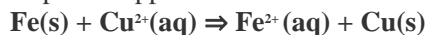**Q1. Copper can be extracted by hydrometallurgy but not zinc. Explain.**

Ans:

Copper has a higher reduction potential than zinc or iron. Thus, in hydro-metallurgy, iron and zinc can be used to displace copper from its solution.
**$Fe(s) + Cu^{2+}(aq) \Rightarrow Fe^{2+}(aq) + Cu(s)$**
However, in order to displace zinc, a metal that is more reactive than it is required e.g. K, Ca, etc. The problem arising now is that all these metals react with water to liberate hydrogen gas. **Thus, they cannot be used for the extraction of zinc using hydro-metallurgy.**

Q2. What is the role of depressants in the froth flotation process?

Ans:

The role of a depressant in the forth flotation is to set apart two sulphide ores through selective prevention of one ore from frothing. For e.g., NaCN is used to separate two sulphide ores, PbS and ZnS. NaCN forms a complex, $Na_2[Zn(CN)_4]$, with zinc on the surface of zinc sulphide, thus selectively preventing ZnS from frothing.
$4NaCN + ZnS \Rightarrow Na_2[Zn(CN)_4] + Na_2S$
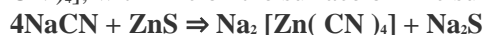
Q3. Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?

Ans:

Hydrogen sulfite and carbon disulfide (CS_2) have a larger $\Delta_f G$ (Gibbs free energy of formation) than copper (I) sulfite. Thus, C and H_2S will not be able to reduce Cu_2S to Cu.
Whereas $\Delta_f G$ of Cu_2O is larger than carbon monoxide's; thus, C can reduce copper (I) oxide to copper.
**Therefore, it is more difficult to extract copper from pyrites than it is to extract from its oxide.**

Q4. Explain (i) Zone refining (ii) Column chromatography.

Ans:

(a) Zone refining:
This method makes use of a principle according to which impurities are more soluble in molten metal than in solid metal. In zone refining, a moving circular heater slowly moves over an impure metal rod/bar. As the circular heater moves, the impurities move into the adjacent molten zone, and the pure metal crystallizes out. This is repeated over several times, causing the segregation of impurities at one end of the bar. This impure end is then cut off. Boron, silicon, gallium, etc., are purified this way.
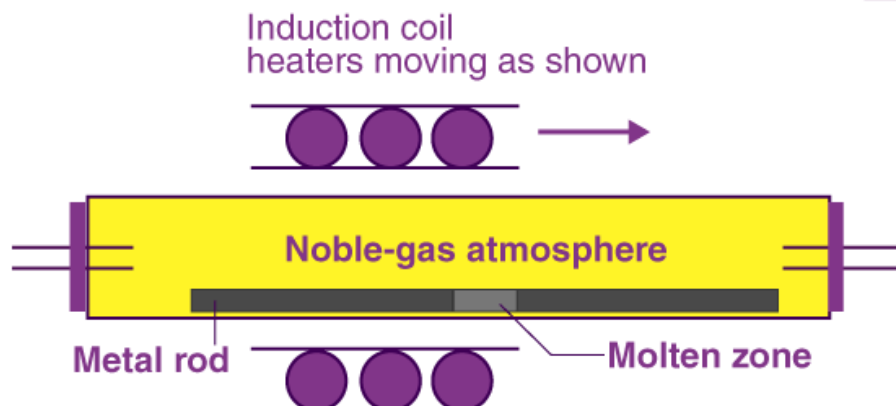
(b) Column chromatography:

