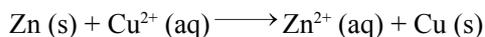


1. Copper can be extracted by hydrometallurgy but not zinc. Explain.

Sol. Copper can be extracted by hydrometallurgy but not zinc, this is because

$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ is lower than that of $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$. Hence, zinc can displace Cu from solutions of Cu^{2+} ions.



In order to displace zinc from zinc solution, a more reactive metal is required, such as Al ($E^\circ_{\text{Al}^{2+}/\text{Al}} = -1.66 \text{ V}$), Mg ($E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ V}$), Ca ($E^\circ_{\text{Ca}^{2+}/\text{Ca}} = -2.87 \text{ V}$), K ($E^\circ_{\text{K}^+/\text{K}} = -2.93 \text{ V}$). But with water, these metals (Al, Mg,

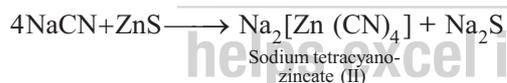
Ca and K) forms their corresponding ions with the evolution of H_2 gas.

Thus, Al, Mg, Ca, K, etc., cannot be used to displace zinc from zinc solution, and only copper can be extracted by hydrometallurgy but not the zinc.

2. What is the role of depressant in froth-floatation process?

Sol. The role of depressant is to prevent one type of sulphide ore particles from forming the froth with air bubbles.

NaCN is used as a depressant to separate lead sulphide (PbS) ore from zinc sulphide (ZnS) ore. NaCN forms a zinc complex, $\text{Na}_2[\text{Zn}(\text{CN})_4]$ on the surface of ZnS thereby preventing it from the formation of the froth.



In this condition, only lead sulphide forms froth and thus can be separated from zinc sulphide ore.

3. Why is the extraction of copper from pyrite difficult than that from its oxide ore through reduction?

Sol. The extraction of copper from pyrite is difficult than that from its oxide ore through reduction. This is because the standard free energy of formation of Cu_2S ($\Delta_f G^\circ_{\text{CS}_2}$) is greater than those of $\Delta_f G^\circ_{\text{H}_2\text{S}}$. Thus, neither carbon nor hydrogen can reduce Cu_2S to Cu metal. But, $\Delta_f G^\circ_{\text{Cu}_2\text{O}}$ is much lower than that of $\Delta_f G^\circ_{\text{CO}_2}$ and hence carbon easily reduces Cu_2O to Cu metal.



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

Sol. This can be explained thermodynamically, taking entropy and free energy changes into account.

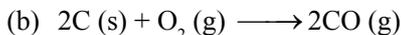
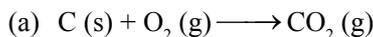
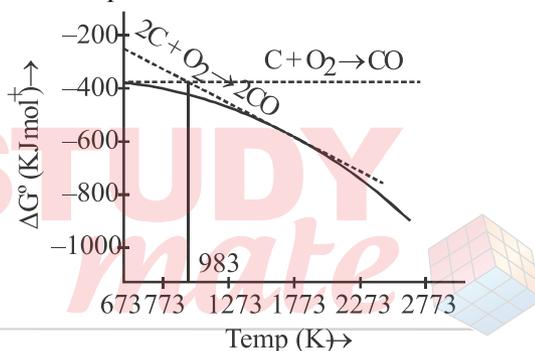
Case (i): Volume of CO_2 produced = Volume of O_2 used. $\therefore \Delta S$ is very small and ΔG does not change with temperature. \therefore Plot of ΔG vs. T is almost horizontal.Case (ii): Volume of CO produced = $2 \times$ Volume of O_2 used. $\therefore \Delta S$ is positive and hence ΔG becomes increasingly negative as the temperature increases. \therefore Plot of ΔG vs. T slopes downwards.

Fig. 6.4

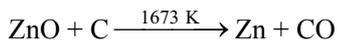
As can be seen from ΔG° vs. T plot (Ellingham diagram), lines for the reactions, $C + O_2 \longrightarrow CO_2$ and $2C + O_2 \longrightarrow 2CO$ cross at 983K. Below 983K, the reaction (a) is energetically more favourable but above 983K, reaction (b) is favourable and preferred. Thus, below 983K both C and CO can act as a reducing agent but since CO can be more easily oxidised to CO_2 than C to CO_2 , therefore, below 983K, CO is more effective reducing agent than carbon.

