General Principles and Processes of Isolation of Elements

Section-A: Learning points

Minerals: Which are naturally occurring chemical substances in the earth's crust which includes Metal and impurities.

Ores: The Minerals in which metal is extracted profitably called ores. Ex: Copper glance (Cu2S), Haematite ($Fe2O_3$)

Gangue: Undesired materials which present along with the metal in the earth crust known as **gangue**.

Metallurgy: The entire scientific and technological process used for isolation of the metal from its ores is known as **metallurgy**

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

> **A) Concentration of the ore (or) Purification of the Ore**
>
> **B) Isolation of the metal from its concentrated ore**
>
> **C) Purification of the metal (Or) Refining of the Metal.**

A) Concentration of the ore (or) Purification of the Ore:

i) Hand picking: In this process the earthy impurities (heavy impurities) which are present in the ore like rocky materials, pellets are picked with hand.

ii) Hydraulic washing:
→In this process the lighter impurities are removed.

→ The ore is fed in to the tank from the top, and the water is allowed with high pressure from the bottom of the tank.

→ During this process the lighter impurities which are adhere to the ore float over the water which can be removed .

→The ore particles will settle down at the bottom of the tank.

iii) Electromagnetic Separation:

→ This process is used for the Iron ore only.

→ The ore is passed through a belt which is connected by two rotating wheels, one among is made up of magnetic material.

→ Once the ore is passed through the belt, the ore particles are attracted by the magnetic wheel, and fall near to it.

→ The impurities which are nonmagnetic are not attracted by the magnetic wheel, and fall away from the magnetic wheel as shown in the figure.

iv) Froth Floatation Process:

Principle: **The mineral particles become wet by oils while the gangue particles by water.**

Method: In this process, a suspension of the powdered ore is made with water. To it, *collectors* and *froth stabilisers* are added. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles

Collectors : The chemical substances which enhance non-wettability of the mineral particles.

Ex : pine oils, fatty acids, xanthates

Froth stabilizers: The chemical substances stabilise the froth. Ex: cresols, aniline.

Depressants: It is possible to separate two sulphide ores by adjusting proportion of oil to water.

For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It electively prevents ZnS from coming to the froth but allows PbS to come with the froth.

V) Leaching: It is often used if the ore is soluble in some suitable solvent. It is chemical method used for purification of ore.

The following examples illustrate the procedure:

(a) Leaching of Alumina from Bauxite:

→ The ore consists of two chemical impurities a) Iron oxide (Fe_2O_3) b) Silica (SiO_2). These impurities are removed in the following process.
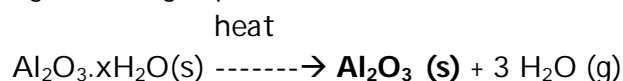
→ The ore is treated with Sodium hydroxide solution (NaOH), in which Iron oxide (Fe_2O_3) impurity does not react with it and can be removed by filtration.

$$Al_2O_3(s) + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4](aq)$$
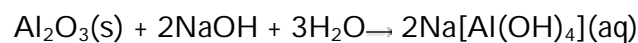
→ The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated.
$$2Na[Al(OH)_4](aq) + CO_2(g) \longrightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3$$
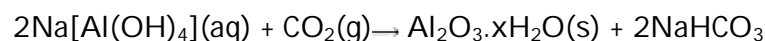
→ $Al(OH)_3$ is ignited to get pure Bauxite called Alumina.
$$Al_2O_3.xH_2O(s) \xrightarrow{\text{heat}} \textbf{Al}_2\textbf{O}_3 \textbf{ (s)} + 3 H_2O \text{ (g)}$$

(b) Leaching of Silver Ore :

→ In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by replacement.
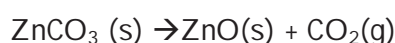
$$4Ag(s) + 8NaCN(aq) + 2H_2O + O_2(g) \rightarrow 4Na[Ag(CN)_2](aq) + 4NaOH$$

$$2Na[Ag(CN)_2](aq) + Zn(s) \rightarrow Na_2[Zn(CN)_4](aq) + 2Ag(s)$$
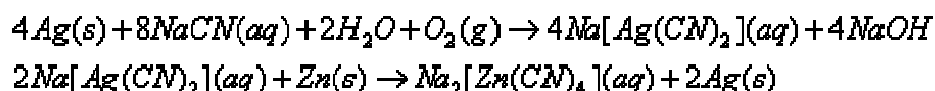
B) Isolation of the metal from its concentrated ore:

i) Conversion of Ore in to Metal oxide:

→ **Roasting**: The process in which the ores are heated in presence of excess of oxygen. This process is mainly used for Sulphide ores.

$$ZnS + O_2 \rightarrow ZnO + SO_2$$
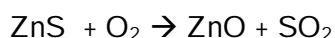
→**Calcination**: It involves heating when the volatile matter escapes leaving behind the metal oxide. This process is mainly used for Carbonate and hydroxide ores.

$$Fe_2O_3.xH_2O(s) \rightarrow Fe_2O_3 (s) + xH_2O(g)$$

$$ZnCO_3 (s) \rightarrow ZnO(s) + CO_2(g)$$

$$CaCO_3.MgCO_3(s) \rightarrow CaO(s) + MgO(s) + 2CO_2(g)$$

ii) Conversion of Metal oxide in to Metal through Thermodynamical principles:

Reduction of the metal oxide usually involves heating it with some other substance acting as a reducing agent (C or CO or even another metal). The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.

$$MxOy + yC \rightarrow xM + y CO$$
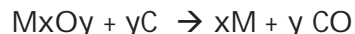
Some metal oxides get reduced easily while others are very difficult to be reduced. In any case, heating is required. To understand the variation in the temperature requirement for thermal reductions *(pyrometallurgy)* and to predict which element will suit as the reducing agent for a given metal oxide ($MxOy$), Gibbs energy interpretations are made. The change in Gibbs energy, ᐁG for any process at any specified temperature, is described by the equation:

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

where, ΔH is the enthalpy change and ΔS is the entropy change for the process.

1. If the value of ΔG *is negative* then only then the reaction will proceed. If ΔS is positive, on increasing the temperature (T), the value of $T\Delta S$ would increase ($\Delta H < T\Delta S$) and then ΔG will become –ve.

2. If reactants and products of two reactions are put together in a system and the net ΔG of the two possible reactions is –ve, the overall reaction will occur. So the process of interpretation involves coupling of the two reactions, getting the sum of their ΔG and looking for its magnitude and *sign*. Such coupling is easily understood through Gibbs energy (ΔG) vs T plots for formation of the oxides in Ellingham Diagram.

Ellingham Diagram provides a suitable reducing agent in the reduction of oxides. Such diagrams help us in predicting the feasibility of thermal reduction of an ore.
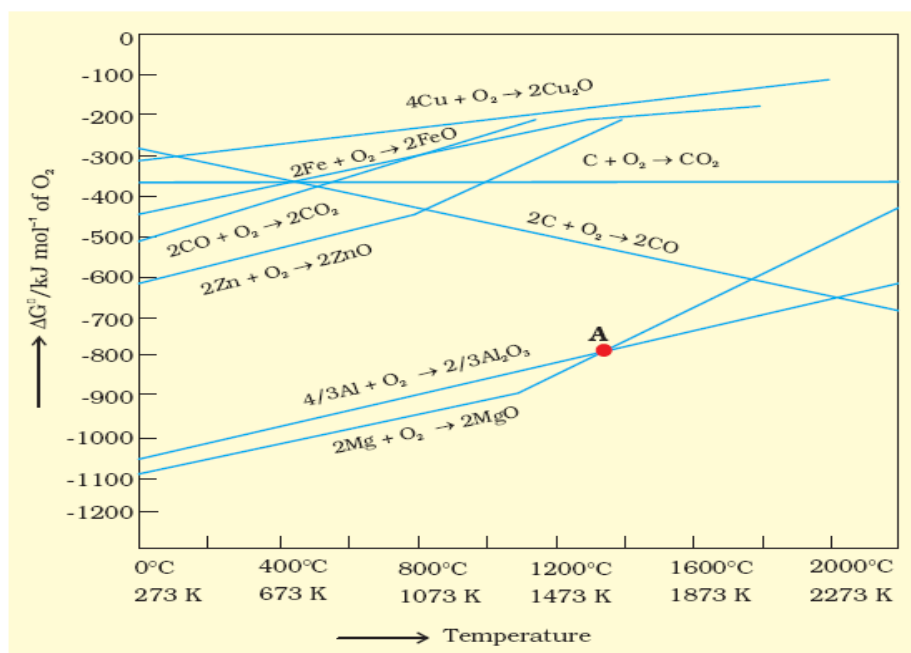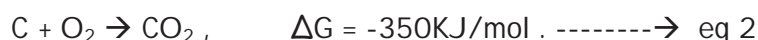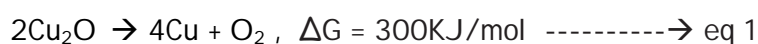
Ellingham Diagram

The following examples explains better understanding of Ellingham Diagram in reduction of metal oxide to metal using suitable reducing agent at different temperatures.

