$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \tag{6.9}$$
$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2 \tag{6.10}$$
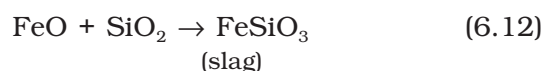$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \tag{6.11}$$

Fig. 6.3: A section of a modern reverberatory furnace

The sulphide ores of copper are heated in **reverberatory furnace** [Fig. 6.3]. If the ore contains iron, it is mixed with silica before heating. Iron oxide 'slags of'* as iron silicate and copper is produced in the form of **copper matte** which contains Cu_2S and FeS.

$$FeO + SiO_2 \rightarrow FeSiO_3 \tag{6.12}$$
$$\text{(slag)}$$

The SO_2 produced is utilised for manufacturing H_2SO_4 .

(b) Reduction of oxide to the metal

Reduction of the metal oxide usually involves heating it with a reducing agent, for example C, or CO or even another metal. The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.

$$M_xO_y + yC \rightarrow xM + y\ CO \tag{6.13}$$

Some metal oxides get reduced easily while others are very difficult to be reduced (reduction means electron gain by the metal ion). In any case, heating is required.

6.4 Thermodynamic Principles of Metallurgy

Some basic concepts of thermodynamics help us in understanding the theory of metallurgical transformations. Gibbs energy is the most significant term. To understand the variation in the temperature required for thermal reductions and to predict which element will suit as the reducing agent for a given metal oxide (M_xO_y), Gibbs energy interpretations are made. The criterion for the feasibility of a thermal reduction is that at a given temperture Gibbs energy change of the reaction must be negative. The change in Gibbs energy, ΔG for any process at any specified temperature, is described by the equation:

$$\Delta G = \Delta H - T\Delta S \tag{6.14}$$

where, ΔH is the enthalpy change and ΔS is the entropy change for the process.

When the value of ΔG is negative in equation 6.14, only then the reaction will proceed. ΔG can become negative in the following situations:

1. If ΔS is positive, on increasing the temperature (T), the value of $T\Delta S$ increases so that $\Delta H < T\Delta S$. In this situation ΔG will become negative on increasing temperature.

2. If coupling of the two reactions, i.e. reduction and oxidation, results in negative value of ΔG for overall reaction, the final reaction becomes feasible. Such coupling is easily understood

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* *During metallurgy, 'flux' is added which combines with 'gangue' to form 'slag'. Slag separates more easily from the ore than the gangue. This way, removal of gangue becomes easier.*

through Gibbs energy ($\Delta_r G^\ominus$) vs T plots for the formation of the oxides (Fig. 6.4). These plots are drawn for free energy changes that occur when one gram mole of oxygen is consumed.

The graphical representation of Gibbs energy was first used by H.J.T. Ellingham. This provides a sound basis for considering the choice of reducing agent in the reduction of oxides. This is known as **Ellingham Diagram**. Such diagrams help us in predicting the feasibility of thermal reduction of an ore.
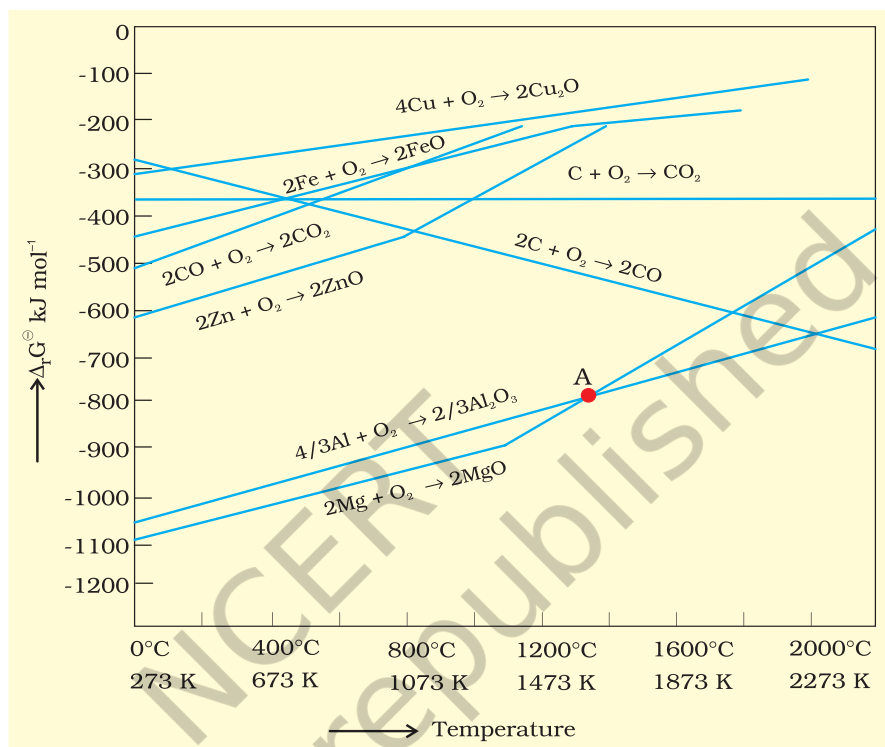

