu}_2\text{O} \rightarrow \text{Cu} + \text{SO}_2 \end{cases}$
- (C) $\begin{cases} \text{PbS} + \text{O}_2 \rightarrow \text{PbO} + \text{SO}_2 \\ \text{PbO} + \text{PbS} \rightarrow \text{Pb} + \text{SO}_2 \end{cases}$ (D) All of these

Section (D) : Electrochemical Principles of Metallurgy

D-1. Magnesium is extracted from ore carnallite by :

- (A) the self-reduction process
(B) the carbon-reduction process
(C) the electrolytic process
(D) treating the ore with aqueous NaCN and then reducing the mixture

D-2. NaCl and CaCl₂ are added to fused MgCl₂ in the electrolysis of MgCl₂ since :

- (A) melting point is decreased and conductivity is increased.
(B) melting point is increased and conductivity is decreased.
(C) melting point and conductivity both are decreased.
(D) melting point and conductivity both are increased.

D-3. Which of the following metals cannot be extracted by the carbon reduction process ?

- (A) Zn (B) Fe (C) Al (D) Sn

D-4. In electrolysis of Al₂O₃ by Hall-Heroult process :

- (A) cryolite Na₃[AlF₆] lowers the melting point of Al₂O₃ and increases its electrical conductivity.
(B) Al is obtained at cathode and probably CO₂ at anode
(C) both (A) and (B) are correct
(D) none of the above is correct

D-5. During the electrolytic reduction of aluminium, the carbon anodes are replaced from time to time because:

- (A) the carbon anodes get decayed
(B) the carbon prevents atmospheric oxygen from coming in contact with aluminium
(C) oxygen liberated at the carbon anodes reacts with anodes to form CO and CO₂
(D) carbon converts Al₂O₃ to Al

Section (E) : Purification or Refining of Impure Metals

E-1. Poling process :

- (A) reduces SnO₂ to Sn (B) oxidises impurities like iron and removes as scum
(C) uses green poles (D) all of the above are correct



- E-2.** Aluminium metal is purified by :
 (A) Hoop's process (B) Hall-Heroult process
 (C) Serpeck's process (D) Baeyer's process
- E-3.** High purity copper metal is obtained by :
 (A) carbon reduction (B) hydrogen reduction
 (C) electrolytic reduction (D) thermite reduction
- E-4.** In the electrolytic refining of lead, Sb, Cu, Ag and Au are found :
 (A) on anode (B) in electrolyte solution
 (C) in anode mud (D) in cathode mud
- E-5.** The anode mud in the electrolytic refining of silver contains :
 (A) Zn, Cu, Ag, Au (B) Zn, Ag, Au (C) Cu, Ag, Au (D) Au only
- E-6.** Silver can be separated from lead by :
 (A) fractional crystallisation (B) liquation
 (C) cupellation (D) addition of zinc (Parke's method)
- E-7.** The method of zone refining of metals is based on the principle of :
 (A) greater mobility of the pure metal than that of 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 the impurity
 (D) greater solubility of the impurity in the molten state than in the solid
- E-8.** Which does not represent correct method ?
 (A) $\text{TiCl}_2 + 2\text{Mg} \longrightarrow \text{Ti} + 2\text{MgCl}_2$: Kroll
 (B) $\text{Ni}(\text{CO})_4 \longrightarrow \text{Ni} + 4\text{CO}$: Mond
 (C) $\text{Ag}_2\text{CO}_3 \longrightarrow 2\text{Ag} + \text{CO}_2 + \frac{1}{2}\text{O}_2$: Van Arkel
 (D) $\text{ZrI}_4 \longrightarrow \text{Zr} + 2\text{I}_2$: Van Arkel

PART - III : MATCH THE COLUMN

1. Match the reactions listed in column (I) with processes listed in column (II).

	Column-I		Column-II
	(reactions)		(processes)
(A)	$4\text{Au} + 8\text{NaCN} + 2\text{H}_2\text{O} + \text{O}_2 (\text{air}) \longrightarrow 4\text{Na}[\text{Au}(\text{CN})_2] + 4\text{NaOH}$	(p)	Leaching
(B)	$\text{CuFeS}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2\text{H}_2\text{S}$	(q)	Smelting
(C)	$\text{CaO} + \text{SiO}_2 \xrightarrow{\Delta} \text{CaSiO}_3$	(r)	Hydrometallurgy
(D)	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \xrightarrow[\text{dry HCl(g)}]{\Delta} \text{MgCl}_2 + 6\text{H}_2\text{O}$	(s)	Calcination

2. **Column-I** and **Column-II** contains four entries each. Entries of **Column-I** are to be matched with some entries of **Column-II**. One or more than one entries of **Column-I** may have the matching with the same entries of **Column-II**.

	Column-I		Column-II
	(Reaction)		(Process)
(A)	$\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$	(p)	Calcination
(B)	$3\text{Mn}_2\text{O}_3 + 8\text{Al} \longrightarrow 4\text{Al}_2\text{O}_3 + 9\text{Mn}$	(q)	Displacement method
(C)	$\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \xrightarrow{\Delta} 6\text{Cu} + \text{SO}_2$	(r)	Smelting
(D)	$2\text{Al}(\text{OH})_3 \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$	(s)	Thermite process
(E)	$2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \longrightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag}$	(t)	Bessemerisation



3. Match the purification processes given in **Column-I** with the metal(s) given in **Column-II**.

	Column-I		Column-II
(A)	Poling	(p)	Titanium
(B)	Cupellation	(q)	Copper
(C)	Liquation	(r)	Silver
(D)	Van Arkel method	(s)	Tin

4. Match the ores given in column-I with type(s) of processes given in column-II.

	Column-I		Column-II
(A)	Haematite	(p)	Slag formation during roasting/smeltering and bessemerisation.
(B)	Copper pyrites	(q)	Reduction by carbon monoxide/carbon at different temperatures.
(C)	Carnallite	(r)	Electrolytic reduction.
(D)	Bauxite	(s)	Calcination.

Exercise-2

Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE

1. Match Column-I with Column-II and select the correct answer using the codes given below :

	Column-I		Column-II
	(Metals)		(Ores)
(A)	Tin	(p)	Calamine
(B)	Zinc	(q)	Cassiterite
(C)	Iron	(r)	Cerrusite
(D)	Lead	(s)	Siderite

Codes:

	(A)	(B)	(C)	(D)		(A)	(B)	(C)	(D)
(A)	p	q	r	s	(B)	q	p	s	r
(C)	s	r	q	p	(D)	q	p	r	s

2. Which is not correct statement ?
 (A) Cassiterite, chromite and haematite may be concentrated by hydraulic washing (Tabling).
 (B) Pure Al_2O_3 is obtained from the bauxite ore by leaching in the Bayer's process.
 (C) Sulphide ore is concentrated by calcination method.
 (D) Roasting can convert sulphide into oxide or sulphate and part of sulphide may also act as a reducing agent.
3. Bauxite is leached with :
 (A) KCl (B) NaCN (C) NaOH (D) Na_2SO_4
4. Froth floatation process for the concentration of sulphide ores is an illustration of the practical application of:
 (A) adsorption (B) absorption (C) sedimentation (D) coagulation
5. Which one of the following is not a method of concentration of ore ?
 (A) electromagnetic separation (B) smelting
 (C) gravity separation (D) froth floatation process
6. The metal which mainly occurs as oxide ore in nature is :
 (A) gold (B) lead (C) aluminium (D) magnesium
7. The reason, for floating of ore particles in concentration by froth floatation process is that :
 (A) they are light (B) they are insoluble
 (C) they are charged (D) they are hydrophobic



8. Choose the correct option using the code regarding roasting process.
 (I) It is the process of heating the ore in air in a reverberatory furnace to obtain the oxide.
 (II) It is an exothermic process.
 (III) It is used for the concentration of sulphide ore.
 (IV) It removes easily oxidisable volatile impurities present in the concentrated ore.
 (A) I, II and III (B) I, II and IV (C) I, III and IV (D) I, II, III and IV
9. Select correct statement for decomposition of metal oxide into solid/liquid metal and oxygen?
 (A) Entropy increases.
 (B) It is an endothermic change.
 (C) To make ΔG° negative, temperature should be high enough so that $T\Delta S^\circ > \Delta H^\circ$.
 (D) All are correct statements.
10. A sulphide ore like ZnS is first roasted into its oxide prior to reduction by carbon because :
 (A) a sulphide ore cannot be reduced to metal at all
 (B) no reducing agent is found suitable for reducing a sulphide ore.
 (C) the Gibb's free energy of formation of most sulphides are less than that for CS_2 .
 (D) a metal oxide is generally less stable than the metal sulphide.
11. Which of the following statements is correct regarding the slag obtained during the extraction of a metal like copper or iron ?
 (A) The slag is lighter and has lower melting point than the metal
 (B) The slag is heavier and has lower melting point than the metal
 (C) The slag is lighter and has higher melting point than the metal
 (D) The slag is heavier and has higher melting point than the metal
12. The slag consists of molten impurities, generally, in the form of :
 (A) metal carbonate (B) metal silicate (C) metal oxide (D) metal nitrate
13. In the metallurgy of iron, the upper layer obtained in the bottom of blast furnace mainly contains :
 (A) $CaSiO_3$ (B) spongy iron (C) Fe_2O_3 (D) $FeSiO_3$
14. Which one of the following reactions occurs during smelting in the reduction zone at lower temperature (in the top zone in blast furnace in iron metallurgy) ?
 (A) $CaO + SiO_2 \longrightarrow CaSiO_3$ (slag)
 (B) $Fe_2O_3 + 3C \longrightarrow 2Fe + CO$
 (C) $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$
 (D) $CO_2 + C \longrightarrow 2CO$
15. Magnesium is extracted by electrolysis of fused magnesium chloride containing NaCl & $CaCl_2$ using :
 (A) a nickel cathode and a graphite anode.
 (B) the iron container as anode and a nickel cathode.
 (C) the iron container as cathode and a graphite rod as anode.
 (D) the nickel container as cathode and iron anode.
16. The process of the isolation of a metal by dissolving the ore in a suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called :
 (A) hydrometallurgy (B) electrometallurgy
 (C) zone refining (D) electro-refining
17. Which method of purification is represented by the equations ?

$$\begin{array}{c} \text{Ti} + 2I_2 \xrightarrow{500\text{ K}} \text{TiI}_4 \xrightarrow{1675\text{ K}} \text{Ti} + 2I_2 \\ \text{(impure)} \qquad \qquad \qquad \text{(Pure)} \end{array}$$

 (A) Cupellation (B) Poling (C) Van Arkel (D) Zone refining
18. Select correct statement regarding silver extraction / purification process.
 (A) When the lead-silver alloy is rich in silver, lead is removed by the cupellation process.
 (B) Lead is removed from argentiferous lead by Parke's process.
 (C) Zinc forms an alloy with lead, from which lead is separated by distillation.
 (D) Zinc forms an alloy with silver, from which zinc is separated by distillation.



