

Physical Chemistry of Blast Furnace Reactions

Chapter 2 presented chemical reactions in various zones of a blast furnace along with the approximate temperature levels (Figure 2.1). It also contained a brief description of the process as well as the internal structure of various regions (Figures 2.1, 2.2 and 2.3). The following regions were identified:

- The upper region, i.e. *Stack* or *Shaft*
- The middle portion of the furnace, i.e. *Belly and Bosh*
- The lower region, i.e. *Hearth*.

The lower region again can be subdivided into various zones—*Cohesive zone*, *Deadman zone* and *Combustion zone* (or *Tuyere zone/Raceway*).

Reactions take place in all these regions, and their control has a major influence on the quality of hot metal produced. An understanding of the reactions is therefore important.

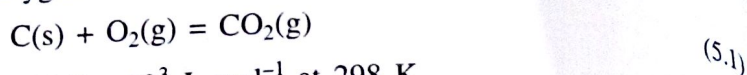
5.1 THERMODYNAMICS OF THE CARBON-OXYGEN REACTION

In Chapter 4, the basics of physical chemistry, i.e. thermodynamics and kinetics of reactions as well as other physicochemical properties of liquid iron and slags of importance to ironmaking and steelmaking were presented. Based on the above, this chapter and some other subsequent chapters shall deal with physicochemical aspects of the reactions and processes of specific interest. In this chapter, the blast furnace reactions are covered.

5.1.1 Combustion of Coke in the Tuyere Zone

Coke is the principal source of carbon in the blast furnace and the principal reducing agent. Carbon combusts with oxygen in the pre-heated air blast at the tuyere zone at temperatures of approximately 1900–2000°C. Carbon is thus also the principal source of heat. The hot gas consisting primarily of CO, N₂ and some CO₂ travels upwards through the bed of solids, which gets heated up and melts. Various reactions take place—the principal ones being the reduction of iron ore and the gasification of coke.

The reactions of carbon with oxygen include:



$$\Delta H_1^0 = -393.7 \times 10^3 \text{ J} \cdot \text{mol}^{-1} \text{ at } 298 \text{ K}$$

$$\Delta G_1^0 = -394,100 - 0.84T \text{ J} \cdot \text{mol}^{-1}$$



$$\Delta H_2^0 = -110.6 \times 10^3 \text{ J} \cdot \text{mol}^{-1} \text{ at } 298 \text{ K}$$

$$\Delta G_2^0 = -111,700 - 87.65T \text{ J} \cdot \text{mol}^{-1}$$

From the above, it may be noted that the combustion of carbon to CO_2 releases much more heat than the conversion to CO. Hence, from the point of view of thermal efficiency, the formation of CO_2 to the maximum possible extent is preferable.

Coke is a mechanical mixture of carbon and ash, which consists of inorganic compounds. From Chapter 4, Section 4.2, it may be noted that for pure carbon, the activity of carbon is 1. Also the activities of gaseous species are equal to their respective partial pressures (in standard atmosphere units). Therefore, on the basis of Eq. (4.17), for reaction (5.1):

$$\Delta G_1^0 = -RT \ln K_1 = -RT \ln \left(\frac{p_{\text{CO}_2}}{p_{\text{O}_2}} \right)_{\text{eq.}} \quad (5.3)$$

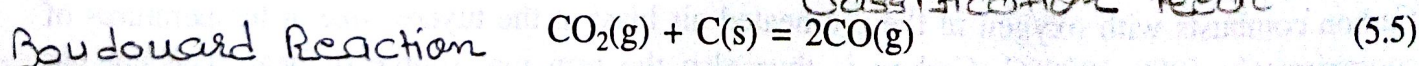
and for reaction (5.2),

$$\Delta G_2^0 = -RT \ln K_2 = -RT \ln \left(\frac{p_{\text{CO}}}{(p_{\text{O}_2})^{1/2}} \right)_{\text{eq.}} \quad (5.4)$$

In the tuyere region of a modern blast furnace, the total pressure is as high as about 4 atmosphere. Since air contains about 79% N_2 by volume, the sum of partial pressures of CO, CO_2 and O_2 will be approximately 1 atmosphere. Taking the tuyere temperature as 1900°C (2173 K), and from values of ΔG_1^0 and ΔG_2^0 , $K_1 = 3.24 \times 10^9$ and $K_2 = 1.75 \times 10^6$. These are large values. Therefore, at equilibrium, from Eqs. (5.3) and (5.4), p_{O_2} is negligible. In other words, oxygen is almost completely converted into CO and CO_2 at the tuyere level. It will be shown later in the following section that the product is essentially CO rather than CO_2 at the tuyere level.

5.1.2 C-CO₂-CO Reaction

On the basis of the above, for reactions in the stack and bosh, O_2 can be ignored and only the following reaction needs to be considered:



Reaction (5.5) is a combination of reactions (5.1) and (5.2). Using Hess' law,

$$\Delta G_3^0 = 2\Delta G_2^0 - \Delta G_1^0 = 170,700 - 174.46T \text{ J} \cdot \text{mol}^{-1} \quad (5.6)$$

Therefore,

$$\begin{aligned} \ln K_5 &= \ln \left(\frac{p_{\text{CO}}^2}{p_{\text{CO}_2}} \right)_{\text{eq.}} = \ln \left(\frac{X_{\text{CO}}^2}{X_{\text{CO}_2}} \right)_{\text{eq.}} \cdot P_T \\ &= -\frac{\Delta G_5^0}{RT} = -\frac{20532}{T} + 20.98 \end{aligned} \quad (5.7)$$

where $P_T = p_{\text{CO}} + p_{\text{CO}_2} = 1$ atmosphere, and X_{CO} , X_{CO_2} are mole fractions of CO and CO_2 respectively. For ideal gases, X is the same as its volume fraction (refer Chapter 4).

