GENERAL PRINCIPLES & PROCESSES OF ELEMENTS

Basic Concepts

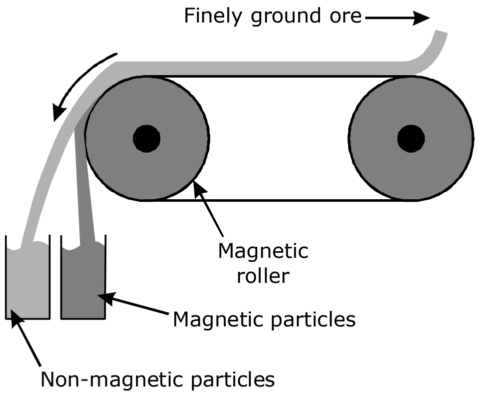
1. **Minerals :** The naturally occurring chemical substances in the earth's crust which are obtained by mining.
2. **Ore :** The mineral from which the metal is conveniently and economically extracted.
3. **Gangue :** The earthy materials associated with the ores.
4. **Occurrence of metals :** Metals which have low chemical reactivity generally occur in free state. For example, gold and platinum. Metals which are chemically reactive occur in combined state. For example, aluminium, iron and zinc.

Metal	Ores	Composition
Aluminium	Bauxite Kaolinite (a form of clay)	$AlO_x(OH)_{3-2x}$ [where 0 < x < 1] $[Al_2(OH)_4Si_2O_5]$
Iron	Haematite Magnetite Siderite Iron pyrite	Fe_2O_3 Fe_3O_4 $FeCO_3$ FeS_2
Copper	Copper pyrite Malachite Cuprite	$CuFeS_2$ $CuCO_3.Cu(OH)_2$ Cu_2O
Zinc	Zinc blende or Sphalerite Calamine Zincite	ZnS $ZnCO_3$ ZnO

5. **Metallurgy :** The scientific and technological process used for isolation of the metals from its ore.

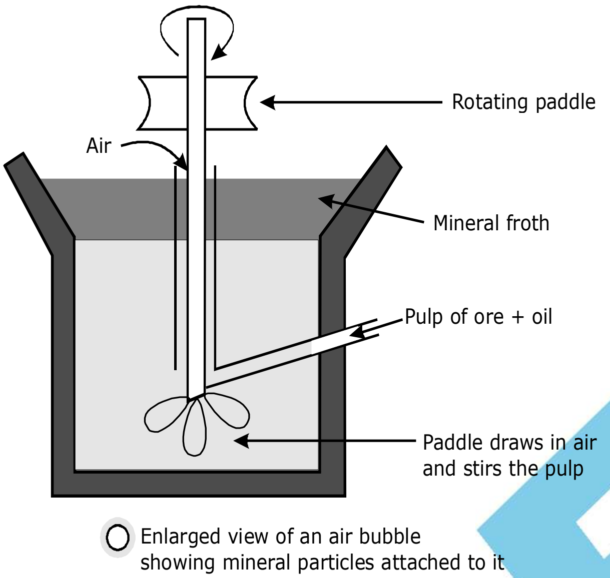
6. **Concentration :** The process of removal of unwanted earthy and silicoius impurities (gangue) from the ore.
Some of the important concentration methods are
(a) Hydraulic washing : It is based on the differences in densities or gravities of the ore and the gangue particles. In one such process an upward stream running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind. The oxide ores are generally concentrated by this method.

(b) Magnetic separation : This method is base on differences in magnetic properties of ore and gangue. For example, magnetic ores, magnetite (Fe_3O_4) and pyrolusite (MnO_2) are separated from the non-magnetic gangue by this method.



(c) Froth floatation : This method is based on preferential wetting of ore particles by oil and gangue particle with water. The sulphide ores of zinc, copper and lead are usually concentrated by this method.
In the froth floatation process a suspension of the powdered ore is made with water. To it collectors and froth stabilisers are added. The suspension is violently agitated by the rotating paddle which

draws in air causing froathing. The ore particles which are preferentially wetted by oil stick to the air bubbles, rise to the surface along with the froth while gangue particles which are preffere initially wetted by water settle at the bottom and are removed as tailing. The forth is skimmed off. It is allowed collapse and finally dried to get the concentrated ore.



- **Froth stabilizers :** Sub like cresols and aniline, which stabilize the froth.
- **Depressants :** These are the substances which selectively prevent certain type of particles from forming the froth with the bubbles. For example, NaCN is added as a depressant for the separation of an ore containing ZnS and PbS. NaCN acts as a depressant for ZnS but not for PbS. NaCN forms a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of ZnS, thereby, preventing it from froth.