Fig. 6.4: Gibbs energy ($\Delta_r G^\ominus$) vs T plots (schematic) for the formation of some oxides per mole of oxygen consumed (Ellingham diagram)

As we know, during reduction, the oxide of a metal decomposes and the reducing agent takes away the oxygen. The role of reducing agent is to provide $\Delta_r G^\ominus$ negative and large enough to make the sum of $\Delta_r G^\ominus$ of the two reactions, i.e, oxidation of the reducing agent and reduction of the metal oxide negative.

$$M_x O(s) \rightarrow xM \text{ (solid or liq)} + \frac{1}{2} O_2 \text{ (g)} \qquad [\Delta_r G^\ominus_{(M,O,M)}] \qquad (6.15)$$
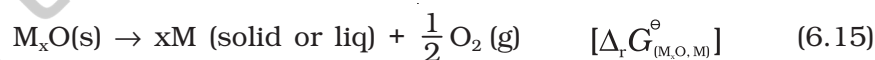
If reduction is carried out by carbon the oxidation of the reducing agent (i.e., C) will be there:

$$C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g) \qquad [\Delta_r G^\ominus_{(C,CO)}] \qquad (6.16)$$

There may also be complete oxidation of carbon to CO_2.

$$\frac{1}{2}C(s) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g) \qquad [\tfrac{1}{2}\Delta_r G^\ominus_{(C,CO_2)}] \qquad (6.17)$$
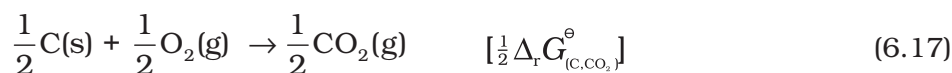
On coupling (combing) reaction 6.15 and 6.16 we get:

$$M_xO(s) + C(s) \rightarrow xM(s \text{ or } l) + CO(g) \qquad (6.18)$$

On coupling reaction 6.15 and 6.17 we have

$$M_xO(s) + \frac{1}{2}C(s) \rightarrow xM(s \text{ or } l) + \frac{1}{2}CO_2(g) \qquad (6.19)$$
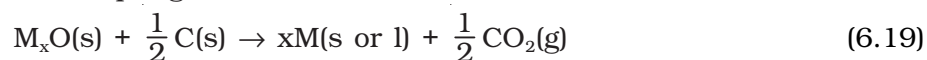
Similarly, if carbon monoxide is reducing agent, reactions 6.15 and 6.20 given below need to be coupled.

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad [\Delta_r G^{\ominus}_{(CO,CO_2)}] \qquad (6.20)$$

Over all reaction will be as follows:

$$M_xO(s) + CO(g) \rightarrow xM(s \text{ or } l) + CO_2(g) \qquad (6.21)$$

Ellingham Diagram

(a) Ellingham diagram normally consists of plots of $\Delta_f G^{\ominus}$ *vs* T for the formation of oxides of common metals and reducing agents i.e., for the reaction given below.

$$2xM(s) + O_2(g) \rightarrow 2M_xO(s)$$
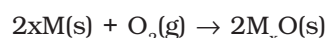
In this reaction, gas is consumed in the formation of oxide hence, molecular randomness decreases in the formation of oxide which leades to a negative value of ΔS as a result sign of $T\Delta S$ term in equation (6.14) becomes positive. Subsequently $\Delta_f G^{\ominus}$ shifts towards higher side despite rising T. The result is positive slope in the curve for most of the reactions for the formation of $M_xO(s)$.