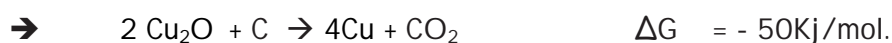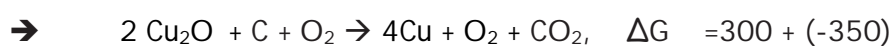Ex : **Q 1)** From the Below Ellinghams diagram,
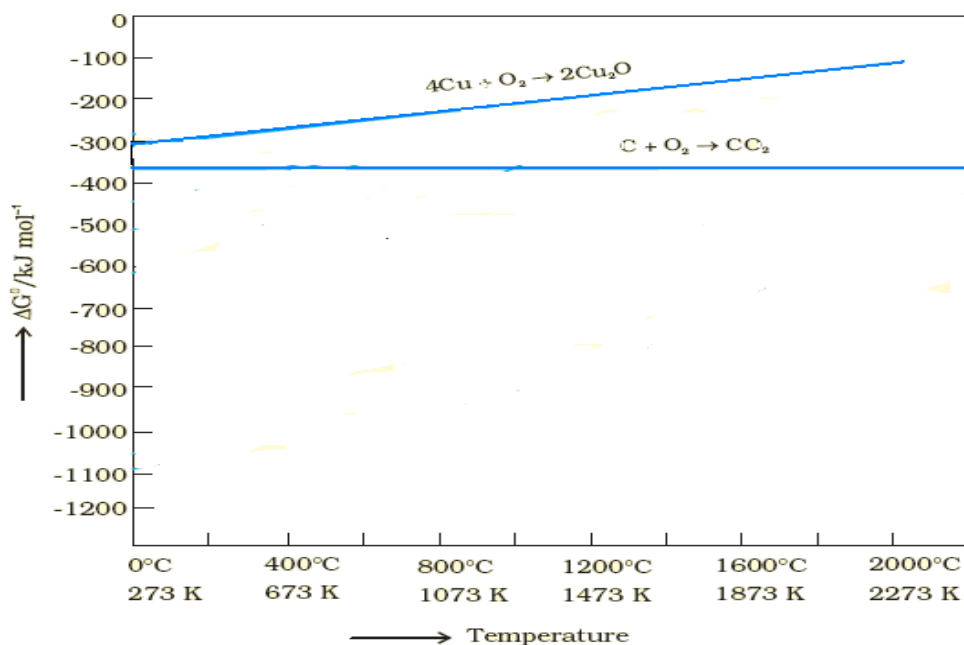
Can carbon acts as a reducing agent for reducing Cu_2O to Cu at 273K ?

ANS: Calculation of ΔG value for the reduction of Cu_2O using Carbon.

$$2Cu_2O \rightarrow 4Cu + O_2 , \quad \Delta G = 300KJ/mol \text{ ----------} \rightarrow eq\ 1$$

$$C + O_2 \rightarrow CO_2 , \quad \quad \Delta G = -350KJ/mol . \text{ --------} \rightarrow eq\ 2$$

Eq 1 + Eq 2 (Coupling of above reactions),

➔ $2\ Cu_2O + C + O_2 \rightarrow 4Cu + O_2 + CO_2, \quad \Delta G = 300 + (-350)$

➔ $2\ Cu_2O + C \rightarrow 4Cu + CO_2 \quad \quad \Delta G = -50Kj/mol.$

Yes, carbon acts as a reducing agent for reducing Cu_2O to Cu, because $\Delta G < 0$.

Ex : **Q 2)** From the Below Ellinghams diagram,
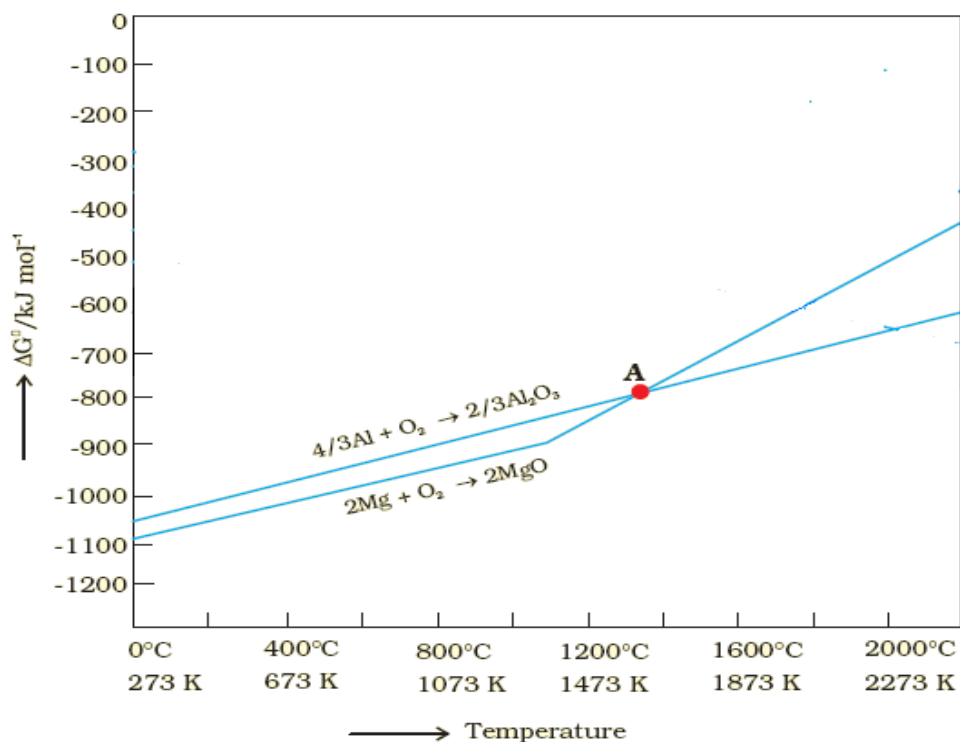
a) Can Al acts as a reducing agent for reducing MgO to Mg at 2273K ?

b) Can Al acts as a reducing agent for reducing MgO to Mg at 1073K ?

ANS: a) Calculation of ΔG value for the reduction of Mg O using Al at 2273K

$2MgO \rightarrow 2Mg + O_2$, $\Delta G = 600KJ/mol$ ----------$\rightarrow$ eq 1

$4/3\ Al + O_2 \rightarrow 2/3\ Al_2O_3$, $\Delta G = -700KJ/mol$. --------$\rightarrow$ eq 2

Eq 1 + Eq 2 (Coupling of above reactions),

$\rightarrow$ 2 MgO + 4/3 Al + O_2 $\rightarrow$ 2Mg + O_2 + 2/3 Al_2O_3, ΔG =600 + (-700)

$\rightarrow$ 2 MgO + 4/3 Al $\rightarrow$ 2Mg + 2/3 Al_2O_3, ΔG = -100Kj/mol.

