6. General Principles and Processes of Isolation of Elements

Exercise Questions:

Question:1 Copper can be extracted by hydrometallurgy but not zinc. Explain?

Answer:

E° value of Zn^{2+}/ Zn =?

0.76 V is less than that of Cu2+/Cu = +0.34V. This means that zinc is a stronger reducing agent than copper and can easily displace Cu from the solution of Cu2+ ions.

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

On the other hand, to displace zinc from the solution of Zn2+ ions, we need a stronger reducing agent like Ca, Mg or Al. But all these metals react with water to evolve hydrogen gas. Thus, these metals cannot be used for this purpose. Hence zinc cannot be extracted by hydrometallurgy.

Question:2 What is the role of depressant in froth floatation process?

Answer:

Depressants prevent certain types of particles from forming froth with bubbles. Due to this, we can separate two sulphide ores.

For example, sodium cyanide is a depressant used for an ore containing ZnS and PbS. NaCN forms a layer of the complex $Na_2[Zn(CN)_4]$ on the surface of ZnS and prevents it from forming a froth. Thus, it acts as a depressant. However, NaCN does not prevent PbS from forming froth and allows it to come with froth.

Question:3 Why is the extraction of copper from pyrides more difficult than that from its oxide ore through reduction?

Answer: The Gibbs free energy of formation ($\Delta_f G$) of CS_2 and H_2S are more than Cu_2S. Therefore, the C and H_2 cannot produce the Cu from the Cu_2S. The Gibbs free energy of formation ($\Delta_f G$) of Cu_2O is more than CO. As a result, C can produce Cu from Cu_2O.

$C(s) + Cu_2O(s) \longrightarrow 2Cu(s) + CO(g)$.

Therefore, the extraction of the copper from the copper pyrite ore is more difficult than from the oxide ore by reduction.

Question:4 Explain:

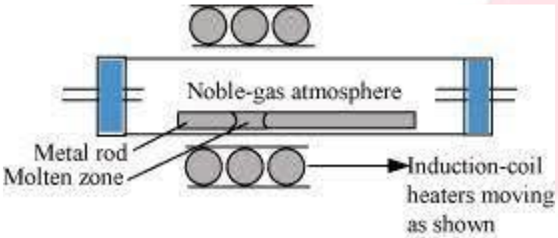
i.) **Zone refining**

ii.) **Column chromatography.**

Answer:

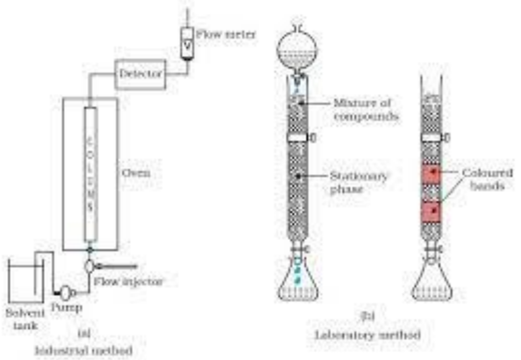
i.) Zone refining:

It is used for refining Si, B, In etc. Impurities are more soluble in the molten state of metal than in solid state. There is a circular mobile heater at one end of a rod of impure metal. Heater and the molten zone moves from one end to another end. Pure metal crystallizes out of the melt and the impurities pass onto the adjacent molten zone. Repetition of this process several times segregates impurities at one end of a rod. The end with impurities can then be cut off.



(ii) Column chromatography:

It is used for the separation and purification. It is based on the difference in the tendency for adsorption of a metal and its impurities on a suitable adsorbent. Different components of a mixture are differently adsorbed on an adsorbent.



Question:5 Out of C and CO, which is a better reducing agent at 673 K?

Answer:

The value of G° for change of C to CO_2 is less than the value of G° for change of CO to CO_2. Therefore, coke (C) is a better reducing agent than CO at 983 K or above temperature. However below this temperature (e.g., at 673 K), CO is more effective reducing agent than C.

Question:6 Name the common elements present in the anode mud in electrolytic refining of copper. Why are they so present?

