CHAPTER - 6
GENERAL PRINCIPLES & PROCESS OF ISOLATION OF ELEMENTS - EXERCISE SOLUTIONS

Question 6.1:

Copper can be extracted by hydrometallurgy but not zinc. Explain.

Answer

The reduction potentials of zinc and iron are lower than that of copper. In hydrometallurgy, zinc and iron can be used to displace copper from their solution.

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

But to displace zinc, more reactive metals i.e., metals having lower reduction potentials than zinc such as Mg, Ca, K, etc. are required. But all these metals react with water with the evolution of H_2 gas.

$$2K_{(s)} + 2H_2O_{(l)} \longrightarrow 2KOH_{(aq)} + H_{2(g)}$$

As a result, these metals cannot be used in hydrometallurgy to extract zinc.

Hence, copper can be extracted by hydrometallurgy but not zinc.

Question 6.2:

What is the role of depressant in froth floatation process?

Answer

In the froth floatation process, the role of the depressants is to separate two sulphide ores by selectively preventing one ore from forming froth. For example, to separate two sulphide ores (ZnS and Pbs), NaCN is used as a depressant which selectively allows PbS to come with froth, but prevents ZnS from coming to froth. This happens because NaCN reacts with ZnS to form $Na_2[Zn(CN)_4]$.

$$4\ NaCN + ZnS \longrightarrow Na_2[Zn(CN)_4] + Na_2S$$

Question 6.3:

Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?

Answer

The Gibbs free energy of formation ($\Delta_f G$) of Cu_2S is less than that of H_2S and CS_2.

Therefore, H_2 and C cannot reduce Cu_2S to Cu.

On the other hand, the Gibbs free energy of formation of Cu_2O is greater than that of

CO. Hence, C can reduce Cu_2O to Cu.

$$C_{(s)} + Cu_2O_{(s)} \longrightarrow 2Cu_{(s)} + CO_{(g)}$$

Hence, the extraction of copper from its pyrite ore is difficult than from its oxide ore through reduction.

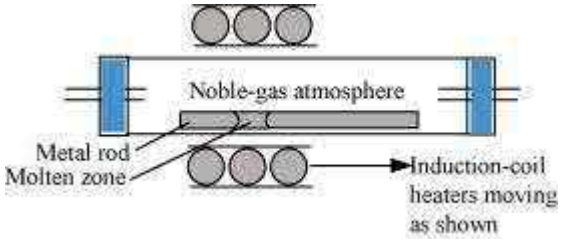
Question 6.4:

Explain: **(i)** Zone refining **(ii)** Column chromatography.

Answer

(i) Zone refining:

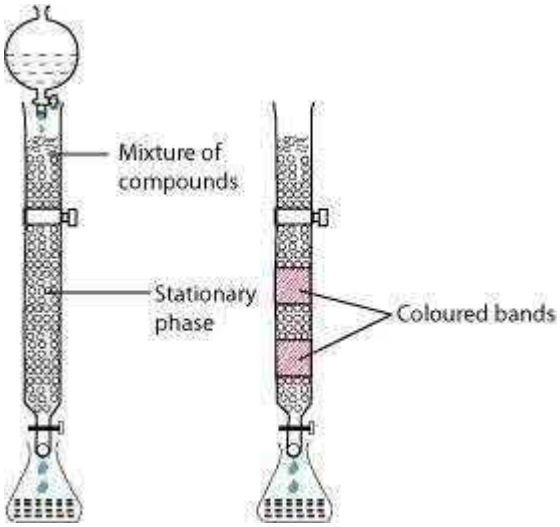
This method is based on the principle that impurities are more soluble in the molten state of metal (the melt) than in the solid state. In the process of zone refining, a circular mobile heater is fixed at one end of a rod of impure metal. As the heater moves, the molten zone of the rod also moves with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



(ii) Column chromatography:

Column chromatography is a technique used to separate different components of a mixture. It is a very useful technique used for the purification of elements available in minute quantities. It is also used to remove the impurities that are not very different in chemical properties from the element to be purified. Chromatography is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. In chromatography, there are two phases: mobile phase and stationary phase. The stationary phase is immobile and immiscible. Al_2O_3 column is usually used as the stationary phase in column chromatography. The mobile phase may be a gas, liquid, or supercritical fluid in which the sample extract is dissolved. Then, the mobile phase is forced to move

through the stationary phase. The component that is more strongly adsorbed on the column takes a longer time to travel through it than the component that is weakly adsorbed. The adsorbed components are then removed (eluted) using a suitable solvent (eluant).