This is a very useful method of purifying elements present in minute amounts. Column chromatography is mostly used in order to take away those impurities which are not very different in chemical properties from the element which needs to be purified. This concept follows the principle various components of a mixture are adsorbed to different extents on an adsorbent.
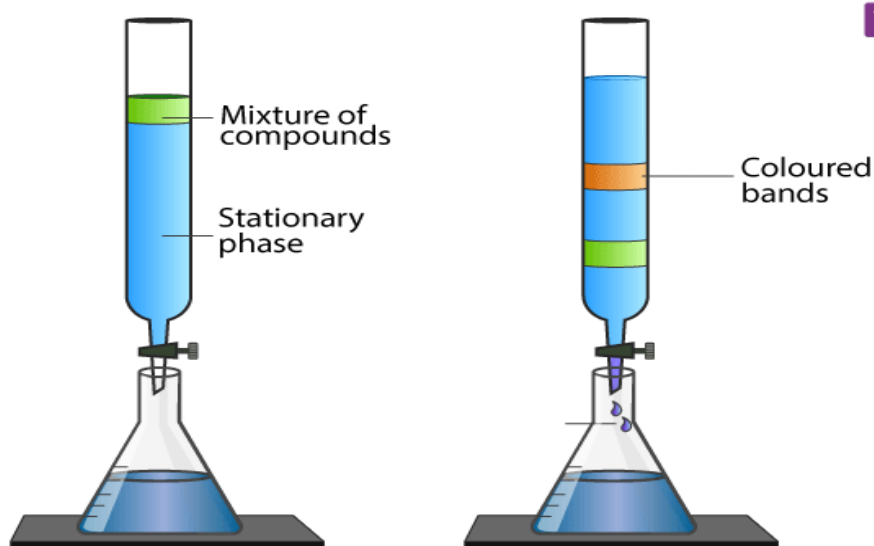
Chromatography includes two phases: mobile phase and stationary phase. The stationary phase is immiscible and immobile. A column of adsorbent, e.g., $Al_2 O_3$, is used as the stationary phase. The mixture to be purified is dissolved in the mobile phase, which can be a liquid, gas or supercritical fluid. This is then poured onto the top of the column. The component which is more strongly adsorbed by the adsorbent takes a greater amount of time to move through it than the component that is weakly adsorbed. This way, the different components of the mixture are separated as they move through the stationary phase.

Q5. Out of C and CO, which is a better reducing agent at 673 K?

Ans:

At 673 K , CO is a more effective reducing agent because, at 673 K, the value of $\Delta G_{(C,CO)}$ is greater than the value of $\Delta G_{(CO,CO2)}$, which means that CO is more easily reduced to CO_2 than C to CO.

Q6. Name the common elements present in the anode mud in the electrolytic refining of copper. Why are they so present?

Ans:

Selenium, silver, tellurium, platinum, antimony and gold are the common elements present in the anode mud during the electrolytic refining of copper.
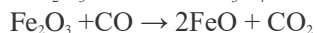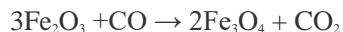As these metals are almost unreactive, they are not affected during the purification method. **Thus, they are present in the anode mud.**

Q7. Write down the reactions taking place in different zones in the blast furnace during the extraction of iron
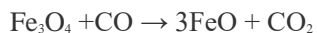
Ans:

Inside a blast furnace, iron oxide is reduced at different temperature ranges, as given below.

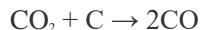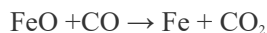**At 500 – 800 K**
$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$
$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$

At 850 K
$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

At 900 – 1500 K
$FeO + CO \rightarrow Fe + CO_2$
$CO_2 + C \rightarrow 2CO$

Above 1570 K
$C + O_2 \rightarrow CO_2$
$FeO + C \rightarrow Fe + CO$
$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$
$SiO_2 + CaO \rightarrow CaSiO_3$ (slag)

Ore, limestone
and coke

Exhaust gases (CO,CO$_2$)