(d) Leaching : This method consists of treating the powdered ore with a suitable reagent which can selectively dissolve the ore but not the impurities. The impurities are filtered out and ore recovered from solution. For example, bauxite ore containing SiO_2, iron oxide and titanium oxide are impurities concentrated by this method.

$$Al_2O_3.xH_2O(s) \xrightarrow{1470\ K} Al_2O_3(s) + xH_2O(g)$$

7. Extraction of Crude Metal from Concentrated Ore : The process used to obtain metals in free state from the concentrated ore is called extraction. It involves the following two major steps.

(a) Conversion of the ore into metal oxide and

(a) Conversion of the ore into metal oxide :
The following two methods are used for conversion of ores into their respective oxides.

(i) Calcination : It is the process of heating an ore below its melting point either in the absence or limited supply of air. During calcination,

- hydrated ores become anhydrous. For example

$$\underset{\text{Limonite}}{Fe_2O_3.3H_2O} \longrightarrow \underset{\text{Calcium oxide}}{Fe_2O_3} + 3H_3O$$

- carbonates are converted into their respective oxides.

$$\underset{\text{Calcium}}{Zn\ CO_3} \xrightarrow{heat} ZnO + CO_2 \uparrow$$

(ii) Roasting : It is process of heating the ore below its melting point in excess of air. The following changes occur during roasting :

- Moisture is drive away.

$$S_8 + 8O_2 \xrightarrow{heat} \underset{\text{Sulphur dioxide}}{8SO_2} \uparrow$$

(b) Reduction of oxide to metal : The role of reducing agent is to provide ΔG negative and large enough to make the sum of ΔG of oxidation of reducing agnet and reduction of metal oxide negative. The free energy change, ΔG is related with other thermodynamic quantities by the expression;

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

where ΔH = enthalpy change, ΔS = entropy change, and T = temperature in Kelvin

As heating, i.e., increase in T, favours a negative value of $\Delta_r G$, therefore, the temperature is chosen such that sum of $\Delta_r G$ in two combined redox processes is negative.

(i) Smelting : In this process metal oxide is reduced to metal with C or CO.

$$Fe_2O_3 + CO \xrightarrow{500-900K} 2FeO + CO_2$$

$$Fe_3O_4 + CO \xrightarrow{500-900K} 3FeO + CO_2$$

8. Flux : A flux is a substance which when mixed with calcinated or roasted ore, chemically combine with impurities present to form an easily fusible material called slag.

Flux + Impurity $\longrightarrow$ Slag

9. Refining : The process of purifying the impure metals is called refined. Various methods are available for refining of impure metals. The choice of purification method depends on the nature of the metal and the impurities there in. Following methods are in general, employed for refining metals.

(a) Distillation : This method is used to remove the non-volatile impurities from volatile metals like zinc, cadmium and mercury. The impure metal is heated in a retort when the pure metal vaporizes and condenses separately leaving behind the non-volatile impurities.

(b) Liquation : This is very useful for low melting metals like tin and led. The impure metal is hated on the sloping hearth of a furnace when the molten metal flows away from the infusible impurities.

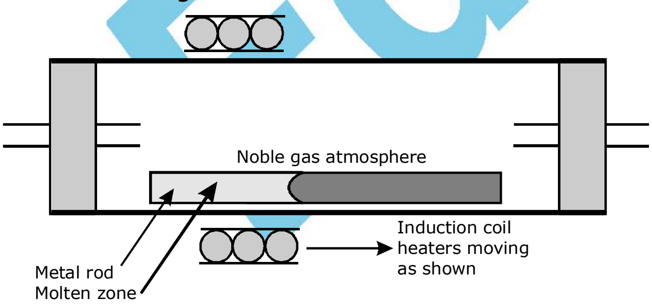
(c) Electrolytic refining : In this method, impure metal is made to act as anode. A strip of same metal in pure form is used as cathode. They are put in a electrolytic bath containing soluble salt of same metal. On passing electric current, metal ions from the electrolyte solution are deposited at the cathode in the form of pure metal while an equivalent amount of metal dissolved from the anode and goes into the electrolyte solution as metal ions, *i.e.*,

At cathode : $M^{n+}_{(aq)} + ne^- \longrightarrow M(s)$

At anode : $M(s) \longrightarrow M^{n+}_{(aq)} + ne^-$

The voltage applied for the electrolysis is such that the impurities of more electropositive metals remain in the solution as ions wheel impurities of less basic metals settle down under the anode as anode mud. A large number of metals such as copper, gold, silver, zinc aluminium etc., are refined by this method.

