

CHAPTER 5

COORDINATION COMPOUNDS

QUESTION AND ANSWERS

2MARKS

1. How is 'cast-iron' different from 'pig iron'?

Ans: Cast iron differs from pig iron with respect to the carbon contents. Whereas carbon contents in pig iron are nearly four percent (4%), cast iron contains carbon to the extent of nearly three percent (3%).

2. Differentiate between "minerals" and "ores".

Ans: Minerals: The natural substances in which the metals or their compounds occur in the earth is called minerals.

Ores: The minerals from which the metals can be conveniently and economically extracted are called ores.

Note : All ores are minerals but all minerals are not ores.

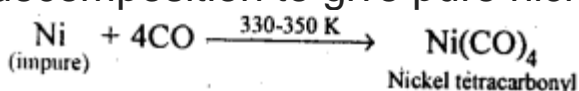
3. What is the role of cryolite in the metallurgy of aluminium?

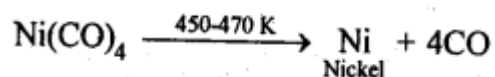
Ans: (a) It lowers the fusion (melting) point of the bath from 2323 K to about 1140 K.

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

4. Describe a method for refining nickel.

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



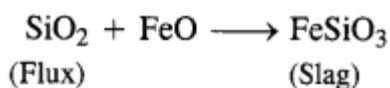


5. What is meant by the term “chromatography”?

Ans: Chromatography is a technique used for separation, purification, identification and characterization 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.

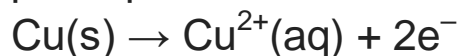
6. State the role of silica in the metallurgy of copper.

Ans: Silica (SiO_2) acts as an acidic flux in the metallurgy of copper and combines with FeO (the main impurity) to form FeSiO_3 which is a slag.



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

Ans: Anode mud contains metals like Ag, Au, Pt etc. which are less reactive than Cu. Actually, they are not in a position to lose electrons though they constitute the electrode which acts as anode. All these metals are left as residue under anode (known as anode mud) while the entire copper present participates in the oxidation half reaction.



5MARKS

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

Ans:

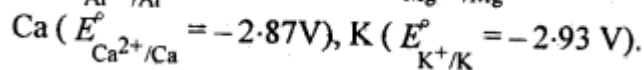
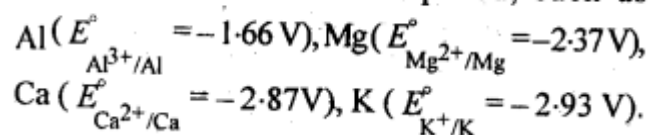
Copper can be extracted by hydrometallurgy but not zinc, this is because $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ is

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

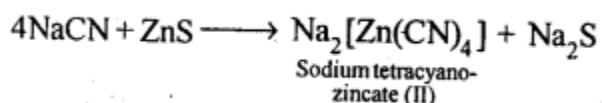


But with water, these metals (Al, Mg, Ca and K) forms their corresponding ions with the evolution of H_2 gas.

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?

Ans: 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.

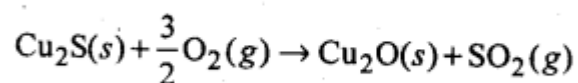


In this condition, only lead sulphide forms froth and thus can be separated from zinc sulphide ore.

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

Ans:

$\Delta_f G^\circ$ of Cu_2S is more negative than $\Delta_f G^\circ$ of CS_2 and H_2S . So Cu_2S can not be reduced by carbon or hydrogen. $\Delta_f G^\circ$ of CO_2 is more negative than $\Delta_f G^\circ$ of Cu_2O . So Cu_2O can be reduced by carbon. So pyrites is first converted to oxide before reduction to copper.

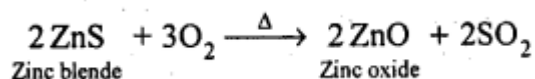


4. Write chemical reactions taking place in the extraction of zinc from zinc blende.

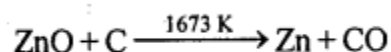
Ans: The following processes are involved in the extraction of zinc from zinc blende:

(i) Concentration: Zinc blende ore is crushed and the concentration done by froth- floatation process.