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

Sol. The common elements present in the anode mud are antimony, selenium, 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.

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

- (iii) **Reduction:** Zinc oxide obtained above is mixed with powdered coke and heated to 1673K in a free clay retort when it is reduced to zinc metal.



At 1673K, zinc metal being volatile (boiling point 1180 K), distills over and is condensed.

- (iv) **Electrolytic refining:** Impure zinc is made the anode while pure zinc sheet is made the anode. ZnSO_4 solution acidified with dil. H_2SO_4 is the electrolyte used. On passing electric current, pure zinc gets deposited on the cathode.

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

Sol. 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 (FeSiO_3) slag which floats over molten matte.

9. What is meant by the term chromatography?

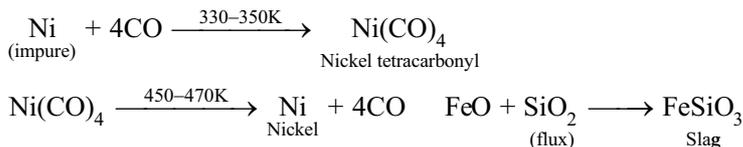
Sol. Chromatography is used for separation, purification identification and characterisation of the components of a mixture whether coloured or colourless. The term chromatography was originally derived from the Greek word '*chroma*' meaning colour and '*graphy*' for writing because the method was first used for the separation of coloured substances (plant pigments) into individual components.

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

Sol. The stationary phase is selected in such a way that the impurities are more strongly adsorbed or are more soluble in the stationary phase than element to be purified. Thus, when the column is extracted, the impurities will be retained by the stationary phase while the pure component is easily eluted.

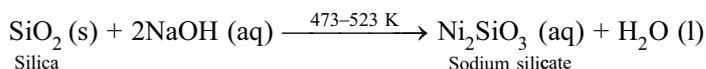
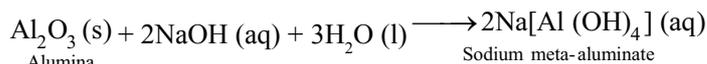
11. Describe the method of refining of nickel.

Sol. When impure nickel is heated in presence of CO at 330–350K, it forms volatile nickel tetracarbonyl leaving behind the impurities. The nickel tetracarbonyl thus obtained is then heated to a higher temperature (450–470K), when it undergoes thermal decomposition to give pure nickel.

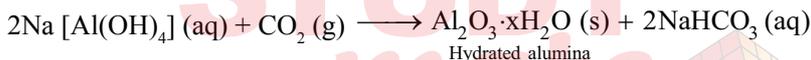


12. How can you separate alumina from silica in bauxite ore associated with silica? Give equations, if any.

Sol. Pure alumina may be separated from silica in bauxite by Baeyer's process. The bauxite ore associated with silica is heated with a concentrated solution of NaOH at 473–523K and 35–36 bar pressure. Under these conditions, alumina dissolves as sodium meta-aluminate and silica as sodium silicate leaving behind the impurities.



The resulting solution is filtered to remove the undissolved impurities, if any and neutralised by passing CO_2 gas. The solution is then seeded with freshly prepared samples of hydrated alumina when hydrated alumina gets precipitated leaving sodium silicate in the solution.

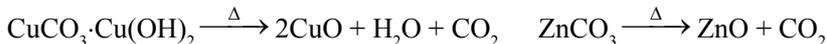


The hydrated alumina is thus precipitated is filtered, dried and heated to give back pure Al_2O_3 .

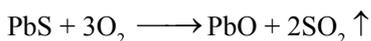
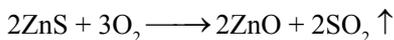


13. Giving examples to differentiate between 'roasting' and 'calcination'.

Sol. Calcination is a process of converting carbonates and hydroxide ores of metals to their respective oxides by heating them strongly below their melting points either in absence or limited supply of air.



Roasting is a process of converting a sulphide ore into its metallic oxide by heating strongly below its melting point in excess of air.



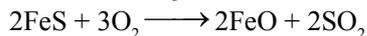
14. How is cast iron different from pig iron?

Sol. The iron obtained from blast furnace is called **pig iron**. It contains about 4% carbon and many other impurities in smaller amount (e.g. S, P, Si and Mn).

Cast iron 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.