(d) Zone refining : It is based on the principle that the impurities are more soluble in the molten state than in the solid state of the metals. The impure metal is heated with the help of a circular mobile heater at one end. This results in the formation of a molten zone or melt. As the heater is moved along the length of the rod, the pure metal crystallizes out of the melt and impurities pass into the adjacent molten zone. This process is repeated several time till the impurities are completely driven to one end of the rode which is then cut off and discarded. This method is very useful for producing semi-conductor and other metals of very high purity, e.g., silicon germanium, boron and gallium



Zone refining process

(e) Vapour phase refining : In this method, the metal is converted into its volatile compound and collected elsewhere. It is then thermally decomposed to get the pure metal.
Following examples will illustrate this technique.

(i) Mond process : In this process, nickel is heated in a stream of carbon monoxide to form a volatile complex, nickel tetracarbonyl.

$$Ni + 4CO \xrightarrow{330-350K}$$

(ii) van Arkel method : This method is very useful for removed all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti. Impure metal is heated with iodine in a evacuated vessel and the resultant tetraiodide is decomposed on a tungsten filament to get the pure metal.

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

10. Extraction of Aluminium from Bauxite : 'Al' is extracted from bauxite $Al_2O_3.2H_2O$.

(i) Concentration of bauxite is done by leaching as explained in Basic Concepts Point 6.

(ii) **Extrolytic reduction (Hall-Heroult Process) :** Purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers its melting point of mixture and brings electrical conductivity. Fused mixture is electroysed using graphite rods as anode carbon lining ad cathode.

The graphite anode is useful for reduction of metal oxide to metal. The overall electrolytic reactions are :

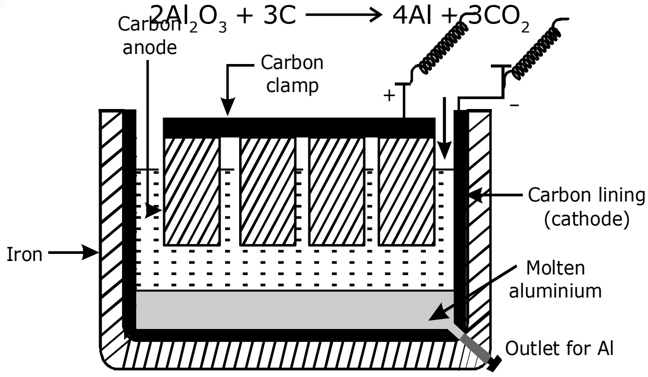
$$Al_2O_3 \xrightarrow{\text{electrolysis}} 2Al^{3+} + 3O^{2-}$$

Cathode : $Al^{3+}(\text{melt}) + 3e^- \longrightarrow Al(\ell)$

Anode : $C(s) + O^{2-}(\text{melt}) \longrightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}(\text{melt}) \longrightarrow CO_2(g) + 4e^-$

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



Electrolytic cell for the extraction of aluminium

11. Copper from Low Grade Ores and Scraps : Copper is extracted by hydrometallurgy from low-grade copper ores and scraps. It is leached out by using acid or bacteria.

Reduction : The solution containing Cu^{2+} is treated with scrap iron or H_2.

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

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

SOLVED PROBLEMS

Q.1 Why is Fe an abundant element on earth, and why are the elements with higher atomic numbers increasingly rare ?

Ans. The high abundance of Fe on earth is due to its very high nuclear binding energy, which imparts stability to Fe. The elements with higher atomic numbers are increasingly rare because they are considered to be produced by a variety of nuclear processes such as capture of neutrons produced from the lighter elements. For Example,

$${}_{10}Ne^{23} + {}_{2}He^{4} \rightarrow {}_{12}Mg^{26} + {}_{0}n^{1}$$

$${}_{42}Mo^{98} + {}_{0}n^{1} \rightarrow {}_{42}Mo^{99} + \gamma + {}_{0}n^{1}$$

$${}_{42}Mo^{99} \rightarrow {}_{43}Tc^{90} + \beta$$

The daughter nuclide may capture more neutrons and may give rise to elements of higher atomic numbers.

Such nuclear phenomenon being relatively less occurring, the abundance of elements of higher atomic numbers is very low.

Q.2 Copper and silver are below hydrogen in electrochemical series and yet they are found in the combined state as sulphides in nature. Comment?

Ans. Though copper and silver are below hydrogen in electrochemical series, they are found in combined state as sulphides because the negative values of their free energies of formation thermodynamically favours their existence as metal sulphides.

Q.3 Describe the principle of froth flotation process. What is the role of a stabilizer and of a depressant? Give one example each.

