

- Q1. The reaction, $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$; $\Delta G^\circ = -421 \text{ kJ}$ is thermodynamically feasible as is apparent from Gibbs energy value. Why does it not take place at room temperature?
- Q2. Copper can be extracted by hydrometallurgy but not zinc. Explain.
- Q3. Name the common elements present in the anode mud in electrolytic refining of copper. Why are they so present?
- Q4. Although thermodynamically feasible, in practice, magnesium metal is not used for the reduction of alumina in the metallurgy of aluminium. Why?
- Q5. Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction?
- Q6. What is the role of depressant in froth floatation process?
- Q7. Why is the extraction of copper from pyrites difficult than that from its oxide ore through reduction?
- Q8. Out of C and CO, which is a better reducing agent at 673 K?
- Q9. State the role of silica in the metallurgy of copper.
- Q10. What criterion is followed for the selection of the stationary phase in chromatography?
- Q11. How is 'cast iron' different from 'pig iron'?
- Q12. Explain why, aluminium cannot be extracted by reducing alumina with carbon.
- Q13. Which metal is used for wrapping the chocolates?
- Q14. Which method can be used in the extraction of zirconium or titanium?
- Q15. What do you mean by metallurgy?
- Q16. Name a method used for refining nickel.
- Q17. Suggest a reducing agent cheaper than aluminium for the reduction of metallic oxide (M_2O_3).
- Q18. At what temperature carbon can be used as a reducing agent for FeO?
- Q19. What is gangue?
- Q20. Give an important ore of aluminium ore.
- Q21. Name the metals do you expect to occur in the native state in nature?
- Q22. What is the role of cryolite in the metallurgy of aluminium?
- Q23. Differentiate between minerals and ores.
- Q24. Out of C and CO, which is a better reducing agent for ZnO?

- Q25. Differentiate between electrolytic reduction and reduction with carbon.
- Q26. Why pine oil is generally added in the froth floatation process?
- Q27. List major steps involved in the extraction of metals.
- Q28. Carbon monoxide is more effective agent than carbon below 983 K but above this temperature reverse is true. How would you explain this?
- Q29. Name three ores which can be concentrated by froth-floatation process.
- Q30. Mention two froth stabilizers used in froth floatation process.
- Q31. How zinc is used for the recovery of silver?
- Q32. Give two difference between hydraulic washing and liquation.
- Q33. What is meant by the term chromatography?
- Q34. Describe the principle of electrolytic refining.
- Q35. What are depressants? How would you separate zinc sulphide (ZnS) and lead sulphide (PbS) ores?
- Q36. Why is it advantageous to roast a sulphide ore to oxide before reduction?
- Q37. Explain zone refining in details.
- Q38. What criterion is followed for the selection of the stationary phase in chromatography?
- Q39. Write chemical reactions taking place in the extraction of zinc from zinc blende.
- Q40. Why is the extraction of copper from pyrite difficult than that from its oxide through reduction?
- Q41. What is the role of graphite rod in the electrometallurgy of aluminium?
- Q42. The value of $\Delta_f G^\ominus$ for formation of Cr_2O_3 is -540 kJ mol^{-1} and that of Al_2O_3 is -827 kJ mol^{-1} . Is the reduction of Cr_2O_3 possible with Al?
- Q43. Why is zinc not extracted from zinc oxide through reduction using CO?
- Q44. How is leaching carried out in case of low grade copper ores?
- Q45. Giving examples, differences between 'roasting' and 'calcination'.
- Q46. Why copper matte is put in silica lined converter?
- Q47. Describe a method for refining nickel.
- Q48. Name various method used for the concentration of ore.
- Q49. Name a metal which is purified by vapour phase refining. Describe the process in brief.
- Q50. Describe in brief the magnetic separation process of the concentrated ore.
- Q51. Predict conditions under which Al might be expected to reduce MgO.
- Q52. Explain the process of leaching or chemical separation for the concentration of ores.
- Q53. Write chemical reactions taking place in the extraction of zinc from zinc blende.