Since, $X_{\text{CO}} + X_{\text{CO}_2} = 1$, $K_5 = \frac{X_{\text{CO}}^2}{1 - X_{\text{CO}}}$ (5.8)

On the basis of Eqs. (5.7) and (5.8), volume fractions (or volume percent) of CO and CO_2 for C-CO- CO_2 equilibrium at any temperature can be calculated. Figure 5.1 presents such calculated volume fraction of CO in CO- CO_2 mixture as a function of temperature. In the above equations, T is in kelvin but for convenience of users the unit of temperature in Figure 5.1 is given in $^{\circ}\text{C}$. Reaction (5.5) is the famous *Boudouard Reaction*. In blast furnace ironmaking the forward reaction is known as the *Solution Loss Reaction*. In general, it is referred to as the *Gasification Reaction*.

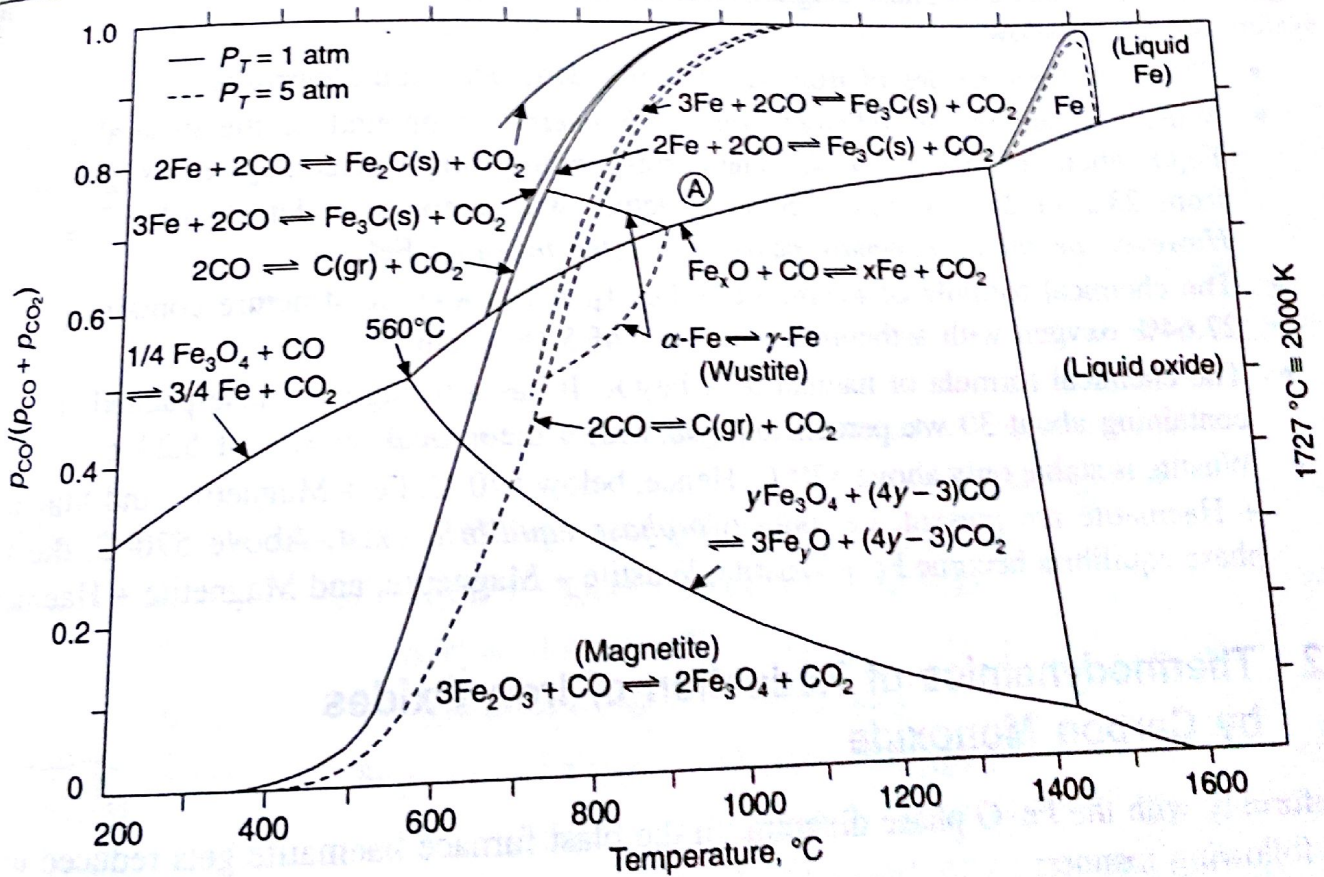


Figure 5.1 Equilibrium $p_{\text{CO}}/(p_{\text{CO}} + p_{\text{CO}_2})$ ratios in gas as a function of temperature for reactions in the Fe-C-O system. The lines are for equilibria of reactions as indicated.

Figure 4.1 shows that CO becomes more and more stable compared with CO₂ as the temperature is increased. This is also demonstrated in Figure 5.1. Therefore, at the tuyeres where the temperatures are the highest, CO is the only stable oxide of carbon and this gas passes through a bed of coke. By neglecting the effects of hydrocarbons or any other tuyere injectants, the composition of the gas as it enters the bottom of the stack can be calculated assuming that air contains 21% O₂, 79% N₂ and that the entire amount of O₂ gets converted into CO. For 100 moles of air, therefore, the number of moles of N₂ and CO would be 79 and 42 respectively. Hence,

$$\text{Volume \% CO} = \frac{42}{79 + 42} \times 100 = 34.7$$

$$\text{Volume \% N}_2 = 100 - 34.7 = 65.3$$

5.2 GAS-SOLID REACTION EQUILIBRIA IN THE BLAST FURNACE STACK

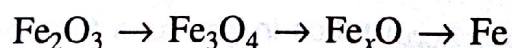
5.2.1 The Fe-O System

Figure 5.2 shows the Fe-O phase diagram (Darken and Gurry, 1946). The salient features of this system are noted below.