Yes, Al can acts as a reducing agent for reducing MgO to Mg at 2273K, because $\Delta G < 0$.

b) Calculation of ΔG value for the reduction of Mg O using Al at 1073K

$2MgO \rightarrow 2Mg + O_2$, $\Delta G = 950KJ/mol$ ----------$\rightarrow$ eq 1

$4/3\ Al + O_2 \rightarrow 2/3\ Al_2O_3$, $\Delta G = -900KJ/mol$. --------$\rightarrow$ eq 2

Eq 1 + Eq 2 (Coupling of above reactions),

$\rightarrow$ 2 MgO + 4/3 Al + O_2 $\rightarrow$ 2Mg + O_2 + 2/3 Al_2O_3, ΔG =950 + (-900)

$\rightarrow$ 2 MgO + 4/3 Al $\rightarrow$ 2Mg + 2/3 Al_2O_3, ΔG = 50Kj/mol.

No, Al can not acts as a reducing agent for reducing MgO to Mg at 1073K, because $\Delta G > 0$.

Ex: **Q 3)** From the Below Ellinghams diagram,
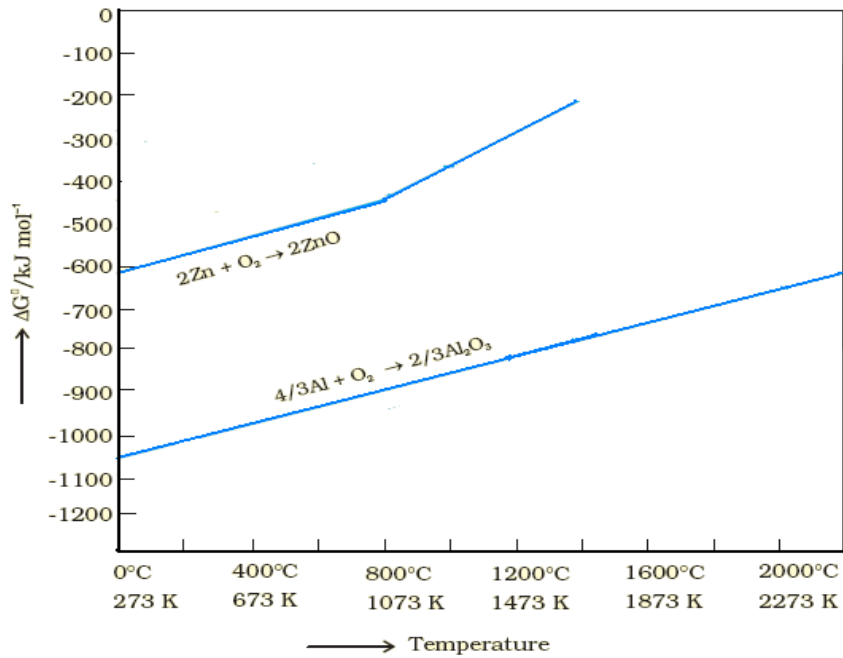
Can Al acts as a reducing agent for reducing ZnO to Zn at 1473K ?

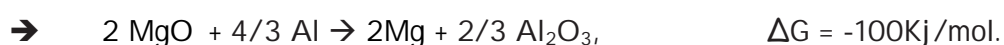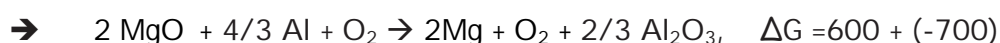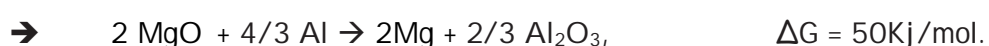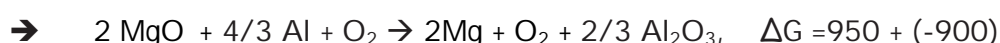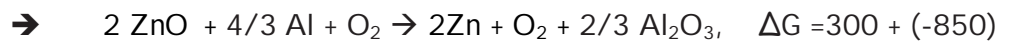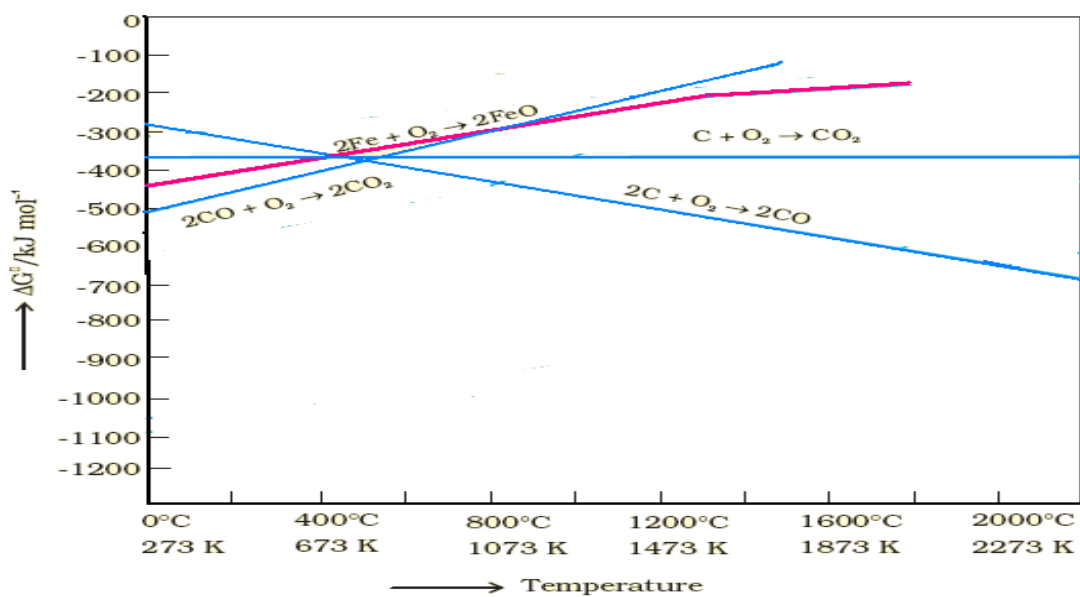**Ans**: Calculation of ΔG value for the reduction of Zn O using Al at 1473K

$$2ZnO \rightarrow 2Zn + O_2 , \qquad\qquad \Delta G = 300KJ/mol \text{ ----------} \rightarrow eq\ 1$$

$$4/3\ Al + O_2 \rightarrow 2/3\ Al_2O_3 , \qquad \Delta G = -850KJ/mol . \text{ --------} \rightarrow eq\ 2$$

Eq 1 + Eq 2 (Coupling of above reactions),

➔ $2\ ZnO + 4/3\ Al + O_2 \rightarrow 2Zn + O_2 + 2/3\ Al_2O_3$, $\Delta G = 300 + (-850)$

➔ $2\ ZnO + 4/3\ Al \rightarrow 2Zn + 2/3\ Al_2O_3$, $\Delta G = -550Kj/mol.$
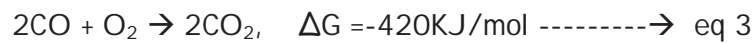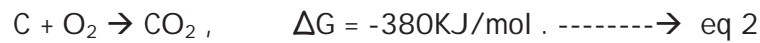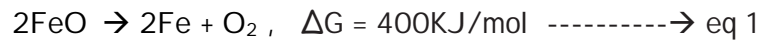
Yes, Al can acts as a reducing agent for reducing ZnO to Zn at 1473K, because ΔG < 0.