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

$Fe_3O_4 + CO_2 \longrightarrow 3FeO + CO_2$

$CaCO_3 \longrightarrow CaO + CO_2$

$CaO + SiO_2 \longrightarrow CaSiO_3$

$FeO + CO \longrightarrow Fe + CO_2$

$C + CO_2 \longrightarrow 2CO$

$C + O_2 \longrightarrow CO_2$

$FeO + C \longrightarrow Fe + CO$

Blast of air and oxygen

Molten iron

Solid waste   Pig iron
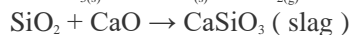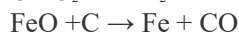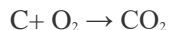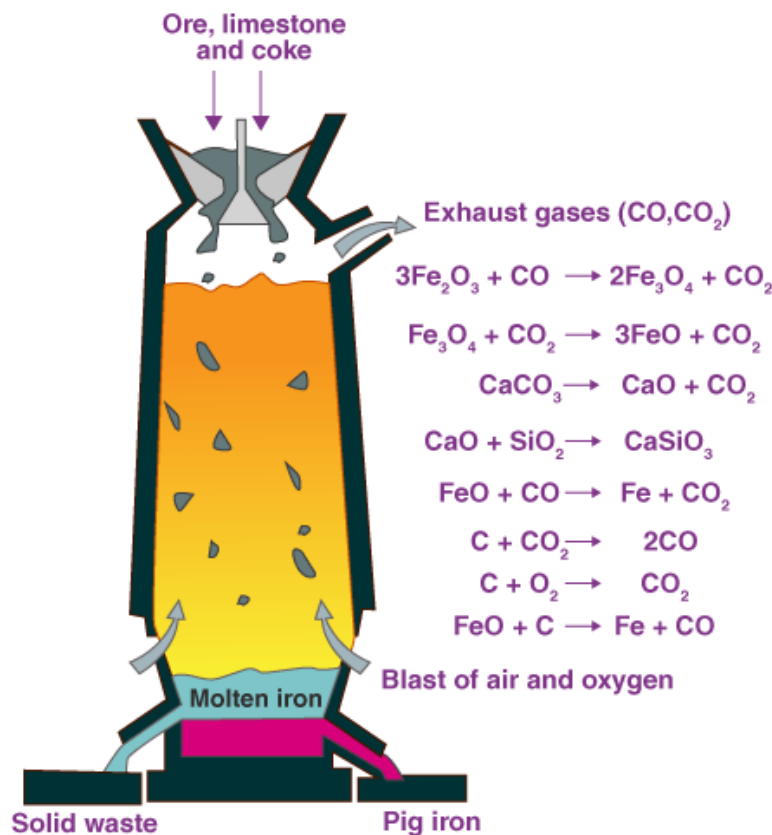
Q8. Write chemical reactions taking place in the extraction of zinc from zinc blende.

Ans:

The various steps involved in zinc extraction are

(1) Concentration of ore
Firstly, to remove the impurities of the ore, zinc blende is crushed, and concentration is done by **froth floatation.**
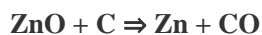
(2) Conversion to oxide (Roasting)
In this step, ZnS is roasted in excess of air in a furnace at a temperature below the melting point of zinc. This results in the formation of zinc oxide.

$2ZnS + 3O_2 \Rightarrow 2ZnO + 2SO_2$
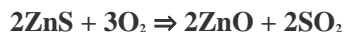
(3) Extraction of Zn from ZnO (Reduction):
To extract zinc from zinc oxide, it is mixed with powdered coke and then heated.

**$ZnO + C \Rightarrow Zn + CO$**

(4) Electrolytic Refining:
In this method, impure zinc becomes the anode, while the cathode is a pure copper strip. The electrolyte is an acidic solution of zinc sulphate (ZnSO$_4$) with dilute sulfuric acid. On passing current, **pure zinc deposits on the copper strip**.

Q9. State the role of silica in the metallurgy of copper.

Ans:

Copper pyrites are converted to a mixture of Cu_2O and FeO during roasting. Acidic silica is added during smelting to separate the FeO from the mixture. SiO_2 and FeO form $FeSiO_3$ (slag), which floats on the molten matter.
$FeO + SiO_2 \Rightarrow FeSiO_3$ (slag)
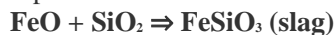
Q10. "Chromatography." What do you understand by this term?

Ans:

Chromatography is a collective term used for a range of laboratory techniques for the purification, separation, characterization and identification of the species of a mixture, whether coloured or colourless. The word has been obtained from two Greek words; 'graphy', meaning 'to write' and 'chroma', meaning 'colour'. **There are numerous chromatographic techniques like column chromatography, paper chromatography, gas chromatography, etc.**

Q11. What is the criterion followed while selecting the stationary phase of chromatography?

Ans:

The choice of stationary phase is done in a way that the elements of the mixture have different solubility in the phase. Thereby, different elements have different movement speeds through the phase, because of which they can be **separated from each other.**

Q12. Describe a method for refining nickel.

Ans:

Mond's process is a technique used to refine nickel. In this method, heat is supplied to nickel in the presence of carbon monoxide to produce nickel tetracarbonyl, which is a volatile complex.