- There are three oxides of iron, viz. *Wustite*, *Magnetite* and *Haematite*.
- Wustite is an *oxygen-deficient non-stoichiometric* compound of the general formula Fe_xO, where 0.835 < x < 0.945. The corresponding weight percentage of oxygen ranges from 23.2 to 25.6. It has a cubic structure with theoretical density of 5.7 g·cm⁻³. However, on an approximate basis, it is often taken as FeO.
- The chemical formula of magnetite is Fe₃O₄. It has a cubic structure containing about 27.64% oxygen with a theoretical density of 5.18 g·cm⁻³.
- The chemical formula of haematite is Fe₂O₃. It has a hexagonal close-packed structure containing about 30 wt. percent oxygen with a theoretical density of 5.24 g·cm⁻³.
- Wustite is stable only above 570°C. Hence, below 570°C, Fe + Magnetite, and Magnetite + Haematite are present, i.e. only *two-phase equilibria* exist. Above 570°C, the two-phase equilibria become Fe + Wustite, Wustite + Magnetite, and Magnetite + Haematite.

5.2.2 Thermodynamics of Reduction of Iron Oxides by Carbon Monoxide

In conformity with the Fe-O phase diagram, in the blast furnace haematite gets reduced to iron in the following manner:



About 75% of oxygen in Fe₂O₃ gets removed at the Fe_xO → Fe stage.

Any gas-solid reaction is much faster than a reaction between two solid species, in this case, solid iron oxide and solid carbon. Therefore, reduction of solid iron oxides in a blast furnace occurs through reaction primarily with carbon monoxide in the stack.

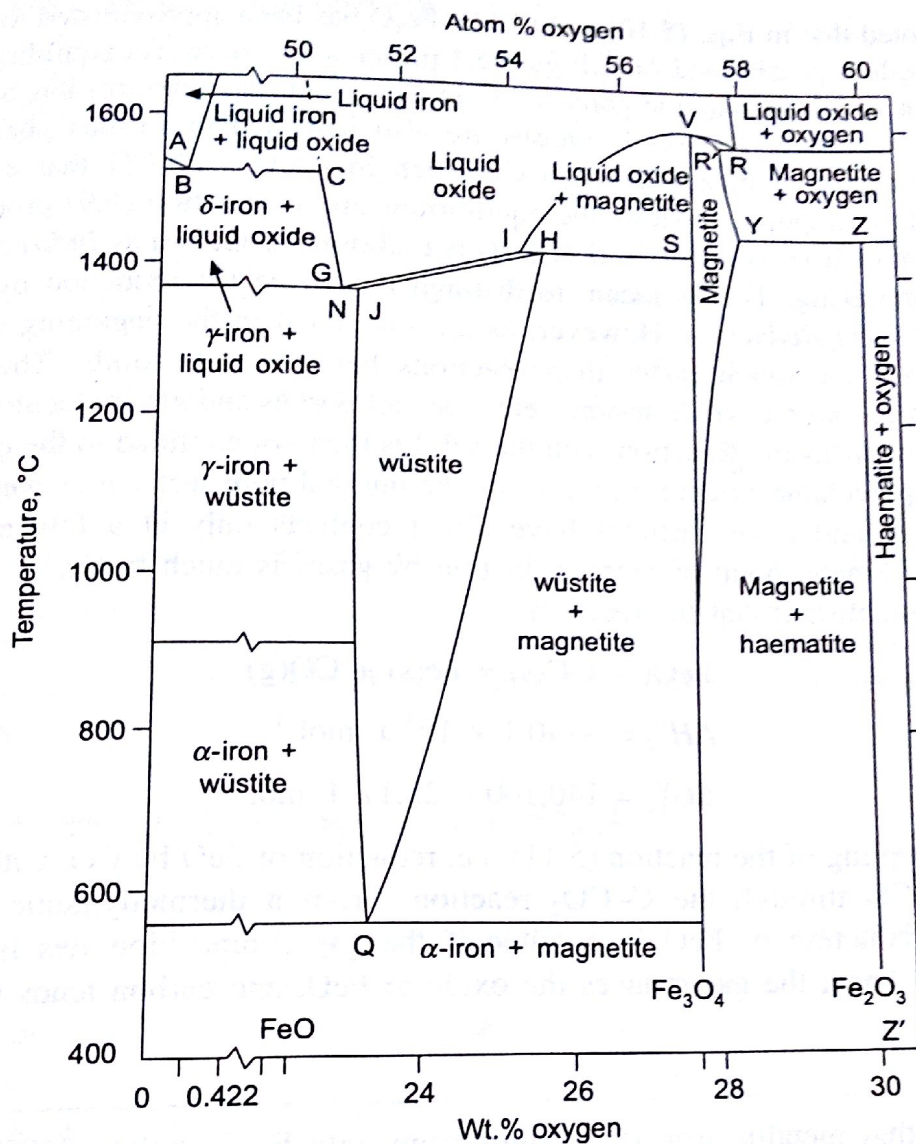
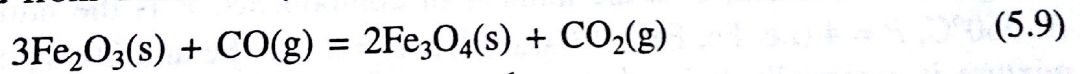


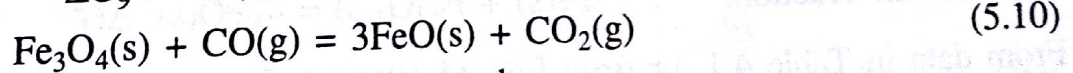
Figure 5.2 Iron–oxygen phase diagram.