19. Formation of volatile $\text{Ni}(\text{CO})_4$ and then its subsequent decomposition into Ni and CO makes basis of Mond's process :
- $$\text{Ni} + 4\text{CO} \xrightarrow{T_1} \text{Ni}(\text{CO})_4 \xrightarrow{T_2} \text{Ni} + 4\text{CO}, T_1 \text{ and } T_2 \text{ are :}$$
- (A) $100^\circ\text{C}, 50^\circ\text{C}$ (B) $50^\circ\text{C}, 100^\circ\text{C}$ (C) $50^\circ\text{C}, 200^\circ\text{C}$ (D) $200^\circ\text{C}, 50^\circ\text{C}$
20. Which one of the following processes involves the principle of fractional crystallisation for the refining of impure metals ?
 (A) Parke's process (B) Mond's process (C) Van Arkel process (D) Zone refining
21. In Van Arkel method, if I_2 is introduced at 1800 K over impure zirconium metal, the product will be :
 (A) iodide of the metal (B) pure metal
 (C) impurities react with iodine (D) none of these

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. How many of the following are oxides ores.
 (i) Carnallite (ii) Cuprite (iii) Cassiterite (iv) Chromite (v) Cinnabar
 (vi) Calamine (vii) Cerussite (viii) Chalcopyrite (ix) Chalcocite.
2. In an ore of iron, iron is present in two oxidation state. Fe^{n+} and $\text{Fe}^{(n+1)+}$. Number of $\text{Fe}^{(n+1)+}$ is twice the number of Fe^{n+} . If empirical formula of ore is Fe_xO . Calculate value of $[x \times 100]$.
3. In extraction of metal how many of the following ores involve calcination process.
 (i) Dolomite (ii) Malachite (iii) Calcite (iv) Copperpyrites (v) Sylvine
 (vi) Cryolite (vii) Siderite (viii) Iron pyrite (ix) Argentite
4. How many of the following metallurgies involve leaching?
 (i) $\text{Al}_2\text{O}_3 \longrightarrow \text{Al}$; (ii) $\text{Ag}_2\text{S} \longrightarrow \text{Ag}$; (iii) $\text{Au} \longrightarrow \text{Au}$; (iv) $\text{CuFeS}_2 \longrightarrow \text{Cu}$; (v) $\text{PbS} \longrightarrow \text{Pb}$
 (vi) $\text{MgCl}_2 \longrightarrow \text{Mg}$; (vii) $\text{FeCO}_3 \longrightarrow \text{Fe}$; (viii) Low grade copper ore $\longrightarrow \text{Cu}$; (ix) $\text{HgS} \longrightarrow \text{Hg}$
5. Among the following metals how many metals are extracted by self-reduction method from their respective ores. Hg, Zn, Cu, Al, Mg, Pb, Fe, Sn.
6. Number of metals among following which are obtained by electrometallurgy in molten state are. Li, Ba, Na, Al, Fe, Cu, Pb, Sn, Ag, Au, Zn, Ca, Mg
7. The number of reducing agents involved in the extraction of iron (as pig iron) using blast furnace from ore haematite is(are).
8. How many of following are correctly matched for electrolytic reduction in molten state.
- | | Ore | Reagent / Process | Remark |
|-----|-------------------------|---|--|
| (a) | Al_2O_3 | AlF_3 and CaF_2 added | Decrease M.P. |
| (b) | MgCl_2 | KCl , CaCl_2 | Increase conductivity |
| (c) | NaCl | AlCl_3 | Decrease M.P. |
| (d) | AlF_3 | Haroult process | Al form at anode |
| (e) | MgBr_2 | Dow process | Br_2 form at anode |
| (f) | Al_2O_3 | conc. NaOH | Leaching process |
| (g) | Carnallite | Dow process | Directly applied to carnallite crystals. |
9. How many of the following reduction processes are correct :
 (1) $\text{B}_2\text{O}_3 + \text{Al} \xrightarrow{\Delta} \text{B}$. (2) $\text{Cr}_2\text{O}_3 + 2\text{Al} \xrightarrow{\Delta} \text{Cr}$.
 (3) $\text{TiCl}_4 + \text{Mg} \xrightarrow{\Delta} \text{Ti}$. (4) $\text{PbS} + \text{PbO} \xrightarrow{\Delta} \text{Pb}$.
 (5) $3\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$ (6) $\text{Fe}_3\text{O}_4 + \text{CO} \longrightarrow 3\text{FeO} + \text{CO}_2$
 (7) $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$ (8) $\text{SnO}_2 + \text{C} \longrightarrow \text{SnO} + \text{CO}$
10. The minimum voltage required to electrolyse of Al_2O_3 in the Hall-Heroult process is
 Given : $\Delta G_f^\circ (\text{Al}_2\text{O}_3) = -1520 \text{ kJ mol}^{-1}$; $\Delta G_f^\circ (\text{CO}_2) = -394 \text{ kJ mol}^{-1}$
 If net reaction in Hall-Heroult process is : $3\text{C} + 2\text{Al}_2\text{O}_3 \longrightarrow 4\text{Al} + 3\text{CO}_2$
 (Report your answer as voltage $\times 10$)



11. Calculate mass of Zn (at. mass = 65) required to recover Ag from a 500 ml solution of 0.5 M sodium argento cyanide (Give your answer by multiplying 8).
12. What is the value of $\frac{\Delta G^\circ}{10}$ required in kJ/mole for preparation of Mg from Dow's process using 2.02 voltage.
13. Oxidation state of Zr in the compound formed by it in Van Arkel process; ' ℓ '
Bond order of the gas involved in Mond's process = ' m '
Total number of ions present in one formula unit of Thomas slag obtained during Bassemmerisation of iron = ' n '
Report your answer as ($\ell \times m \times n$)
14. How many of the following process of refining is/are chemical methods.
(i) Liquation process (ii) Fractional distillation process (iii) Zone refining method
(iv) Chromato graphic method (v) Cupellation (vi) Poling process
(vii) Hoop's process (viii) Kroll's process (ix) Mond's process

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Which of the following manufactured by the electrolysis of their fused salts.
(A) Copper (B) Sodium (C) Aluminium (D) Platinum
2. On the basis of ellingham diagram plotted for formation of metal oxide from metal and one mole of oxygen, which of the following is/are correct.
(A) Entropy change for all metal oxides is roughly same.
(B) Below the boiling point, ' $T\Delta S$ ' factor is nearly same irrespective of metal.
(C) Above $\Delta G = 0$ line, oxide decomposes into metal & oxygen.
(D) If randomness increases the slope increases
3. The smelting of iron in a blast furnace involves, which of the following process/(es) ?
(A) Combustion (B) Reduction (C) Slag formation (D) Sublimation
4. Addition of high proportion of manganese makes steel useful in making rails of rail roads, because manganese :
(A) gives hardness to steel (B) helps the formation of oxides of iron
(C) can remove oxygen and sulphur (D) can show highest oxidation state of +7
5. Complexes formed in the cynide process are :
(A) $[\text{Au}(\text{CN})_2]^-$ (B) $[\text{Ag}(\text{CN})_2]^-$ (C) $[\text{Cu}(\text{CN})_4]^{2-}$ (D) $[\text{Zn}(\text{CN})_4]^{2-}$
6. In poling process of purification of Cu, O_2 oxidises following group of elements :
(A) S, Sb, As (B) Sb, As, Fe (C) S, Sb, As (D) As, Ag, Au
7. Which of the following process(es) occur(s) during the extraction of copper from chalcopyrites ?
(A) Froth floatation (B) Roasting (C) Bessemerisation (D) calcination
8. Calcium silicate (slag) formed in the slag formation zone in extraction of iron from haematite ore :
(A) does not dissolve in molten iron.
(B) being lighter floats on the molten iron
(C) is used in cement industry and as building material.
(D) prevents the re-oxidation of molten iron.
9. Which of the following statement(s) is (are) incorrect ?
(A) In Serpeck's process silica is removed by heating the bauxite to 1800°C with coke in a current of N_2
(B) In extraction of lead from galena roasting and self reduction takes place in the same furnace but under different conditions of temperature and supply of air
(C) The tin is obtained by the carbon reduction of black tin.
(D) None
10. Parting of gold may be done with :
(A) Sulphuric acid (B) Sodium hydroxide (C) Borax (D) Chlorine (Cl_2)



11. Liquefaction process may be applied for the purification of :
 (A) copper (B) tin (C) iron (D) zinc
12. Of the following reduction processes, the correct process(es) is/are :
 (A) $\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow \text{Fe} + \text{CO}_2$ (B) $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$
 (C) $\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow \text{Cu} + \text{SO}_2$ (D) $\text{PbO} + \text{C} \longrightarrow \text{Pb} + \text{CO}$
13. ✖ Roasting of copper pyrites is done :
 (A) to remove moisture.
 (B) to oxidise free sulphur and antimony.
 (C) to convert pyrites completely into Cu_2O and FeO .
 (D) to remove volatile organic impurities.
14. ✖ Select the correct statement(s) with respect to the differences between roasting and calcination.
 (A) In roasting at higher temperature sulphide ores of the some metal like Cu, Pb, Hg etc. are reduced directly to metal but not in calcination.
 (B) Partial fusion occurs in calcination but not in roasting.
 (C) Calcination is done in limited supply of air or absence of air but in roasting supply of excess air is required.
 (D) Combustion reaction occurs in roasting but not in calcination.

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

Amongst the various ores of a metal (M) (sulphide, carbonates, oxides, hydrated or hydroxides) two ores [X] and [Y] show the following reactivity.

(i) [X] on calcination gives a black solid (S), water and a colourless gas which produces milkiness when passed through lime water. But this colourless gas does not decolourise the acidified KMnO_4 .

(ii) [X] dissolved in dilute HCl on reaction with KI gives a white precipitate (P) and iodine gas.

(iii) [Y] on roasting at high temperature gives metal (M) and a gas (G_1) which turns starch iodate solution blue.

(iv) [Y] on reaction with dilute HCl gives a white precipitate (MS) and another gas (G_2) which turns lead acetate solution black and also reacts with gas (G_1) to precipitate colloidal sulphur in presence of moisture.

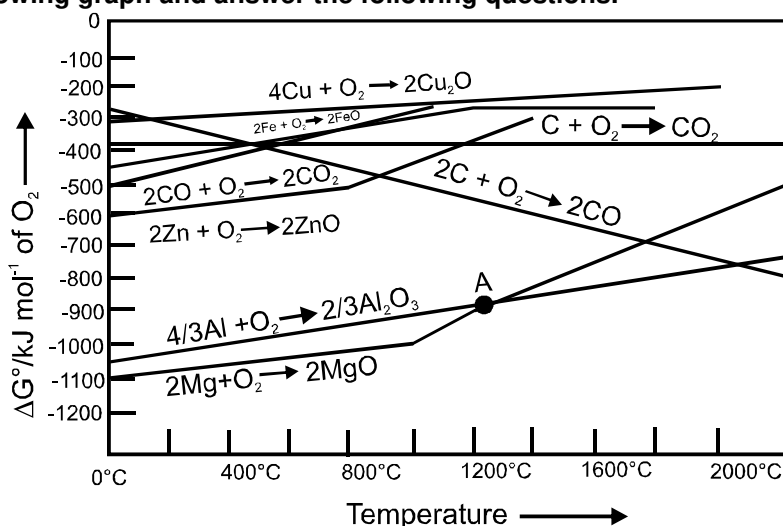
The M, S, [X] and [Y] gives greenish blue flame.

1. ✖ The metal ores [X] and [Y] are respectively :
 (A) Carbonate and sulphide ores (B) Sulphide and carbonate ores
 (C) Carbonate and hydroxide ores (D) Carbonate and oxide ores
2. ✖ Which of the following statements is correct about [Y] ?
 (A) [Y] is converted to metal (M) by self reduction.
 (B) Carbonate extract of [Y] gives yellow precipitate with suspension of CdCO_3 .
 (C) [Y] is copper glance or copper pyrite
 (D) All of these
3. The gas (G_1) acts as
 (A) oxidising agent (B) reducing agent
 (C) oxidising and reducing agent (D) fluxing agent
4. The white precipitate (P) is of :
 (A) Cu_2I_2 (B) CuI_2 (C) $\text{K}_2[\text{CuI}_4]$ (D) none
5. Identify the correct statement about [X].
 (A) It is malachite or azurite ore
 (B) Its solution in dil. HCl gives white ppt of Cu_2I_2 with KI
 (C) It on calcination gives black cupric oxide
 (D) All of these



Comprehension # 2

Read the following graph and answer the following questions.



6. At what approximate temperature, zinc and carbon have equal affinity for oxygen.
 (A) 1000°C (B) 1500°C (C) 500°C (D) 1200°C
7. To make the following reduction process spontaneous, temperature should be :
 $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}$
 (A) < 1000°C (B) > 1000°C (C) < 500°C (D) > 500°C but < 1000°C
8. Which of the following statement is true ?
 (A) In the extractive metallurgy of iron, the reduction of calcined / roasted haematite ore in blast furnace takes place in the lower temperature range as well as in the higher temperature range by carbon monoxide and carbon respectively.
 (B) The reduction of zinc oxide by carbon takes place at higher temperature than that in case of copper.
 (C) It is quite easy to reduce oxide ores of copper directly to the metal by heating with coke after 500-600K.
 (D) All of these

Comprehension # 3

Answer Q.9, Q.10 and Q.11 by appropriately matching the information given in the three columns of the following table.