Ex: **Q 4)** From the Below Ellinghams diagram

Predict the best reducing agent 'carbon' or 'carbon monoxide' for reducing FeO to Fe in a blast furnace at the temperatures i) 673K   ii) 1073K   iii) 1473K

ANS: **a) Calculation of ΔG value for the reduction of FeO using Carbon / CO at 673K**

$$2FeO \rightarrow 2Fe + O_2, \quad \Delta G = 400KJ/mol \text{ ----------} \rightarrow eq 1$$

$$C + O_2 \rightarrow CO_2, \quad \Delta G = -380KJ/mol. \text{ --------} \rightarrow eq 2$$

$$2CO + O_2 \rightarrow 2CO_2, \quad \Delta G = -420KJ/mol \text{ ---------} \rightarrow eq 3$$

Eq 1 + Eq 2 (Coupling of above reactions), $\rightarrow \Delta G = 400 - 380 = 20Kj/mol$

Eq 1 + Eq 3 (Coupling of above reactions), $\rightarrow \Delta G = 400 - 420 = -20Kj/mol$

From the above, we can infer that carbon monoxide acts as a reducing agent for reducing FeO to Fe, at 673K because $\Delta G < 0$.

b) Calculation of ΔG value for the reduction of FeO using Carbon / CO at 1073K

$$2FeO \rightarrow 2Fe + O_2, \quad \Delta G = 320KJ/mol \text{ ----------} \rightarrow eq 1$$

$$C + O_2 \rightarrow CO_2, \quad \Delta G = -380KJ/mol. \text{ --------} \rightarrow eq 2$$

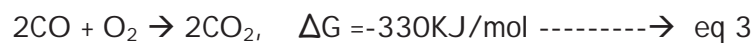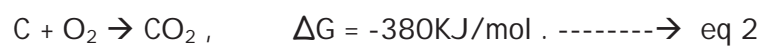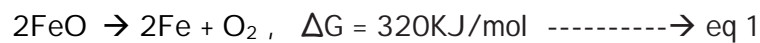$$2CO + O_2 \rightarrow 2CO_2, \quad \Delta G = -330KJ/mol \text{ ---------} \rightarrow eq 3$$

Eq 1 + Eq 2 (Coupling of above reactions), $\rightarrow \Delta G = 320 - 380 = -60Kj/mol$

Eq 1 + Eq 3 (Coupling of above reactions), $\rightarrow \Delta G = 320 - 330 = -10Kj/mol$

From the above, we can infer that carbon monoxide aswell as Carbon acts as a reducing agent for reducing FeO to Fe, at 1073K because $\Delta G < 0$. a)

c) Calculation of ΔG value for the reduction of FeO using Carbon / CO at 1473K

$$2FeO \rightarrow 2Fe + O_2, \quad \Delta G = 290KJ/mol \text{ ----------} \rightarrow eq 1$$

$$C + O_2 \rightarrow CO_2, \quad \Delta G = -380KJ/mol. \text{ --------} \rightarrow eq 2$$

$$2CO + O_2 \rightarrow 2CO_2, \quad \Delta G = -250KJ/mol \text{ ---------} \rightarrow eq 3$$
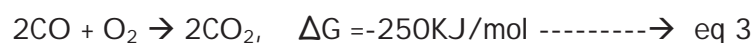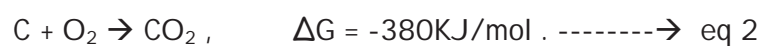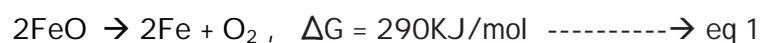
Eq 1 + Eq 2 (Coupling of above reactions), $\rightarrow \Delta G = 290 - 380 = -90Kj/mol$

Eq 1 + Eq 3 (Coupling of above reactions), $\rightarrow \Delta G = 290 - 250 = 40Kj/mol$

From the above, we can infer that carbon acts as a reducing agent for reducing FeO to Fe, at 1473K because $\Delta G < 0$.

Extraction of some metals from their metal oxides:

1) Iron from Iron oxide:

    a) Removal of chemical impurity:

→Silica (SiO_2) is a chemical impurity which is acidic in nature present along with the ore.

→ **A basic flux** like calcium oxide (CaO) is added to remove Silica.

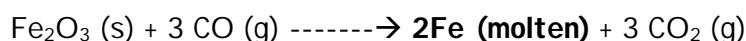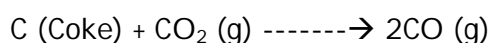→ CaO is obtained from the Lime stone ($CaCO_3$) which decomposes to CaO and CO_2 in the furnace due to intense heat.

$$CaCO_{3\ (s)} \text{-------} \rightarrow CaO_{\ (s)} + CO_{2\ (g)}.$$
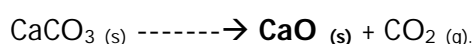
→The impurity SiO_2, combines with CaO to form calcium silicate ($CaSiO_3$) called Slag.

$$CaO_{\ (s)} + SiO_{2\ (s)} \text{--------} \rightarrow CaSiO_3.$$
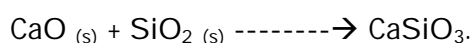
    b) Extraction of Iron:

→ The pure Haematite ore, Ferric oxide (Fe_2O_3) is reduced to iron in presence of a reducing agent Coke (carbon).

→ Coke (C) combines with CO_2 to form carbon monoxide which is a very good reducing agent which reduces Fe_2O_3 in to Iron (Fe).

$$C\ (Coke) + CO_2\ (g) \text{-------} \rightarrow 2CO\ (g)$$

$$Fe_2O_3\ (s) + 3\ CO\ (g) \text{-------} \rightarrow 2Fe\ (molten) + 3\ CO_2\ (g)$$

→ The **slag** calcium silicate ($CaSiO_3$), is lighter than molten Iron which floats over the molten iron and also which also prevents the molten Iron to oxidize in presence of oxygen in the furnace.

→ The slag and the molten Iron are collected separately as shown in the figure.

2) Aluminium from Alumina (Aluminium oxide):

   **Electrolytic Reduction** : **Hall's Process** :

→The Pure Alumina having high melting point i.e 2348K., it is highly expensive to carry the electrolytic reduction process at this temperature.

→To reduce the melting point and by increase the electrical conductivity of Alumina a substance called Cryolite (Na_3AlF_6) is added.

→The electrolytic reduction process carried as shown as

Cathode reaction : $Al^{+3} + 3e^- \longrightarrow$ **Al**

Anode Reaction : $2O^{-2} - 4e^- \longrightarrow O_2$ (g)
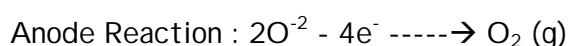
→ The oxygen gas liberated at anode reacts with graphite anode and form CO_2 gas, so anode is to be replaced from time to time.

$$C(graphite) + O_2 \text{ (g)} \longrightarrow CO_2(g) \, .$$
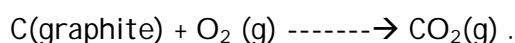
→ The pure aluminium (Al) is collected from the cathode from time to time.

3) Copper from Copper Oxide :

a) Removal of chemical impurity:

→The ore contains FeO is a basic impurity which is removed by adding an **acidic flux** silica.

→Iron oxide 'slags of' as iron silicate and copper is produced in the form of ***copper matte.*** This **contains Cu_2S and FeS.**

$$FeO + SiO_2 \rightarrow FeSiO_3$$
(Slag)
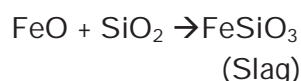
→Copper matte is then charged into **silica lined convertor**. hot air blast is blown to convert the remaining FeS_2, FeO and Cu_2S/Cu_2O to the metallic copper. Following reactions take place:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \rightarrow FeSiO_3$$
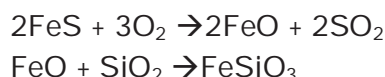
b) Extraction of Copper:Auto reduction/ Self Reduction:

Method 1: Process takes place in a reverbatory furnace:

→Hot air is blown to convert the Cu_2S to Cu_2O. The Cu_2O formed converted in to metallic copper in the presence of remaining Cu_2S which acts as a reducing agent.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$
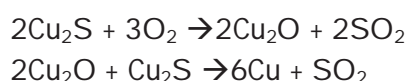
→The solidified copper obtained has blistered appearance **due to the evolution of SO_2** and so it is called **blister copper.**

Method 2: Process takes place with the help of a reducing agent C / CO :

→In the Ellingams diagram 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).

→ The sulphide ores are roasted/smelted to give oxides
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
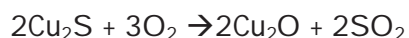
→The oxide can then be easily reduced to metallic copper using coke:
$$Cu_2O + C \rightarrow 2\,Cu + CO$$
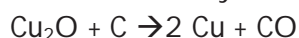
4) Extraction of zinc from zinc oxide:

→The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.

$$ZnO + C \text{ (coke)} \rightarrow Zn + CO \text{ at 673K}$$

→The metal is distilled off and collected by rapid chilling.

C) Purification of the metal (Or) Refining of the Metal:

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below.
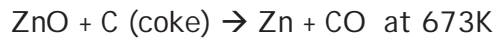
a) Distillation
b) Liquation
c) Electrolysis
d) Zone refining
e) Vapour phase refining
f) Chromatographic methods

(a) Distillation:

This is very useful for **low boiling metals like zinc and mercury**. The impure metal is evaporated to obtain the pure metal as distillate.