Using Hess' law, and from Table 4.1 (for ΔG^0 only),



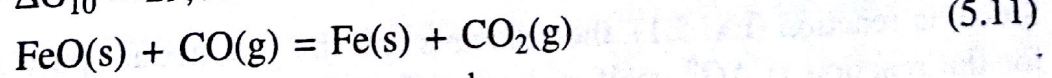
$$\Delta H_9^0 = -52.8 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$$

$$\Delta G_9^0 = -44,300 - 39.89T \text{ J} \cdot \text{mol}^{-1}$$



$$\Delta H_{10}^0 = +36.3 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$$

$$\Delta G_{10}^0 = 29,860 - 38.29T \text{ J} \cdot \text{mol}^{-1}$$



$$\Delta H_{11}^0 = -17.3 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$$

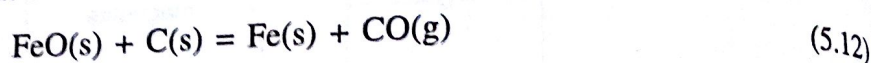
$$\Delta G_{11}^0 = -22,800 - 24.26T \text{ J} \cdot \text{mol}^{-1}$$

(Note: Since the values of ΔH^0 and ΔG^0 could not be collected from the same source, some minor discrepancies may be present).

It may be noted that in Eqs. (5.10) and (5.11), Fe_xO has been approximated to FeO in order to use concrete values of ΔH^0 and ΔG^0 . Figure 5.1 presents the curves for equilibria of reactions (5.9) to (5.11), in which the volume percent CO in $CO + CO_2$ gas mixtures has been plotted as a function of temperature. The stable phases are also indicated in various phase fields. The reduction of haematite to magnetite occurs at such low levels of CO that a different gas composition scale is required to show the equilibrium line of reaction (5.9) properly.

The reduction of iron oxides by CO and H_2 is traditionally known as *Indirect Reduction* in blast furnace ironmaking. This is meant to distinguish it from the reduction by solid carbon, which is called *Direct Reduction*. However, as already stated in the beginning of this section, gas-solid reactions are much faster than reactions between two solids. The solid burden materials—iron ore, sinter, coke, limestone, etc.—are all porous and gas molecules can penetrate into these pores by diffusion. Reaction with the solid is then not confined to the external surface alone, but to an appreciable extent it proceeds on the internal pore surfaces as well. On the other hand, adjacent ore and coke particles have direct contacts only at a few point locations. Therefore, from a kinetic point of view, reduction by gases is much faster.

It has been established that the reaction:



$$\Delta H_{12}^0 = +140.1 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$$

$$\Delta G_{12}^0 = 140,100 - 25.1T \text{ J} \cdot \text{mol}^{-1}$$

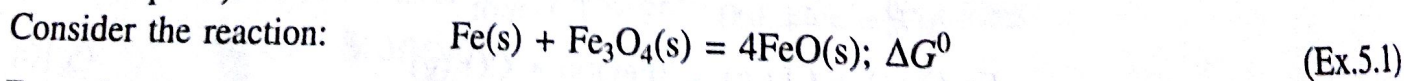
occurs through coupling of the reaction (5.11), i.e. reduction of FeO by CO , with reaction (5.5), which generates CO through the $C-CO_2$ reaction. From a thermodynamic point of view, therefore, direct reduction of FeO is possible if the gas composition lies in region (A) of Figure 5.1. In this zone, the gas reduces the oxide to FeO , and carbon tends to form CO .

EXAMPLE 5.1

Figure 5.1 shows that metallic iron is at equilibrium with Fe_3O_4 below $560^\circ C$ and with FeO above $560^\circ C$. Justify this through thermodynamic considerations.

Solution: Since gas phase is also involved, according to phase rule, $F = C - P + 2$, where F is degrees of freedom, C is the number of components, P is the number of phases.

At $560^\circ C$, $P = 4$ (i.e. $Fe, FeO, Fe_3O_4, \text{gas}$), $C = 2$ (i.e. Fe and O), since the role of CO and CO_2 mixture is essentially to control oxygen potential in gas. Hence, $F = 0$ at $560^\circ C$ (i.e. it is an invariant point).



From data in Table 4.1, or from Eqs. (5.10) and (5.11), it is obtained that

$$\Delta G^0 = 4\Delta G_f^0(FeO) - \Delta G_f^0(Fe_3O_4) = 52,325 - 62.58T \text{ J} \cdot \text{mol}^{-1} \tag{Ex.5.2}$$

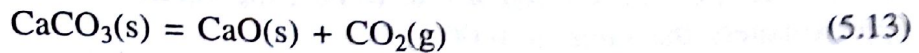
Since, in reaction (Ex. 5.1), the reactants and the product are pure solids, the feasibility criterion for the reaction is ΔG^0 itself and not ΔG . See Chapter 4 for further clarification.

Let the temperature at which reaction (Ex. 5.1) is at equilibrium be T_0 . Then, at T_0 , $\Delta G^0 = 0$. This gives $T_0 = 836 \text{ K} = 563^\circ C$, which is slightly different from that in Figure 5.1, due to different thermodynamic data sources.