Ans. Froth floatation process is based on the preferential wetting properties of the ore and gangue. For example, sulphide ores are preferentially wetted by oil than water, and the gangue particles are wetted by water.

In the process, the powdered ore is mixed with water and a small quantity of pine oil. The mixture is vigorously stirred by passing compressed air. Froth is produced and it rises to the surface and carries the ore particles along with it. Ore is recovered from the froth collected in the process and the gangue is left behind.

The substances which stabilize the froth are called stabilizers, e.g. cresols and aniline. The substances which prevent certain type of particles from forming the froth with the bubbles are called depressants.

For example, sodium cyanide can be used as a depressant in the separation of zinc sulphide ore (ZnS) and lead sulphide ore(PbS). Sodium cyanide acts as a depressant for ZnS but does not prevent PbS from froth formation.

Q.4 Describe the principle of each of the following processes in detail.
(a) Mond's process
(b) Zone refining (c) Electrolytic refining

Ans. **(a) Vapour phase refining: Mond's process** When nickel oxide is heated with water gas ($CO + H_2$), H_2 reduces nickel oxide to nickel, which readily combines with CO to form $Ni(CO)_4$, a highly inflammable, volatile vapours.

This gas, when separated out and heated to 230ºC, decomposes to give pure nickel.

Impure Ni + CO $\rightarrow Ni(CO)_4 \rightarrow Ni + 4CO$

(b) Zone refining method is based on the principle that the impurities are more soluble in the melt than in the pure metal. Impure metal rod is taken and heat is applied at a narrow region. By slowly moving the heat source, the molten region is gradually transferred from one end of the rod to another. The impurities, which remain in the molten part, are progressively shifted to one end of the rod. The process could be repeated many times still the desired level of purity is attained. The method is especially useful for producing B, Ge, Si, Ga (semiconductors).

(c) To get metal of high purity, electrochemical refining is done making impure metal as anode.

In an aqueous solution: It is used in cases when the electrolyte is soluble in water and product does not react with it. Cu, Zn, Ag and other metal are obtained by the electrolysis of aqueous solution of their salts ($ZnSO_4$, $AgNO_3$, $CuSO_4$). Impure metal is made anode of electrolytic cell (consists of same metal salt) having pure metal plate of cathode. On electrolysis pure metal from crude form gets dissolved at anode whereas at cathode pure metal is deposited. The soluble impurities pass into solution while the insoluble ones collected below the anode as **anodic mud or anode sludge.**

In fused melts: Na, K, Ca, Mg etc., react with H_2O hence they are extracted by electrolysis of fused halides.

– Na and Cl_2 are obtained by electrolysis of fused NaCl.

– Al is obtained by the electrolysis of fused mixture of Al_2O_3 and $Na_3(AlF_6)$ (cryolite).

In other solvents: Electrolysis can be carried out in solvents other than water.

F_2 reacts violently with H_2O hence it is produced by electrolysis of KHF_2 in HF.

Q.5 You are provided with samples of some impure metals such as zinc, copper and germanium. Which methods would you recommend for the purification of each of these metals?

Ans. Zinc: distillation, electrolysis; Copper: poling, electrolysis; Germanium: zone refining

Q.6 Name the chief forms of the occurrence of the following in the earth's crust:

(a) aluminium (b) calcium
(c) sodium (d) lead

Ans. (a) Aluminium: Bauxite, Al_2O_3, $2H_2O$; Cryolite, Na_3AlF_6; Aluminosilicates

(b) Calcium: Limestone, $CaCO_3$; Dolomite, $MgCO_3$, $CaCO_3$; Gypsum $CaCO_3$, $2H_2O$

(c) Sodium: Rock Salt, NaCl; Feldspar, $Na_3AlSi_3O_8$; Chile saltpeter, $NaNO_3$

(d) Lead: Galena, PbS; Cerrusite, $PbCO_3$; Anglesite, $PbSO_4$

Q.7 Discuss some of the factors which need consideration before deciding on the method of extraction of metal from its ore.

Ans. Some of the factors which need consideration before deciding on the method of extraction of metal from its ore are:

(i) Depending upon the type of impurity, the ore may be concentrated by different methods like

(a) magnetic separation
(b) hydraulic washing
(c) froth floatation method
(d) leaching
(e) electrostatic concentration

(ii) If the ore is in the oxide form, it is directly reduced. However, if the ore is a hydroxide, carbonate or sulphide, it is first converted to the oxide form by calcinations or roasting/smelting.

(iii) Chemical nature of the ore greatly affects the extraction process.
For example, various oxide ores may be reduced by carbon, hydrogen, aluminium or other metals auto-reduction, displacement method or electrolytic method depending on the nature of the metal.