(ii) Roasting: The concentrated ore is then roasted in presence of excess of air at about 1200 K as a result zinc oxide is formed.



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



At 1673 K, 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 strip is made the cathode. ZnSO_4 solution acidified with dil. H_2SO_4 is the electrolyte used. On passing electric current, pure zinc gets deposited on the cathode.

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

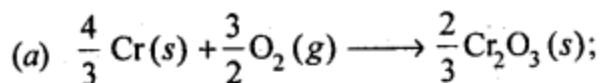
Ans: In chromatography, particularly in adsorption chromatography, the stationary phase is the adsorbent. It should fulfil certain criteria for better results.

- (i) It should have high but selective adsorption power.
- (ii) The particles should be spherical in shape and of uniform size.
- (iii) The adsorbent should not react chemically with the solvents used for elution or with the components of the mixture under investigation.
- (iv) The adsorbent should contain as small amount of the soluble components as possible.
- (v) The adsorbent should be catalytically inactive and must have a neutral surface.
- (vi) The adsorbent should be easily available.
- (vi) The adsorbent should be perfectly white.

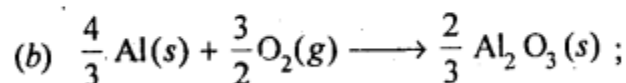
6. The value of $\Delta_f G^\circ$ for formation of Cr_2O_3 is -540 kJ mol^{-1} and that of Al_2O_3 is -827 kJ mol^{-1} . Is the reduction of Cr_2O_3 possible with Al?

Ans: Chemical equation for the formation of Cr_2O_3 and Al_2O_3 are

as follows :

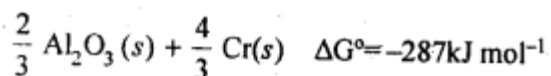
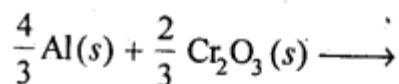


$$\Delta G_f^\circ = -540 \text{ kJ mol}^{-1}$$



$$\Delta G_f^\circ = -827 \text{ kJ mol}^{-1}$$

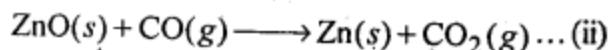
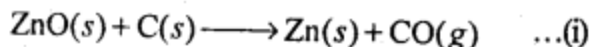
Substrating equation (a) from equation (b), we get



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

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

Ans: The two reduction reactions are :

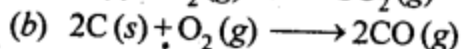
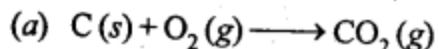


In the first case, there is increase in the magnitude of ΔS° while in the second case, it almost remains the same. In other words ΔG° will have more negative value in the first case when C(s) is used as the reducing agent than in the second case when CO(g) acts as the reducing agent. Therefore, C(s) is a better reducing agent.

7MARKS

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

Ans: 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.

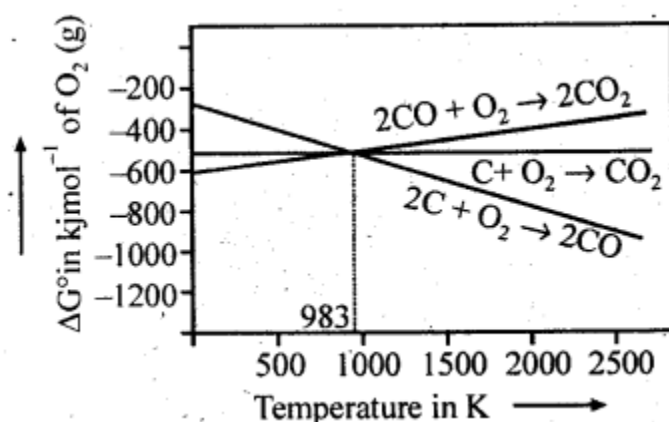
$\therefore \Delta S$ is very small and ΔG does not change with temperature.

\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.