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5.2.3 Dissociation of Limestone

Limestone in lump form often constitutes one of the burden materials (in many cases, the entire lime requirement is met through sinter). Limestone decomposes in the stack region of the furnace through the reaction



$$\Delta H_{13}^0 = 179 \times 10^3 \text{ J} \cdot \text{mol}^{-1} \text{ at } 298 \text{ K}$$

$$\Delta G_{13}^0 = 168,500 - 144T \text{ J} \cdot \text{mol}^{-1}$$

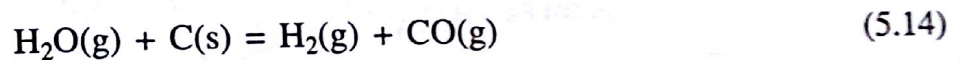
Consider a temperature of 850°C, which is typical in the lower part of the stack. p_{CO_2} in the gas in this region of a blast furnace may be assumed to range between 0.3 and 0.4 atmosphere. Based on the value of ΔG_{13}^0 , p_{CO_2} in equilibrium with CaCO_3 and CaO is 0.48 atmosphere.

Since $p_{\text{CO}_2}(\text{actual}) < p_{\text{CO}_2}(\text{eq.})$, calcium carbonate should completely decompose at this level. But this does not happen because of kinetic limitations, and, in a blast furnace, significant decomposition occurs only at 1000–1100°C. Decomposition of limestone is endothermic and requires heat to be supplied. During the progress of decomposition, a layer of porous CaO forms on the outer layer of limestone. This layer has very poor thermal conductivity, and consequently, slows down heat transfer into the interior of the limestone lumps. This factor also affects the rate of decomposition.

5.2.4 Reactions of Hydrogen in the Stack

In the tuyere area, steam has been traditionally injected to control the flame temperature. Injection of hydrocarbon in the form of natural gas or oil was also resorted to in some blast furnaces around the world. A recent development is the injection of pulverised coal. The coal decomposes at the tuyere level liberating hydrocarbons and volatile H–C–O compounds. All these compounds become a source of hydrogen in the furnace.

Hydrocarbons are unstable at a high temperature and readily decompose into carbon and hydrogen. Also steam reacts with carbon in coke, thus generating more hydrogen.



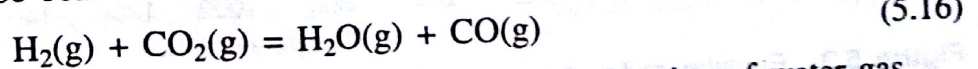
$$\Delta H_{14}^0 = 131.4 \times 10^3 \text{ J} \cdot \text{mol}^{-1} \text{ at } 298 \text{ K}$$

$$\Delta G_{14}^0 = 134300 - 142.45T \text{ J} \cdot \text{mol}^{-1}$$

Again,

$$\Delta G_{14}^0 = -RT \ln K_{14} = -RT \ln \left(\frac{p_{\text{CO}} \times p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right)_{\text{eq.}} \quad (5.15)$$

At the tuyere level, assuming $T = 2173 \text{ K}$ (i.e. 1900°C), $p_{\text{CO}} = 1$ atmosphere, a sample calculation shows that at equilibrium, $p_{\text{H}_2}/p_{\text{H}_2\text{O}}$ ratio is 1.63×10^4 : 1, i.e. H_2O would be almost completely converted into H_2 . Therefore, the gas mixture in the lower part of the stack (typically at a temperature of 1000°C or so) would consist of CO , CO_2 , H_2 and N_2 . In the stack, the following reaction needs to be considered.



This is known as the Water Gas Reaction, since it occurs during generation of water gas.

For reaction (5.16),

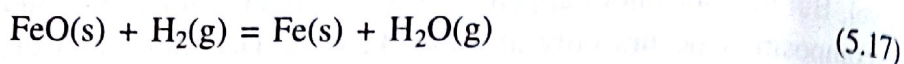
$$\Delta H_{16}^0 = 32.0 \times 10^3 \text{ J} \cdot \text{mol}^{-1} \text{ at } 298 \text{ K}$$

$$\Delta G_{16}^0 = 30,470 - 28.48T \text{ J} \cdot \text{mol}^{-1}$$

At 1000 K (i.e. 727°C), $K_{16} = 0.8$. Hence, the equilibrium ratios of $\text{H}_2/\text{H}_2\text{O}$ and CO/CO_2 are approximately the same at 1000 K.

The rates of all gaseous reactions are very high at high temperatures (say, above 700–800°C). Hence, the general assumption is that equilibrium is attained at such temperatures. The water gas reaction is no exception. As far as the blast furnace is concerned, it has been observed that this equilibrium exists above 800–1000°C, but in the upper stack (below a temperature of 600–700°C), equilibrium does not exist.

H_2 is a reducing agent like CO , and equations analogous to Eqs. (5.9)–(5.11) can be written for the reduction of iron oxides by hydrogen. For example, the reduction of FeO would occur as



$$\Delta H_{17}^0 = 8.0 \times 10^3 \text{ J} \cdot \text{mol}^{-1} \text{ at } 298 \text{ K}$$

$$\Delta G_{17}^0 = 7800 - 4.22T \text{ J} \cdot \text{mol}^{-1}$$

It may be noted that the reduction of FeO by CO is exothermic, while that by H_2 is endothermic. The equilibrium relations for iron oxide reduction by H_2 as a function of temperature are plotted in Figure 5.3 as volume fraction H_2 in $\text{H}_2 + \text{H}_2\text{O}$ mixtures. The slope of the FeO–Fe equilibrium line is just opposite to that for reduction by CO . Therefore, hydrogen is thermodynamically a better reductant than carbon monoxide at higher temperatures.