(iv) Thermodynamic considerations are very important in metallurgical processes.
These can help in deciding the temperature and the choice of reducing agents in the reduction processes.

(v) Availability of facilities greatly determines the method of extraction.

Q.9 The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinions with examples?

Ans. Thermodynamic factor affects the choice of a reducing agent in a particular case. The Gibb's free energy change, which is defined in terms of enthalpy and entropy changes, decides the direction of the process at constant temperature and pressure. For Example, ΔG of most sulphides are greater than those of CS_2 and H_2S.

Thus neither carbon nor hydrogen is a suitable reducing agent for such metal sulphides. Such metal sulphides are roasted to the oxide form prior to reduction. ZnS, PbS, Cu_2S etc. are converted to their oxides before reduction.

Q.9 Which is a better reducing agent at 710°C, C or CO?

Ans. CO is a better reducing agent at 710°C

Q.10 Indicate the temperature at which carbon can be used as a reducing agent for FeO.

Ans. T > 1123 K

Q.11 Is it true that under certain conditions Mg can reduce SiO_2 and Si can reduce MgO?

Ans. **(i)** $SiO_2 + 2Mg \rightarrow Si + 2MgO$

Well powdered quartz is mixed with magnesium and heated in a fire clay crucible along with some quantity of calcined magnesia.

(ii) $2MgO + Si \xrightarrow{2000^0C} SiO_2 + 2Mg$

Q.12 Giving appropriate examples (at least three); explain how the reactivity of a metal is related to its mode of occurrence in nature.

Ans. The reactivity of a metal is related to its mode of occurrence.

For example, gold and platinum are highly unreactive and thus occur in the native state. Most metals are quite reactive and thus occurs in the combined form e.g., calcium being highly reactive does not occur is native form and is found in the combined form as $CaCO_3$, $CaCl_2$, $CaSO_4$, $2H_2O$ etc.

Q.13 Name three metals which are obtained by the reduction of their oxides though they do not occur as such in the earth's crust.

Ans. The metals which occur as sulphide ores are generally converted to oxide forms before reduction.

A few such example are ores of lead (PbS), zinc (ZnS), copper (Cu_2S) etc.

Q.14 Outline the principles of refining of metals by the following methods:

(i) Electrolytic refining

(ii) Zone refining

(iii) Vapour phase refining

Ans. Refer to Q.4.

Q.15 Predict the modes of occurrence of the following three types of metals:

(i) Highly reactive (e.g. Na);

(ii) Moderately reactive (e.g. Fe);

(iii) Noble metal (e.g. Au)

Ans. (i) Highly reactive metals like Na, K, Mg, Ca etc. are not found in the free or native form. They occur in the combined form as minerals. The compounds of the highly reactive metals, especially the halides which are soluble in water are found in sea water or in the large salt bed deposits formed by the evaporation of inland seas.

(ii) Moderately reactive metals like Fe, Zn, Pb, etc. also do not occur in the native state and are found in the combined form as oxides, carbonates, sulphides, sulphates, etc.

(iii) Noble metals like Au, Ag, etc being highly unreactive occur in native form.

Q.16 How do non-metals occurs in nature? How are they extracted/isolated form their natural sources?

Ans. Non-metals occur in nature in the elemental as well as combined form. Nitrogen, oxygen, noble gases, hydrogen etc are some non-metals which occur in the elemental form and are available from air.

The non-metals which occur in the combined form are generally extracted by oxidation, e.g., halogens etc. are obtained by oxidation by electrolysis.

Non-metals like carbon, sulphur and phosphorus are extracted either from native ores or by oxidation from their compounds occurring in nature. There are no general methods of extraction of non-metals.

Q.17 Name the processes from which chlorine is obtained as a bye product.
What will happen if an aqueous solution of NaCl is subjected to electrolysis?

Ans. Chlorine is obtained as a bye product in the electrolytic reduction of metal chlorides like NaCl, KCl etc.

When an aqueous solution of NaCl is subjected to electrolysis, H^+ ions are preferentially discharged at the cathode by accepting electrons and thereby producing H_2 gas. This pushes the dissociation equilibrium of water in the forward direction. The net reaction at cathode can be represented as

At cathode $2H_2O + 2e^- \rightarrow 2\,OH^-(aq) + H_2(g)$

Cl^- ions are preferentially liberated at the anode.

At anode $Cl^- \rightarrow Cl + e^-$ $Cl + Cl \rightarrow Cl_2(g)$

The overall reaction during the electrolysis of aqueous solution of sodium chloride is

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

Q.18 Name the chief ores of tin, iron and aluminium. What methods are employed for the concentration/purification of their ores?