- Q54.** Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.
- Q55.** State the role of silica in the metallurgy of copper.
- Q56.** Outline the principles of refining of metals by the following methods:
(a) Electrolytic refining (b) Vapour phase refining
- Q57.** 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.
- Q58.** Explain: (1) Zone refining (2) Column chromatography.
- Q59.** Suggest a condition under which magnesium could reduce alumina.
- Q60.** (a) Name the processes from which chlorine is obtained as a by-product.
(b) What will happen if an aqueous solution of NaCl is subjected to electrolysis?
- Q61.** How can you separate alumina from bauxite ore associated with silica? Give equations.

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S1. The reaction is thermodynamically favourable. Since in the given redox reaction, all the reactants and the products are solids at room temperature, therefore, it does not occur at room temperature. However, at high temperature when chromium melts, the reaction proceeds rapidly. Thus, heating is required for this reaction to start.

S2. Zinc is more electropositive ($E^\circ = -0.76\text{ V}$) and therefore, is highly reactive metal. Hence, it cannot be easily displaced from its solution of ZnSO_4 . On the other hand, copper is less electropositive ($E^\circ = +0.34\text{ V}$) and can be readily displaced from its solution by some more active metal such as zinc.



S3. The anode mud in the electrolytic refining of copper contains antimony, selenium, tellurium, silver, gold and platinum. These are present as impurities in blister copper. These are less reactive and are not affected by $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ solution and hence settle down under anode as anode mud.

S4. Above the temperature corresponding to the point of intersection of the Al_2O_3 and MgO curves, magnesium could reduce alumina. But the temperature required would be so high that the process will be uneconomic and technologically difficult.

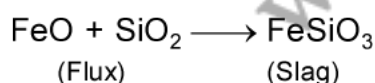
S5. The entropy of metal in liquid state is higher than solid state. The value of entropy change (ΔS) in reduction process is more on +ve side when the metal formed is in liquid state and the metal oxide being reduced is in solid state. Thus the value of ΔG° becomes more on negative side and the reduction becomes easier.

S6. Depressants prevent certain type of particles from forming froth during froth floatation process. For example, NaCN acts as depressant for ZnS but not for PbS . Thus, when an ore containing PbS and ZnS is subjected to froth floatation process only PbS forms the froth. In this way, PbS can be separated from ZnS .

S7. Copper pyrites contain FeS which needs to be oxidised to FeO and then removed as FeSiO_3 (slag) whereas in oxide ore, such impurities are not present.

S8. At 673 K, CO is better reducing agent.

S9. In the metallurgy of copper, silica (SiO_2) acts as flux. It reacts with impurity (FeO) and removes it as slag (FeSiO_3).

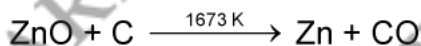


S10. In chromatography method adsorbent acts as stationary phase. It should have high adsorption power, greater surface area for adsorption. It should not react chemically with sample component.

- S11.** Cast iron contains about 3% carbon whereas pig iron contains about 4% carbon. Pig iron is converted into cast iron by heating molten pig iron with scrap iron and coke in specially designed furnace.
- S12.** Alumina (Al_2O_3) cannot be reduced by using carbon because aluminium has more affinity for oxygen than carbon has.
- S13.** Aluminium.
- S14.** Van Arkel method.
- S15.** Operations used in the extraction of metal from its ore is known as metallurgy.
- S16.** Mond's Process.
- S17.** Coke. (C)
- S18.** Above 1123 K, carbon can reduce FeO to Fe.
- S19.** The earthy and siliceous impurities associated with the ores is called gangue.
- S20.** Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$).
- S21.** Metals are Cu, Ag, Au, Pt.
- S22.** Cryolite performs two functions in the metallurgy of aluminium:
- It lowers the melting point of the mixture to about 1140 K.
 - It improves the electrical conductivity of the cell.
 - It acts as solvent.
- S23. Minerals:** Mineral are the naturally occurring chemical substances in the earth's crust which can be extracted by mining.

Ores: The minerals from which a metal can be extracted economically and conveniently are called ores. For example, minerals of copper are copper glance (Cu_2S) cuprite (Cu_2O) and copper pyrites (CuFeS_2) but its ore is copper pyrites. All ores are minerals but all minerals are not ores.

- S24.** C is better reducing agent for reduction of ZnO.