Answer: The common elements present in the anode mud are antimony, tellurium, silver, gold and platinum. These elements settle down under anode as anode mud because they are less reactive and are not effected by $CuSO_4 - H_2SO_4$ solution.

Question:7 Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.

Answer:

In blast furnace, iron oxides are reduced at different temperature ranges. In the lower part of the blast furnace, the temperature is as high as 2200 K. It is called combustion zone. At the top, the temperature is as low as 500−800 K. It is called reduction zone. In the lower temperature range, carbon is the reducing agent and in the higher temperature range, CO is the reducing agent. In the reduction zone (500−800 K), following reactions occur.

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

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

$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$

In the temperature range 900-1500 K, following reactions occur.

$C + CO_2 \longrightarrow 2CO$

$FeO + CO \longrightarrow Fe + CO_2$

Around 1270 K (middle portion), decomposition of limestone gives lime (CaO) and CO_2. Lime is a flux and combines with silicate impurity to form slag of calcium silicate.

$CaCO_3 \longrightarrow CaO + CO_2$

$CaO + SiO_2 \longrightarrow CaSIO_3$

Question:8 Write chemical reactions taking place in the extraction of zinc from zinc blende.

Answer:

During extraction of Zn from zinc blende (ZnS), following reactions occur:

(i) ZnS is roasted in excess air at 1200 K to form ZnO.

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

(ii) ZnO is heated with crushed coke at 1673 K, where it is reduced to Zn.

$ZnO + C \xrightarrow{1676K} Zn + CO$

(iii) Electrorefining is carried out for refining of impure zinc. Anode is impure zinc and cathode is pure zinc. Electrolyte is a mixture of zinc sulphate and dilute sulphuric acid (small amount). When current is passed, zinc is deposited on cathode and is collected.

At anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

At cathode: $Zn^{2+} + 2e^- \longrightarrow Zn$

Question:9 State the role of silica in metallurgy of copper.

Answer:

During roasting, copper pyrites are converted into a mixture of FeO and Cu_2O. Thus, acidic flux silica is added during smelting to remove FeO (basic). FeO combines with SiO_2 to form famous silicate slag which floats over molten matte.

Question:10 What is meant by the term "chromatography".

Answer:

It is the technique of separating the components of a mixture in which separation is achieved by the differential movement of individual components through a stationary phase under the influence of a mobile phase. The stationary is made up of aluminium oxide or silica gel.

Question: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 impurities are more strongly absorbed or are more soluble in the stationary phase than component to be purified. Thus, when the column is extracted, the impurities will be retained by stationary phase while the pure component is easily eluted.

Question:12 Describe the method of refining nickel.

Answer:

When impure nickel is heated in presence of CO at 330 - 350 K, it forms volatile nickel tetra carbonyl leaving behind the impurities. The nickel tetra carbonyl thus obtained is than heated to high temperature (450 – 470 K), then it undergoes thermal decomposition to give pure nickel.

$Ni + 4CO \xrightarrow{330-350\,K} Ni(CO)_4$

(Impure) Nickel teracarbonyl

$Ni(CO)_4 \xrightarrow{450-470\,K} Ni + 4CO$

Question:13 How can you separate alumina from silica in a bauxite ore associated with silica? Give equations, if any.

Answer:

Bauxite ore containing silica is heated with conc. NaOH solution at 473−523 K and 35−36 bar pressure. Alumina forms sodium aluminate and silica forms sodium silicate. Impurities are left behind.

$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]$

Carbon dioxide neutralizes the aluminate to precipitate hydrated alumina.

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

Sodium silicate remains in the solution and hydrated alumina is filtered and dried. On heating, hydrated alumina gives pure alumina.

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

Question:14 Giving examples, differentiate b/w 'roasting' and 'calcination'.