$Ni + 4CO \Rightarrow Ni(CO)_4$ [330k – 350k]

The **nickel tetracarbonyl** so obtained is then decomposed by heating it at a higher temperature (450 − 470 K) to form pure nickel.
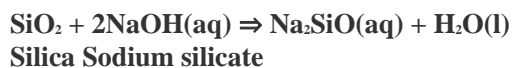
$Ni(CO)_4 \Rightarrow Ni + CO$ [450k – 470k]

Q13. How can you separate alumina from silica in a bauxite ore associated with silica? Give equations, if any.

Ans:

The separation of alumina from silica in bauxite ore associated with silica is as follows:
Firstly, a concentrated NaOH solution is used to digest the powdered ore at 473 − 523 K and at a pressure of 35 − 36 bar. This causes alumina (Al_2O_3) and silica (SiO_2) to leach as sodium aluminate and sodium silicate, respectively, abandoning the impurities behind.

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O (f) \Rightarrow 2Na [Al (OH)_4](aq)$
Alumina sodium aluminate

$SiO_2 + 2NaOH(aq) \Rightarrow Na_2SiO(aq) + H_2O(l)$
**Silica Sodium silicate**

Now, to neutralise the aluminate present in the solution, carbon dioxide gas is passed through the solution we obtained. This causes the sodium meta-aluminate to precipitate as hydrated alumina.
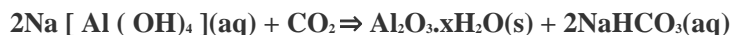
$2Na [Al (OH)_4](aq) + CO_2 \Rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3(aq)$
hydrated alumina
Sodium silicate cannot be precipitated, so it is filtered off. The hydrated alumina is dried, heated and filtered to obtain pure alumina.

$Al_2O_3.xH_2O(s) \Rightarrow Al_2O_3(s) + xH_2O(g) [1470 k]$
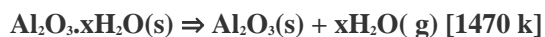
Q14. Giving examples, differentiate between 'roasting' and 'calcination'.

Ans:

Calcination is the conversion of carbonate and hydroxide ores to oxides by heating them at a temperature below their melting points and in the absence or in a very limited supply of air.
For example, carbonates of Ca, Mg, and Zn are turned into their respective oxides through this process.
$ZnCO_3 \Rightarrow ZnO + CO_2$

$Fe_2O_3.3H_2O \Rightarrow Fe_2O_3 + 3H_2O[Heat]$

Roasting is the conversion of sulfide ores into their metallic oxides by heating at a temperature below their melting points in the excess presence of air.
For e.g., sulfide ores of Pb and Zn are turned into their respective oxides through this process.
$2Zns + 3O_2 \Rightarrow 2ZnO + 2SO_2$

$2Pbs + 3O_2 \Rightarrow 2PbO + 2SO_2$
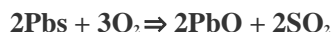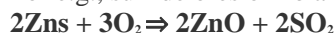
Q15. How is 'cast iron' different from 'pig iron"?

Ans:

Pig iron is the iron obtained from a blast furnace. It is 4% carbon and contains many other impurities like Si, P, S, and Mn in lesser amounts.
Cast iron is made by melting pig iron and coke with the help of a hot air blast. It has lower levels of carbon in it
(3%). **Unlike pig iron, cast iron is brittle and extremely hard.**

Q16. Differentiate between "minerals" and "ores".

Ans:

Minerals are naturally available substances having metals or their compounds.
Ores are rocks and minerals from which metals are economically and conveniently obtained.
For e.g., there are a lot of minerals that contain, but zinc cannot be conveniently and economically extracted from all of them. Zinc is extracted from calamine ($ZnCO_3$), zinc blende (ZnS), etc. **Hence, these minerals qualify as ores of zinc.**

Q17. Why copper matte is put in silica lined converter?

Ans:

Copper matte has Cu_2S and some FeS. So, when a hot blast of air is blown through a molten matte placed in a silica-lined converter, FeS of the matte oxidises to FeO. This FeO combines with SiO_2 (silica) to produce $FeSiO_3$ (slag).