Ans. **Tin** Cassiterite, SnO_2

- Concentration by hydraulic washing
- Roasting to remove arsenic and sulphur as volatile oxides
- Smelting in a reverberatory furnace to reduce metal oxide
- Refining by liquation method.

Iron Haematite, Fe_2O_3

- Concentration by hydraulic washing and magnetic separation Magnetic, Fe_2O_3
- Roasting to remove moisture and remove arsenic and sulphur as

volatile oxides and to convert FeO to Fe_2O_3.

Limonite, $(Fe_2O_3)_2$, $3H_2O$

- Smelting in a blast furnace which yields pig iron.
- Pig iron is purified /alloyed/treated in different ways to get different varieties of iron and steel.

Aluminium Bauxite, $Al_2O_3.2H_2O$ Bauxite is the most commonly used ore.

Different steps involved in extraction are

Cryolite, Na_3AlF_6

- Purification of bauxite by either Baeyer's process, Hall's process or Serpeck's process.

Aluminosilicates

- Electrolysis of fused aluminium oxide to obtain metal.
- Refining by Hoop's electrolytic process.

Q.19 Name three ores which are concentrated by froth-floatation process. What is meant by a depressant?

Ans. Sulphide ores like argentite (Ag_2S), zinc blende (ZnS), cinnabar (HgS), galena (PbS) are concentrated by froth flotation process.

Depressants: Which suppress the floatation of a particular particle selectively, e.g. when ore containing PbS and ZnS is floated in presence of CN^-, floatation of ZnS is suppressed and only PbS is removed.

CN^- is then destroyed by any oxidizing agent and ZnS is floated again.

Q.20 What is the thermodynamic consideration in the choice of a reducing agent in metallurgy?

Ans. Same as Question 8.

Q.21 Carbon monoxide is more effective agent than carbon below 983 K but above this temperature the reverse is true. How would you explain this?

Ans. The difference in the action of carbon monoxide and carbon at different temperatures can be explained on the basis of thermodynamic considerations. The Gibbs free energy change decides the direction of the process at constant temperature and pressure. It is defined in terms of temperature, enthalpy and entropy changes as

$\Delta G = \Delta H - T\Delta S$
The magnitude of T largely affects the value of ΔG and therefore affects the direction of the process.
At temperatures below 980 K, carbon monoxide is energetically a better reducing agent than carbon.
Above this temperature, the reduction with carbon becomes more favourable.

Q.22 Describe the principle of extraction of each of the following:
(i) Sn from SnO_2 **(ii) Zn from ZnO**
(iii) Cr from Cr_2O_3

Ans. **(i)** Sn from SnO_2 , SnO_2 is crushed, concentrated, roasted and washed.
It is smelted (reduced) with powdered anthracite in blast furnace to obtain tin.

$$SnO_2 + 2C \rightarrow Sn + 2CO$$

(ii) Zinc oxide is mixed with powdered coke and heated to 1673 K in a fire clay retort when it is reduced to zinc metal.

$$ZnO + C \xrightarrow{1673\ K} Zn + CO$$

(iii) Cr is obtained from Cr_2O_3 by reduction by employing aluminothermy process.
In this process, a mixture of aluminium powder and Cr_2O_3 is ignited in a closed crucible by inserting a burning magnesium ribbon into the ignition mixture consisting of magnesium powder and barium peroxide.

$$2Al + Cr_2O_3 \rightarrow Al_2O_3 + 2Cr$$

Q.23 Which metals are generally extracted by the electrolytic processes?
What positions these metals generally occupy in the periodic table?

Ans. Highly electropositive metals are generally extracted by the electrolytic process.
These metals which occur as chlorides or oxosalts are converted into their chlorides.
When electric current is passed through a fused chloride, the Mg^{2+} ions are discharged at cathode and deposited.
These metals generally occupy groups 1 and 2 in the periodic table.

Q.24 Name the main steel plants which are operated by the Steel Authority of India.

Ans. The main steel plants operated by Steel Authority of India (SAIL) are:
(i) Bhilai Steel plants, Bhilai, Chattisgarh
(ii) Bokaro Steel plants, Bokaro, Jharkhand
(iii) Durgapur Steel plants, Durgapur, West Bengal
(iv) Alloy Steel plants, Durgapur, West Bengal
(v) Rourkela Steel plants, Rourkela, Orissa
(vi) Salem Steel plants, Salem, Tamil Nadu
(vii) Visvesvaraya Iron and Steel plants, Bhadravati, Karnataka

Q.25 Name the metals which are associated with the following terms in their extraction from their ores:
(i) Bessemer's converter
(ii) Blast furnace
(iii) Alumino thermic process
(iv) Magnetic separation

Ans. (i) Bessemer's converter: Copper, iron.
(ii) Blast furnace: Iron, Copper
(iii) Alumino thermic process
: Chromium, manganese.
(iv) Magnetic separation: Tin, iron, chromium and manganese.