The scientific and technological process used for the extraction isolation of the metal from its are is called as metallurgy. Following information is given in columns :
 Column-1 : Ore
 Column-2 : Process desirable in metallurgy.
 Column-3 : Process involved in column-II.

Column-1		Column-2		Column-3	
(I)	Copper pyrite	(i)	Dow's process	(P)	Electrolytic reduction in fused state
(II)	Bauxite	(ii)	Mac-Arthur Forrest process	(Q)	Molten $\text{MgCl}_2 + \text{CaCl}_2 + \text{NaCl}$ electrolysis
(III)	Silver argentite	(iii)	Hall-Heroult process	(R)	Molten impure aluminum + fluorides of Na^+ , Ba^{2+} and Al^{3+} electrolysis
(IV)	MgCl_2 from sea water	(iv)	Hoop's process	(S)	Complex formation and displacement by metal.

9. For Ag, the only correct combination is :
 (A) (III) (i) (S) (B) (III) (iv) (P) (C) (III) (ii) (S) (D) (III) (iii) (R)
10. Metal which is obtained from carnallite can be extracted by following combination :
 (A) (III) (iii) (R) (B) (II) (iv) (S) (C) (IV) (i) (S) (D) (IV) (i) (Q)
11. Select the only correct combination for Al :
 (A) (II) (iv) (P) (B) (II) (iii) (R) (C) (II) (iii) (S) (D) (II) (iv) (R)



Exercise-3

* Marked Questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. In the process of extraction of gold,

$$\text{Roasted gold ore} + \text{CN}^- + \text{H}_2\text{O} \xrightarrow{\text{O}_2} [\text{X}] + \text{OH}^-$$

$$[\text{X}] + \text{Zn} \longrightarrow [\text{Y}] + \text{Au}$$
 Identify the complexes [X] and [Y]. [JEE-2003(S), 3/84]
 (A) $\text{X} = [\text{Au}(\text{CN})_2]^-$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$ (B) $\text{X} = [\text{Au}(\text{CN})_4]^{3-}$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
 (C) $\text{X} = [\text{Au}(\text{CN})_2]^-$, $\text{Y} = [\text{Zn}(\text{CN})_5]^{4-}$ (D) $\text{X} = [\text{Au}(\text{CN})_4]^-$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
2. Write down the reaction involved in the extraction of lead. What is the oxidation number of lead in litharge ? [JEE-2003(M), 2/60]
3. Pb and Sn are extracted from their chief ores by : [JEE-2004(S), 3/84]
 (A) carbon reduction and self reduction.
 (B) self reduction and carbon reduction.
 (C) electrolytic reduction and self reduction.
 (D) self reduction and electrolysis.
4. Two ores A1 and A2 of a metal M show the following reactivity :

$$\begin{array}{l} \text{A1} \xrightarrow{\text{Calcination}} \text{S (black solid)} + \text{CO}_2 + \text{H}_2\text{O} \\ \text{A1} \xrightarrow[\text{(ii) KI}]{\text{(i) dil. HCl}} \text{P (precipitate)} + \text{I}_2 \end{array}$$

$$\text{A2} \xrightarrow{\text{Roasting}} \text{G (gas)} + \text{M (metal)}$$

$$\text{G} \xrightarrow{\text{Acidified K}_2\text{Cr}_2\text{O}_7 \text{ solution}} \text{green solution}$$
 Write the chemical formulae of A1, A2, S, P and G. Explain using required chemical reactions. [JEE-2004, 4/144]
5. Which of the following ore contains both Fe and Cu ? [JEE - 2005, 3/144]
 (A) Chalcopryite (B) Malachite (C) Cuprite (D) Azurite
6. Match the extraction processes listed in column-I with metals listed in column-II. [JEE - 2006, 6/184]
- | | Column-I | | Column-II |
|-----|---|-----|-----------|
| (A) | Self reduction | (p) | Lead |
| (B) | Carbon reduction | (q) | Silver |
| (C) | Complex formation and displacement by metal | (r) | Copper |
| (D) | Decomposition of iodide | (s) | Boron |
7. Extraction of zinc from zinc blende is achieved by : [JEE - 2007, 3/162]
 (A) electrolytic reduction
 (B) roasting followed by reduction with carbon
 (C) roasting followed by reduction with another metal
 (D) roasting followed by self-reduction
8. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of: [JEE - 2008, 3/163]
 (A) nitrogen (B) oxygen (C) carbon dioxide (D) argon



9. Match the conversions in Column-I with the type(s) of reaction(s) given in Column-II. [JEE-2008, 6/163]

	Column-I		Column-II
(A)	$\text{PbS} \rightarrow \text{PbO}$	(p)	Roasting
(B)	$\text{CaCO}_3 \rightarrow \text{CaO}$	(q)	Calcination
(C)	$\text{ZnS} \rightarrow \text{Zn}$	(r)	Carbon reduction
(D)	$\text{Cu}_2\text{S} \rightarrow \text{Cu}$	(s)	Self reduction

Comprehension :

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$). However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS_2). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction.

10. Partial roasting of Chalcopyrite produces : [JEE - 2010, 3/163]
 (A) Cu_2S and FeO (B) Cu_2O and FeO (C) CuS and Fe_2O_2 (D) Cu_2O and Fe_2O_2
11. Iron is removed from chalcopyrite as : [JEE - 2010, 3/163]
 (A) FeO (B) FeS (C) Fe_2O_3 (D) FeSiO_3
12. In self-reduction, the reducing species is : [JEE - 2010, 3/163]
 (A) S (B) O^{2-} (C) S^{2-} (D) SO_2
- 13.* Extraction of metal from the ore **cassiterite** involves [JEE - 2011, 4/180]
 (A) carbon reduction of an oxide ore (B) self-reduction of a sulphide ore
 (C) removal of copper impurity (D) removal of iron impurity
14. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are : [JEE - 2011, 3/180]
 (A) II, III in haematite and III in magnetite (B) II, III in haematite and II in magnetite
 (C) II in haematite and II, III in magnetite (D) III in haematite and II, III in magnetite
15. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are [JEE-2012, 3/136]
 (A) O_2 and CO respectively (B) O_2 and Zn dust respectively
 (C) HNO_3 and Zn dust respectively. (D) HNO_3 and CO respectively
16. Sulfide ores are common for the metals : [JEE(Advanced) 2013, 2/120]
 (A) Ag , Cu and Pb (B) Ag , Cu and Sn (C) Ag , Mg and Pb (D) Al , Cu and Pb
- 17.* The carbon-based reduction method is **NOT** used for the extraction of: [JEE(Advanced) 2013, 3/120]
 (A) tin from SnO_2 (B) iron from Fe_2O_3
 (C) aluminium from Al_2O_3 (D) magnesium from MgCO_3 , CaCO_3
- 18.* Upon heating with Cu_2S , the reagent(s) that give copper metal is/are: [JEE(Advanced) 2014, 3/120]
 (A) CuFeS_2 (B) CuO (C) Cu_2O (D) CuSO_4
- 19.* Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is (are): [JEE(Advanced) 2015, 4/168]
 (A) Impure Cu strip is used as cathode (B) Acidified aqueous CuSO_4 is used as electrolyte
 (C) Pure Cu deposits at cathode (D) Impurities settle as anode-mud
20. Match the anionic species given in Column-I that are present in the ore(s) given in Column-II. [JEE(Advanced) 2015, 8/168]

	Column-I		Column-II
(A)	Carbonate	(P)	Siderite
(B)	Sulphide	(Q)	Malachite
(C)	Hydroxide	(R)	Bauxite
(D)	Oxide	(S)	Calamine
		(T)	Argentite



- 21.* Extraction of copper from copper pyrite (CuFeS_2) involves [JEE(Advanced) 2016, 4/124]
 (A) crushing followed by concentration of the ore by froth-flotation
 (B) removal of iron as slag
 (C) self-reduction step to produce 'blistercopper' following evolution of SO_2
 (D) refining of 'blister copper' by carbon reduction
22. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnace such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of O_2 consumed is _____. [JEE(Advanced) 2018, 3/120]
 (Atomic weights in g mol^{-1} : O = 16, S = 32, Pb = 207)

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. Refining of impure copper with zinc impurity is to be done by electrolysis using electrodes as : [AIEEE-2002, 3/225]
- | Cathode | Anode | Cathode | Anode |
|-----------------|---------------|---------------|-------------|
| (1) pure copper | pure zinc | (2) pure zinc | pure copper |
| (3) pure copper | impure copper | (4) pure zinc | impure zinc |
2. Aluminium is extracted by the electrolysis of : [AIEEE-2002, 3/225]
 (1) alumina (2) bauxite
 (3) molten cryolite (4) alumina mixed with molten cryolite
3. The metal extracted by leaching with a cyanide is : [AIEEE-2002, 3/225]
 (1) Mg (2) Ag (3) Cu (4) Na
4. Which one of the following ores is best concentrated by froth floatation method ? [AIEEE-2004, 3/225]
 (1) magnetite (2) cassiterite (3) galena (4) malachite.
5. Heating mixture of Cu_2O and Cu_2S will give : [AIEEE-2005, 3/225]
 (1) Cu_2SO_3 (2) $\text{CuO} + \text{CuS}$ (3) $\text{Cu} + \text{SO}_3$ (4) $\text{Cu} + \text{SO}_2$
6. During the process of electro-refining of copper some metals present as impurity settle as anode mud. These are : [AIEEE-2005, 3/225]
 (1) Sn and Ag (2) Pb and Zn (3) Ag and Au (4) Fe and Ni
7. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly ? [AIEEE-2008, 3/105]
 (1) CO_2 is thermodynamically more stable than CS_2
 (2) Metal sulphides are less stable than the corresponding oxides
 (3) CO_2 is more volatile than CS_2
 (4) Metal sulphides are thermodynamically more stable than CS_2
8. Which method of purification is represented by the following equation : [AIEEE-2012, 4/120]

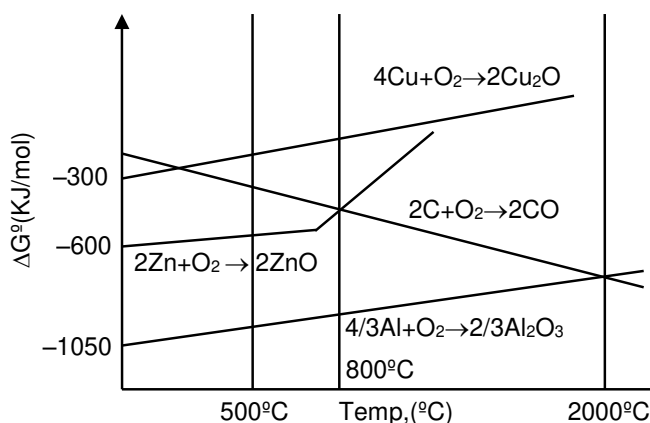
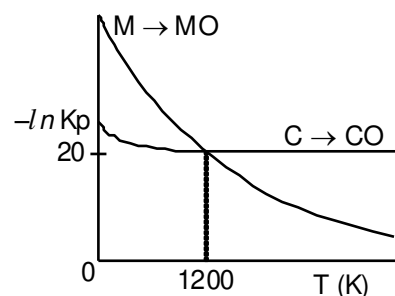
$$\text{Ti (s)} + 2\text{I}_2(\text{g}) \xrightarrow{523\text{K}} \text{TiI}_4(\text{g}) \xrightarrow{1700\text{K}} \text{Ti (s)} + 2\text{I}_2(\text{g})$$
 (1) Zone refining (2) Cupellation (3) Polling (4) Van Arkel
9. In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false? [JEE-Main 2015, 4/120]
 (1) CO and CO_2 are produced in this process
 (2) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity
 (3) Al^{3+} is reduced at the cathode to form Al
 (4) Na_3AlF_6 serves as the electrolyte
10. Which one of the following ores is best concentrated by froth floatation method? [JEE-Main 2016, 4/120]
 (1) Siderite (2) Galena (3) Malachite (4) Magnetite
11. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is : [JEE-Main 2018, 4/120]
 (1) Al (2) Fe (3) Zn (4) Ca