Question 6.5:

Out of C and CO, which is a better reducing agent at 673 K?

Answer

At 673 K, the value of $\Delta G_{(CO,CO_2)}$ is less than that of $\Delta G_{(C,CO)}$. Therefore, CO can be reduced more easily to CO_2 than C to CO. Hence, CO is a better reducing agent than C at 673 K.

Question 6.6:

Name the common elements present in the anode mud in electrolytic refining of copper. Why are they so present ?

Answer

In electrolytic refining of copper, the common elements present in anode mud are selenium, tellurium, silver, gold, platinum, and antimony.

These elements are very less reactive and are not affected during the purification process. Hence, they settle down below the anode as anode mud.

Question 6.7:

Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.

Answer

During the extraction of iron, the reduction of iron oxides takes place in the blast furnace. In this process, hot air is blown from the bottom of the furnace and coke is burnt to raise the temperature up to 2200 K in the lower portion itself. The temperature is lower in the upper part. Thus, it is the lower part where the reduction of iron oxides (Fe_2O_3 and Fe_3O_4) takes place.

The reactions taking place in the lower temperature range (500 – 800 K) in the blast furnace are:

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

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

$$Fe_2O_3 + CO \longrightarrow 2Fe_3 + CO_2$$

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

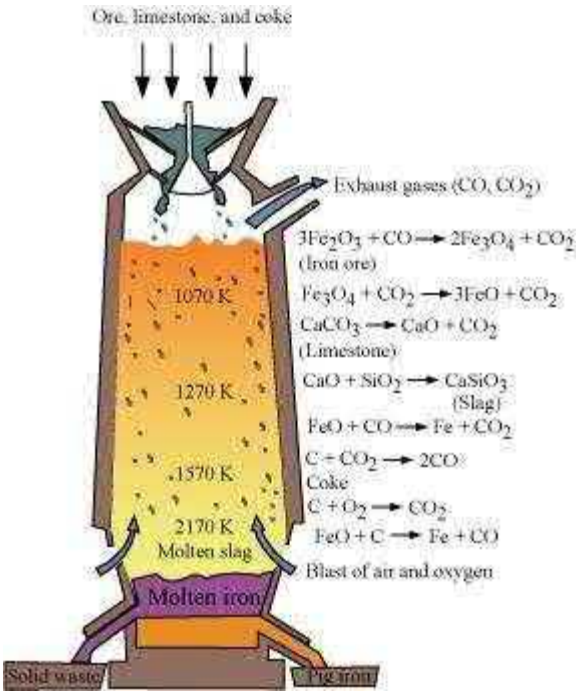
$$C + CO_2 \longrightarrow 2CO$$

$$FeO + CO \longrightarrow Fe + CO_2$$

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

$$CaCO_3 \longrightarrow CaO + CO_2$$

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



Question 6.8:

Write chemical reactions taking place in the extraction of zinc from zinc blende.

Answer

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

(i) Concentration of ore

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

(ii) Conversion to oxide (Roasting)

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

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

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

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

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

(iv) Electrolytic Refining

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

$$\text{Anode}: \quad Zn \longrightarrow Zn^{2+} + 2e^-$$
$$\text{Cathode}: Zn^{2+} + 2e^- \longrightarrow Zn$$

Question 6.9:

State the role of silica in the metallurgy of copper.

Answer

During the roasting of pyrite ore, a mixture of FeO and Cu_2O is obtained.

$$2\,CuFeS_2 + O_2 \xrightarrow{\Delta} Cu_2S + 2\,FeS + SO_2$$
$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$
$$2FeS + 3O_2 \xrightarrow{\Delta} 2FeO + 2SO_2$$

The role of silica in the metallurgy of copper is to remove the iron oxide obtained during the process of roasting as 'slag'. If the sulphide ore of copper contains iron, then silica (SiO_2) is added as flux before roasting. Then, FeO combines with silica to form iron silicate, $FeSiO_3$ (slag).

$$FeO + SiO_2 \xrightarrow{\Delta} \underset{(\text{Slag})}{FeSiO_3}$$

Question 6.10:

What is meant by the term "chromatography"?

Answer

Chromatography is a collective term used for a family of laboratory techniques for the separation of mixtures. The term is derived from Greek words 'chroma' meaning 'colour' and 'graphein' meaning 'to write'. Chromatographic techniques are based on the principle that different components are absorbed differently on an absorbent. There are several

chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc.