Q.26 What do you understand by the following terms
(i) Roasting **(ii) Calcination**
(iii) Smelting

Ans. (i) Roasting is the process of converting an ore into its metallic oxide by heating strongly below its melting point in excess of air. The following changes occur during roasting:
(a) Moisture is removed
(b) Organic matter is destroyed
(c) Non-metallic impurities like that of sulphur, phosphorus & arsenic are oxidized & are removed as volatile gases

$$S_8 + 8O_2 \rightarrow 8SO_2(g)$$

$$P_4 + 5O_2 \rightarrow P_4O_{10}(g)$$

$$4As + 3O_2 \rightarrow 2As_2O_3(g)$$

(d) Ores are generally converted into metallic oxides

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2(g)$

$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2(g)$

(e) It makes the ore porous and hence easily workable in subsequent changes.

(ii) Calcination is the process of converting an ore into its oxide by heating it strongly below its melting point either in absence or limited supply of air.

During the process of calcinations, the following chemical changes occur:

(a) moisture is driven out

(b) volatile impurities of S, As and P are removed as their volatile oxide.

(c) water is removed from hydrated oxides and hydroxide ores.

(d) carbonate ores are converted into their respective oxides by loss of carbon dioxide.

(e) It makes the ore porous and hence easily workable in subsequent stages.

(iii) Smelting is he process of extracting the metal by fusing of its oxide ore with carbon is called smelting.

In this process, the roasted or the calcined ore is mixed with a calculated quantity of carbon and heated to a high temperature above its melting, when carbon reduces the metal oxide to the free metal. For example,

$Zn + C \rightarrow Zn + CO$; $Pb + C \rightarrow Pb + CO$

The carbon monoxide thus produced can also bring about the reduction of metal oxides to free metals.

$Fe_2O_3 + 3CO \rightarrow 2\ Fe + 3CO_2(g)$

$PbO + CO \rightarrow Pb + CO_2(g)$

Q.27 Which method would you suggest for the separation of the metals in the following mixtures?

(i) Zinc and iron

(ii) Copper and magnesium

(iii) Rare earths. Give reasons for your choice.

Ans. **(i) Zinc and iron** can be separated from the mixture by distillation. The mixture is distilled, when zinc with low boiling point distills over leaving behind iron.

(ii) Copper and magnesium metals can be separated fro the mixture by electrolytic refining.

The mixture is converted into a rod and made the anode while a thin plate of pure copper serves as the cathode.

The electrolytic tank contains a solution of copper sulphate acidified with dil. H_2SO_4 which acts as the electrolyte.

On passing electricity, cupric ions from the solution are discharged at the cathode as pure metal.

(iii) Rare earths can be separated by chromatography. Since the rare earths do not differ much in their chemical behaviors, they are separated by physical process like column chromatography, which is based on the differential adsorption properties (physical phenomenon) of the constituents of the mixture.

EXERCISE-I UNSOLVED PROBLEMS

Q.1 Copper and silver lie below in the electrochemical series and yet they are found in the combined state as sulphides in nature. comment.

Q.2 What types of ores are roasted ?

Q.3 What is the role of flux in metallurgical processes ?

Q.4 What is gangue ?

Q.5 What name is given to carbon reduction process for extra cting the metal ?

Q.6 What are fluxes ? How are they useful ?

Q.7 Name one each of (a) acidic flux (b) basic flux

Q.8 An ore sample of galena (PbS) is contaminated with zinc blende (ZnS). Name one chemical which can be used to concentrate galena selectively by froth floatation method .

Q.9 Indicate the temperature at which carbon cambe used as a reducing agent for FeO.

Q.10 What is a slag ?

Q.11 What is meant by beneficiation process ?

Q.12 What is liquation ?

Q.13 What is the principle of zone refining ?

Q.14 When is electrolytic reduction applied for getting a metal ?

Q.15 Give two requirements for vapour phase refining

Q.16 What should be the considerations during the extraction of metals by electrochemical method

Q.17 The purest form of iron is prepared by oxidizing impurities from cast iron in a reverberatory furnace. Which iron ore is used to line the furnace ? Explain by giving reaction ?