JEE(MAIN) ONLINE PROBLEMS

- The form of iron obtained from blast furnace is : [JEE(Main) 2014 Online (09-04-14), 4/120]
(1) Steel (2) Cast Iron (3) Pig Iron (4) Wrought Iron
- Which One of the following ores is known as Malachite : [JEE(Main) 2014 Online (19-04-14), 4/120]
(1) Cu_2O (2) Cu_2S (3) CuFeS_2 (4) $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$
- In the isolation of metals, reaction process usually results in : [JEE(Main) 2015 Online (10-04-15), 4/120]
(1) Metal sulphide (2) metal carbonate
(3) metal hydroxide (4) metal oxide
- Calamine is an ore of : [JEE(Main) 2015 Online (11-04-15), 4/120]
(1) Zinc (2) Aluminium (3) Iron (4) Copper
- The plot shows the variation of $-\ln K_p$ versus temperature for the two reactions.

$$\text{M(s)} + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{MO(s)} \quad \text{and} \quad \text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO(s)}$$
Identify the correct statement: [JEE(Main) 2016 Online (09-04-16), 4/120]
(1) At $T > 1200 \text{ K}$, carbon will reduce MO(s) to M(s) .
(2) At $T < 1200 \text{ K}$, oxidation of carbon is unfavourable.
(3) Oxidation of carbon is favourable at all temperatures.
(4) At $T < 1200 \text{ K}$, the reaction $\text{MO(s)} + \text{C(s)} \rightarrow \text{M(s)} + \text{CO(g)}$ is spontaneous.
- Extraction of copper by smelting uses silica as an additive to remove : [JEE(Main) 2016 Online (10-04-16), 4/120]
(1) FeS (2) FeO (3) Cu_2S (4) Cu_2O
- In the leaching method, bauxite ore is digested with a concentrated solution of NaOH that produces 'X'. When CO_2 gas is passed through the aqueous solution of 'X', a hydrated compound 'Y' is precipitated. 'X' and 'Y' respectively are : [JEE(Main) 2018 Online (15-04-18), 4/120]
(1) NaAlO_2 and $\text{Al}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ (2) $\text{Al}(\text{OH})_3$ and $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
(3) $\text{Na}[\text{Al}(\text{OH})_4]$ and $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (4) $\text{Na}[\text{Al}(\text{OH})_4]$ and $\text{Al}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$
- In the extraction of copper from its sulphide ore, metal is finally obtained by the oxidation of cuprous sulphide with : [JEE(Main) 2018 Online (16-04-18), 4/120]
(1) SO_2 (2) Fe_2O_3 (3) Cu_2O (4) CO
- The ore that contains both iron and copper is : [JEE(Main) 2019 Online (09-01-19), 4/120]
(1) azurite (2) copper pyrites (3) malachite (4) dolomite
- The correct statement regarding the given Ellingham diagram is: [JEE(Main) 2019 Online (09-01-19), 4/120]



[JEE(Main) 2019 Online (09-01-19), 4/120]

- At 1400°C , Al can be used for the extraction of Zn from ZnO
- Coke cannot be used for the extraction of Cu from Cu_2O
- At 800°C , Cu can be used for the extraction of Zn from ZnO
- At 500°C , coke can be used for the extraction of Zn from ZnO



11. Hall-Heroult's process is given by : [JEE(Main) 2019 Online (10-01-19), 4/120]
 (1) $2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$ (2) $\text{Cu}^{+2}(\text{aq}) + \text{H}_2(\text{g}) \rightarrow \text{Cu}(\text{s}) + 2\text{H}^+(\text{aq})$
 (3) $\text{ZnO} + \text{C} \xrightarrow{\text{Coke, 1673 K}} \text{Zn} + \text{CO}$ (4) $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$
12. Match the ores (column A) with the metals (column B) : [JEE(Main) 2019 Online (11-01-19), 4/120]

(Column A) Ores	(Column B) Metals
(I) Siderite	(a) Zinc
(II) Kaolinite	(b) Copper
(III) Malachite	(c) Iron
(IV) Calamine	(d) Aluminium

 (1) (I) \rightarrow (c); (II) \rightarrow (d); (III) \rightarrow (b); (IV) \rightarrow (a)
 (2) (I) \rightarrow (b); (II) \rightarrow (c); (III) \rightarrow (d); (IV) \rightarrow (a)
 (3) (I) \rightarrow (c); (II) \rightarrow (d); (III) \rightarrow (a); (IV) \rightarrow (b)
 (4) (I) \rightarrow (a); (II) \rightarrow (b); (III) \rightarrow (c); (IV) \rightarrow (d)
13. The reaction that does NOT define calcination is : [JEE(Main) 2019 Online (11-01-19), 4/120]
 (1) $\text{CaCO}_3 \cdot \text{MgCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{MgO} + 2\text{CO}_2$
 (2) $2\text{Cu}_2\text{S} + 3\text{O}_2 \xrightarrow{\Delta} 2\text{Cu}_2\text{O} + 2\text{SO}_2$
 (3) $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O} \xrightarrow{\Delta} \text{Fe}_2\text{O}_3 + \text{XH}_2\text{O}$
 (4) $\text{ZnCO}_3 \xrightarrow{\Delta} \text{ZnO} + \text{CO}_2$
14. In the Hall-Heroult process, aluminium is formed at the cathode. The cathode is made out of : [JEE(Main) 2019 Online (12-01-19), 4/120]
 (1) Carbon (2) Copper (3) Pure aluminium (4) Platinum
15. The pair that does NOT require calcination is : [JEE(Main) 2019 Online (12-01-19), 4/120]
 (1) ZnO and MgO (2) ZnCO_3 and CaO
 (3) Fe_2O_3 and $\text{CaCO}_3 \cdot \text{MgCO}_3$ (4) ZnO and $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$



Answers

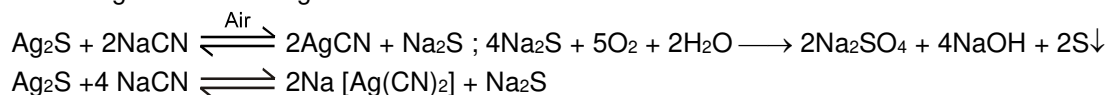
EXERCISE - 1

PART - I

- A-1.** This method is commonly used for the concentration of low grade sulphide ores like. ZnS , Cu_2S , PbS .
- A-2.** Substances which are used to prevent certain type of particles, from forming the froth with the bubbles by complexation.
- A-3.** By magnetic separation as wolframite ($\text{FeWO}_4 + \text{MnWO}_4$) has magnetic property.
- A-4.** Copper, Lead, Mercury etc.
- A-5.** By heating in a current of dry hydrogen chloride gas.
- A-6.** Stabiliser like cresol and aniline tend to stabilise the froth (i.e. the froth last for longer period).
- B-1.** All three oxidation curves for the carbon system lie above that for oxidation of zinc, until a temperature of approximately 1000°C is reached. At this point, C is thermodynamically capable of reducing ZnO to Zn. Since this temperature is greater than the boiling point of Zn (907°C), it will be formed as a vapour. The overall equation for reduction is, $\text{ZnO(s)} + \text{C(s)} \longrightarrow \text{Zn(g)} + \text{CO(g)}$.
- B-2.** When the temperature is raised a point will be reached where the graph crossed the $\Delta G = 0$ line. Below this temperature the free energy of formation of oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of the oxide is positive, and the oxide becomes unstable and should decompose into metal and oxygen. This explains why HgO , for instance, decomposes spontaneously into its elements when heated.
- B-3.**
- | | |
|--|---|
| $\text{CuO} + \text{H}_2 \longrightarrow \text{Cu} + \text{H}_2\text{O}$ | $\text{CuO} + \text{C} \longrightarrow \text{Cu} + \text{CO}$ |
| $\Delta G_f^\circ = -237.2 - (-129.7)$ | $\Delta G_f^\circ = -137.2 - (-129.7)$ |
| $\Delta G_f^\circ = -107.9 \text{ kJ}$ | $\Delta G_f^\circ = -7.5 \text{ kJ}$ |
- So, reduction of CuO is quite feasible with H_2 than C.
- C-1.** Oxide of Pb and Hg are unstable while that of zinc is stable towards heat, therefore, oxides of mercury and lead are reduced by their respective sulphides to the corresponding metals but zinc oxide does not.
- C-2.** MgO acts as a basic flux and removes certain acidic impurities present in steel in the form of slag.
 $\text{MgO} + \text{SiO}_2 \longrightarrow \text{MgSiO}_3$; $3\text{MgO} + \text{P}_2\text{O}_5 \longrightarrow \text{Mg}_3(\text{PO}_4)_2$
- C-3.** It will combine with tin to form calcium stannate.
- C-4.** $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3(\text{slag})$; $\text{PbO} + \text{SiO}_2 \longrightarrow \text{PbSiO}_3$
 CaO converts the PbSiO_3 to PbO , $\text{PbSiO}_3 + \text{CaO} \longrightarrow \text{PbO} + \text{CaSiO}_3$, and also prevents the formation of PbSO_4 .
- C-5.** It reduces ZnO to Zn and also reduces CO_2 to CO which is used as a fuel.
- C-6.** Remove the infusible impurities of silica as slag
 $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$; $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3(\text{slag})$
 formed CO_2 reacts with carbon and form CO which works as reducing agent
 $\text{CO}_2 + \text{C} \longrightarrow 2\text{CO}$
- C-7.** Silica removes iron oxide impurity remaining in the matte by forming silicate, FeSiO_3 .



- D-1.** Na_2S is oxidised to Na_2SO_4 in the presence of air and thus equilibrium is shifted in the forward direction according to the following reactions.



- D-2.** As they have low ionisation energies and are more electropositive elements, they themselves act as strong reducing agent.
- D-3.** To lower the melting point and increase conductivity of the mixture.
- E-1.** (A) liquation process, (B) fractional distillation process,
(C) zone refining method and (D) chromatographic methods.
- E-2.** This method is used for the purification of those impure metals which contain their own oxides as one of the impurities. This process is used for the purification of copper and tin.
- E-3.** Ni, Zr, Ti etc.

PART - II

- | | | | | |
|-----------------|-----------------|-----------------|-----------------|------------------|
| A-1. (A) | A-2. (C) | A-3. (C) | A-4. (B) | A-5. (B) |
| A-6. (C) | A-7. (D) | A-8. (C) | A-9. (B) | A-10. (C) |
| B-1. (A) | B-2. (A) | B-3. (A) | C-1. (A) | C-2. (C) |
| C-3. (B) | C-4. (C) | C-5. (D) | D-1. (C) | D-2. (A) |
| D-3. (C) | D-4. (C) | D-5. (C) | E-1. (D) | E-2. (A) |
| E-3. (C) | E-4. (C) | E-5. (D) | E-6. (D) | E-7. (D) |
| E-8. (C) | | | | |

PART - III

- | | |
|--|--|
| 1. (A \rightarrow p,r); (B \rightarrow p,r); (C \rightarrow q); (D \rightarrow s) | 2. (A \rightarrow r,t); (B \rightarrow q,s); (C \rightarrow t); (D \rightarrow p); (E \rightarrow q). |
| 3. (A \rightarrow q,s); (B \rightarrow r); (C \rightarrow s); (D \rightarrow p) | 4. (A \rightarrow p,q,s); (B \rightarrow p); (C \rightarrow r,s); (D \rightarrow r,s) |

EXERCISE - 2

PART - I

- | | | | | |
|----------------|----------------|----------------|----------------|----------------|
| 1. (B) | 2. (C) | 3. (C) | 4. (A) | 5. (B) |
| 6. (C) | 7. (D) | 8. (B) | 9. (D) | 10. (C) |
| 11. (A) | 12. (B) | 13. (A) | 14. (C) | 15. (C) |
| 16. (A) | 17. (C) | 18. (D) | 19. (C) | 20. (D) |
| 21. (D) | | | | |