S25.	Electrolytic Reduction	Reduction with carbon
	<ol style="list-style-type: none"> In this, cathode acts as a reducing agent by supplying electrons to reduce metal ions into metal. It is used for reduction of salts of less reactive metal. 	<ol style="list-style-type: none"> In this, carbon is used as reducing agent. It can be used for the reduction of oxide of highly reactive metals.

S26. When impure ore is mixed with water and pine oil in a tank and steam is passed through it. Now gangue particles are wetted by water while the ore by oil. With the sulphide ore rises in the form of a foam while the gangue impurities settle at the bottom of the container.

S27. (a) Concentration of the ore.

(b) Isolation of metal from concentrated ore.

(c) Purification of metal.

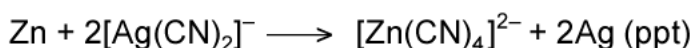
S28. Below 983 K CO is effective reducing agent because it does not decompose to carbon and oxygen rather gets oxidized to CO₂ and reduces the metal oxide to metal.

At high temperature, it gets reduced by metal oxide to carbon and oxygen.

S29. (a) Copper pyrites (CuFeS₂) (b) Galena (PbS) (c) Zinc blende (ZnS)

S30. (a) Cresol (b) Aniline

S31. Zinc is a powerful reducing agent and it readily displaces silver present in the complex.



S32.	Hydraulic Washing	Liquation
	1. It is used for concentration of the ore. 2. In this process ore is washed with water.	1. It is used for refining of metals. 2. In this process the metal is heated.

S33. Chromatography is a technique for the separation and purification based on the differences in the adsorbing tendencies of the metal and its impurities on a suitable adsorbent. It is based on the principle that different components of a mixture are differently adsorbed on an adsorbent.

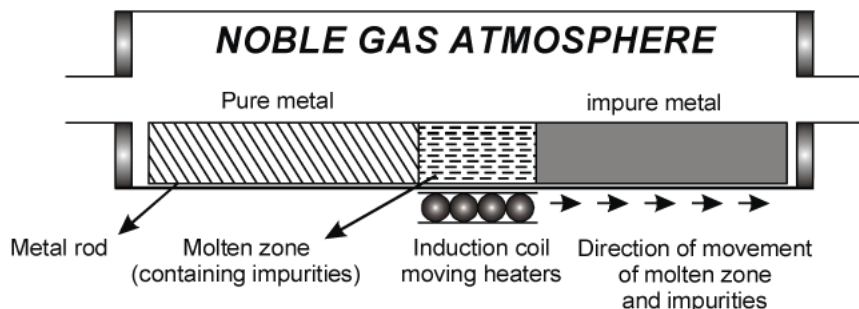
S34. Electrolytic refining: Many metals like copper, nickel, silver etc, are refined by this method. The impure copper is refined in the following way. The impure copper metal is made the anode of an electrolytic cell. The cathode is made of a thin plate of pure copper. The electrolyte is a solution of copper salt in water, e.g., copper sulphate. On passing electric current, copper is dissolved from the anode and deposited on the cathode. The impurities collect at the bottom below the anode.

S35. Depressants are the chemicals which are used for preventing certain type of particles from forming the froth. Zinc sulphide ore can be separated from lead sulphide ore by froth floatation process using sodium cyanide (NaCN) as depressant. Sodium cyanide acts as depressant for ZnS but does not prevent PbS from the formation of froth. Thus, the two ores can be separated.

S36. Oxides can be more easily reduced to the respective metals using carbon or hydrogen as reducing agent. On the other hand sulphides cannot be reduced by carbon or hydrogen because $\Delta_r G$ for such reactions are positive and hence these reactions are not feasible.

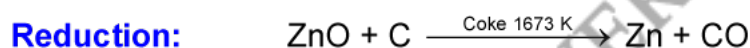
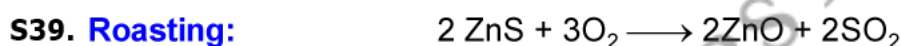
S37. This method is used for metal which are required very high purity. For example, extremely pure silicon, germanium, boron, gallium, and indium are refined by this method. This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. Therefore, an impure metal on solidification will deposit crystals of pure metal and the impurities will remain behind in the molten part of the metal. In this method, the impure metal is cast into a thin bar.