(b) Liquation:

In this method a **low melting metal like tin** can be made to flow on a sloping surface. In this way it is separated from higher melting impurities.

(c) Electrolytic refining:

In this method,

*The impure metal is made to act as anode.
*A strip of the same metal in pure form is used as cathode.
*They are put in a suitable electrolytic bath containing soluble salt of the same metaL
*The more basic metal remains in the solution and the less basic ones go to the anode mud.
.   *The reactions are:

$$\text{Anode:} \quad M \rightarrow M^{n+} + ne-$$
$$\text{Cathode:} \quad M^{n+} + ne^- \rightarrow M$$

Example: **Copper** is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:

$$\text{Anode: } Cu \rightarrow Cu^{2+} + 2 e-$$
$$\text{Cathode: } Cu^{2+} + 2e- \rightarrow Cu$$
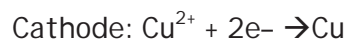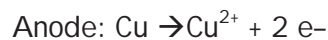
Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum.

(d) Zone refining :
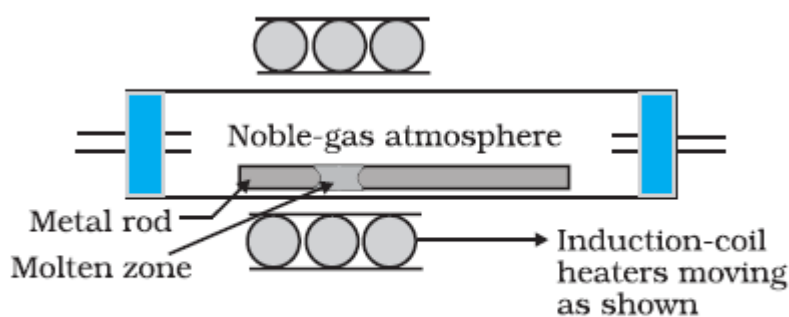
Zone refining

Principle: The impurities are more soluble in the melt than in the solid state of the metal.

Method: Circular mobile heater is fixed at one end of a rod of the impure metal. The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off. This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

(e) Vapour phase refining :

In this method, the metal is converted into its volatile compound. It is then decomposed to give pure metal. So, the two requirements are:

(i) The metal should form a volatile compound with an available reagent,
(ii) The volatile compound should be easily decomposable, so that the recovery is easy.

Examples :.

1) Mond Process for Refining Nickel:

In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl.

$$Ni + 4CO \rightarrow Ni(CO)_4 \text{ at } 330 - 350 \text{ K.}$$

The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal

$$Ni(CO)_4 \rightarrow Ni + 4CO \text{ at } 450 - 470 \text{ K.}$$

2) Van Arkel Method for Refining Zirconium or Titanium:

This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti.

The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilizes.

$$Zr + 2I_2 \rightarrow ZrI_4$$

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$$ZrI_4 \rightarrow Zr + 2I_2$$
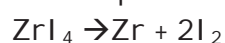
(f) Chromatographic methods:

Principle: This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent.

Method: The mixture is put in a liquid medium which is moved through the adsorbent. Different components are adsorbed at different levels on the column. Later the adsorbed components are removed by using suitable solvents.

Column chromatography: 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 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.

Section –B: Important Conceptual questions and answers:

1Q. Give the name and composition of the ore chosen for extraction of aluminium. (1 Mark)
(**Ans**) The ore chosen for the extraction of aluminium is bauxite and its composition is
$Al_2O_3.xH_2O$.

2Q. What is leaching? (1 Mark)
(**Ans**) Leaching is the process of extracting a substance from a solid by dissolving it in a liquid. In metallurgy leaching is used for the ores that are soluble in a suitable solvent.

3Q. Why are cryolite and fluorospar added to alumina during electrolytic reduction?(1 Mark)
(**Ans**) Cryolite and fluorospar are added to alumina during elctrolytic reduction to reduce the melting point of alumina and to increase its conductivity.

4Q. Reduction with C for Cu_2O can be done at a lower temperature than ZnO. Why? (1 M)
(**Ans**) In the ellingham diagram the curve for Cu_2O lies higher than ZnO i.e. for the reduction of Cu_2O with C the negative value of gibbs energy can be reached at a lower temparature than ZnO.

5Q. Although thermodynamically feasible in practice magnesium metal is not used for the reduction of alumina. Why? (1 Mark)
(**Ans**) Magnesium can reduce alumina at the temperature above 1500^0c (The intersection point of the curves for Al_2O_3 and MgO in the Gibbs Energy vs T plot (ellingham diagram)). But the temperature at which this is feasible is too high to be achieved economically and is also technologically difficult. So this reduction is not done.

6Q. Define Metallurgy. (1 Mark)
(**Ans**) Metallurgy is the process of extraction of metals from their ores that includes various steps.

7Q. Why is hydraulic washing a type of gravity separation? (1 Mark)
(**Ans**) The process of hydraulic washing is based on the differences in gravity of the ore and the gangue particles and so is known as gravity separation.

8Q. What is the use of van Arkel method? (1 Mark)
(**Ans**) Van Arkel method is used for removal of impurities like oxygen and nitrogen from the metals like zirconium and titanium.

9Q. How is distillation used for metal refining? (1 Mark)

(**Ans**) Distillation is used for the metals with boiling point lower then the impurities. So the metals can be evaporated and separately obtained as distillate.

10Q. Why do the anodes used in the elctrolytic cell for the reduction of alumina need to be replaced regularly?
(1 Mark)

(**Ans**) The oxygen liberated at the anode during the reduction of alumina, reacts with the carbon of the anode to form CO and CO burning away the anode and hence the anodes need to be replaced.

11Q. What is the role of depressant in froth floatation process?   (1 Mark)

(**Ans**) In froth floatation process the depressant selctively prevents one of the ores from coming to the froth in a mixture of two ores hence enabling the separation of the other one with the froth.

12Q. State the role of silica in the matallurgy of copper.   (1 Mark)

(**Ans**) Silica in the metallurgy of copper helps in the removal of iron oxide as iron silicate (slag).

13Q. What is the role of graphite rods in the electrometallurgy of aluminium? (1 Mark)

(**Ans**) In the electrometallurgy of aluminium graphite rods act as anodes in the electrolytic cell of reduction and are the site for release of oxygen.

14Q. What is refining of metals?   (1 Mark)

(**Ans**) Refining of metal is the process of purification of a metal extracted from its ore.

15Q. What is vapour phase refining?   (1 Mark)

(**Ans**) Vapour phase refining is the method of metal refining by changing the metal into volatile compound that can be collected separately leaving behind the impurities and can be decomposed to give the pure metal

16Q. Give the principle underlying the process used for refining of gallium. (1 Mark)

(**Ans**) The process used for the refining of gallium is **zone refining** and the principle underlying it is that the impurities are more soluble in the melt than in the solid state of the metal.

17Q. State the principle on which the chromatographic methods of metal refining are based?   (1 M)

(**Ans**) Chromatographic methods of metal refining are based on the principle that different components of a mixture are differently adsorbed on an adsorbent.

18Q. Which is the purest form of iron and what are its uses?   (1 Mark)

(**Ans**) The purest form of iron is **wrought** iron and is used in making anchors, wires, bolts etc.

19Q. What are minerals and how are they different from ores?   (2 Marks)

(**Ans**) Minerals are the naturally occurring chemical substances in the earth's crust obtained by mining. It is different from ores, as ores are the minerals that are used for the extraction of metals profitably.

20Q. Name one ore each for iron and copper and give their chemical compositions. (2 Marks)

(**Ans**) The ore of iron is haematite- Fe_2O_3 and the ore for copper is copper pyrites- $CuFeS_2$.

21Q. What is the purpose of adding collectors and froth stabilisers during froth floatation? Give an example for each.   (2 Marks)

(**Ans**) During froth floatation process collectors like pine oil and fatty acids are added to enhance non wettability of the mineral particles and the froth stabilisers like cresol and aniline stabilise the froth.