Answer:

Calcination	**Roasting**
1.) Calcination is a process in which ore is heated in the absence of air or air might be supplied in limited quantity.	1.) Roasting involves heating of ore lower than its melting point in the presence of air or oxygen.
2.) Calcination involves thermal decomposition of carbonate ores.	2.)Roasting is carried out mostly for sulphide minerals.
3.) During calcination, moisture is driven out from an ore.	3.)Roasting does not involve dehydrating an ore.
4.) Carbon dioxide is given out during calcination.	4.)During roasting large amount of toxic, metallic and acidic compounds are released.
For example: Decomposition of limestone to lime. **$CaCO_3 \rightarrow CaO + CO_2$**	**For example: Zinc sulphide to zinc oxide.** **$2ZnS + 3O_2 \rightarrow 2ZnO + 2\ SO_2$**

Question:15 How is 'cast iron' different from 'pig iron'?

Answer:

The iron obtained from blast furnace is called pig iron. It contains about 4% carbon and many other impurities like S, P, Si, Mn etc. in smaller amounts.

Cast iron, on the other hand, is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

Question:16 Differentiate b/w 'minerals' and 'ores'.

Answer:

Minerals are naturally occurring chemical substances. They are present in earth's crust and obtained by mining. Ores are the minerals from which a metal can be economically and conveniently extracted. Thus, bauxite (Al_2O_3. $2H_2O$) and clay (Al_2O_2. $2SiO_2$. $2H_2O$) are minerals of Al. However, bauxite is an ore of Al as Al can be economically and conveniently extracted from bauxite.

Question:17 Why copper matte is put in silica lined converter?

Answer:

In the Ellingham diagram, the graph of ΔG^0 vs T for the formation of oxide, the Cu_2O quite easy to reduce copper oxide to copper by simple heating the coke. But most of the copper ores are sulphate and in some ways contains iron. The sulphide ores are roasted to give oxides as:

$Cu_2s + 3O_2 \rightarrow 2Cu2O + 2SO2$

The oxide is converted to copper metal using coke as:

$Cu2O + C \rightarrow 2Cu + CO$

But in actual process, the ore is heated in the reverberatory furnace after mixing with silica. In the reverberatory furnace iron oxide slags of as iron silicate and copper is produced as copper matte which contains Cu2S, FeS.

$FeO + SiO2 \rightarrow FeSiO3$ (slag)

Copper matte is than charged into a silica lined converter. Some silica is also added and hot air blast is blown to convert the remaining FeS, FeO AND Cu2S / Cu2O to metallic copper. The reaction take place in the silica lined converter are as –

$Cu2O + C \rightarrow 2Cu + CO$

$FeO + SiO2 \rightarrow FeSiO3$

$2Cu2O + 3O2 \rightarrow 2Cu2O + 2SO2$

$2FeS + 3O2 \rightarrow 2FeO + 2SO2$

Question:18 What is the role of cryolite in the metallurgy of aluminium?

Answer:

In the metallurgy of aluminium, the metal is to be isolated from alumina (Al_2O_3) by carrying out its electrolytic reduction. The melting point of alumina as such is 2323 K. It is therefore, mixed with cryolite (Na_3AlF_6) which lowers its melting point to 1173 K. Moreover, cryolite also increases the electrical conductivity of alumina which is a poor conductor.

Question:19 How is leaching carried out in case of low grade copper ores?

Answer:

For low grade copper ores, leaching is carried out with acid or bacteria in the presence of air. During this process, copper goes into the solution as Cu_2^+ ions. The solution is then reacted with scrap iron or H_2 to get metallic copper.

Acid in presence of air is used to leach out copper from low grade copper.

$Cu + 2H^+ + ½ O_2 \longrightarrow Cu^{2+} + 2H_2O$

Solution is then treated with scrap iron or hydrogen.

$Cu^{2+} + H_2 \longrightarrow Cu + 2H^+$

Question:20 Why is zinc not extracted from zinc oxide through reduction using CO?

Answer:

The chemical reaction involving the reduction of ZnO by CO is not feasible thermodynamically: This is because the standard free energy of formation of CO2 from CO is higher than that of the formation of ZnO from Zn. Thus, CO cannot be used to reduce ZnO to Zn.