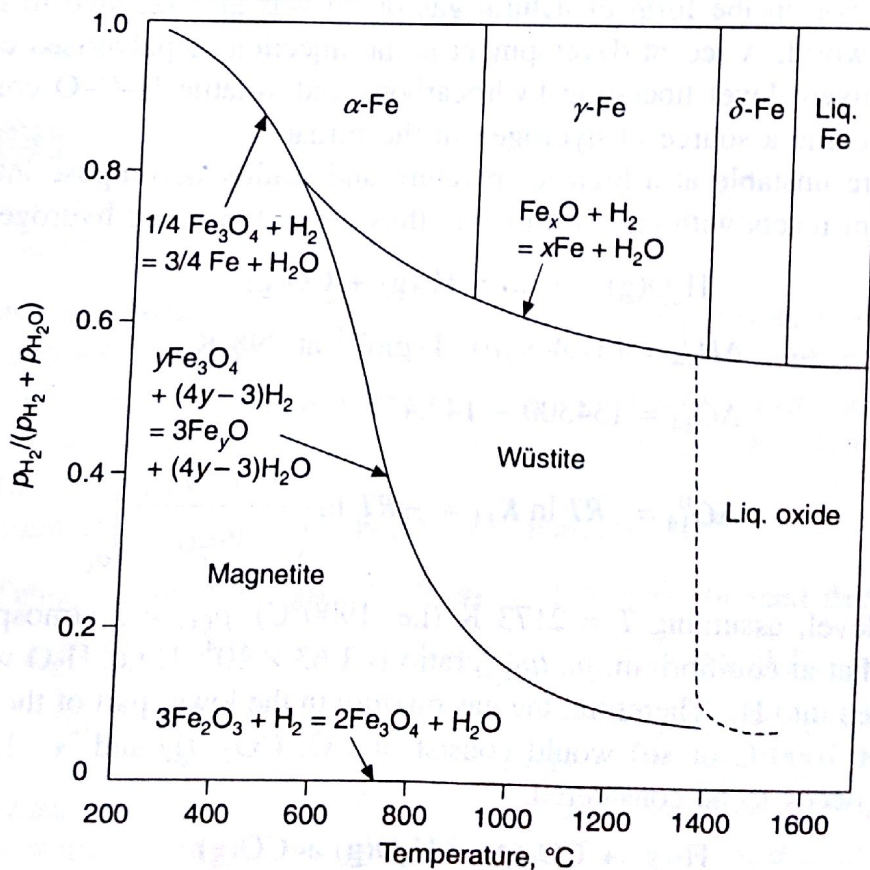


Figure 5.3 Equilibrium $[\rho_{\text{H}_2}/(\rho_{\text{H}_2} + \rho_{\text{H}_2\text{O}})]$ ratios in gas as a function of temperature for reactions in Fe–H–O system. The lines are for equilibria of reactions as indicated.

EXAMPLE 5.2

A gas mixture containing 50% CO₂ and 50% H₂, is introduced into a furnace at 1000 K. Assuming that it attained equilibrium at the furnace temperature quickly, predict whether it will deposit carbon as solid. Assume total pressure (P_T) = 1 atmosphere.

Solution: Consider equilibrium of the reaction



From the data given, ΔG^0 for the above reaction at 1000 K = 1990 J·mol⁻¹

So,
$$1990 = -R \times 1000 \ln \left(\frac{P_{\text{H}_2\text{O}} \cdot P_{\text{CO}}}{P_{\text{H}_2} \cdot P_{\text{CO}_2}} \right)_{\text{eq.}} \quad (\text{Ex.5.3})$$

Assume that initially 1 gmol of H₂ + CO₂ mixture was introduced into the furnace. Let x moles of each react, before equilibrium is reached. Then the number of gmol of H₂, CO₂, H₂O and CO are $0.5 - x$, $0.5 - x$, x and x respectively. Since partial pressures are proportional to number of moles,

$$1990 = -R \times 1000 \ln \left[\frac{x^2}{(0.5 - x)^2} \right]$$

Calculations give
$$\frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \frac{X_{\text{CO}_2}}{X_{\text{CO}}} = \frac{0.5 - x}{x} = 3.20$$

Noting that $p_{\text{CO}_2} + p_{\text{CO}} = (0.5 - x) + x = 0.5$ atmosphere, the values of p_{CO_2} and p_{CO} are 0.381 and 0.119 atmosphere respectively.

Now, consider the reaction,



From Eq. (5.7), at 1000 K, K for reaction (5.5) is 1.565.

$$J = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} (\text{actual}) = \frac{0.119^2}{0.381} = 0.037$$

$\Delta G = RT \ln (J/K) = -31,095 \text{ J}\cdot\text{mol}^{-1}$. Since it is negative, reaction (5.5) shall proceed in the forward direction. Therefore, carbon deposition shall not occur.

5.3 KINETICS OF REACTIONS IN THE STACK

The major reactions are:

- Reduction of iron oxides by CO and H₂
- Gasification of carbon by CO₂
- Reduction of FeO by carbon.

The first two are gas–solid reactions while the last reaction is a combination of the first two reactions as mentioned earlier.

5.3.1 Kinetics of Reduction of Iron Oxides by CO and H₂

General features

The general features of kinetics and mechanism of iron oxide reduction by CO and H₂ are similar. Hence, they will be discussed together. Straightway it needs to be pointed out that the major difference is that reduction by H₂ is 5-10 times faster than that by CO. Numerous fundamental investigations carried out in the laboratory over a period of six decades have confirmed this finding.

