

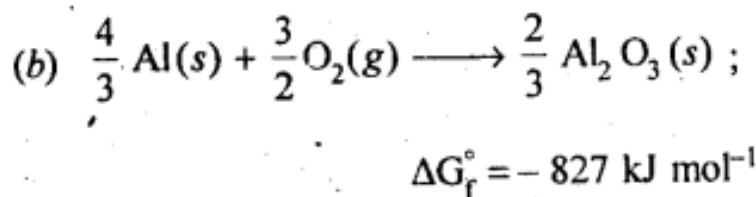
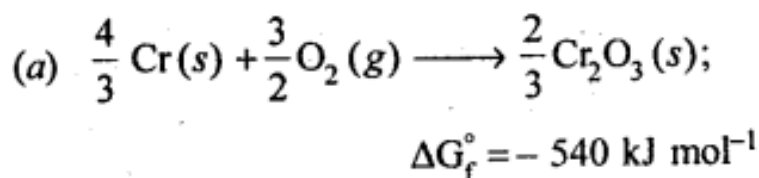


6.20. Why is zinc not extracted from zinc oxide through reduction using CO?

Ans: This is because the standard free energy of formation of  $\text{CO}_2$  from CO is higher than that of standard free energy of formation of ZnO from Zn.

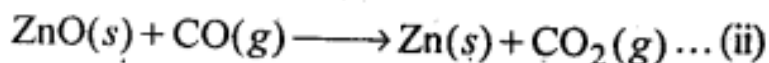
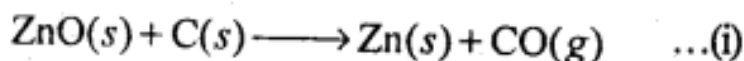
6.21. The value of  $\Delta_f G^\circ$  for formation of  $\text{Cr}_2\text{O}_3$  is  $-540 \text{ kJ mol}^{-1}$  and that of  $\text{Al}_2\text{O}_3$  is  $-827 \text{ kJ mol}^{-1}$ . Is the reduction of  $\text{Cr}_2\text{O}_3$  possible with Al?

Ans: Chemical equation for the formation of  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  are as follows :



6.22. 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  $\Delta S^\circ$  while in the second case, it almost remains the same. In other words  $\Delta G^\circ$  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.

6.23. 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.

Ans: 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 ( $\Delta_r G^\circ$ ) 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

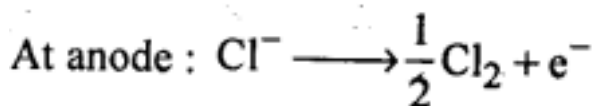
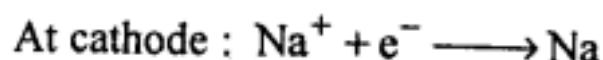
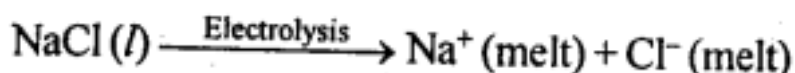
$\text{Al}_2\text{O}_3$  to Al and  $\text{ZnO}$  to Zn. In the same way, G can reduce  $\text{ZnO}$  to Zn but not CO.

Note : Only that reagent will be preferred as reducing agent which will lead to decrease in free energy value ( $\Delta G^\circ$ ) at a certain specific temperature.

6.24. 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: Down 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  $\text{CaCl}_2$  at 873

K. Sodium is discharged at the cathode while  $\text{Cl}_2$  is obtained at the anode as a by-product.



If, an aqueous solution of NaCl is electrolysed,  $\text{H}_2$  is evolved at the cathode while  $\text{Cl}_2$  is obtained at the anode.

6.25. What is the role of graphite rod in the electrometallurgy of aluminium?

Ans: In the electrometallurgy of aluminium, oxygen gas is evolved at anode.  $\text{O}_2$  reacts with graphite or carbon (graphite electrodes) to form carbon monoxide and carbon dioxide. In case if some other metal electrodes is used as anode, then oxygen will react with aluminium formed during the process to form aluminium oxide ( $\text{Al}_2\text{O}_3$ ) which will pass into the reaction mixture resulting into wastage of Al. Since graphite is cheaper than aluminium, its wastage or can be tolerated.

6.26. 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, Ca 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.

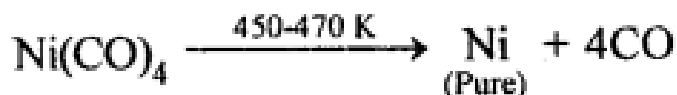
(ii) Electrolytic refining: Many metals, such as Cu, Ag, Au, Al, Pb, etc., are purified by this method. The impure metal is made the anode while a thin sheet of pure metal acts as a cathode. The electrolytic solution consists of a salt or a complex salt solution of the metal.

On passing the current, the pure metal is deposited on the cathode while the impurities fall down as anode mud.

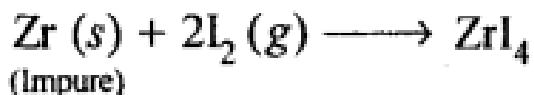
(iii) Vapour-phase refining: The crude metal is freed from impurities by first converting it into a suitable volatile compound by heating it

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 in 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.

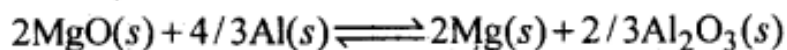


6.27. Predict conditions under which Al might be expected to reduce MgO.

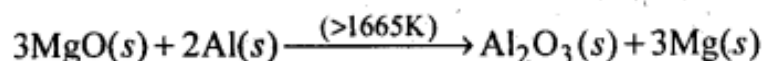
Ans. The equations for the formation of the two oxides are



If we look at the plots for the formation of the two oxides of the Ellingham diagram, we find that they intersect at certain point. The corresponding value of  $\Delta G^\circ$  becomes zero for the reduction of MgO by Al metal.



This means that the reduction of MgO by Al metal can occur below this temperature. Aluminium (Al) metal can reduce MgO to Mg above this temperature because  $\Delta^\circ G$  for  $\text{Al}_2\text{O}_3$  is less as compared to that of MgO.



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