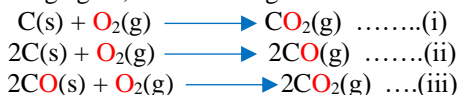


Industrial Metallurgy

❖ Reducing Nature of Carbon:

Carbon in the form of coke, charcoal or carbon monoxide is used as a reducing agent in *pyrometallurgical* operations. Such a reduction process used in the extraction of a metal is termed smelting.

When carbon is to act as a reducing agent, the following three reactions are possible:



In the first reaction (formation of CO_2) there is hardly any change in entropy, *i.e.*, $\Delta S^\circ = 0$ and therefore, ΔG° remains nearly the same with rise in temperature *i.e.*, ΔG° is independent of temperature.

In the second reaction (formation of CO), there is increase in entropy (ΔS° is positive) and therefore, ΔG° becomes more negative with increase in temperature.

However, in third reaction, there is decrease in entropy (ΔS° is negative) and therefore, ΔG° becomes less negative with increase in temperature.

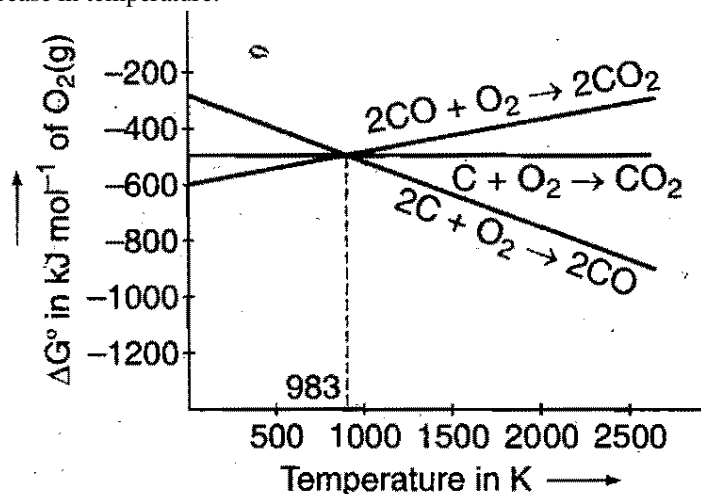


Figure 1: Ellingham diagram for the reducing nature of carbon.

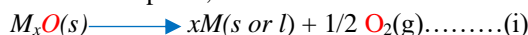
The three curves have been found to intersect at 983 K. It implies that above this temperature, the reaction (ii) is most suitable. It means that carbon can reduce any metal oxide at very high temperatures and is then itself oxidised to CO. However, the reduction with carbon at high temperatures is not preferred in all cases due to the following reasons:

- ❖ It involves high cost.
- ❖ Some metals react with carbon at high temperatures and form carbides.
- ❖ There are many practical difficulties in the maintenance of high temperature.

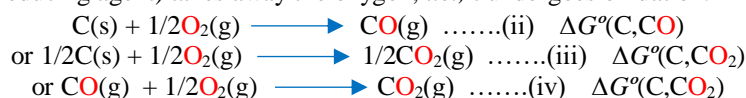
From the plot for the reaction of carbon monoxide with oxygen, it is evident that carbon monoxide acts as a better reducing agent than carbon at temperatures below 983 K.

Theory of Reduction of Metal Oxide with Carbon:

During reduction the metal oxide decomposes,



and the carbon (reducing agent) takes away the oxygen, *i.e.*, it undergoes oxidation.

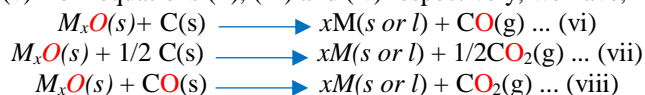


The role of the reducing agent is to provide a large negative ΔG° to make the sum of the $\Delta_r G^\circ$ of the above two reactions, (*i.e.*, reduction of metal oxide and oxidation of carbon or carbon monoxide) negative.

Reversing the equation (i)



Subtracting equation (v) from equations (ii), (iii) and (iv) respectively, we have,



The equations (vi), (vii) and (viii) describe the reduction of the metal oxide, M_xO . The $\Delta_r G^\circ$ values of these equations can be obtained from Ellingham diagram (Fig.). If $\Delta_r G^\circ$ values are negative, the reduction is feasible otherwise not. Greater the difference, easier is the reduction.

Without making any calculations for $\Delta_r G^\circ$ the prediction about the feasibility of a reduction process can be made by looking at the Ellingham diagram. **Metal oxide placed higher in the diagram can be reduced by the element (metal) involved in the formation of the oxide placed lower in the diagram.**

It is important to note that if a particular reduction process does not take place at a lower temperature, it may take place at a higher temperature. Ellingham diagram also helps in selecting such a temperature. The temperature is indicated by the intersection of the two curves.

Theory of Reduction of Haematite

In the Ellingham diagram (Fig.), there are three curves which illustrate the formation of ferric oxide from iron, formation of CO from carbon and formation of CO_2 from CO. The curves cross each other at 1073 K.

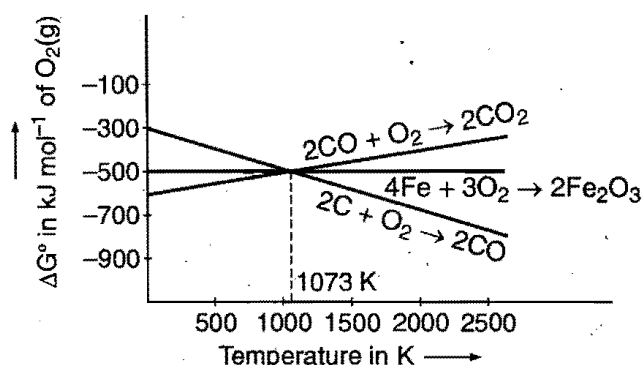


Figure 2: Ellingham diagram for the reduction of haematite.

Above 1073 K, $\Delta_r G^\circ$ for the formation of Fe_2O_3 is less negative than $\Delta_r G^\circ$ for the formation of carbon monoxide from carbon. Thus, above 1073 K, carbon (coke) can reduce Fe_2O_3 , i.e., $\Delta_r G^\circ$ for the reaction, is negative (T greater than 1073 K).



Below 1073 K, $\Delta_r G^\circ$ for formation of CO from carbon is less negative than $\Delta_r G^\circ$ for the formation of Fe_2O_3 . $\Delta_r G^\circ$ for the reduction of Fe_2O_3 with carbon will be positive and hence, reduction- is not possible. However, it is observed from the diagram that $\Delta_r G^\circ$ formation of CO_2 from CO is more negative than $\Delta_r G^\circ$ of formation of Fe_2O_3 . This means that Fe_2O_3 can be reduced by CO below 1073 K, i.e., $\Delta_r G^\circ$ for the reaction, is negative.



Thus, in the blast furnace, reduction of Fe_2O_3 occurs in different temperature ranges either below 1073 K by carbon monoxide or above 1073 K by carbon (coke).