Question 6.11:

What criterion is followed for the selection of the stationary phase in chromatography?

Answer

The stationary phase is selected in such a way that the components of the sample have different solubility's in the phase. Hence, different components have different rates of movement through the stationary phase and as a result, can be separated from each other.

Question 6.12:

Describe a method for refining nickel.

Answer

Nickel is refined by Mond's process. In this process, nickel is heated in the presence of carbon monoxide to form nickel tetracarbonyl, which is a volatile complex.

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

Then, the obtained nickel tetracarbonyl is decomposed by subjecting it to a higher temperature (450 – 470 K) to obtain pure nickel metal.

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

Question 6.13:

How can you separate alumina from silica in bauxite ore associated with silica?

Give equations, if any.

Answer

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

$$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Na\left[Al(OH)_4\right]_{(aq)}$$

Alumina Sodium aluminate

$$SiO_2 + 2NaOH_{(aq)} \longrightarrow Na_2SiO_{3(aq)} + H_2O_{(l)}$$

Silica Sodium silicate

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

$$2Na\left[Al(OH)_4\right]_{(aq)} + CO_{2(g)} \longrightarrow Al_2O_3.xH_2O_{(s)} + 2NaHCO_{3(aq)}$$

Sodium aluminate Hydrated alumina Sodium hydrogen carbonate

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

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

Hydrated alumina Alumina

Question 6.14:

Giving examples, differentiate between 'roasting' and 'calcination'.

Answer

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

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

Zinc blende

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$$

Galena

$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$

Copper glance

On the other hand, calcination is the process of converting hydroxide and carbonate ores to oxides by heating the ores either in the absence or in a limited supply of air at a

temperature below the melting point of the metal. This process causes the escaping of volatile matter leaving behind the metal oxide. For example, hydroxide of Fe, carbonates of Zn, Ca, Mg are converted to their respective oxides by this process.

$$Fe_2O_3.3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$$

Limonite

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

Calamine

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

Dolomite

Question 6.15:

How is 'cast iron' different from 'pig iron"?

Answer

The iron obtained from blast furnaces is known as pig iron. It contains around 4% carbon and many impurities such as S, P, Si, Mn in smaller amounts.

Cast iron is obtained by melting pig iron and coke using a hot air blast. It contains a lower amount of carbon (3%) than pig iron. Unlike pig iron, cast iron is extremely hard and brittle.

Question 6.16:

Differentiate between "minerals" and "ores".

Answer

Minerals are naturally occurring chemical substances containing metals. They are found in the Earth's crust and are obtained by mining.

Ores are rocks and minerals viable to be used as a source of metal.

For example, there are many minerals containing zinc, but zinc cannot be extracted profitably (conveniently and economically) from all these minerals.

Zinc can be obtained from zinc blende (ZnS), calamine ($ZnCO_3$), Zincite (ZnO) etc.

Thus, these minerals are called ores of zinc.

Question 6.17:

Why copper *matte* is put in silica lined converter?

Answer

Copper *matte* contains Cu_2S and FeS. Copper *matte* is put in a silica-lined converter to remove the remaining FeO and FeS present in the *matte* as slag ($FeSiO_3$). Also, some silica is added to the silica-lined converter. Then, a hot air blast is blown. As a result, the remaining FeS and FeO are converted to iron silicate ($FeSiO_3$) and Cu_2S is converted into metallic copper.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \longrightarrow FeSiO_3$$

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

Question 6.18:

What is the role of cryolite in the metallurgy of aluminium?

Answer

Cryolite (Na_3AlF_6) has two roles in the metallurgy of aluminium:

1. To decrease the melting point of the mixture from 2323 K to 1140 K.

2. To increase the electrical conductivity of Al_2O_3.

Question 6.19:

How is leaching carried out in case of low grade copper ores?

Answer

In case of low grade copper ores, leaching is carried out using acid or bacteria in the presence of air. In this process, copper goes into the solution as Cu^{2+} ions.

$$Cu_{(s)} + 2H^+_{(aq)} + \frac{1}{2}O_{2(g)} \longrightarrow Cu^{2+}_{(aq)} + 2H_2O_{(l)}$$

The resulting solution is treated with scrap iron or H_2 to get metallic copper.

$$Cu^{2+}_{(aq)} + H_{2(g)} \longrightarrow Cu_{(s)} + 2H^+_{(aq)}$$

Question 6.20:

Why is zinc not extracted from zinc oxide through reduction using CO?