**PART - II**

- | | | | |
|--------------------|-------------------------------|-------------------------|-------------------------|
| 1. 3 (ii, iii, iv) | 2. 75 | 3. 4 (i, ii, iii & vii) | 4. 4 (i, ii, iii, viii) |
| 5. 3 (Hg, Cu, Pb) | 6. 6 (Li, Ba, Na, Al, Ca, Mg) | 7. 2 | |
| 8. 4 (a, b, e, f) | 9. 7 (except 8) | 10. 16 | 11. 65 |
| 12. 39 | | | |
| 13. 60 | 14. 5 (v, vi, viii, ix) | | |

PART - III

- | | | | | |
|----------|------------|-----------|----------|----------|
| 1. (BC) | 2. (BCD) | 3. (ABC) | 4. (AC) | 5. (ABD) |
| 6. (ABC) | 7. (ABC) | 8. (ABCD) | 9. (D) | 10. (AD) |
| 11. (BD) | 12. (ABCD) | 13. (ABD) | 14. (AC) | |

PART - IV

- | | | | | |
|---------|--------|--------|--------|---------|
| 1. (A) | 2. (D) | 3. (C) | 4. (A) | 5. (D) |
| 6. (A) | 7. (B) | 8. (D) | 9. (C) | 10. (D) |
| 11. (D) | | | | |

EXERCISE - 3**PART - I**

- | | | |
|---|--|--|
| 1. (A) | 2. O.N. is +2, litharge is PbO. | 3. (B) |
| 4. $A1 = \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ or $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$; $A2 = \text{Cu}_2\text{S}$; $S = \text{CuO}$; $P = \text{Cu}_2\text{I}_2$; $G = \text{SO}_2$ | | |
| 5. (A) | 6. (A - p,r), (B - p), (C - q), (D - s). | 7. (B) |
| 8. (B) | | |
| 9. (A - p); (B - q); (C - p,r); (D - p, s) | 10. (A) | 11. (D) |
| 12. (C) | | |
| 13.* (AD) | 14. (D) | 15. (B) |
| 16. (A) | 17.* (CD) | |
| 18.* (BCD) | 19.* (BCD) | 20. (A - P,Q,S); (B - T); (C - Q,R); (D - R) |
| 21.* (ABC) | | |
| 22. 6.47 kg | | |

PART - II**JEE(MAIN) OFFLINE PROBLEMS**

- | | | | | |
|---------|--------|--------|--------|---------|
| 1. (3) | 2. (4) | 3. (2) | 4. (3) | 5. (4) |
| 6. (3) | 7. (3) | 8. (4) | 9. (4) | 10. (2) |
| 11. (1) | | | | |

JEE(MAIN) ONLINE PROBLEMS

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (3) | 2. (4) | 3. (4) | 4. (1) | 5. (4) |
| 6. (2) | 7. (3) | 8. (3) | 9. (2) | 10. (1) |
| 11. (1) | 12. (1) | 13. (2) | 14. (1) | 15. (1) |



Additional Problems for Self Practice (APSP)

➤ Marked questions are recommended for Revision.

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.

Max. Marks : 120

Important Instructions

1. The test is of **1 hour** duration.
2. The Test Booklet consists of **30** questions. The maximum marks are **120**.
3. Each question is allotted **4 (four)** marks for correct response.
4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. $\frac{1}{4}$ (**one fourth**) marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
5. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

1. The rocky and silicious matter associated with an ore is called :
(1) slag (2) mineral (3) matrix or gangue (4) flux
2. The process of removing lighter gangue particles by washing in a current of water is called :
(1) levigation (2) liquation (3) leaching (4) cupellation.
3. Gravity separation method is based upon :
(1) preferential washing of ores and gangue particles.
(2) difference in densities of ore particles and impurities.
(3) difference in chemical properties of ore particles and impurities.
(4) none of these.
4. In the froth floatation process for the purification of minerals the particles float because :
(1) they are light. (2) they are insoluble.
(3) their surface is preferentially wetted by oil. (4) they bear an electrostatic charge.
5. An ore of tin containing FeCr_2O_4 is concentrated by :
(1) magnetic separation (2) froth floatation
(3) leaching method (4) gravity separation.
6. ➤ Process of heating ore in air to remove sulphur is :
(1) calcination (2) roasting (3) smelting (4) none of these.
7. ➤ In roasting :
(1) moisture is removed. (2) non-metals as their volatile oxide are removed.
(3) ore becomes porous. (4) all the above.
8. Which one of the following reactions is an example of calcination process ?
(1) $2\text{Ag} + 2\text{HCl} + [\text{O}] \rightarrow 2\text{AgCl} + \text{H}_2\text{O}$ (2) $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$.
(3) $2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2$ (4) $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$.
9. ➤ Roasting is carried out in case of :
(1) galena (2) iron pyrites (3) copper glance (4) all.
10. Slag is a product of :
(1) flux and coke. (2) coke and metal oxide.
(3) flux and impurities. (4) metal and flux.
11. An ore after levigation is found to have basic impurities. Which of the following can be used as flux during smelting ?
(1) H_2SO_4 (2) CaCO_3 (3) SiO_2 (4) Both CaO and SiO_2 .



12. Among the following statements, the incorrect one is :
 (1) calamine and siderite are carbonates (2) argentite and cuprite are oxides
 (3) zinc blende and iron pyrites are sulphides (4) malachite and azurite are ores of copper
13. Electrolytic reduction method is used in the extraction of :
 (1) highly electronegative elements. (2) highly electropositive elements.
 (3) transition metals. (4) noble metals.
14. Which one of the following metals cannot be extracted by carbon reduction ?
 (1) Pb (2) Fe (3) Zn (4) Al.
15. Among the following groups of oxides, the group that cannot be reduced by carbon to give the respective metals.
 (1) Cu_2O , SnO_2 (2) Fe_2O_3 , ZnO (3) CuO , K_2O (4) PbO , FeO .
16. The process of bringing the metal or its ore into solution by the action of a suitable chemical reagent followed by extraction of the metal either by electrolysis or by a suitable precipitating agent i.e. more electropositive metal is called :
 (1) electrometallurgy (2) hydrometallurgy
 (3) electro-refining (4) zone refining.
17. Cryolite is :
 (1) Na_3AlF_6 and is used in the electrolysis of alumina for decreasing electrical conductivity.
 (2) Na_3AlF_6 and is used in the electrolysis of alumina for lowering the melting point of alumina.
 (3) Na_3AlF_6 and is used in the electrolytic purification of alumina.
 (4) Na_3AlF_6 and is used in the electrolysis of alumina for increasing the melting point and electrical conductivity.
18. In the extraction of Cu the reaction takes place in Bessemer converter is :
 (1) $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$ (2) $2\text{CuFeS}_2 + \text{O}_2 \rightarrow \text{Cu}_2\text{S} + \text{FeS} + \text{SO}_2$
 (3) $2\text{Cu}_2\text{S} + 3\text{O}_2 \rightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$ (4) $2\text{FeS} + 3\text{O}_2 \rightarrow 2\text{FeO} + 2\text{SO}_2$
19. Which of the following statement is incorrect about the extractive metallurgy of copper ?
 (1) Matte chiefly consists of iron sulphide and some ferrous oxide.
 (2) The impurity of iron sulphide is removed as fusible slag, FeSiO_3 during roasting.
 (3) The copper pyrite is concentrated by froth floatation process.
 (4) Copper is obtained by self reduction in bessemer converter.
20. Van Arkel method of purification of metals involves converting the metal to :
 (1) volatile stable compound. (2) volatile unstable compound.
 (3) non-volatile stable compound. (4) none of these.
21. Copper and tin are refined by :
 (1) liquation (2) cupellation (3) bessemerisation (4) poling.
22. The process of zone refining is used for :
 (1) silicon (2) germanium (3) gallium (4) all the above.
23. Tin and zinc can be refined by :
 (1) cupellation (2) liquation (3) poling (4) bessemerisation.
24. Match column I with column II and select the correct answer using the codes given below the lists :

	Column I		Column II
I.	Cyanide process.	(a)	Ultra pure Ge
II.	Froth floatation process.	(b)	Pine oil.
III.	Electrolytic reduction.	(c)	Extraction of Al.
IV.	Zone refining.	(d)	Extraction of Au.



Code :

(1) I-(c), II-(a), III-(d), IV-(b)

(2) I-(d), II-(b), III-(c), IV-(a)

(3) I-(c), II-(b), III-(d), IV-(a)

(4) I-(d), II-(a), III-(c), IV-(b)

25. Match the ores listed in column-I with the type of ores listed in column-II and select the correct alternate.

	Column-I		Column-II
(a)	Limonite.	(p)	Carbonate ore.
(b)	Argentite.	(q)	Halide ore.
(c)	Carnallite	(r)	Sulphide ore.
(d)	Calamine.	(s)	Oxide ore.

Code :

- (a) (b) (c) (d) (a) (b) (c) (d)
 (1) (s) (r) (q) (p) (2) (p) (s) (q) (r)
 (3) (p) (q) (r) (s) (4) (s) (r) (p) (q)

26. Match the method of concentration of the ore in column I with the ore in column II and select the correct alternate.

	Column I		Column II
(a)	Leaching.	(p)	Copper pyrite.
(b)	Calcination.	(q)	Siderite.
(c)	Froth floatation.	(r)	Bauxite.
(d)	Magnetic separation.	(s)	Chromite.

Code :

- (a) (b) (c) (d) (a) (b) (c) (d)
 (1) (s) (q) (p) (r) (2) (r) (q) (p) (s)
 (3) (p) (q) (r) (s) (4) (q) (r) (p) (s).

27. Match the extraction process listed in column I with metals listed in column II and choose the correct option.

	Column I		Column II
(a)	Self reduction.	(p)	Copper from copper glance
(b)	Carbon and carbon monoxide reduction.	(q)	Silver from argentite.
(c)	Electrolytic reduction in fused state.	(r)	Aluminium from bauxite.
(d)	Complex formation and displacement by metal.	(s)	Iron from haematite.

Code :

- (a) (b) (c) (d) (a) (b) (c) (d)
 (1) (p) (s) (r) (q) (2) (p) (r) (s) (q)
 (3) (s) (p) (r) (q) (4) (p) (r) (s) (q)

28. The iron obtained from the blast furnace is called :

(1) pig iron (2) cast iron (3) wrought iron (4) steel

29. The extraction of zinc from zinc blende involves :

- (1) the electrolytic reduction.
 (2) the roasting followed by reduction with carbon.
 (3) the calcination followed by reduction with another metal.
 (4) the roasting at molten temperature.

30. Carbon cannot be used in the reduction of Al_2O_3 because :

- (1) it is non-metal
 (2) the heat of formation of CO_2 is more than that of Al_2O_3
 (3) pure carbon is not easily available
 (4) the heat of formation of Al_2O_3 is too high



Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

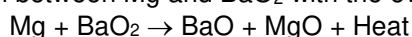
- Which of the following metal is extracted by thermal reduction process : [NSEC-2000]
(A) Al (B) Fe (C) Cu (D) Mg
- In the gold plating process, sodium cyanide solution is used as an electrolyte instead of nitric acid because [NSEC-2003]
(A) cyanide forms a complex with gold and thus helps uniform deposition of gold.
(B) sodium cyanide is a better solvent for gold ions.
(C) cyanide binds with impurity ions and keeps the impurities in solution.
(D) deposition of gold from nitric acid bath is slow.
- Goldsmiths use borax while making gold jewelry. They heat the mixture of a gold sample and borax on a flame, through which air is passed using a blow pipe because [NSEC-2003]
(A) heat and air convert the impurities into their oxides that react with molten borax forming a slag which can be separated from gold
(B) gold oxide formed by heat and air gets reduced by borax to pure gold
(C) air increases the heating temperature at which gold dissolves in borax, and on cooling gets recrystallised in pure form
(D) borax reduces the hardness of gold at high temperature so that it can be stretched to form jewelry easily.
- High purity germanium is obtained by a technique that is based on [NSEC-2004]
(A) fractional distillation (B) recrystallization
(C) fractional crystallisation (D) diffusion.
- The metal that cannot be displaced from its aqueous solution by zinc is [NSEC-2004]
(A) Cu (B) Ag (C) Al (D) Hg.
- Stainless steel contains iron along with [NSEC-2006]
(A) Cr + Cu + C (B) Ni + Zn + Cr (C) Cr + Ni + C (D) Ni + Cu + Mn.
- Sapphire is a mineral of : [NSEC-2008]
(A) Cu (B) Zn (C) Al (D) Mg
- Van Arkel method of purification of metals involves converting the metal to a [NSEC-2013]
(A) Volatile compound (B) Volatile unstable compound
(C) Non-volatile stable compound (D) Non-volatile unstable compound
- Out of the following metal extraction processes, those in which carbon – based reduction methods are not used are [NSEC-2014]
(I) Sn from SnO_2 (II) Fe from Fe_2O_3 (III) Al from Al_2O_3 (IV) Mg from $\text{MgCO}_3 \cdot \text{CaCO}_3$
(A) (I) and (IV) (B) (II) and (III) (C) (III) and (IV) (D) (II) and (IV)