(b) Each plot is a straight line and slopes upwards except when some change in phase $(s\rightarrow l \text{ or } l\rightarrow g)$ takes place. The temperature at which such change occurs, is indicated by an increase in the slope on positive side (e.g., in the Zn, ZnO plot, the melting is indicated by an abrupt change in the curve) [Fig. 6.4].

(c) When temperature is raised, a point is reached in the curve where it crosses $\Delta_r G^{\ominus}=0$ line. Below this temperature, $\Delta_r G^{\ominus}$ for the formation of oxide is negative so M_xO is stable. Above this point, free energy of formation of oxide is positive. The oxide, M_xO will decompose on its own.

(d) Similar diagrams are constructed for sulfides and halides also. From them it becomes clear that why reduction of M_xS is difficult.

Limitations of Ellingham Diagram

1. The graph simply indicates whether a reaction is possible or not, i.e., the tendency of reduction with a reducing agent is indicated. This is so because it is based only on the thermodynamic concepts. It does not explain the kinetics of the reduction process. It cannot answer questions like how fast reduction can proceed? However, it explains why the reactions are sluggish when every species is in solid state and smooth when the ore melts down. It is interesting to note here that ΔH (enthalpy change) and the ΔS (entropy change) values for any chemical reaction remain nearly constant even on varying temperature. So the only dominant variable in equation(6.14) becomes T. However, ΔS depends much on the physical state of the compound. Since entropy depends on disorder or randomness in the system, it will increase if a compound melts $(s\rightarrow l)$ or vapourises $(l\rightarrow g)$ since molecular randomness increases on changing the phase from solid to liquid or from liquid to gas.

2. The interpretation of $\Delta_r G^{\ominus}$ is based on K ($\Delta G^{\ominus} = -RT \ln K$). Thus it is presumed that the reactants and products are in equilibrium:

$$M_xO + A_{red} \rightleftharpoons xM + A_{red}O$$
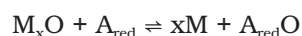
This is not always true because the reactant/product may be solid. In commercial processes reactants and products are in contact for a short time.

The reactions 6.18 and 6.21 describe the actual reduction of the metal oxide, M_xO, that we want to accomplish. The $\Delta_r G^\ominus$ values for these reactions in general, can be obtained from the corresponding $\Delta_f G^\ominus$ values of oxides.

As we have seen, heating (i.e., increasing T) favours a negative value of $\Delta_r G^\ominus$. Therefore, the temperature is chosen such that the sum of $\Delta_r G^\ominus$ in the two combined redox processes is negative. In $\Delta_r G^\ominus$ vs T plots (Ellingham diagram, Fig. 6.4), this is indicated by the point of intersection of the two curves, i.e, the curve for the formation of M_xO and that for the formation of the oxide of the reducing substance. After that point, the $\Delta_r G^\ominus$ value becomes more negative for the combined process making the reduction of M_xO possible. The difference in the two $\Delta_r G^\ominus$ values after that point determines whether reduction of the oxide of the element of the upper line is feasible by the element of which oxide formation is represented by the lower line. If the difference is large, the reduction is easier.

Example 6.1 Suggest a condition under which magnesium could reduce alumina.

Solution The two equations are:

(a) $\frac{4}{3} Al + O_2 \rightarrow \frac{2}{3} Al_2O_3$ (b) $2Mg + O_2 \rightarrow 2MgO$

At the point of intersection of the Al_2O_3 and MgO curves (marked "A" in diagram 6.4), the $\Delta_r G^\ominus$ becomes ZERO for the reaction:

$$\frac{2}{3} Al_2O_3 + 2Mg \rightarrow 2MgO + \frac{4}{3} Al$$
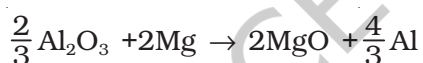
Below that point magnesium can reduce alumina.

Example 6.2 Although thermodynamically feasible, in practice, magnesium metal is not used for the reduction of alumina in the metallurgy of aluminium. Why ?

Solution Temperatures below the point of intersection of Al_2O_3 and MgO curves, magnesium can reduce alumina. But the process will be uneconomical.

Example 6.3 Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction?