Answer

The standard Gibbs free energy of formation of ZnO from Zn

is lower than that of CO_2 from CO. Therefore, CO cannot reduce ZnO to Zn. Hence, Zn is not extracted from ZnO through reduction using CO.

Question 6.21:

The value of $\Delta_f G^\theta$ for formation of Cr_2O_3 is – 540 $kJmol^{-1}$ and that of Al_2O_3 is – 827 $kJmol^{-1}$. Is the reduction of Cr_2O_3 possible with Al?

Answer

The value of $\Delta_f G^\theta$ for the formation of Cr_2O_3 from Cr (−540 $kJmol^{-1}$) is higher than that of Al_2O_3 from Al (−827 $kJmol^{-1}$). Therefore, Al can reduce Cr_2O_3 to Cr. Hence, the reduction of Cr_2O_3 with Al is possible.

Alternatively,

$$2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3 \qquad \Delta_r G^\theta = -827\ kJmol^{-1}$$

$$2Cr + \frac{3}{2}O_2 \longrightarrow Cr_2O_3 \qquad \Delta_r G^\theta = -540\ kJmol^{-1}$$

Subtracting equation (ii) from (i), we have

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

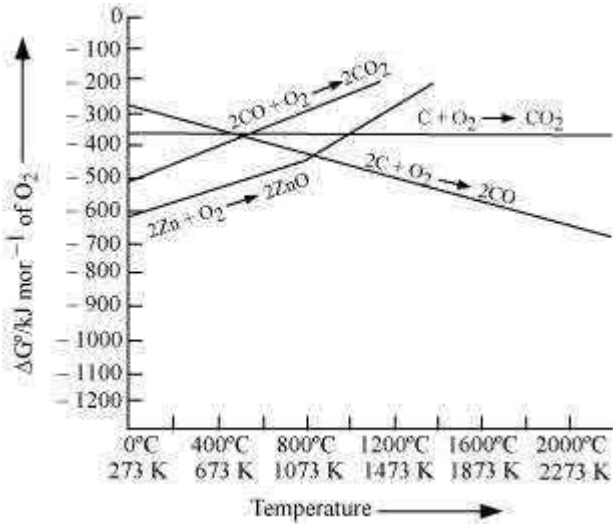
$$\Delta_r G^\theta = -827 - (-540) = -287\ kJmol^{-1}$$

As $\Delta_f G^\theta$ for the reduction reaction of Cr_2O_3 by Al is negative, this reaction is possible.

Question 6.22:

Out of C and CO, which is a better reducing agent for ZnO ?

Answer



Reduction of ZnO to Zn is usually carried out at 1673 K. From the above figure, it can be observed that above 1073 K, the Gibbs free energy of formation of CO from C and above 1273 K, the Gibbs free energy of formation of CO_2 from C is lesser than the Gibbs free energy of formation of ZnO. Therefore, C can easily reduce ZnO to Zn.

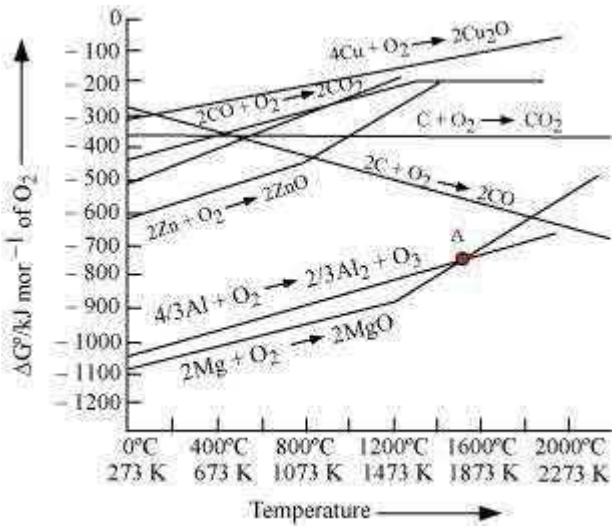
On the other hand, the Gibbs free energy of formation of CO_2 from CO is always higher than the Gibbs free energy of formation of ZnO. Therefore, CO cannot reduce ZnO.

Hence, C is a better reducing agent than CO for reducing ZnO.

Question 6.23:

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.