22Q. How can the ores ZnS and PbS be separated from a mixture using froth floatation process? **(2 Marks)**

(**Ans**) During the froth floatation process a depressent like NaCN is added to the tank. The depressent selectively prevents ZnS from coming to the froth but allows PbS to come to the froth and hence helps the separation of PbS with the froth.

23Q. Give the equations involved in the concentration of bauxite ore. **(2 Marks)**

(**Ans**) i) $Al_2O_3(s) + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4](aq)$

ii) $2Na[Al(OH)_4](aq) + CO_2(g) \longrightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3$

iii) $Al_2O_3.xH_2O(s) \longrightarrow Al_2O_3(s) + xH_2O$

24Q. Why is coke preferred over CO for reducing FeO? **(2 Marks)**
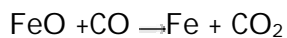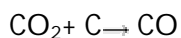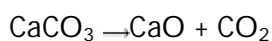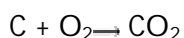
(**Ans**) According to ellingham diagram the point of intersection of the curves of C, CO and Fe, FeO lies at temperature lower than that of the point of intersection of CO, CO_2 and Fe, FeO curves. This means the reduction of FeO will occur at much lower temperature with C than with CO. So C is preferred to CO for reduction.

25Q. How is cast iron different from pig iron? **(2 Marks)**

(**Ans**) Pig iron has 4% carbon and can be easily cast into varity of shapes. Whereas cast iron has lower carbon content and is extremely hard and brittle.

26Q. Give the reactions involved in the reduction of iron oxide to give iron in a blast furnace. (3 M)

(**Ans**) The reactions are as follows:

$$C + O_2 \longrightarrow CO_2$$
$$CaCO_3 \longrightarrow CaO + CO_2$$
$$CO_2 + C \longrightarrow CO$$
$$3Fe_2O_3 + CO \longrightarrow Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$$
$$FeO + CO \longrightarrow Fe + CO_2$$
$$FeO + C \longrightarrow Fe + CO$$
$$CaO + SiO_2 \longrightarrow CaSiO_3$$
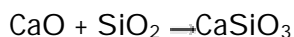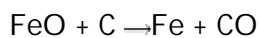
27Q. How is copper extracted from low grade ores and scraps? **(3 Marks)**

(**Ans**) For extraction of copper from low grade ores and scraps the ore is first leached out using acid or bacteria. The solution containing Cu^{2+} is treated with scarp iron or H_2 and Cu is obtained.

$$Cu^{2+}(aq) + H_2(g) = Cu(s) + 2H^+(aq)$$
$$Cu^{2+} + Fe = Cu(s) + Fe^{2+}$$
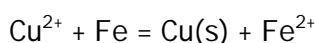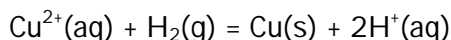
28Q. How is nickel refined? **(3 Marks)**

(**Ans**) Nickel is refined by Mond process which is based upon vapour phase refining.
In this process nickel is heated in stream of carbon monoxide giving a volatile complex, leaving the impurities behind. The complex is further subjected to higher temperature so that it gets decomposed to giving pure metal.330-350K

$$Ni + 4CO \text{ --------------> } Ni(CO)_4$$
450-470K

$$Ni(CO)_4 \text{ -----------------> } Ni + 4CO$$
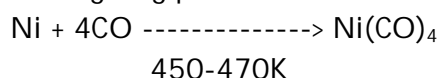
Section C: CBSE sample paper, Question and answer:

1Q: 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 Aluminium is thermodynamically feasible, yet it does not occur at room temperature.
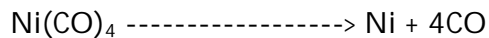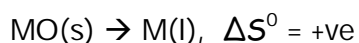
c) Pine oil is used in Froth floatation method.   **(CBSE –SAM Paper–1 – 3M)**

Ans: a) This is because if the metal is in liquid state, its entropy is higher than when it is in solid state. When the metal oxide (solid state) reduced to metal (liquid state), the entropy increases.

$$MO(s) \rightarrow M(l), \ \Delta S^0 = \text{+ve}$$

We know, $\Delta G^0 = \Delta H^0 - T\Delta S^0$, the ΔG^0 becomes more negative, and hence reduction occurs easier.

b) The reduction of Cr_2O_3 with Al is thermodynamically, feasible, because ΔG is negative.

$$Cr_2O_3 + Al \text{ --} \rightarrow Al_2O_3 + Cr, \ \Delta G = \text{-ve.}$$
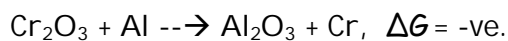
By increasing temperature, fraction of activated molecules increase which help in crossing over the energy barriers.

c) Pine oil enhances non-wetting property of ore particles and acts as a froth collector.

2Q: An Ore sample of Gelena (PbS) is contaminated with Zinc blend (ZnS). Name one chemical whichcan be used to concentrate galena selectively by Froth floatation method.

(CBSE-SAMPaper2–1M)

Ans: NaCN (sodium cyanide) is used as depressant.

3Q: Free energies of formation (ΔfG) of MgO (l) and $CO(g)$ at 1273K and 2273K are given below.

ΔfG (MgO(s)) = - 941 kj/mol at 1273K, ΔfG(MgO(s)) = -314 KJ/mol at 2273K,

 $\Delta fG(CO(g))$ = -439KJ/mol at 1273K, $\Delta fG(CO(g))$ = -628KJ/mol at 2273K.

On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for MgO (s).   **(CBSE –SAM Paper-2 – 2M)**

Ans: Reduction of MgO (s) with carbon can be written as MgO (s) + C (s) --→ Mg(s) + CO (g)

$$\Delta_rG= \Delta_fG(\text{products}) -\Delta_fG(\text{reactants})$$

$$\Delta_rG= \Delta_fG(CO(g)) -\Delta_fG(MgO(s))$$

At 1273K, Δ_rG = (-439) – (-941) =502Kj/mol, i.e $\Delta_rG > 0$

At 2273K, Δ_rG = (-628)-(-314) = -314Kj/mol, i.e $\Delta_rG < 0$

At 2273K, $\Delta_rG < 0$ So, the reaction is spontaneous.

4Q: (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.   **(CBSE –SAM Paper–3 – 3M)**

Ans: a) i) Mond's process ii) Van Arkel Method.

b) Step 1: Gold is leached with NaCN solution in the presence of oxygen. It is an oxidation reaction.

$$4Au \text{ (s)} + 8 CN\text{-} + 2 H_2O \text{ (l)} + O_2 \text{ (g)} \text{ --→ } 4 [Au (CN)_2]^- + 4 OH^-$$
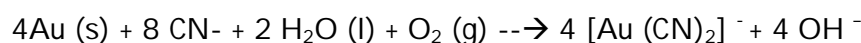
Step 2: The Cyano complex is treated with the highly reactive metal Zn, to remove Gold. This is a reduction reaction.

$$4 [Au (CN)_2]^- + Zn \text{ --→ } 4 [Zn (CN)_4]^{-2} + 2 Au(s)$$
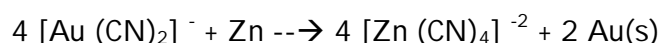
5Q: On what principle froth floatation process is carried for sulphide ores?

          (CBSE–SAM Paper–4 – 1M)

Ans: Wetting of Ore particles with the oil and the impurities with water.

6Q: Account for the following   **(CBSE –SAM Paper–4 – 2M)**

 a) Mond process for refining of Ni metal b) Zone refining

Ans: a) Nickel is refined by Mond process which is based upon vapour phase refining.

In this process nickel is heated in stream of carbon monoxide giving a volatile complex, leaving the impurities behind. The complex is further subjected to higher temperature so that it gets decomposed to giving pure metal.330-350K.

$$Ni + 4CO \text{ -------------> } Ni(CO)_4$$
$$450\text{-}470K$$
$$Ni(CO)_4 \text{ -----------------> } Ni + 4CO$$
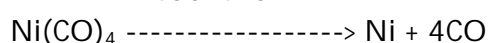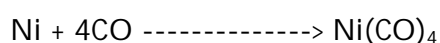
b) **Principle:** The impurities are more soluble in the melt than in the solid state of the metal.

Method: Circular mobile heater is fixed at one end of a rod of the impure metal. The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off.