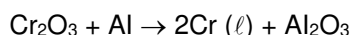
10. Aluminium and copper are extracted from their oxide and sulphide ores respectively. Which of the following is correct? [NSEC-2018]
- Copper is extracted by the auto reduction of copper oxide by copper sulphide
 - Aluminium cannot be obtained by chemical reduction due to its strong affinity for oxygen
 - In electrometallurgy of Al, graphite is used as cathode to avoid reoxidation of Al into Al_2O_3 by preventing formation of O_2 .
 - Sulphide ores of copper are difficult to be reduced than the oxide ores
- (A) I, II, IV (B) II and III (C) II and III (D) II and IV

PART - III : ADDITIONAL THEORY

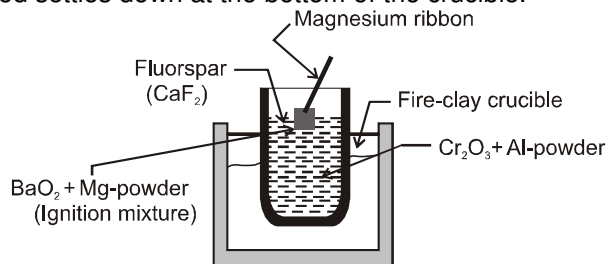
Cr_2O_3 is mixed with requisite amount of Al-powder (this mixture is called thermite mixture) and is placed in a large fire-clay crucible. An intimate mixture of Na_2O_2 or BaO_2 and Mg powder (called *ignition mixture* or *igniter*) is placed in a small depression made in the thermite mixture. The crucible is surrounded by sand which prevents the loss of heat by radiation. A piece of Mg ribbon is struck into the ignition mixture and the charge is covered by a layer of fluorspar (CaF_2) which acts as a heat insulator. Now Mg-ribbon is ignited so that ignition mixture catches fire and flame is produced, leading to a violent reaction between Mg and BaO_2 with the evolution of large amount of heat.



Heat produced in the above reaction makes Cr_2O_3 and Al-powder react together.



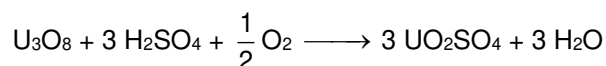
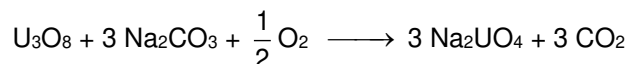
Molten Cr-metal formed settles down at the bottom of the crucible.



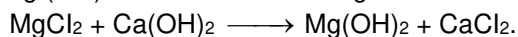
Reduction of Cr_2O_3 by Al-powder (Aluminothermic process).

An application of aluminothermic process has been used for joining the broken pieces of iron (welding). In this process thermite mixture consisting of Fe_2O_3 and Al-powder in 3 : 1 ratio is placed in a funnel shaped crucible lined internally with magnesite and having a plug hole at its bottom. The thermite mixture is covered with a mixture of BaO_2 plus Mg-powder (ignition mixture) in which a piece of Mg ribbon is inserted. The ends of the iron pieces to be welded are thoroughly cleaned and surrounded by a fire-clay mould. When Mg ribbon is ignited, ignition mixture catches fire and Fe_2O_3 gets reduced to Fe by Al-powder.

Leaching pitch blends with H_2SO_4 or sodium carbonate to dissolve uranium:



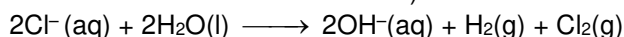
Precipitation of $\text{Mg}(\text{OH})_2$ from sea water using lime solution :



Oxidation Reduction :

Besides reductions, some extractions are based on oxidation particularly for non-metals.

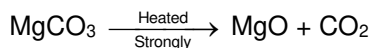
(a) A very common example of extraction based on oxidation is the extraction of chlorine from brine (chlorine is abundant in sea water as common salt).



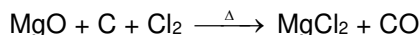
The ΔG° for this reaction is + 422 kJ. When it is converted to E° (using $\Delta G^\circ = -nE^\circ F$), we get $E^\circ = -2.2$ V. Naturally, it will require an external e.m.f. that is greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions. Thus, Cl_2 is obtained by electrolysis giving out H_2 and aqueous NaOH as by-products. Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH .



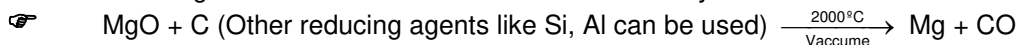
From Magnesite : The concentrated ore is calcined at higher temperature



The calcined ore is heated with coke in a current of dry chlorine gas.



The magnesium chloride is fused and then electrolysed.



PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 66

Important Instructions

A. General :

1. The test is of 1 hour duration.
2. The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format :

3. Each part consists of five sections.
4. Section-1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5. Section-2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6. Section-3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
7. Section-4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8. Section-5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme :

9. For each question in Section-1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.
10. For each question in Section-2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
11. For each question in Section-3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

This section contains 7 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

1. Give the correct order of initials **T** or **F** for following statements. Use **T** if statement is true and **F** if it is false.
 - (i) In Gold Schmidt thermite process aluminium acts as a reducing agent.
 - (ii) Mg is extracted by electrolysis of aqueous solution of MgCl_2
 - (iii) Extraction of Pb is possible by carbon reduction of PbO in smelting.
 - (iv) Red bauxite is purified by Serpeck's process
 (A) T T T F (B) T F F T (C) F T T T (D) T F T F
2. Leaching of Ag_2S is carried out by heating it with a dilute solution of :
 (A) NaCN only (B) HCl (C) NaOH (D) NaCN in presence of O_2
3. In which of the following pair of metals, both are commercially extracted from their respective ores by self reduction method ?
 (A) Zn, Cu (B) Pb, Cu (C) Sn, Zn (D) Al, Ag



4. Consider the following isolation / purification processes.
 (I) Heating impure metal with I_2 at $150-200^\circ\text{C}$ and passing the resulting volatile iodide on hot tungsten filament at 1400°C to get the pure metal.
 (II) Heating the sulphide ore in air until a part is converted to oxide and then further heating in the absence of air to let the oxide react with unchanged metal sulphide to get the metal.
 (III) Electrolysis of the molten electrolyte containing metal oxide and cryolite or florspar to obtain the metal.
 The processes used for obtaining aluminium, titanium and lead are respectively :
 (A) (I), (II) and (III) (B) (II), (III) and (I)
 (C) (III), (I) and (II) (D) (II), (I) and (III)
5. Consider the following statements :
 S_1 : In extraction of iron from haematite ore, the reduction reactions take place only in the lower temperature range in the blast furnace.
 S_2 : Calamine is an carbonate ore of zinc.
 S_3 : The principal ore of aluminium, bauxite, usually contains silica, iron oxides and titanium oxide as impurities.
 S_4 : Solidified copper obtained from silica lined convertor (Bessemer converter) has blistered appearance due to the evolution of SO_2 .
 and arrange in the order of true/false.
 (A) F T T T (B) F T F F (C) F F T T (D) T F F T
6. In the extraction of aluminium
 Process X : employed for red bauxite to remove iron oxide (main impurity)
 Process Y : (Serpeck's process) : used for white bauxite to remove Z (main impurity) then,
 Select correct option for the process X and impurity Z.
 (A) X = Hall and Heroult's process and Z = SiO_2
 (B) X = Bayer's process and Z = SiO_2
 (C) X = Serpeck's process and Y = iron oxide
 (D) X = Bayer's process and Y = iron oxide
7. Which of the following metals may be present in the anode mud during electrorefining of copper?
 I. Gold ; II. Iron, III. Silver ; IV Magnesium
 (A) I and II (B) II and IV (C) I and III (D) III and IV

Section-2 : (One or More than one options correct Type)

This section contains 5 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

8. Select the correct statement :
 (A) Dolomite contains both magnesium and calcium.
 (B) Extraction of lead from galena involves roasting in limited supply of air at moderate temperature followed by self reduction at higher temperature (to melt the charge).
 (C) Extraction of zinc from zinc blende involves roasting followed by reduction with carbon.
 (D) The chemical composition of 'slag' formed during the extraction of iron and copper is FeSiO_3 .
9. The reaction(s) which does (do) not occur in the reduction zone in the extraction of iron from haematite ore is (are) :
 (A) $\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2$ (B) $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$
 (C) $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$ (D) $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$
10. Which of the following is a correct statement ?
 (A) Calamine is the ore of zinc. (B) Proustite is the ore of silver.
 (C) Cassiterite is the ore of tin. (D) Diaspore is the ore of aluminium.



11. Froth floatation :
 (A) is a physical method of separating mineral from the gangue
 (B) is a method of concentration of ore depending on the difference in wetability of gangue and the ore particles.
 (C) is used for the concentration of sulphide ores
 (D) is a method in which impurities sink to the bottom and ore particles pass on to the surface with froth.
12. Which of the following reduction reactions are actually employed in commercial extraction of metals?
 (A) $\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$
 (B) $\text{Cr}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$
 (C) $2\text{Na}[\text{Au}(\text{CN})_2] + \text{Zn} \rightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Au}$
 (D) $\text{Cu}_2\text{S} + 2\text{CuO} \rightarrow 6\text{Cu} + \text{SO}_2$

Section-3 : (One Integer Value Correct Type.)

This section contains 6 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

13. The minimum potential difference needed to reduce Al_2O_3 at 500°C is :
 The reaction for decomposition is :

$$\frac{2}{3} \text{Al}_2\text{O}_3 \longrightarrow \frac{4}{3} \text{Al} + \text{O}_2 \quad \Delta G = + 960 \text{ kJ at } 500^\circ\text{C}.$$

 (Report your answer as potential difference $\times 2$)
14. How many of the following minerals are oxides of metals/metalloids.
 (i) Bauxite (ii) Corundum (iii) Dolomite
 (iv) Malachite (v) Magnetite (vi) Pyrolucite
 (vii) Argentite (viii) Horn silver (ix) Quartz
 (x) Cryolite (xi) Siderite (xii) Zincite
 (xiii) Calamine (xiv) Syline (xv) Carnellite
15. Calculate number of metals which can be extracted by self reduction method –
 Cu, Al, Fe, Mg, Zn, Sb, Sn, Pb
16. Poling process is applied when impurity is a compound of a metal and a non-metal. Atomic number of non-metal is
17. How many of following metals can be purified by electro refining by using metal as impure anode.
 Cu, Al, Pb, Sn, Ag, Zn, Ca, Mg
18. How many of the following refining processes are correctly matched with their element ?
 Liquation-Tin, Fractional distillation-Zinc, Zone refining-Germanium, Poling-Tin, Van Arkel-Titanium, Cupellation-Silver.

SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 19 to 21

Metallic gold frequently is found in aluminosilicate rocks and it is finely dispersed among other minerals. It may be extracted by treating the crushed rock with aerated sodium cyanide solution. During this process metallic gold is slowly converted to $[\text{Au}(\text{CN})_2]^-$, which is soluble in water. After equilibrium has been reached, the aqueous phase is pumped off and the metallic gold is recovered from it by reacting the gold complex with zinc, which is converted to $[\text{Zn}(\text{CN})_4]^{2-}$. Gold in nature is frequently alloyed with silver which is also oxidised by aerated sodium cyanide solution.