Answer



The above figure is a plot of Gibbs energy $(\Delta G^{\ominus})$ vs. T for formation of some oxides.

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

Question 6.24:

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

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

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

At cathode: $Na^+_{(melt)} + e^- \longrightarrow Na_{(s)}$

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

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

The overall reaction is as follows:

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

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

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

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

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

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

Question 6.25:

What is the role of graphite rod in the electrometallurgy of aluminium?

Answer

In the electrometallurgy of aluminium, a fused mixture of purified alumina (Al_2O_3), cryolite (Na_3AlF_6) and fluorspar (CaF_2) is electrolysed. In this electrolysis, graphite is used as the anode and graphite-lined iron is used as the cathode. During the electrolysis, Al is liberated at the cathode, while CO and CO_2 are liberated at the anode, according to the following equation.

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

$$\text{Anode}: C_{(s)} + O^{2-}_{(melt)} \longrightarrow CO_{(g)} + 2e^-$$

$$C_{(s)} + 2O^{2-}_{(melt)} \longrightarrow CO_{2(g)} + 4e^-$$

If a metal is used instead of graphite as the anode, then O_2 will be liberated. This will not only oxidise the metal of the electrode, but also convert some of the Al liberated at the cathode back into Al_2O_3. Hence, graphite is used for preventing the formation of O_2 at the anode. Moreover, graphite is cheaper than other metals.

Question 6.27:

Outline the principles of refining of metals by the following methods:

(i) Zone refining

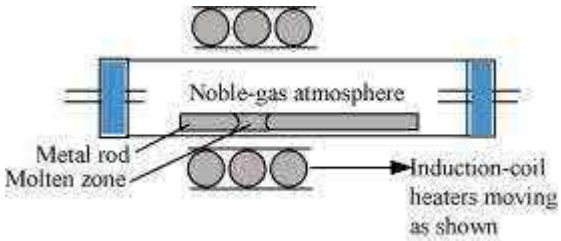
(ii) Electrolytic refining

(iii) Vapour phase refining

Answer

(i) Zone refining:

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



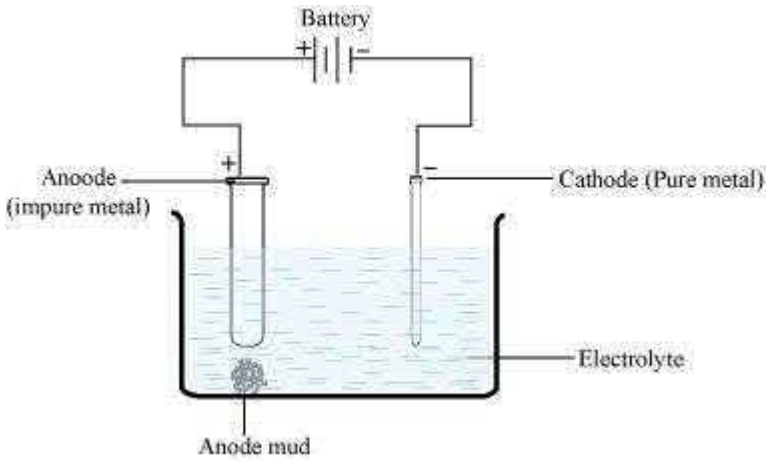
(ii) Electrolytic refining;

Electrolytic refining is the process of refining impure metals by using electricity. In this process, impure metal is made the anode and a strip of pure metal is made the cathode. A solution of a soluble salt of the same metal is taken as the electrolyte. When an electric current is passed, metal ions from the electrolyte are deposited at the cathode as pure metal and the impure metal from the anode dissolves into the electrolyte in the form of ions. The impurities present in the impure metal gets collected below the anode.

This is known as anode mud.

Anode: $M \longrightarrow M^{n+} + ne^-$

Cathode: $M^{n+} + ne^- \longrightarrow M$



(iii) Vapour phase refining

Vapour phase refining is the process of refining metal by converting it into its volatile compound and then, decomposing it to obtain a pure metal. To carry out this process,

(i) the metal should form a volatile compound with an available reagent, and

(ii) the volatile compound should be easily decomposable so that the metal can be easily recovered.

Nickel, zirconium, and titanium are refined using this method.

Question 6.28:

Predict conditions under which Al might be expected to reduce MgO.

Answer

Above 1350°C, the standard Gibbs free energy of formation of Al_2O_3 from Al is less than that of MgO from Mg. Therefore, above 1350°C, Al can reduce MgO.