Solution The entropy is higher if the metal is in liquid state than when it is in solid state. The value of entropy change (ΔS) of the reduction process is more on positive side when the metal formed is in liquid state and the metal oxide being reduced is in solid state. Thus the value of $\Delta_r G^\ominus$ becomes more on negative side and the reduction becomes easier.

6.4.1 Applications

(a) Extraction of iron from its oxides

After concentration, mixture of oxide ores of iron (Fe_2O_3, Fe_3O_4) is subjected to **calcination/roasting** to remove water, to decompose carbonates and to oxidise sulphides. After that these are mixed with limestone and coke and fed into a *Blast furnace* from its top, in which the oxide is reduced to the metal. In the Blast furnace,
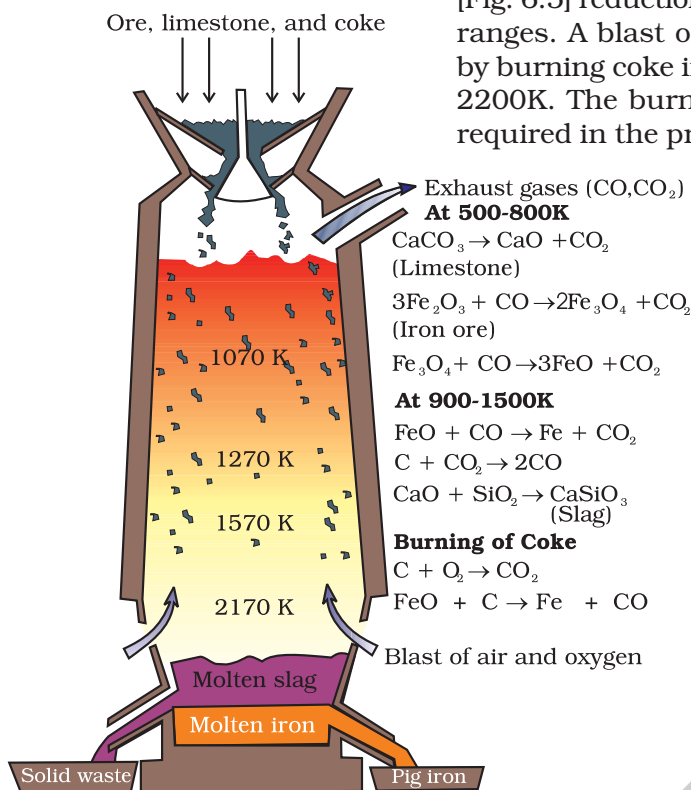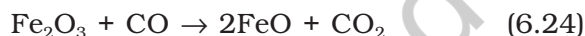
Ore, limestone, and coke

Exhaust gases (CO, CO_2)

At 500-800K

$CaCO_3 \rightarrow CaO + CO_2$
(Limestone)

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$
(Iron ore)

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

At 900-1500K

$FeO + CO \rightarrow Fe + CO_2$

$C + CO_2 \rightarrow 2CO$

$CaO + SiO_2 \rightarrow CaSiO_3$
(Slag)

Burning of Coke

$C + O_2 \rightarrow CO_2$

$FeO + C \rightarrow Fe + CO$

Blast of air and oxygen

1070 K
1270 K
1570 K
2170 K

Molten slag
Molten iron
Solid waste
Pig iron

Fig. 6.5: Blast furnace

[Fig. 6.5] reduction of iron oxides takes place at different temperature ranges. A blast of hot air is blown from the bottom of the furnace by burning coke in the lower portion to give temperature upto about 2200K. The burning of coke, therefore, supplies most of the heat required in the process. The CO and heat move to the upper part of the furnace. In upper part, the temperature is lower and the iron oxides (Fe_2O_3 and Fe_3O_4) coming from the top are reduced in steps to FeO. These reactions can be summarised as follows:

At 500 – 800 K (lower temperature range in the blast furnace),

Fe_2O_3 is first reduced to Fe_3O_4 and then to FeO

$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2 \qquad (6.22)$$

$$Fe_3O_4 + 4\ CO \rightarrow 3Fe + 4\ CO_2 \qquad (6.23)$$

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \qquad (6.24)$$

Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.