A circular mobile heater is fixed at one end of the rod of impure metal. One zone of the bar is melted by a circular mobile heater in the atmosphere of an inert gas like argon. At the heated zone, the metal melts (see figure). As the heater moves slowly, the impurities also move into the adjacent molten part. In this way, the impurities are made to move into one end which is finally cut off and discarded.



The molten metal present at the colder region solidifies in the mean time since it is away from the heater. Thus, we get completely pure metal by this method. This method is specially useful for producing semiconductors of very high purity. Germanium, for example, purified by this method contains impurities only upto 7 – 10 ppm.

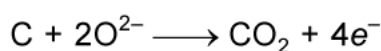
- S38.** The stationary phase acts as adsorbent and may have the following characteristics:
- It should have high and selective adsorption power.
 - It should be finely divided to offer greater surface area for adsorption.
 - The mechanical stability of stationary phase must be high to prevent the formation of dust which might be deposited in the channels of packing.
 - It should not react chemically either with the sample components or with the eluting solvents.
 - It should be pure.

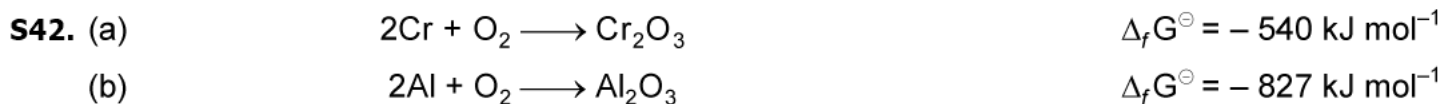


- S40.** The graph of $\Delta_r G^\circ$ vs T in Ellingham diagram for the formation of oxides shows that the copper-copper oxide line is almost at the top. Therefore, it is very easy to reduce oxide ores of copper directly to metal by heating with coke. This is because, $\Delta_r G^\circ$ vs T lines for CO has negative slope at higher temperature and therefore, can easily reduce Cu_2O to copper. However, the Gibbs energies of formation of most sulphides are greater than that for CS_2 . In fact, CS_2 is an endothermic compound. Moreover, there is no CS analogous to CO for which $\Delta_r G^\circ$ vs T graphs slop downward. Therefore, extraction of copper from pyrite ore (Cu_2S) is difficult.

- S41.** Graphite act as anode because in electro metallurgy of Al to prevent the liberation of O_2 at the anode which may otherwise oxidise some of the liberated Al back to Al_2O_3 .

Carbon reacts with oxygen liberated at anode producing CO and CO_2 .





Subtracting equation (a) from (ii), we get



Since the $\Delta_r G^\ominus$ for the reduction of Cr_2O_3 with Al is negative therefore, the reaction is possible.

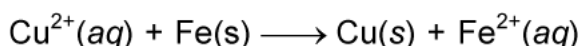
S43. Because difference in Gibbs energy charge of carbon monoxide and zinc oxide is not very large. So lesser the difference more difficult will be reduction. Hence, reduction of ZnO with CO is not possible as the $\Delta_r G^\ominus$ for this reaction would be positive.



On the other hand, coke can reduce zinc oxide to zinc as the energy Gibbs for this reaction would be negative and hence the reaction is feasible.



S44. Copper is leached out using acid. The solution containing Cu^{2+} ions is treated with iron scrap or H_2 to recover copper.



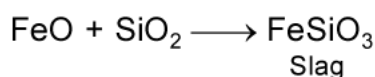
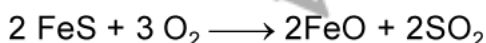
S45. Roasting: Roasting is the process of heating the ore in the excess supply of air below its melting point. This process is applied for sulphide ores. As a result sulphide ore changes into oxide.

Calcination: Calcination is the process of heating the ore in limited supply of air below its melting point. This process is applied for oxide and carbonate ores. Carbonates are changed into oxide ores. For example:

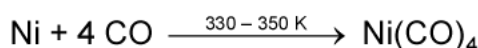
Zinc blende is roasted whereas haematite is subjected to calcination.