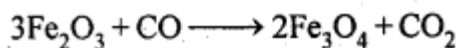


As can be seen from ΔG° Vs T plot (Ellingham diagram), lines for the reactions, $\text{C} \longrightarrow \text{CO}_2$ and $\text{C} \longrightarrow \text{CO}$ cross at 983 K. Below 983 K, the reaction (a) is energetically more favourable but above 673 K, reaction (b) is favourable and preferred. Thus, below 673 K 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 673 K, CO is more effective reducing agent than carbon.

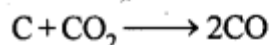
2. Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.

Ans: In the blast furnace reduction of iron oxides take place at different temperature ranges as shown below.

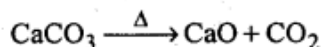
At 500 – 800 K



At 900 – 1500 K

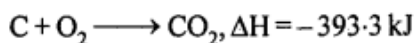


Above 1570 K

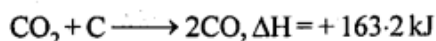


The following reactions occur in the blast furnace:

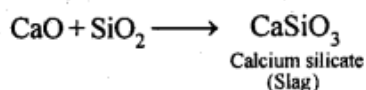
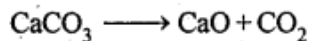
(a) In zone of combustion,



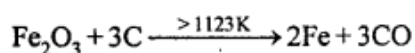
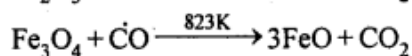
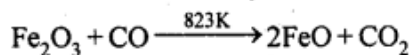
(b) In zone of heat absorption,



(c) In zone of slag formation,

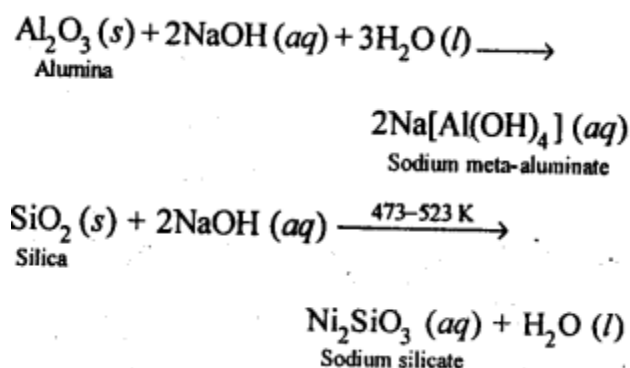


(d) In zone of reduction,

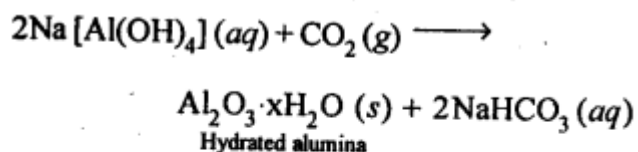


3. How can you separate alumina from silica in a bauxite ore associated with silica? Give equations, if any.

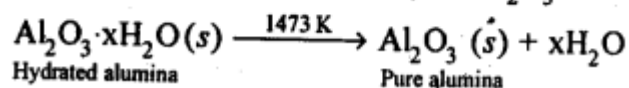
Ans: Pure alumina can be separated from silica in bauxite by Baeyer's process. The bauxite ore associated with silica is heated with a concentrated solution of NaOH at 473-523 K and 35-36 bar pressure. Under these conditions, alumina dissolves as sodium meta-aluminate and silica as sodium silicate leaving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



The resulting solution is filtered to remove the undissolved impurities, sodium meta-aluminate can be precipitated as hydrated aluminium oxide by passing CO₂ vapours. The sodium silicate formed cannot be precipitated and can be filtered off.



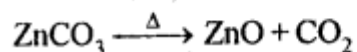
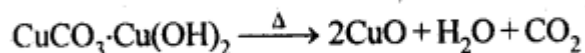
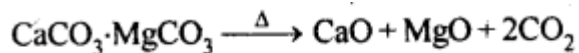
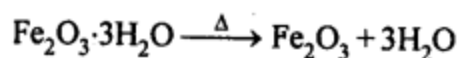
The hydrated alumina thus precipitated is filtered, dried and heated to give back pure Al₂O₃.