7Q: What chemical principle is involved in choosing a reducing agent for getting the metal from its oxide Ore? Considering the metal oxides, Al_2O_3 and Fe_2O_3, and justify the choice of reducing agent in each case. **(CBSE –2008 – 3M)**

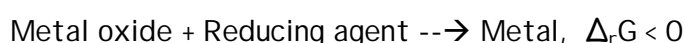Ans: In choosing the reducing agents for the reduction of metal oxides in to metal, a chemical principle like Thermodynamic principle i.e Gibbs energy involved. For the reduction process to be spontaneous Δ_rG value is less than zero at a given temperature.

Metal oxide + Reducing agent --→ Metal, $\Delta_rG < 0$

i) In an Ellingams diagram MgO line is below Al_2O_3 line so, Al_2O_3, can be reduced by the metal Mg which acts as a reducing agent. Thermodynamically the reaction is favarouble ($\Delta_rG < 0$)

ii) Fe_2O_3, can be reduced to Fe with the help of reducing agent Carbon monoxide below 1273K in a blast furnace. Thermodynamically the reaction is favarouble ($\Delta_rG < 0$)

8Q; State the basis of refining a substance by chromatographic method. Under what circumstances is this method specially useful? **(CBSE –Suply –2008 – 3M)**

Ans: This method is based on difference in extent of adsorption of different components of a mixture on an adsorbent. The mixture is put in a liquid which is moved through the adsorbent, different components are adsorbed at different levels in the column. Later the adsorbed components are removed by using suitable solvents.

Column chromatography is useful for purification of elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

9Q: The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with two examples. **(CBSE–SAM Paper–5 – 3M)**

Ans: It is true that choice of a reducing agent in a particular case depends on thermodynamic factor.
For the reducing of metal oxide in to its metal, a suitable reducing agent is required, if the Δ_rG for the coupling reaction is less than zero, then the reaction is feasible.

Ex: 1) At 1000K

Cr2O3 + 2 Al --→ Al2O3 + Cr, Δ_rG = -Ve
2MgO + 2 Al --→ Al2O3 + 3 Mg, Δ_rG = +ve
Thus, Al is correct choice for the reduction of Cr2O3 and not for MgO.
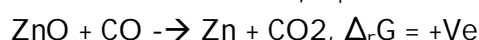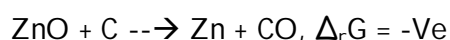
2) At 1500K,
ZnO + C --→ Zn + CO, Δ_rG = -Ve
ZnO + CO -→ Zn + CO2, Δ_rG = +Ve
Thus, coke (carbon) is correct choice for the reduction of ZnO to Zn.

10Q. What is vapour phase refining? What are the necessary requirements for the compound to be purified by vapour phase refining? (CBSE–SAM Paper–6 – 2M)

Ans. Vapour phase refining, the metal is converted into volatile compound and collected. Then it is decomposed separately to obtain pure metal.
Two necessary requirements for a compound to be purified by vapour phase refining are:-

(i) The metal should form a volatile compound with a common reagent.

(ii) The compound should be easily decomposable.

11Q. Why does CaO react with SiO$_2$ to form a slag? (CBSE–SAM Paper–6 – 1M)

Ans. CaO is basic oxide and SiO$_2$ is acidic oxide. I t is an example of acid –base reaction

Q. Explain the following:–
   (a) Role of cresols in froth flotation method.
   (b) Significance of leaching in extraction of silver. (CBSE–SAM Paper–7 – 3M)

Ans. (a) I t acts as froth stabilizer and stabilizes the froth.
(b) Leaching of silver ore converts it into soluble cyanide complex from where the metal is extracted by distillation with zinc.
$$4Ag(s) + 8NaCN(aq) + 2H_2O + O_2(g) \rightarrow 4Na[Ag(CN)_2](aq) + 4NaOH$$
$$2Na[Ag(CN)_2](aq) + Zn(s) \rightarrow Na_2[Zn(CN)_4](aq) + 2Ag(s)$$

12Q. What is meant by the term "chromatography"? (CBSE–SAM Paper–8 – 1M)

Ans. This method firstly used for the separation of coloured substances (plant pigments) into individual components. But nowadays this method is widely used for separation, purification, identification and characterization of the components of a mixture whether coloured or colourless.

13Q. How will you differentiate in between 'roasting and calcination'?
(CBSE–SAM Paper–8 – 2M)

Ans. Roasting:- The process of converting a sulphide ore into its metallic oxide by heating strongly below its melting point in excess of air is called roasting.
$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2(g)$$
Calcination:- The process of converting carbonates and hydroxides ores of metals to their respective oxides by heating them strongly below their melting points either in absence or limited supply of air is called calcination.
$$Fe_2O_3.3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$$
$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$
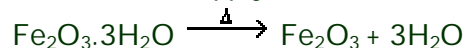
14Q. (a) What is the meant by the term electrolytic refining?
   (b) What is the signification of leaching in the extraction of Aluminium?
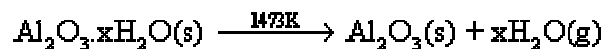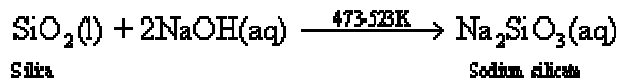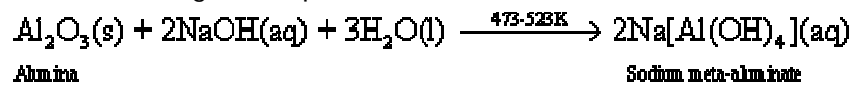(CBSE–SAM Paper–9 – 3M)

Ans. (a) This method is used for the purification of very reactive metals like Zn, Al, Ni etc.

In this method, the impure metal is attached to anode while cathode is made up of a pure metal rod. These electrodes are suspended in an metal salt solution (electrolyte). When electricity is passed through in metal salt solution, the pure metal transfer from anode to cathode via electrolyte. The impurities remains near the anode, this is called anode mud.

(b) Aluminium usually contains silica, iron oxide and titanium oxide as impurities.

These impurities can be removed by the process of leaching.

During leaching, the powdered bauxite ore is heated with a concentrated solution of NaOH at 473-523K, when alumina dissolves as sodium meta-aluminate and silica as sodium silicate leaving the impurities.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \xrightarrow{473-523K} 2Na[Al(OH)_4](aq)$$
Alumina   Sodium meta-aluminate

$$SiO_2(l) + 2NaOH(aq) \xrightarrow{473-523K} Na_2SiO_3(aq)$$
Silica   Sodium silicate

$$Al_2O_3.xH_2O(s) \xrightarrow{1473K} Al_2O_3(s) + xH_2O(g)$$

Thus, the signification of leaching in the extraction of aluminium is to prepare pure alumina from the bauxite ore.

15Q. (a) Copper and silver lie below in the electrochemical series and yet they are found in the combined state as sulphides in nature. Comment.

(b) Describe froth floatation process.   **(CBSE-SAM Paper–10 – 3M)**

Ans. (a) Due to high polarizing power of Cu and Ag ions, their sulphides are more stable than the metals.

(b) This method is widely used for the concentration of sulphides ores. In this method, we take the mixture of powdered ore, water, pine oil and xanthates in tank and fitted a below pipe in the tank. Below the air with help of below pipe, froth is formed in the tank. Light ores particles go with the froth and heavy gangue particles at the bottom of the tank. Skimmed off the concentrated ores particles washed with water and dry it. This ore is called concentrated ore.