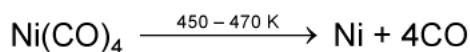
S46. Copper matte contains Cu_2S and FeS . In the converter FeS gets converted into FeO . Silica helps in removal of FeO impurity as slag.



S47. Mond Process for refining Nickel: In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl:



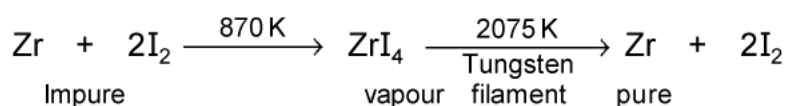
Now carbonyl is heat at higher temperature so that it is decomposed into pure metal and carbon-monoxide.



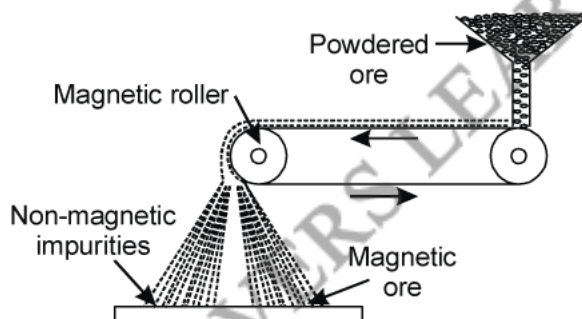
S48. Various methods used for the concentration of ores are:

- Hand picking
- Gravity separation or levitation
- Froth floatation process
- Magnetic separation
- Leaching or chemical separation.

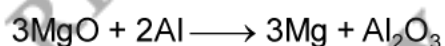
S49. Zirconium is purified by vapour phase refining the process is known as Van Arkel Process. In this process impure zirconium is heated with iodine vapour at about 870 K. Zirconium volatilizes as ZrI_4 . When ZrI_4 is passed over tungsten filament at 2075 K, it decomposes to give pure zirconium



S50. Magnetic separation: Some ores are attracted by a magnet whereas gangue is not attracted. The magnetic ores like chromite, $\text{Fe(CrO}_3)_3$ and pyrolusite, MnO_2 are concentrated by this method as shown below



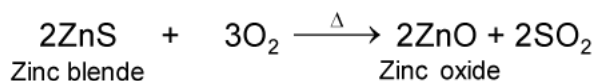
S51. Aluminium can reduce magnesium oxide at a temperature of about 2000 K because in this temperature range the line of $\Delta G^\ominus_{(\text{Mg, MgO})}$ lies above the line of $\Delta G^\ominus_{(\text{Al, Al}_2\text{O}_3)}$ in the Ellingham diagram. Therefore, under these condition $\Delta_r G^\ominus$ for reduction of MgO with Al will be negative and hence the reaction,



would be feasible.

S52. Leaching: It is a process used for the concentration of ores. In this process the impure ore is treated with a suitable reagent such as an acid or a base, when ore particles dissolve due to the chemical reaction called **leaching**, while the gangue particles do not react. The ore can be recovered from the solution with the help of a suitable method. This process of concentration has been successfully used for the aluminium ore bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$). It has also been successfully used for the silver ore argentite (Ag_2S) and also for gold ores.

- S53.** (a) The concentrated zinc blende ore (ZnS) is roasted in the presence of excess air at about 1200 K to convert it to zinc oxide.



- (b) Zinc oxide is reduced to zinc by heating with crushed coke at 1673 K.

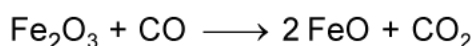
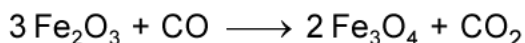


- (c) The impure zinc is refined by electrorefining method. In this method, the impure zinc is made anode and a plate of pure zinc is made cathode in an electrolytic bath containing zinc sulphate and a small amount of dilute H_2SO_4 . On passing current, the following reactions occur:

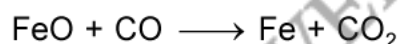
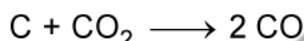


- S54.** In blast furnace, reduction of iron oxides takes place in different temperature ranges. The lower part of the blast furnace has high temperature of the order of 2200 K (called combustion zone) and the top of the furnace has low temperature of the order of 500–800 K (called reduction zone). The reduction occurring in the lower temperature range (upper part) is by carbon and in the higher temperature range (lower part) is by carbon monoxide.