$2FeS + 3O_2 \Rightarrow 2FeO + 2SO_2$
$FeO + SiO_2 \Rightarrow FeSiO_3$
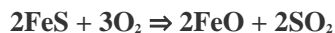
When all of the iron has been removed as slag, Cu_2S is oxidised to Cu_2O, which then undergoes a reaction with Cu_2S to give copper metal.

$2Cu_2S + 3O_2 \Rightarrow 2CuO_2 + 2SO_2$
$2Cu_2O + Cu_2S \Rightarrow 6Cu + SO_2$
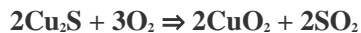
Q18. What is the role of cryolite in the metallurgy of aluminium?

Ans:

Na_3AlF_6 **(Cryolite) has two basic roles:**

1. The melting point of the solution is decreased from 2323 K to 1140 K due to the presence of cryolite.
**2.** Cryolite makes alumina a good conductor of electricity.

Q19. How is leaching carried out in the case of low-grade copper ores?

Ans:

When dealing with low-grade copper ores, bacteria or acids are used in the presence of air to leach the copper. In this method, copper enters the solution as Cu^{2+} ions.

$Cu + 2H^+ + \frac{1}{2} O_2 \Rightarrow Cu^{2+} + 2H_2O$

The solution so obtained is then treated with H_2 or scrap iron to get copper metal.

$Cu + 2H^+ \Rightarrow 2H^{2+} + Cu$
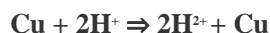
**Q20. Why is zinc not extracted from zinc oxide through reduction using CO?**

Ans:

As the standard Gibbs free energy of the formation of CO to CO_2 is higher than that of Zn to ZnO, CO will not be able to reduce ZnO to Zn. **Thereby, zinc oxide reduction using CO isn't used to extract zinc.**
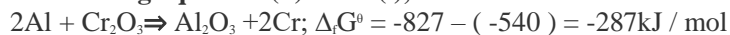
**Q21. The value of $\Delta_f G^0$ for formation of $Cr_2 O_3$ is – 540 kJmol^{-1} and that of $Al_2 O_3$ is – 827 kJmol^{-1}
Is the reduction of $Cr_2 O_3$ possible with Al?**

Ans:

As Cr_2O_3 has a higher value of formation (-540 kJ mol^{-1}) than Al_2O_3 (-827 kJ /mol), Al can thus reduce Cr_2O_3 to Cr.
Alternatively,
$2Al + (3/2)O_2 \Rightarrow Al_2O_3$

$2Cr + (3/2)O_2 \Rightarrow Cr_2O_3$
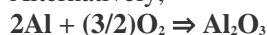
Subtracting equation (ii) from (i), we have
$2Al + Cr_2O_3 \Rightarrow Al_2O_3 + 2Cr$; $\Delta_f G^0$ = -827 – (-540) = -287kJ / mol

As $\Delta_f G^0$ is negative for the reduction reaction of Cr_2O_3 by Al, the reaction can take place.

**Q22. Out of C and CO, which is a better reducing agent for ZnO?**

Ans:
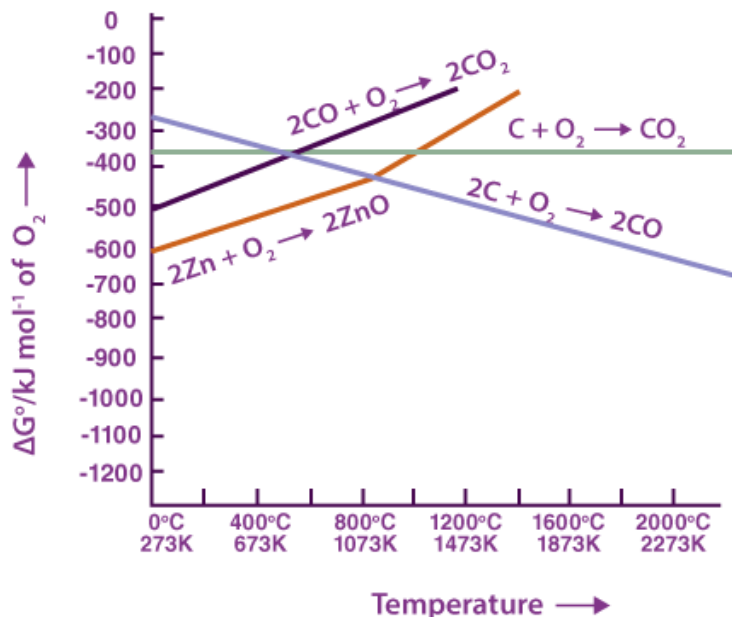
ZnO is reduced to Zn at around 1673 K. From the figure above, we can observe that beyond 1073 K, the Gibbs free energy of the formation of CO from C and beyond 1273 K, the Gibbs free energy of the formation of CO_2 from C is smaller than the Gibbs free energy of formation of ZnO. Thus, C can reduce ZnO to Zn. However, the Gibbs free energy of the formation of CO_2 from CO is greater than the Gibbs free energy of the formation of ZnO. **Thus, CO is not able to reduce ZnO, making C a better reducing agent for ZnO.**