At 900 – 1500 K (higher temperature range in the blast furnace):

$$C + CO_2 \rightarrow 2\ CO \qquad (6.25)$$

$$FeO + CO \rightarrow Fe + CO_2 \qquad (6.26)$$

Thermodynamics helps us to understand how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process involves reaction 6.27 given below.

$$FeO(s) + C(s) \rightarrow Fe(s/l) + CO\ (g) \qquad (6.27)$$
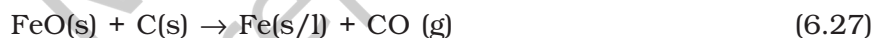
This reaction can be seen as a reaction in which two simpler reactions have coupled. In one the reduction of FeO is taking place and in the other, C is being oxidised to CO:

$$FeO(s) \rightarrow Fe(s) + \frac{1}{2} O_2(g) \qquad [\Delta_r G^{\ominus}_{(FeO,Fe)}] \qquad (6.28)$$

$$C(s) + \frac{1}{2} O_2\ (g) \rightarrow CO\ (g) \qquad [\Delta_r G^{\ominus}_{(C,CO)}] \qquad (6.29)$$

When both the reactions take place to yield the equation (6.27), the net Gibbs energy change becomes:

$$\Delta_r G^{\ominus}_{(C,\ CO)} + \Delta_r G^{\ominus}_{(FeO,\ Fe)} = \Delta_r G^{\ominus} \qquad (6.30)$$

Naturally, the resultant reaction will take place when the right hand side in equation 6.30 is negative. In $\Delta_r G^{\ominus}$ vs T plot representing the change Fe$\rightarrow$ FeO in Fig. 6.6 goes upward and that representing the change C$\rightarrow$ CO (C,CO) goes downward. They cross each other at about 1073K. At temperatures above 1073K (approx.), the C, CO line is below the Fe, FeO line $[\Delta_r G^{\ominus}_{(C,CO)}] < [\Delta_r G^{\ominus}_{(FeO,Fe)}]$. So above 1073 K in the range of temprature 900–1500 K coke will reduce FeO and will itself be oxidised to CO. Let us try to understand this through Fig. 6.6 (approximate values of $\Delta_r G^{\ominus}$ are given). At about 1673K (1400°C) $\Delta_r G^{\ominus}$ value for the reaction:
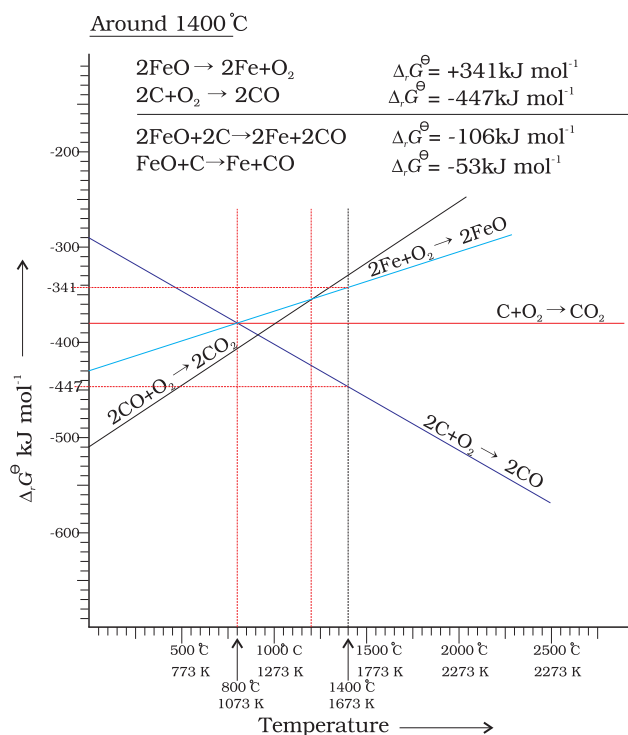
Around 1400°C

$2FeO \rightarrow 2Fe+O_2$	$\Delta_r G^\ominus = +341kJ\ mol^{-1}$
$2C+O_2 \rightarrow 2CO$	$\Delta_r G^\ominus = -447kJ\ mol^{-1}$
$2FeO+2C \rightarrow 2Fe+2CO$	$\Delta_r G^\ominus = -106kJ\ mol^{-1}$
$FeO+C \rightarrow Fe+CO$	$\Delta_r G^\ominus = -53kJ\ mol^{-1}$