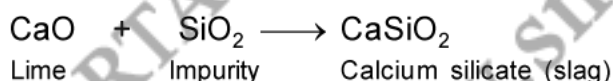
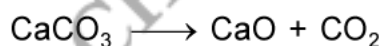
At lower temperature range (500–800 K) in upper part of furnace the reactions occurring are :



At higher temperature range (900–1500 K) in lower part of furnace the reactions occurring are:

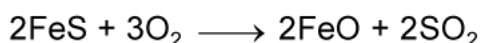
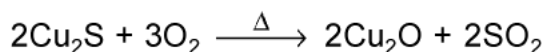
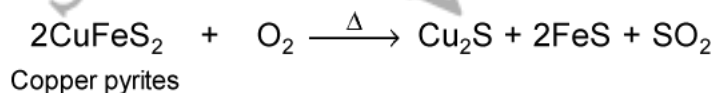


In the middle portion (at about 1270 K), limestone decomposes to give lime (CaO) and CO_2 . Lime acts as a flux and combines with silicate impurity to form slag.



Slag is in the molten state and separates out from iron.

- S55.** During roasting the copper pyrites are converted into a mixture of FeO and Cu_2O .



S57. It is true that choice of a reducing agent in a particular case depends on thermodynamic factor. For a reaction to be feasible, the reaction of metal oxide with the reducing agent should have negative $\Delta_r G^\ominus$. Therefore, that reducing agent is suitable for which $\Delta_r G^\ominus$ for the reduction reaction is negative. For example, at 1000 K, Al can reduce Cr_2O_3 but it cannot reduce MgO.



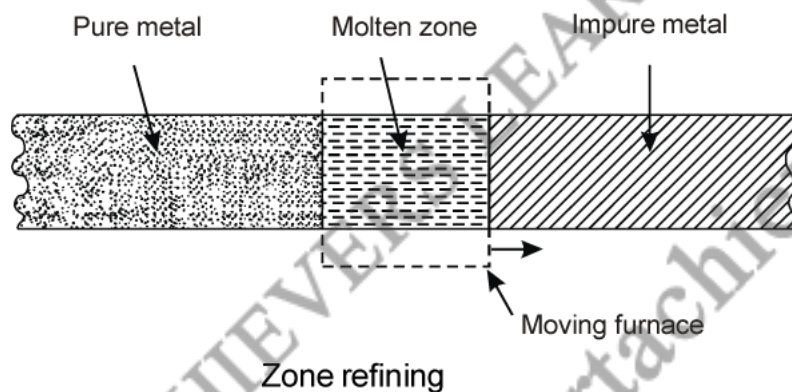
Thus, Al is correct choice for the reduction of Cr_2O_3 and not for MgO.

Similarly, ZnO can be reduced with coke at about 1500 K but it cannot be reduced with CO.

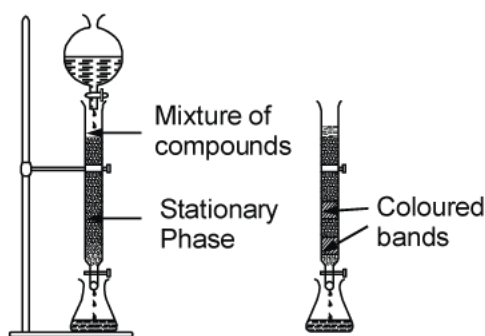


Therefore for the reduction of ZnO, coke is the correct choice.

S58. 1. **Zone Refining:** This method is particularly used when metals are required in high degree of purity. In this method, a metal rod is placed inside a small high frequency induction furnace. A narrow zone of metal is melted (see given figure). The furnace is now slowly moved along the rod. The pure metal recrystallises out of the melt while impurities remain in the melt which moves along with the melted zone of the rod with the movement of the furnace. The process is repeated several times. The end of the rod where the impurities have collected is cut off. This method is employed for the purification of germanium, silicon, gallium, etc., which is used in semiconductors.