Q23. 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 examples.

**Ans:**
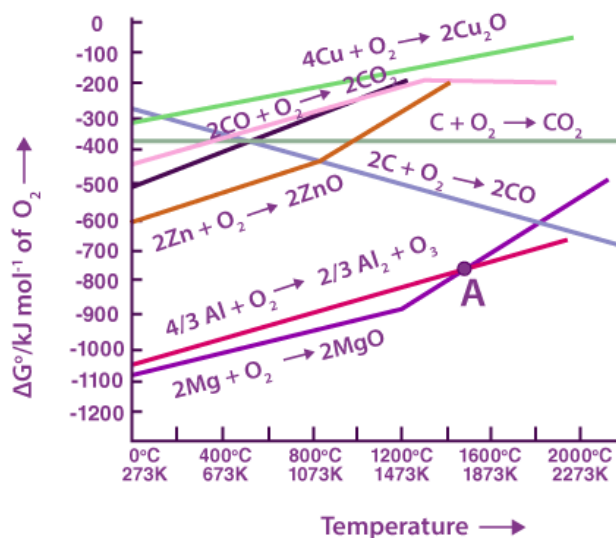
The figure given above is a graph of Gibbs energy ΔG^θ vs Temperature for the formation of solid oxides. We can see from this graph that if $\Delta_f G^\theta$ of a metal's oxide is more negative than another metal's oxide, then the former metal can reduce the oxide of the latter metal (i.e., the oxide with less negative $\Delta_f G^\theta$). For example, $\Delta_f G^\theta$ (Al, Al$_2$O$_3$) is more negative than $\Delta_f G^\theta$ (Cu, Cu$_2$O); thus, Al can readily reduce Cu$_2$O to Cu, but it is not possible for Cu to reduce Al$_2$O$_3$. Likewise, **it isn't possible for Zn to reduce MgO, but Mg can reduce ZnO to Zn. This is because $\Delta_f G^\theta$ (Mg, MgO) is more negative than $\Delta_f G^\theta$ (Zn,ZnO).**

Q24. 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?

Ans:

In the Down process, chlorine is obtained as a byproduct. In this process fused mixture of CaCl$_2$ and NaCl is electrolyzed at 873 K. Sodium is obtained from the cathode, and Cl$_2$ is discharged at the anode.

When an aqueous solution of NaCl is subjected to electrolysis, Cl$_2$ is discharged at the anode. At the cathode, H$_2$ is obtained (in place of Na). This is because the standard reduction potential of H$_2$O (E° = − 0.83 V) is less negative than that of Na (E°= − 2.71 V). Thus, H$_2$O will get a higher preference to get reduced at the cathode, thereby discharging H$_2$.
NaCl ⇒ Na$^+$ + Cl $^-$
At cathode : 2H$_2$O + 2e $^-$ ⇒ H$_2$ + 2OH $^-$
At anode: Cl $^-$ ⇒ Cl + e$^-$
2Cl ⇒ Cl$_2$
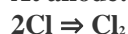
Q25. What is the role of a graphite rod in the electrometallurgy of aluminium?

Ans:

In the **electrometallurgy of aluminium**, the anode is graphite, and the cathode iron is graphite lined. The O$_2$ being liberated due to electrolysis reacts with the graphite anode to liberate CO$_2$ and CO. Had it been any other metal besides graphite, the oxygen would have reacted with the aluminium during the electrolysis to form Al$_2$O$_3$. This would have

resulted in the wastage of aluminium, and as graphite is cheaper than aluminium, it is expandable.
This is the role of a graphite rod in the electrometallurgy of aluminium.