Froth floatation process
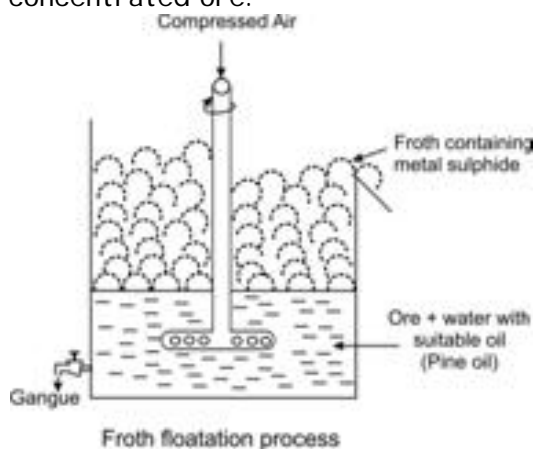
16Q. Name the chief ore of silver. Describe with chemical equations the extraction of silver from this ore.   **(CBSE-SAM Paper–11 – 3M)**

Ans. Silver glance (Argentite), Ag_2S is the chief ore of silver. The method involves leaching of the crude metal or ore with sodium cyanide solution (0.5% or less concentration) through which air is blown.

$$2Ag_2S + 8CN^- + O_2 + 2H_2O \rightarrow 4[Ag(CN)_2]^- + 2S + 4OH^-$$
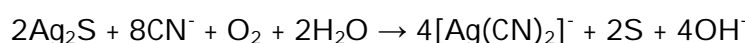
Silver goes into solution as complex cyanide and the pure metal is precipitated by addition of zinc.

$$2[Ag(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Ag(s)$$
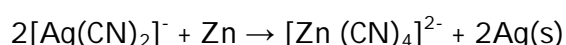
Section –D : Higher Order Questions for high achievers:

Q1. In the extraction of Copper, a process called "Poling" is used. Explain the process "poling".

Q2. How do non-metals occur in nature? Illustrate with an example.

Q3. How does NaCN act as a depressant in preventing ZnS from forming the froth?

Q4. Name the chief ore of Iron. How is the pig iron converted in to Steel? Describe any one method of steel making in details.

Q5. What do you understand by terms "Quenching" and "Tempering" ?

Q6. Explain the term "Smelting process" with an example.

Q7. Which method would you suggest for the separation of the metals in the following mixtures.

    i) Copper and Magnesium   ii) Copper and Zinc   iii) Rare earth elements.

Q8. What is Ellingams diagram? What are its important features? How it helps in selection of proper reducing agent and temperature during reduction of an Ore?

Multiple choice questions:

(Q.1) Cyanide process is used for the extraction of   (1 mark)

    (a) barium,
    (b) aluminium
    (c) boron
    (d) silver.

(Q.2) In the commercial electrochemical process for aluminium extraction the electrolyte used is

(1 mark)

(a) Al(OH)$_3$ in NaOH solution
(b) An aqueous solution of Al2(SO)3.
(c) A molten mixture of Al2O3 and Na3AlF6.
(d) A molten mixture of Al2O3 and Al(OH)3.

(Q.3) The natural materials from which an element can be extracted economically are called

(1 mark)

(a) Ores
(b) Minerals
(c) Gangue
(d) None of the above.

(Q.4) The impurities associated with minerals used in metallurgy are called collectively?

(1 mark)

(a) Slag
(b) Flux
(c) Gangue
(d) Ore

(Q.5) When a metal is to be extracted from its ore and the gangue associated with the silica, then

(1 mark)

(a) An acidic flux is needed
(b) A basic flux is needed
(c) Both acidic and basic fluxes are needed
(d) Neither of them is needed

(Q.6) A basic lining is given to a furnace by using

(1 mark)

(a) Calcined dolomite
(b) Lime stone
(c) Haematite
(d) Silica

(Q.7) Cryolite is

(1 mark)

(a) used in the electrolysis of alumina for decreasing electrical conductivity
(b) used in the electrolysis of alumina for lowering the melting point of alumina
(c) used in the electrolytic purification of alumina
(d) used in the electrolysis of alumina

(Q.8) Cassiterite is concentrated by   (1 mark)

    (a) Levigation
    (b) Electromagnetic separation
    (c) Floatation
    (d) Liquefaction

(Q.9) For which ore of the metal, froth floatation method is used for concentration?

                                                                       (1 mark)

    (a) Horn silver
    (b) Bauxite
    (c) Cinnabar
    (d) Haematite

(Q.10) Calcination is used in metallurgy for removal of?   (1 mark)

    (a) Water and sulphide
    (b) Water and CO_2
    (c) CO_2 and H_2S
    (d) H_2O and H_2S.

(Q.11) Heating of ore in the absence of air below its melting point is called   (1 mark)

    (a) Leaching
    (b) Roasting
    (c) Smelting
    (d) Calcination

(Q.12) Mac Arthur process is used for   (1 mark)

    (a) Ag
    (b) Fe
    (c) Cl
    (d) O_2

(Q.13) In Goldschmidt aluminothermic process, which of the following reducing agent is used

                                                                       (1 mark)

    (a) Coke
    (b) Al powder
    (c) Na
    (d) Ca

(Q.14) Match list I with list II and select the correct answer using the codes given below the lists

	List I		List II
I.	Cyanide process	A.	Ultrapure Ge
II.	Floatation process	B.	Pine oil
III.	Electrolytic reduction	C.	Extraction of Al
IV.	Zone refining	D.	Extraction of Au

(1 mark)

(a) I-C, II-A, III-D, IV-B
(b) I-D, II-B, III-C, IV-A
(c) I-C, II-B, III-D, IV-A
(d) I-D, II-A,   III-C, IV-B

(Q.15) Among the following statements the incorrect one is   (1 mark)

(a) Calamine and siderite are carbonates
(b) Argentite and cuprite are oxides
(c) Zinc blende and iron pyrites are sulphides
(d) Malachite and azurite are ores of copper.

(Q.16) Pyrolusite is a/an   (1 mark)

(a) Oxide ore
(b) Sulphide ore
(c) Carbide ore
(d) Not an ore

(Q.17) Cassiterite is an ore of   (1 mark)

(a) Mn
(b) Ni
(c) Sb
(d) Sn

(Q.18) Silver containing lead as an impurity is removed by   (1 mark)

(a) Poling
(b) Cupellation
(c) Lavigation
(d) Distillation

(Q.19) When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are?

Cathode   Anode

(a) pure zinc   pure copper

(b) impure sample   pure copper

(c) impure zinc   impure sample

(d) pure copper   impure sample.   (1 mark)

(Q.20) The substance not likely to contain CaCO3is   (1 mark)

(a) calcined gypsum
(b) sea shells
(c) dolomite
(d) a marble statue

(Q.21) Thomas stag is   (1 mark)

(a) Calcium silicate
(b) Calcium phosphate
(c) Tricalcium phosphate and calcium silicate
(d) Calcium ammonium phosphate

(Q.22) Before introducing FeO in blast furnace , it is converted to Fe2O3by roasting so that
                                                                            (1 mark)

(a) I t may not be removed as slag with silica
(b) I t may not evaporate in the furnace
(c) Presence of it may increase the m.pt. of charge
(d) None.

(Q.23) Among the following groups of oxides, the group containing oxides that cannot be reduced by carbon to give the respective metals is   (1 mark)

(a) Cu_2O, SnO_2
(b) Fe_2O_3, ZnO
(c) CaO, K_2O
(d) PbO, Fe_3O_4

(Q.24) Which process represents the change,

$$Ti + 2I_2 \longrightarrow TiI_4 \longrightarrow Ti + 2I_2$$

Impure metal   volatile
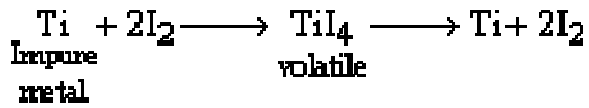
(1 mark)

    (a) Cupellation
    (b) Van Arkel
    (c) Poling
    (d) Zone Refining

(Q.25) Granulated Zn is obtained by   (1 mark)

    (a) Suddenly cooling molten Zinc
    (b) Adding molten Zn to H2O
    (c) Heating Zn to 100-150°C
    (d) Dropping molten Zn drop by drop

(Q.26) In which of the following minerals, aluminium is not present?   (1 mark)

    (a) Cryolite
    (b) Mica
    (c) Fledsper
    (d) Fluorspar

(Q.27) Which of the following metals is obtained by leaching the ore with dilute cyanide solution?

(1 mark)

    (a) Silver
    (b) Titanium
    (c) Vanadium
    (d) Zinc

(Q.28) Which of the following metals is sometimes found native in nature?   (1 mark)

    (a) Aluminium
    (b) Copper
    (c) Iron
    (d) Magnesium

◇◇◇◇◇◇◇ ALL THE BEST ◇◇◇◇◇◇◇