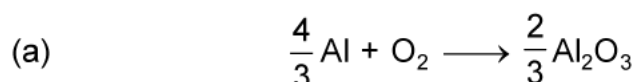
2. This method is based on difference in extent of adsorption of different components of a mixture on an adsorbent. In column chromatography, a suitable adsorbent such as alumina (Al_2O_3) is packed in glass tube having a stop-cock near the bottom (see the given figure). This constitutes the **stationary phase**. The mixture to be separated is dissolved in some suitable solvent and added to the column. The different components of the mixture gets adsorbed to different extent. Some suitable solvent (called **eluant**) is then added to the column. The eluant constitutes the **mobile phase**.



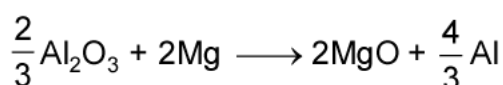
Column chromatography. (Laboratory Method)

The weakly adsorbed components reach the bottom of the column first. It is followed by more strongly adsorbed components. Thus, different components of the mixture reach the bottom one by one and in this way get separated. This method is suitable for purification of those elements which are available in small quantities and the impurities are not much different in chemical behaviour from the element to be purified. Lanthanides (rare earth elements) are purified by this technique.

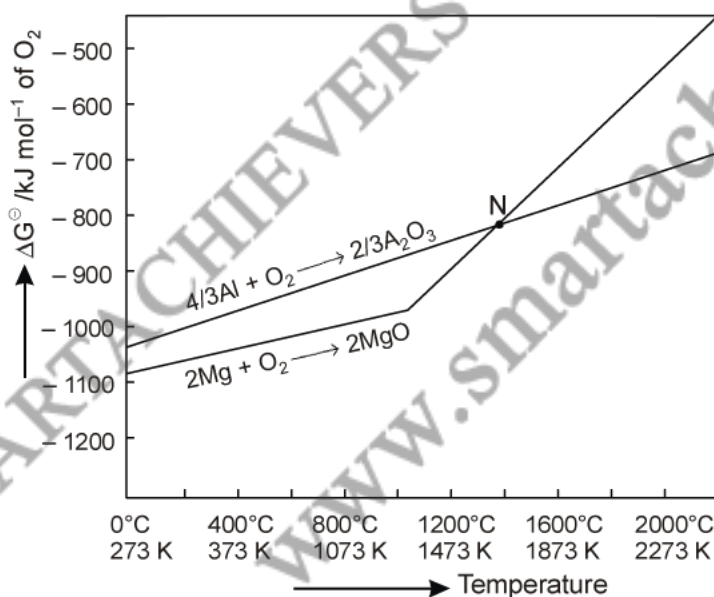
S59. The two equations are :



At the point of intersection of the Al_2O_3 and MgO curves, the ΔG° becomes Zero for the reaction:



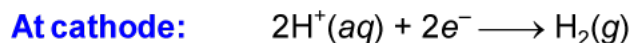
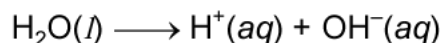
Above the point magnesium can reduce alumina.



Gibbs energy (ΔG°) vs T plots (schematic) for formation of some oxides (Ellingham diagram)

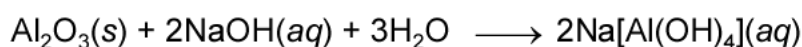
S60. (a) Electrolysis of molten NaCl (Down's Process) and electrolysis of aqueous NaCl (Castner – Kellner Process).

(b) Electrolysis of aqueous solution of NaCl



Hydrogen gas is formed at cathode, chlorine is liberated at anode. Sodium hydroxide is formed in the electrolyte.

S61. Bauxite, a principal ore of aluminium contains silica, iron oxide and titanium oxide as impurities. The ore is digested with a concentrated solution of NaOH at 473–523 K and 35 – 36 bar pressure. Al_2O_3 is leached out as sodium aluminate and silica as sodium silicate while impurities are left behind



The aluminate in the solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated.



The sodium silicate remains in the solution while hydrated alumina is filtered and dried.

The hydrated alumina thus precipitated is filtered, dried and heated to give back pure alumina.