19. The correct ionic reaction for the process are
 (A) $4\text{Au} + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 (\text{air}) \rightarrow 4[\text{Au}(\text{CN})_2]^- (\text{soluble}) + 4\text{OH}^-$
 (B) $\text{Au} + 2\text{CN}^- \rightarrow \text{Au}[(\text{CN})_2]^-$
 (C) $\text{Zn} + 2\text{CN}^- \rightarrow \text{Zn}[(\text{CN})_2]^-$
 (D) $\text{Zn} + 4\text{CN}^- \rightarrow \text{Zn}[(\text{CN})_4]^{2-}$
20. There have been several efforts to develop alternative gold extraction processes which could replace this one. Why ?
 (A) Sodium cyanide solutions corrode mining machinery
 (B) Sodium cyanide escapes into ground water and produces hydrogen cyanide which is toxic to many animals.
 (C) Gold obtained by this process is not pure.
 (D) The amount of gold in aluminosilicate rocks is very less.
21. The process described above in the passage is represents :
 (A) ore concentration (B) pyrometallurgical extraction
 (C) hydrometallurgical extraction (D) purification of metal

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct.

22. Match the name of the processes given in **column-I** with type(s) of metallurgical methods given in **column-II**.

	Column – I		Column – II
(P)	Hall–Heroult process	(1)	Molten $\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6$ electrolysis.
(Q)	Dow's sea water process	(2)	Molten $\text{MgCl}_2 + \text{CaCl}_2 + \text{NaCl}$ electrolysis.
(R)	Hoop's process	(3)	Molten impure aluminium + fluorides of Na^+ , Ba^{2+} and Al^{3+} electrolysis.
(S)	Mac-Arthur Forrest process	(4)	Complex formation and displacement method.

Code :

	P	Q	R	S		P	Q	R	S
(A)	4	2	3	1	(B)	1	2	4	3
(C)	2	1	3	4	(D)	1	2	3	4

Practice Test-2 (IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22								
Ans.										



APSP Answers

PART - I

1. (3)	2. (1)	3. (2)	4. (3)	5. (1)
6. (2)	7. (4)	8. (4)	9. (4)	10. (3)
11. (3)	12. (2)	13. (2)	14. (4)	15. (3)
16. (2)	17. (2)	18. (1)	19. (1)	20. (2)
21. (4)	22. (4)	23. (2)	24. (2)	25. (1)
26. (2)	27. (1)	28. (1)	29. (2)	30. (4)

PART - II

1. (B)	2. (A)	3. (A)	4. (C)	5. (C)
6. (C)	7. (C)	8. (B)	9. (C)	10. (A)

PART - IV

1. (D)	2. (D)	3. (B)	4. (C)	5. (A)
6. (B)	7. (C)	8. (ABC)	9. (CD)	10. (ABCD)
11. (ABCD)	12. (BCD)	13. 5	14. 06	15. 3
16. 8	17. 08	18. 6	19. (A)	20. (B)
21. (C)	22. (D)			

APSP Solutions

PART - I

- The rocky and silicious impurities associated with an ore is called matrix or gangue.
- Lighter gangue particles are washed in a current of water by a process called levigation. In levigation the powdered ore is agitated with water or washed with an upward stream of running water, the lighter particles of sand, clay etc are washed away leaving behind heavier ore particles.
- Hydraulic washing or Gravity separation or Levigation method is based on the difference in the densities of the gangue and ore particles.
- This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb); copper pyrites CuFeS_2 (ore of copper); zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil.
- An ore of tin containing FeCr_2O_4 is concentrated by magnetic separation as FeCr_2O_4 is ferromagnetic.
- Roasting is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or O_2 below its melting point. During roasting impurities of As, Sb, P and S escape as their volatile oxides.

$$\text{S(s)} + \text{O}_2\text{(g)} \longrightarrow \text{SO}_2\text{(g)}$$
- Roasting removes easily oxidisable volatile impurities like arsenic (as As_2O_3), sulphur (as SO_2), phosphorus (as P_4O_{10}) and antimony (as Sb_2O_3).

$$4\text{M (M = As, Sb)} + 3\text{O}_2 \longrightarrow 2\text{M}_2\text{O}_3 \uparrow$$

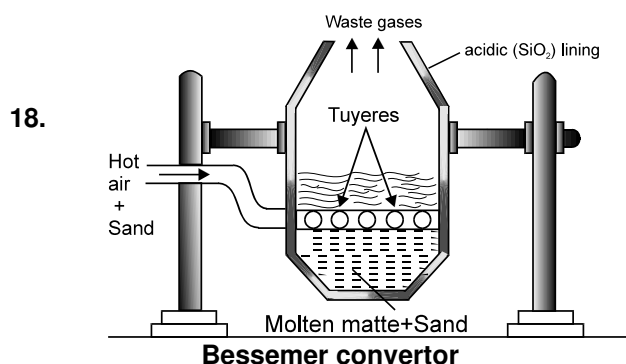
$$\text{S} + \text{O}_2 \longrightarrow \text{SO}_2 \uparrow; \text{P}_4 + 4\text{O}_2 \longrightarrow \text{P}_4\text{O}_{10} \uparrow$$

Organic matter, moisture if present in the ore, also get expelled and the ore becomes porous.

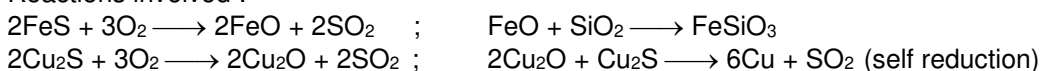


8. Conversion of a carbonate into oxide is an example of calcination

$$\text{MgCO}_3 \xrightarrow[\text{absence of air}]{\Delta} \text{MgO} + \text{CO}_2 \uparrow$$
9. Generally the sulphides of Zn, Pb, Fe, Cu etc. are subjected to roasting to convert in to their oxides prior to reduction by carbon.
10. In many extraction processes, an oxide is added deliberately to combine with other impurities and form a stable molten phase immiscible with molten metal called a slag. The principle of slag formation is essentially the following.
 Nonmetal oxide (acidic oxide) + Metal oxide (basic oxide) \longrightarrow Fusible (easily melted) slag.
11. Acidic flux is used. It is an acidic oxide (oxide of a non-metal) like SiO_2 , P_2O_5 , B_2O_3 (from borax). It is used to remove the basic impurity like CaO , FeO , MgO etc. The acidic flux combines with the basic impurity and forms a slag.
12. (1) Calamine is ZnCO_3 and siderite is FeCO_3 .
 (2) Argentite is Ag_2S while cuprite is Cu_2O .
 (3) Zinc blende is ZnS and iron pyrites is FeS_2 .
 (4) Malachite is $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ and azurite is $2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$.
13. Electrolytic reduction method is used in the extraction of highly electropositive elements as they themselves are stronger reducing agents. They lie above hydrogen in electrochemical series.
14. Electrolytic reduction method is used in the extraction of highly electropositive elements as they themselves are stronger reducing agents. They lie above hydrogen in electrochemical series. The heat of formation of Al_2O_3 is very high and therefore, at higher temperature there will be the possibility of formation of Al_4C_3 with carbon.
15. (1) $\text{Cu}_2\text{O} + \text{C} \xrightarrow{\Delta} 2\text{Cu} + \text{CO}$; $\text{SnO}_2 + 2\text{C (anthracite)} \xrightarrow{1800^\circ\text{C}} \text{Sn} + 2\text{CO}$.
 (2) $2\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 4\text{Fe (spongy iron)} + 3\text{CO}_2$; $\text{ZnO} + \text{C} \xrightarrow{1200^\circ\text{C}} \text{Zn} + \text{CO}$.
 (3) Oxides of highly reactive metals (like K_2O) are not reduced by carbon. K lie above hydrogen in electrochemical series and so it acts as strong reducing agent. K is obtained by electrolytic reduction of their fused salts.
 (4) $\text{FeO} + \text{C} \longrightarrow \text{Fe} + \text{CO}$; $\text{PbO} + \text{C} \longrightarrow \text{Pb} + \text{CO}$
16. A hydrometallurgical process for the extraction of metals from ores, concentrates, or secondary materials essentially contains three basic steps—dissolution of the valuable metal in the aqueous solution (leaching) purification of leach solution and subsequent recovery of metal from the purified solutions either by electrolysis or by adding some electropositive metal to it.
17. Cryolite is Na_3AlF_6 and is used in the electrolysis of alumina. It reduces the melting point of alumina and increase the electrical conductivity of electrolyte.

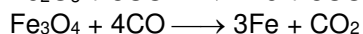
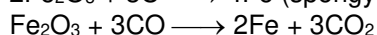
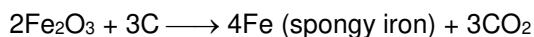


Reactions involved :



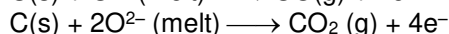
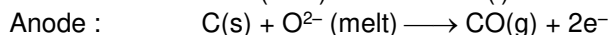
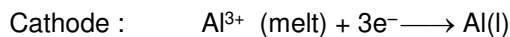


19. In actual process the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags off' as iron silicate and copper is produced in the form of copper matte which contains mostly Cu_2S and some FeS .
20. $\text{Ti (impure)} + 2\text{I}_2(\text{g}) \xrightarrow[50-250^\circ\text{C}]{\text{Tungsten filament}} \text{TiI}_4(\text{g}) \xrightarrow{1400^\circ\text{C}} \text{Ti(pure)} + 2\text{I}_2(\text{g})$
21. This process is used for the purification of copper and tin to remove the impurities of their oxides.
 Green wood \rightarrow Hydrocarbons $\rightarrow \text{CH}_4$; $4\text{CuO} + \text{CH}_4 \rightarrow 4\text{Cu (pure metal)} + \text{CO}_2 + 2\text{H}_2\text{O}$
 Green wood \rightarrow Hydrocarbon $\rightarrow \text{CH}_4$; $2\text{SnO}_2 + \text{CH}_4 \rightarrow 2\text{Sn} + \text{CO}_2 + 2\text{H}_2\text{O}$
22. This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.
23. This process is used for the purification of the metal, which itself is readily fusible, but the impurities present in it are not, i.e., the impurities are infusible. This process is used for the purification of Sn and Zn, and for removing Pb from Zn-Ag alloy, which is obtained at the end of Parke's process and contains Pb as impurity.
24. (I) $4\text{Au / Ag (s)} + 8\text{CN}^-(\text{aq}) + 2\text{H}_2\text{O}(\text{aq}) + \text{O}_2(\text{g}) \longrightarrow 4[\text{Au / Ag (CN)}_2]^-(\text{aq}) + 4\text{OH}^-(\text{aq})$
 $2[\text{Au / Ag (CN)}_2]^-(\text{aq}) + \text{Zn(s)} \longrightarrow 2\text{Au / Ag (s)} + [\text{Zn(CN)}_4]^{2-}(\text{aq})$
 (II) This method is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil.
 (III) Electrolytic reduction (Hall-Heroult process) :
 The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar) which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed. The electrolytic reactions are :
 Cathode : $\text{Al}^{3+}(\text{melt}) + 3\text{e}^- \longrightarrow \text{Al(l)}$
 Anode : $\text{C(s)} + \text{O}^{2-}(\text{melt}) \longrightarrow \text{CO(g)} + 2\text{e}^-$
 $\text{C(s)} + 2\text{O}^{2-}(\text{melt}) \longrightarrow \text{CO}_2(\text{g}) + 4\text{e}^-$
 (IV) This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors and hence are purified by this method. Zone refining method is based on the principle that an impure molten metal on gradual cooling will deposit crystals of the pure metal, while the impurities will be left in the remaining part of the molten metal.
25. (a) Limonite is $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. (b) Argentite is Ag_2S .
 (c) Carnallite is $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. (d) Calamine is ZnCO_3 .
26. (a) Bauxite is leached with NaOH (concentrated) to form soluble $\text{Na[Al(OH)}_4]$ complex and insoluble impurities are filtered off.
 (b) Carbonate and hydroxide ores are heated in absence of air below their melting point to convert in to their oxides in reverberatory furnace. This is called calcination. So siderite, FeCO_3 is subjected to calcination.
 (c) This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb) ; copper pyrites CuFeS_2 (ore of copper) ; zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil.
 (d) Chromite ore ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) having magnetic properties is separated from non-magnetic silicious impurities by magnetic separator.
27. (a) **Self-reduction method** : This method is also called auto-reduction method or air reduction method. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb etc. are heated in air, a part of these is changed into oxide or sulphate that then reacts with the remaining part of the sulphide ore to give its metal and SO_2 .
 $\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 3\text{Cu}_2\text{O} + 2\text{SO}_2$
 $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$

**(b) Reduction with carbon / carbon monoxide :**

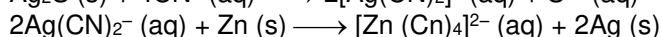
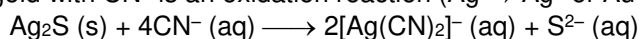
(c) Electrolytic reduction (Hall-Heroult process) : The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar) which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed.