Lump ores, sinter and pellets contain iron oxide mostly as Fe₂O₃, but in some ore bodies, the oxide is in the form of magnetite. The gangue minerals contain primarily SiO₂ and Al₂O₃ besides other minor compounds. In the stack region, CO and H₂ can reduce only the oxides of iron. The fundamental measure of the extent of reduction is the Degree of Reduction (F₀) defined as

$$F_0 = \frac{\text{loss of mass of the ore due to removal of oxygen}}{\text{total mass of removable oxygen in ore}} \quad (5.18)$$

Figure 5.4 shows the relationship between F₀ and time t for the reduction of iron oxide pellets by hydrogen at 900°C (Bogdandy and Engell, 1971). Salient kinetic features that need to be noted are as follows:

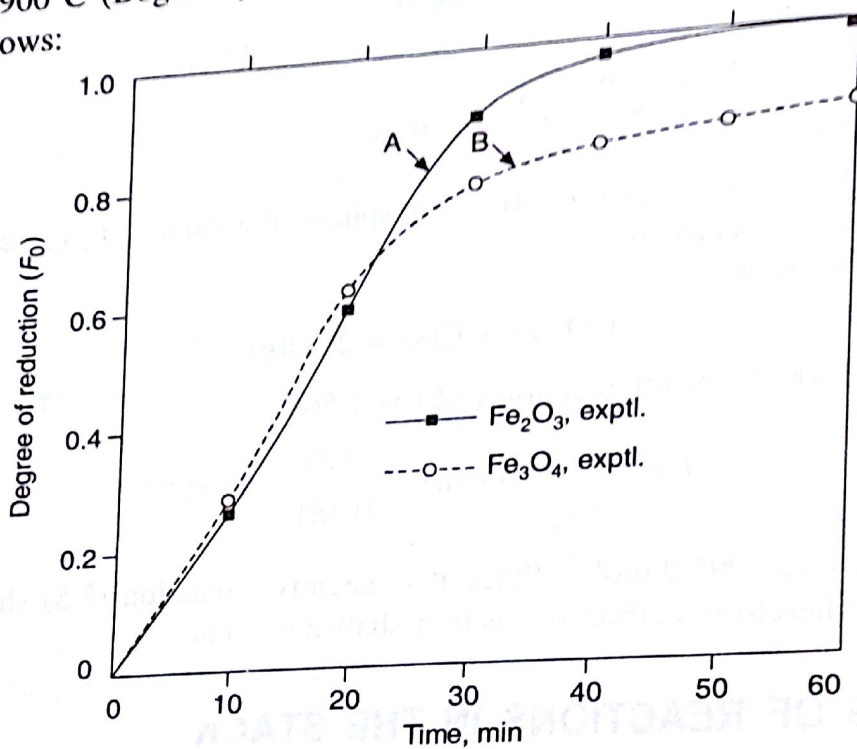


Figure 5.4 F₀ vs. t plots for reduction of Fe₂O₃ and Fe₃O₄ in H₂ at 900°C.

- Lump ore, sinter and pellets are porous solids.
- Reduction is characterised by the formation of a porous product layer.
- Fe₂O₃ is reduced in stages, viz. Fe₂O₃ → Fe₃O₄ → Fe_xO → Fe.
- Additional porosity develops during reduction owing to density differences of the product solids. The relative volumes per unit mass of Fe are:

$$\text{Fe} : \text{Fe}_x\text{O} : \text{Fe}_3\text{O}_4 : \text{Fe}_2\text{O}_3 = 1 : 1.79 : 2.08 : 2.14$$

Handwritten notes:
 9/cm
 7.87
 5.74
 5.24
 5.14

As a result, when haematite is reduced to magnetite, additional porosity develops, enhancing the rate of further reduction of haematite. Hence, as shown in Figure 5.4, haematite is more reducible than magnetite.

- A measure of the rate of reduction (r_0) is dF_0/dt , where t is the time after reduction starts.
- The term *Reducibility* is popular in technical literature. The higher the reducibility of an iron oxide bearing solid, the faster is the rate of reduction. Hence, dF_0/dt may be considered as a measure of reducibility.
- Figure 5.4 shows that dF_0/dt is a function of time, which gives rise to problems in assigning a characteristic value to reducibility. Different conventions have been adopted, out of which the following alternatives are popular.

$$\begin{aligned} \underline{r_0} &= \frac{dF_0}{dt} \text{ at } F_0 = 0.4 \text{ or } 0.5 \\ \underline{r_0} &= \frac{[1 - (1 - F_0)^{1/3}]}{t} = \text{constant} \end{aligned} \quad (5.19)$$

With respect to gas composition, the rate is first order, reversible, i.e.

$$\text{for CO reduction of FeO,} \quad r_0 = k_C \left(p_{\text{CO}} - \frac{p_{\text{CO}_2}}{K_{11}} \right) \quad (5.20)$$

$$\text{for H}_2 \text{ reduction of FeO,} \quad r_0 = k_H \left(p_{\text{H}_2} - \frac{p_{\text{H}_2\text{O}}}{K_{17}} \right) \quad (5.21)$$

where k_C , k_H are rate constants, and K_{11} and K_{17} are equilibrium constants of reactions (5.11) and (5.17) respectively.

Mechanism of reduction

If the reduction of FeO in any ore proceeds in the manner depicted in Figure 5.5, the kinetic

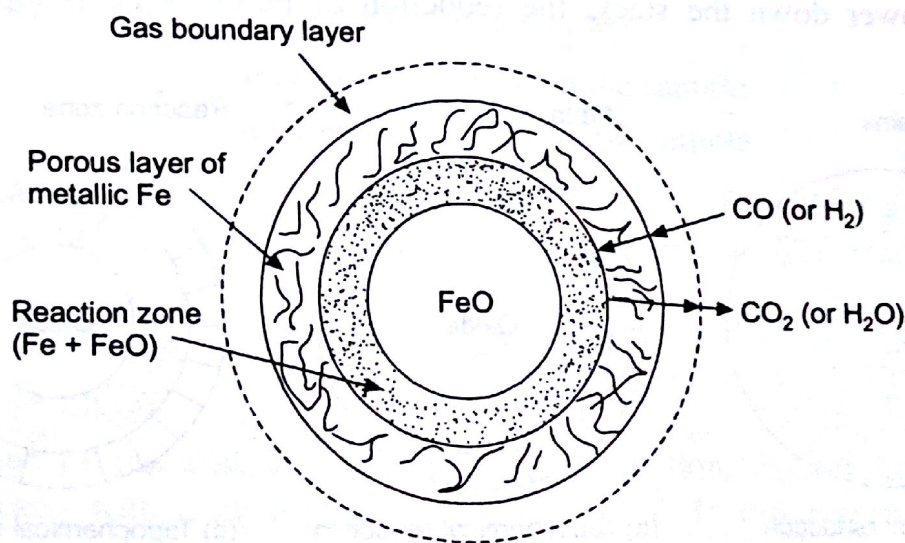


Figure 5.5 Sketch of a partially reduced sphere of FeO showing layers and kinetic steps.