Fig. 6.6: *Gibbs energy Vs T plot (schematic) for the formation of oxides of iron and carbon (Ellingham diagram)*

$2FeO \rightarrow 2Fe+O_2$ is $+341$ kJmol^{-1} because it is reverse of $Fe \rightarrow FeO$ change and for the reaction

$2C+O_2 \rightarrow 2CO$ $\Delta_r G^\ominus$ is -447 kJmol^{-1}. If we calculate $\Delta_r G^\ominus$ value for overall reaction (6.27 the value will be -53 kJmol^{-1}). Therefore, reaction 6.27 becomes feasible. In a similar way the reduction of Fe_3O_4 and Fe_2O_3 by CO at relatively lower temperatures can be explained on the basis of lower lying points of intersection of their curves with the CO, CO_2 curve.

The iron obtained from Blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn). This is known as **pig iron**. It can be moulded into variety of shapes. **Cast iron** is different from *pig iron* and 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.

Further Reductions

Wrought iron or malleable iron is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite. The haematite oxidises carbon to carbon monoxide:

$$Fe_2O_3 + 3\ C \rightarrow 2\ Fe + 3\ CO \tag{6.31}$$

Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag. The metal is removed and freed from the slag by passing through rollers.

(b) Extraction of copper from cuprous oxide [copper(I) oxide]

In the graph of $\Delta_r G^\ominus$ vs T for the formation of oxides (Fig. 6.4), the Cu_2O line is almost at the top. So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke. The lines (C, CO) and (C, CO_2) are at much lower positions in the graph particularly after 500 – 600K. However, many of the ores are sulphides and some may also contain iron. The sulphide ores are roasted/smelted to give oxides:

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \tag{6.32}$$
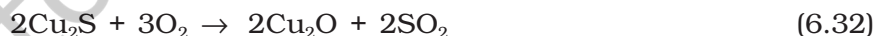
The oxide can then be easily reduced to metallic copper using coke:

$$Cu_2O + C \rightarrow 2\ Cu + CO \tag{6.33}$$

In actual process, the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags of' as iron slicate is formed. Copper is produced in the form of **copper matte**. This contains Cu_2S and FeS.

$$FeO + SiO_2 \rightarrow FeSiO_3 \tag{6.34}$$
(Slag)

Copper matte is then charged into silica lined convertor. Some silica is also added and hot air blast is blown to convert the remaining

FeS, FeO and Cu_2S/Cu_2O to the metallic copper. Following reactions take place:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2 \tag{6.35}$$

$$FeO + SiO_2 \rightarrow FeSiO_3 \tag{6.36}$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \tag{6.37}$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2 \tag{6.38}$$

The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called **blister copper**.

(c) Extraction of zinc from zinc oxide

The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in the case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.

$$ZnO + C \xrightarrow{\text{coke,1673K}} Zn + CO \tag{6.39}$$

The metal is distilled off and collected by rapid chilling.

Intext Questions

6.3 The reaction,

$$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr \qquad (\Delta_rG^\ominus = -421kJ)$$

is thermodynamically feasible as is apparent from the Gibbs energy value. Why does it not take place at room temperature?

6.4 Is it true that under certain conditions, Mg can reduce Al_2O_3 and Al can reduce MgO? What are those conditions?


6.5
Electrochemical Principles of Metallurgy

We have seen how principles of thermodyamics are applied to **pyrometallurgy**. Similar principles are effective in the reductions of metal ions in solution or molten state. Here they are reduced by electrolysis or by adding some reducing element.

In the reduction of a molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation,

$$\Delta G^\ominus = -nE^\ominus F \tag{6.40}$$

here n is the number of electrons and $E^\ominus$ is the electrode potential of the redox couple formed in the system. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two $E^\ominus$ values corresponds to a positive $E^\ominus$ and consequently negative $\Delta G^\ominus$ in equation 6.40, then the less reactive metal will come out of the solution and the more reactive metal will go into the solution, e.g.,

$$Cu^{2+} (aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+} (aq) \tag{6.41}$$
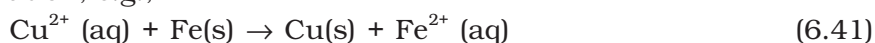
In simple electrolysis, the M^{n+} ions are discharged at negative electrodes (cathodes) and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added for making the molten mass more conducting.