The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2 .



(d) Complex formation and displacement by metal : Extraction of Ag and Au. Metals like Au and Ag can be precipitated for their salt solution by electropositive metals for example, Zn.

Metallic Ag is dissolved from its ore in dilute NaCN solution, and the solute so obtained is treated with scrap Zn when Ag is precipitated. Air is blown into the solution oxidize Na_2S . Leaching the metals like silver, gold with CN^- is an oxidation reaction ($\text{Ag} \rightarrow \text{Ag}^+$ or $\text{Au} \rightarrow \text{Au}^+$)



Here Zn acts as reducing agent.

28. Molten iron from blast furnace is taken in to sand pigs for solidification. Therefore iron obtained from blast furnace is called pig iron.
29. $2\text{ZnS} + 3\text{O}_2 \xrightarrow{\text{roasting}} 2\text{ZnO} + 2\text{SO}_2$; $\text{ZnO} + \text{C} \xrightarrow{1100^\circ\text{C}} \text{Zn} + \text{CO}$.
Therefore, (2) option is correct.
30. In Ellingham diagram, the $\Delta_f G^\circ$ of Al_2O_3 lies below that of CO_2 . If reduction is carried out at very high temperature, the Al produced will react with carbon forming Al_4C_3 .

PART - IV

1. (i) $\text{Cr}_2\text{O}_3 + 2\text{Al} \xrightarrow{\Delta} 2\text{Al}_2\text{O}_3 + 2\text{Cr}$
(ii) Mg is extracted by electrolytic reduction of fused MgCl_2 . As Mg lies above hydrogen in electrochemical series.
(iii) $\text{PbO} + \text{C} \xrightarrow{\Delta} \text{Pb} + \text{CO}$; $\text{CaO} + \text{SiO}_2 \xrightarrow{\Delta} \text{CaSiO}_3$
(iv) Red bauxite (contains impurity of iron oxide) is purified by Bayer's / Hall's process.
2. $\text{Ag}_2\text{S (conc. ore)} + 2\text{NaCN} \xrightarrow{\text{Air}} 2\text{AgCN} + \text{Na}_2\text{S}$.
 Ag_2S and AgCN are in equilibrium so Na_2S is oxidised by air in to Na_2SO_4 . Hence equilibrium shifts towards right side.
$$4\text{Na}_2\text{S} + 5\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Na}_2\text{SO}_4 + 4\text{NaOH} + 2\text{S}$$

$$\text{AgCN} + \text{NaCN} \longrightarrow \text{Na[Ag(CN)}_2\text{]} (\text{soluble complex})$$

$$2\text{Na[Ag(CN)}_2\text{]} + \text{Zn (dust)} \longrightarrow 2\text{Ag}\downarrow + \text{Na}_2[\text{Zn(CN)}_4]$$
3. (i) Extraction of tin (carbon reduction) :
$$\text{SnO}_2 + \text{C} \rightarrow \text{SnO} + \text{CO}\uparrow$$

(ii) Extraction of zinc (carbon reduction) :
$$\text{ZnO} + \text{C} \xrightarrow{\text{coke, } 673} \text{Zn} + \text{CO}$$

(iii) Extraction of lead (self reduction) :
$$\text{PbS} + 2\text{O}_2 \longrightarrow \text{PbSO}_4$$
 ;
$$\text{PbS} + 3\text{O}_2 \longrightarrow 2\text{PbO} + 2\text{SO}_2$$

$$\text{PbS} + 2\text{PbO} \longrightarrow 3\text{Pb} + \text{SO}_2$$
 ;
$$\text{PbS} + \text{PbSO}_4 \longrightarrow 2\text{Pb} + 2\text{SO}_2$$

(iv) Extraction of copper (self reduction) :
$$2\text{CuFeS}_2 + 4\text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeO} + 3\text{SO}_2$$

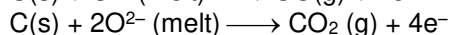
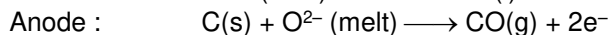
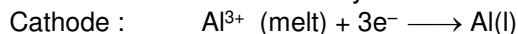
$$\text{Cu}_2\text{S} + \text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3 (\text{fusible slag}) + \text{Cu}_2\text{S} (\text{matte})$$

$$2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$$
 ;
$$2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$$

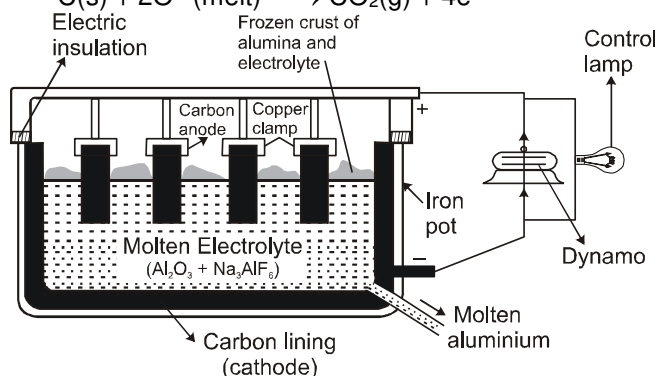
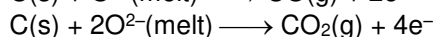
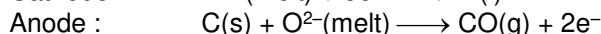
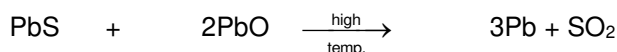
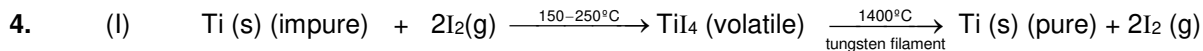
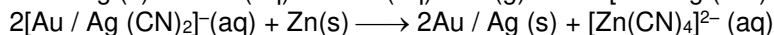
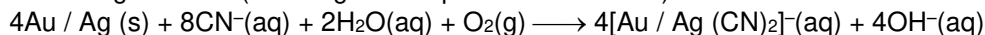


(v) Extraction of aluminium (electrolytic reduction, Hall-Heroult process) :

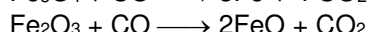
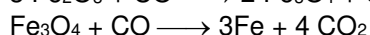
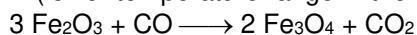
The purified Al_2O_3 is mixed with Na_3AlF_6 (cryolite) or CaF_2 (fluorspar) which lowers the melting point of the mixture and increases conductivity. The fused matrix is electrolysed.



(vi) Extraction of gold/silver (leaching and displacement method) :



5. S_1 : At 500–800 K (lower temperature range in the blast furnace)



At 900–1500 K (higher temperature range in the blast furnace): $\text{FeO} + \text{CO} \longrightarrow \text{Fe} + \text{CO}_2$

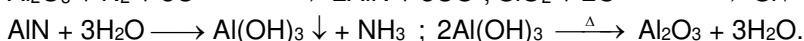
S_2 : calamine is ZnCO_3

S_3 : It contains Fe_2O_3 , SiO_2 and TiO_2 as impurities

S_4 : The surface of solidified copper has blistered like appearances due to the evolution of SO_2 and so it is called blister copper.

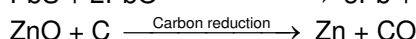
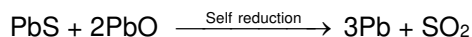
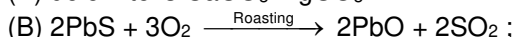
6. (X) Red bauxite contains the impurities of oxides of iron and silicates. In Bayer process, alumina is dissolved by reacting sodium hydroxide solution leaving behind the insoluble oxide of iron.

(Y) White bauxite contains the impurity of silica which is removed by Serpeck's method.



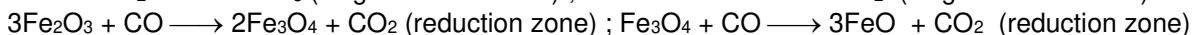
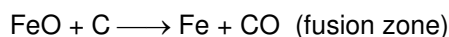
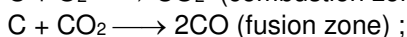
7. Anode mud contains Ag, Au as impurities.

8. (A) dolomite is $\text{CaCO}_3 \cdot \text{MgCO}_3$



(D) In extraction of iron the slag obtained is CaSiO_3 where as in copper it is FeSiO_3 .

9. $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$ (combustion zone)





10. (A) Calamine, ZnCO_3 is the ore of zinc. (B) Proustite, Ag_3AsS_3 is the ore of silver.
(C) Cassiterite, SnO_2 is the ore of tin. (D) Diaspore, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is the ore of aluminium.
11. This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb); copper pyrites CuFeS_2 (ore of copper); zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil.
12. (A) $2\text{Al} + \text{Fe}_2\text{O}_3 \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$ (molten); $\Delta H = -3230 \text{ kJ}$ (The reaction is used for thermite welding)
(B) Aluminothermic process : $\text{Cr}_2\text{O}_3 + \text{Al} \rightarrow 2\text{Cr}$ (molten) + Al_2O_3
(C) Extraction of gold : $4\text{Au} (\text{s}) + 8 \text{CN}^- (\text{aq}) + \text{O}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l}) \longrightarrow 4 [\text{Au}(\text{CN})_2]^- (\text{aq}) + 4\text{OH}^- (\text{aq})$
 $2[\text{Au}(\text{CN})_2]^- (\text{aq}) + \text{Zn} (\text{s}) \longrightarrow [\text{Zn}(\text{CN})_4]^{2-} (\text{aq}) + 2 \text{Au} (\text{s})$
(D) Self-reduction method : $\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 3\text{Cu}_2\text{O} + 2 \text{SO}_2$; $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$
13. Hence, the change in oxidation number of aluminium is 3 per mole. Since $4/3$ moles of Al are produced
 $n = 3 \times 4/3 = 4$
$$E_{\text{ext}} = \frac{960000}{4 \times 96490} = 2.5 \text{ V}$$

A potential difference of at least 2.5 V must be applied to the oxide to bring about reduction.
14. (i), (ii), (v), (vi), (ix), (xii)
15. Self reduction method can be used for Cu, Pb, and Sb
16. Impurity is of metal oxide.
17. Cu, Pb, Sn, Zn, Ag : In aqueous medium
Al, Ca, Mg : In molten state
19. Dissolution of gold in NaCN forming soluble complex is reversible, so it is carried out in presence of air bubbling. Oxygen contained in air oxidises Au to Au^+ which then complexes with CN^- to form soluble complex.
20. (B) HCN produced with water by NaCN and KCN is poisonous and have carcinogenic activity.
21. The process which involves the dissolution of ore in to a suitable reagent and then extraction of metal from the solution by more electropositive element is called hydrometallurgy.
22. (A) Hall- Heroult process is the electrolytic reduction of molten Al_2O_3 dissolved in cryolite or fluorspar.
(B) Dow's sea water process involves the isolation of Mg from sea water as MgCl_2 and then electrolytic reduction of molten MgCl_2 dissolved in CaCl_2 and NaCl.
(C) Hoop's process is the electrolytic purification of impure aluminium. The cell has three liquid layers upper most layer contains impure Al, middle one contains fluorides of Na^+ , Ba^{2+} and Al^{3+} , lower most layer has pure Al (obtained by cathodic oxidation).
(D) Mac-Arthur forest cyanide process is the process used for the extraction of gold and silver. Extraction of gold and silver involves leaching the metal with CN^- . The metal is later recovered by displacement method.