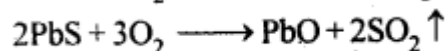
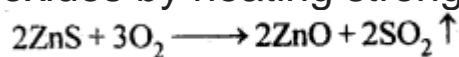
4. Giving examples, differentiate between 'roasting' and 'calcination'.

Ans: 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 sulphide ores into its metallic oxides by heating strongly below its melting point in excess of air.



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

(i) Zone refining

(ii) Electrolytic refining

(iii) Vapour phase refining

Ans: (i) Zone refining: This method is used for production of semiconductors and other metals of very high purity, e.g., Ge, Si, B, Ga and In.

It is, based on the principle that the impurities are more soluble in the molten state (melt) than in the solid state of the metal.

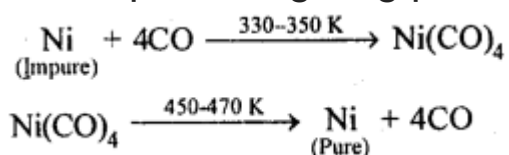
The impure metal in the form of bar is heated at one end with a moving circular heater. As the heater is slowly moved along the length of the rod, the pure metal crystallises out of the melt whereas the impurities pass into the adjacent molten zone. This process is repeated several times till the impurities are completely driven to one end of the rod which is then cut off and discarded.

(ii) Electrolytic refining: Many metals, such as Cu, Ag, Au, Al, Pb, etc., are purified by this method. The impure metal is made the anode while a thin sheet of pure metal acts as a cathode. The

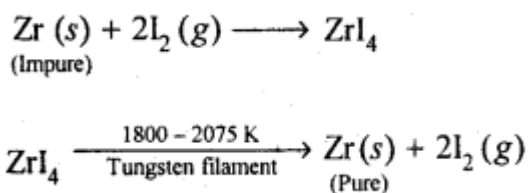
electrolytic solution consists of a salt or a complex salt solution of the metal. On passing the current, the pure metal is deposited on the cathode while the impurities fall down as anode mud.

(iii)Vapour-phase refining: The crude metal is freed from impurities by first converting it into a suitable volatile compound by heating it with a specific reagent at a lower temperature and then decomposing the volatile compound at some higher temperature to give the pure metal.

(a)Mond's process: When impure nickel is heated with a current of CO at 330-350 K, it forms volatile nickel tetracarbonyl complex leaving behind the impurities. The complex then heated to a higher temperature (450-470K) when it undergoes thermal decomposition giving pure nickel.



(b)Van Arkel method: This method is Used for preparing ultra-pure metals by removing all the oxygen and nitrogen present as impurities in metals like zirconium and titanium (which are used in space technology).Crude Zr is heated in an evacuated vessel with iodine at 870 K. Zirconium tetraiodide thus formed is separated. It is then decomposed by heating over a tungsten filament at 1800 – 2075 K to give pure Zr.



SUMMARY

1. Coordination compounds contain a central atom (or cation) which is coordinated to a suitable number of anions or neutral molecules and usually retain their identity in solution as well as in solid state. These may be a positively charged, negatively charged or a neutral species, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{NiCl}_4]^{2-}$, $[\text{Ni}(\text{CO})_4]$ etc.

2. In 1893, Werner proposed a theory to explain the structure and bonding in coordination compounds:

(a) In coordination compounds, metals show two types of valencies : Primary valency and secondary valency.

(b) Primary valencies are ionisable.

(c) Secondary valencies are not ionisable.

(d) This theory was successful to very limited extent and could not explain many aspects of coordination compounds.

3. In modern formulations, such spatial , arrangements are called coordination polyhedra.

The species within the square bracket are coordination entities or complexes and the ions outside the square brackets are called counter ions.

4. The compounds which have the same molecular formula but differ in their structural arrangements are known as isomers.

5. The types of isomerism shown by coordination compounds are :

(a) Geometrical (or cis-trans) isomerism: Two coordination compounds are said to be **geometrical isomers**, when they differ in the arrangement of their ligands in space. When two identical ligands occupy adjacent position, the isomer is called 'cis-form' and when they arranged opposite to one another,