Question:21 The value of $\Delta_r G^0$ for the formation of Cr_2O_3 is -540 kjmol^{-1}and that of Al2O3 is -827 kjmol^{-1}. Is the reduction of Cr_2O_3 possible with Al?

Answer:

Chemical equation for the formation of Cr_2O_3 and Al_2O_3 are as follows:

(a) $4/3\ Cr(s) + 3/2\ O_2(g) \rightarrow 2/3\ Cr_2O_3\ (s)\quad : \Delta_f G^0 = -\ 540\ kJmol^{-1}$

b.) $4/3\ Al\ (s) + 5/2\ O_2\ (g) \rightarrow 2/3\ Al_2O_3\ (s)\quad : \Delta_f G^0 = -827\ kJmol^{-1}$

Substracting equation (a) from (b), we get

$4/3\ Al\ (s) + 2/3\ Cr_2O_3 \rightarrow\ 2/3\ Al_2O_3 + 4/3\ Cr\ (s)\ : \Delta G^0 = -287\ kJ\ mol^{-1}$

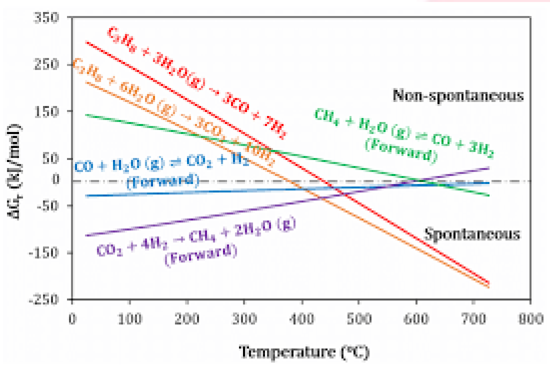
Now ΔG^0 is negative thus, reduction of Cr_2O_3 by Al is possible.

Question: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 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:23 The choice of a reducing agent in a particular case depends on the thermodynamic factor. How far do you agree with this statement? Support your opinion with two example

Answer:

Yes, The choice of a reducing agent in a particular case depends on thermodynamic factor. Example:

The free energies of formation ($\Delta_f G^0$) of most sulphides are greater than those or CS_2 and H_2S. Carbon disulphide is, in fact, an endothermic compound.

Therefore, neither carbon nor hydrogen is a suitable reducing agent for metal sulphides.

Question:24 Name the process 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. The overall reaction is as follows: If an aqueous solution of NaCl is electrolyzed, Cl_2 will be obtained at the anode but at the cathode, H_2 will be obtained (instead of Na).

(1) In Down's process for the manufacture of sodium, the electrolysis of NaCl gives chlorine as a byproduct.

$NaCl(l) \xrightarrow{\text{Electrolysis}} Na^+(melt) + Cl^-\ (melt)$

At anode : $Cl^-(melt) \longrightarrow Cl(g) + e^-$

$Cl(g) + Cl(g) \longrightarrow Cl_2\ (g)$

At cathode : $Na^+(melt) + e^- \longrightarrow Na(s)$

(2) In Castner Kellner cell, electrolysis of brine solution is carried out to manufacture NaOH (caustic soda). Chlorine is obtained as a byproduct.

Question:25 What is the role of graphite rod in the electrometallurgy of aluminium?

Answer:

The role of graphite in electrometallurgy of aluminium is to avoid the release of oxygen so that the aluminium is not oxidized by oxygen.

Question:26 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 the impurities are more soluble in the melt then in the solid state of the metal. A 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 move forward. As the heater moves forward the pure metal crystallises out of the melt and the impurity pass on into the adjacent molten zone. The process is repeated several times so that the impurities get concentrated at one end. Example: silicon, boron, etc.

ii.)Electrolytic refining: This method is used in refining of copper. 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 cathode.

Anode: $Cu \rightarrow Cu^{2+} + 2e^-$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

iii.)Vapour phase refining: In this method, the metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal. This method is used for the refining of Ni, Zn, Ti.

Mond process for refining nickel: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl:

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

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

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