Q.18 Although carbon and hydrogen are better reducing agents but they are not used to reduce metallic oxides at high temperatures. Why ?

Q.19 Differentiate between a mineral and an ore.

Q.20 Why is it that only sulphide ores are concentrated by froth floatation process ?

Q.21 Account for the following facts :
(a) the reduction of a metal oxide is easier if the metal formed is in liquid state at the temperature of reduction.
(b) the reduction of Cr_2O_3 with Al is thermodynamically feasible, yet it does not occur at room temperature.
(c) pine oil is used in froth floatation method.

Q.22 (a) Name the method used for refining of
(i) Nickel (ii) Zirconium
(b) The extraction of Au by leaching with NaCN involves both oxidation and reduction. Justify giving equations.

Q.23 Explain the following
(i) NaCN acts as depressant in preventing ZnS from forming the froth.
(ii) Role of cryolite in the metallurgy of aluminum.

Q.24 Out of C and CO, which is better reducing agent at 673 K.

Q.25 How is the concept of coupling reactions useful in explaining the occurrence of non-spontaneous thermochemical reactions ? Explain giving an example.

Q.26 Free energies of formation (ΔG_p) of MgO(s) and CO(g) at 1273 K and 2273 K are given below.
$\Delta_f G[MgO(s)] = -94$ KJ/mol at 1273 K
$\Delta_f G[MgO(s)] = -314$ KJ/mol at 2273 K
$\Delta_f G[CO(g)] = -439$ KJ/mol at 1273 K
$\Delta_f G[CO(g)] = -628$ KJ/mol at 2273 K
On the basis of abve data, predict the temperature at which carbon can be used as a reducing agent for MgO(s).

Q.27 Explain the following :
(i) Generally sulphide ores are converted into oxides before reduction.
(ii) Carbon and hydrogen are not used as reducing agents at high temperature.
(iii) Silica is added to sulphide ore of copper in the reverberatory furnace.

EXERCISE-II BOARD PROBLEMS

Q.1 How is the concept of coupling reactions useful in explaining the occurrence of non-spontaneous thermochemical reactions ? Explain giving an example.

Q.2 Name the chief ore of silver. Describe with chemical equations in the extraction of silver from this ore.

Q.3 Write the chemical reactions which take place in the following operations :
(i) Electrolytic reduction of Al_2O_3
(ii) Isolation of zinc from zinc blende
(iii) Mond's process for refining nickel.

Q.4 Explain the role of
(i) Cryolite in the electrolytic of alumina.
(ii) Carbon monoxide in the purification of nickel.

Q.5 Describe the role of the following :
(i) NaCN in the extraction of silver from a silver ore.
(ii) Cryolite in the extraction of aluminium from pure alumina.

Q.6 State briefly the principles which serve as basis for the following operations in metallurgy :
(i) Froth floatation process
(ii) Zone refining
(iii) Refining by liquation

Q.7 Explain the basic principles of following metallurgical operations :
(i) Zone refining
(ii) Vapour phase refining
(iii) Electrolytic refining

Q.8 Describe how the following change are brought about :
(i) Pig iron into steel.
(ii) Zinc oxide into metallic zinc.
(iii) Impure titanium into pure titanium.

Q.9 Describe how the following changes are brough about :
(i) Pig iron into steel.
(ii) Bauxite into pure alumina
(iii) Impure copper into pure copper

Q.10 Describe the role of
(i) NaCN in the extraction of gold from gold ore
(ii) SiO_2 in the extraction of copper from copper matte
(iii) Iodine in the refining of zirconium
Write chemical equations for the involved reactions.

Q.11 Describe the principle behind each of the following processes :
(i) Vapour phase refining of a metal.
(ii) Electrolytic of a metal
(iii) Recovery of silver after silver ore was leached with NaCN.

Q.12 Explain the role of each of the following in the extraction of metals from their ores :
(i) CO in the extraction of nickel
(ii) Zinc in the extraction of silver
(iii) Silica in the extraction of copper

Q.13 Describe the principle controlling each of the following processes :
(i) Vapour phase refining of titanium metal
(ii) Froth floatation method of concentration of a sulphide ore

Q.14 Describe the principle controlling each of the following processes :
(i) Zone refining of metals,
(ii) Electrolytic refining of metals

Q.15 Describe the principle controlling each of the following processes :
(i) Preparation of cast iron from pig iron
(ii) Preparation of pure alumina (Al_2O_3) from bauxite ore

Q.16 Write the reactions involved in the following processes :
(i) Leaching of bauxite ore to prepare pure alumina
(ii) Refining of zironium by van Arkel method
(iii) Recovery of gold after gold ore has been leached with NaCN solution.