Q26. Outline the principles of refining metals by the following methods:
(i) Zone refining
(ii) Electrolytic refining
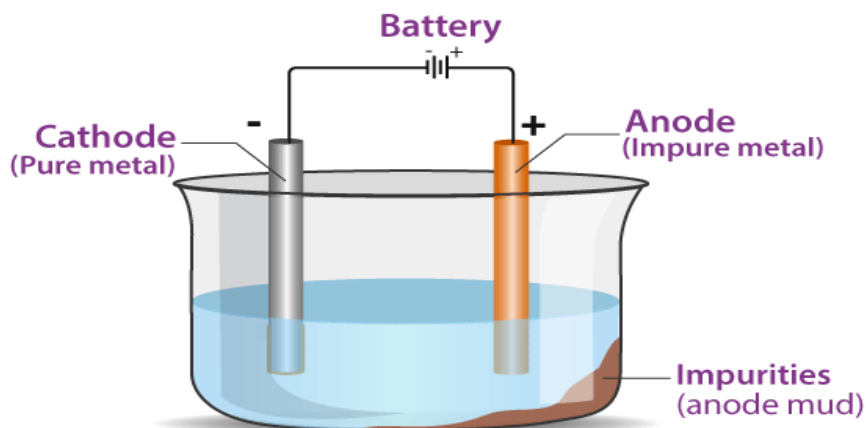**(iii) Vapour phase refining**

Ans:

(a) Zone refining:
This method makes use of a principle according to which impurities are more soluble in molten metal than in solid metal. In zone refining, a moving circular heater slowly moves over an impure metal rod/bar. As the circular heater moves, the impurities move into the adjacent molten zone, and the pure metal crystallises out. This is repeated over several times, causing the segregation of impurities at one end of the bar. This impure end is then cut off. Boron, silicon, gallium, etc., are purified this way.
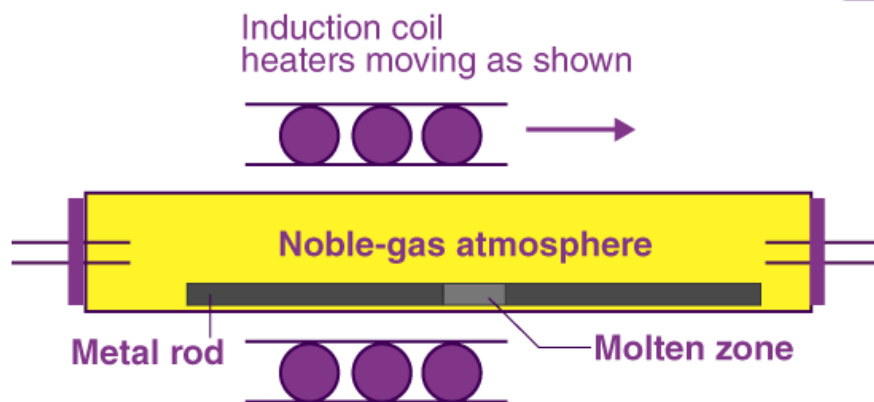
(b) Electrolytic refining:
It is the refining of impure metals using electricity. In this method, the anode is the impure metal, and the cathode is a thin sheet of pure metal. The electrolyte is a salt solution of the same metal.
On passing the electric current, the metal ions from the electrolyte collect at the cathode as a pure metal, and the impure metal of the anode dissolves into the solution (electrolyte) in the form of ions. The impurities of the metal deposits below the anode. This is called the anode mud.

(c) Vapour phase refining:
It is a method of metal refining by converting the metal into its volatile compound and then decomposing it to get pure metal.
To achieve this:
(1) The metal should convert into a volatile compound with a reagent.
(2) The volatile compound of the metal has to be able to decompose easily so that the pure metal can be conveniently recovered.
Zirconium, titanium and nickel are refined through this method.

Q27. Predict conditions under which Al might be expected to reduce MgO

Ans:

The standard Gibbs free energy of the formation of Al_2O_3 from Al is smaller than that of MgO from Mg after 1350 ^{0}C. **Thus, at a temperature beyond 1350°C, Al can reduce MgO.**