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

Sol. Copper matte consists of Cu_2S along with some unchanged FeS . When a blast of hot air is passed through molten matte placed in silica lined converter, FeS present in matte is oxidised to FeO which combines with silica (SiO_2) to form FeSiO_3 slag.



When whole of iron has been removed as slag, some of the Cu_2S undergoes oxidation to form Cu_2O which then reacts with more Cu_2S to form copper metal.



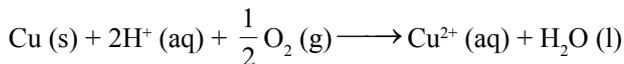
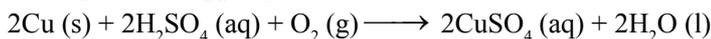
16. What is the role of cryolite in the metallurgy of aluminium?

Sol. (a) It lowers the fusion (melting) point of the bath from 2323K to about 1140K.

(b) It makes alumina a good conductor of electricity.

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

Sol. Leaching in case of low grade copper ores is carried out with acids in presence of air. In this process, copper goes into the solution as Cu^{2+} ions.

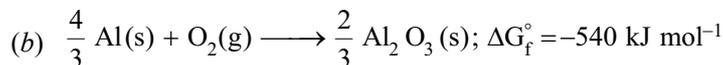
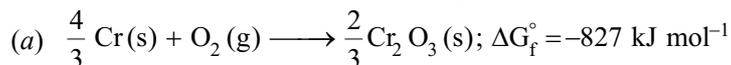


18. Why is zinc not extracted from zinc oxide through reduction using CO ?

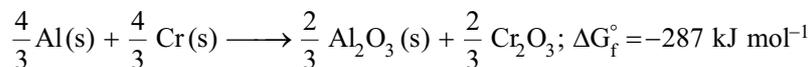
Sol. This is because the standard free energy of formation of CO_2 from CO is higher than that of standard free energy of formation of ZnO from Zn .

19. The value of $\Delta_f G^\circ$ 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 aluminium?

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



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



As can be seen $\Delta_f G^\circ$ is negative, thus, reduction of Cr_2O_3 by Al is possible.

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

Sol. The standard free energy of formation of CO from C becomes lower at temperatures above 1120K while that of CO_2 from C becomes lower above 1323K than standard free energy of formation of ZnO. Also, $\Delta_f G^\circ$ of CO_2 from CO is always higher than that of ZnO. Therefore, C can reduce ZnO.

21. 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.

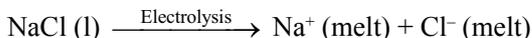
Sol. We can study the choice of a reducing agent in a particular case using Ellingham diagram.

It is evident from the diagram that metals for which the standard free energy of formation of their oxides is more negative can reduce those metal oxides for which the standard free energy of formation of their respective oxides is less negative. It means that any metal will reduce the oxides of other metals which lie above it in the Ellingham diagram. This is because the standard free energy change ($\Delta_f G^\circ$) of the combined redox reaction will be negative by an amount equal to the difference in $\Delta_f G^\circ$ of the two metal oxides. Thus both Al and Zn can reduce FeO to Fe but Fe cannot reduce Al_2O_3 to Al and ZnO to Zn. In the same way, C can reduce ZnO to Zn but not CO.

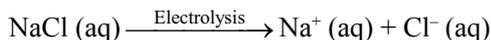
22. Name the process from which chlorine is obtained as a by-product. What will happen if an aqueous solution of NaCl is subjected to electrolysis?

Sol. Down's process is used for the preparation of sodium metal, where chlorine is obtained as a by-product. This process involves the electrolysis of a fused mixture of NaCl and CaCl_2 at 873K.

Sodium is discharged at the cathode while Cl_2 is obtained at the anode as a by-product.

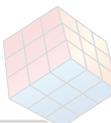


If, an aqueous solution of NaCl is electrolysed, H_2 is evolved at the cathode while Cl_2 is obtained at the anode. This is because $E^\circ_{\text{Na}^+/\text{Na}} = -0.83 \text{ V}$, and hence, water is reduced to H_2 in preference to Na^+ ions. However, NaOH is obtained in the solution.



23. What is the role of graphite in the electrometallurgy of aluminium?

Sol. The role of graphite in electrometallurgy of Al is to prevent the liberation of O_2 at the anode which may otherwise oxidise some of the liberated Al back to Al_2O_3 .

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