steps involved are:

- Transfer of reactant gas to the solid surface (CO or H₂) across the gas boundary layer around the piece of solid
- Inward diffusion of reactant gas through the pores of the solid
- Chemical reaction (5.11) or (5.17)
- Outward diffusion of the product gas (CO₂ or H₂O) through the pores
- Transfer of the product gas from the solid surface into the bulk gas across the boundary layer.

It has been established by laboratory investigations that the rates of all these steps are comparable. Therefore, generally speaking, all of them have to be considered as partially rate controlling steps. The overall rate would depend on:

- Temperature
- Gas composition
- Size of the particle
- Nature of the solid in terms of its structure and composition.

Depending on the situation, the pattern of ore reduction has been classified into the following:

1. *Uniform internal reduction* is obtained when diffusion through the pores is faster than chemical reaction (smaller particles, lower temperature, slower reduction, higher porosity).
2. *Topochemical reduction with a sharp interface* is obtained when pore diffusion is slower than chemical reaction (large particles, higher temperature, low porosity).
3. *Topochemical reduction with a diffused interface* is obtained when the chemical reaction rate is comparable with the pore diffusion rate.

These phenomena are illustrated in Figure 5.6. In the blast furnace, reduction of Fe₂O₃ → Fe₃O₄ → Fe_xO (i.e. stagewise reduction) occurs in the upper part of stack at lower temperature. The pattern is basically internal reduction, and thus stagewise reduction occurs throughout the entire particle. Lower down the stack, the reduction of Fe_xO → Fe is topochemical with a diffused interface.

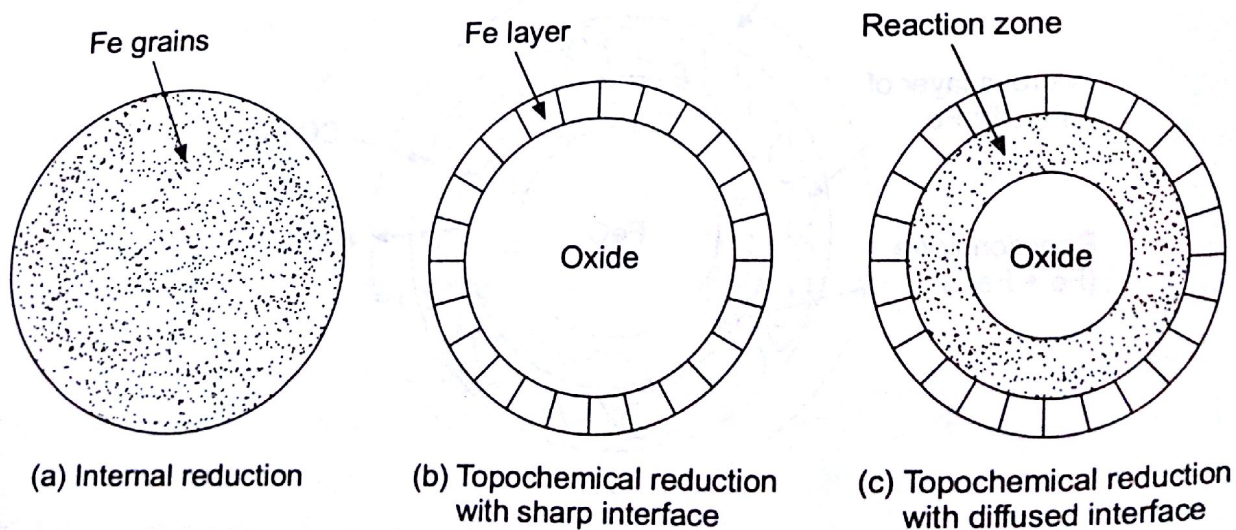


Figure 5.6 Sketches of sections of partially reduced iron ore pellets, showing three patterns; (Fe₂O₃, Fe₃O₄ and FeO have not been shown separately).

It is interesting to note that at a fixed temperature and gas composition, and for any type of ore/sinter/pellet burden of a given size range, the reducibility values do not differ by more than a small factor.

The overall kinetics of iron ore reduction is complex because of:

- Dependence of the rate on the structure of the solid, especially its porosity and pore structure
- Changes in the structure of the solid during reduction on account of swelling/contraction, recrystallisation and grain growth
- Comparable rates of chemical reaction, pore diffusion and in many cases, boundary layer mass transfer.

Several rate equations have been proposed, and mathematical modelling exercises have been reported in the literature. The best results are obtained by a combination of (i) experimental rate measurements, (ii) characterisation of the ore-pore size distribution, pore surface area, mineralogical details, etc., and (iii) quantitative analysis/mathematical modelling.

In a blast furnace, as the solid burden moves downwards, it undergoes changes in the surrounding environment (in terms of temperature, gas composition, overlying load, etc.). In view of this as well as complex kinetics, in actual practice, integrated tests are preferred where the blast furnace situation is simulated in the laboratory for small batches of ore/sinter/pellets. On this basis, an attempt is made to assess the overall performance.

5.3.2 Kinetics of Gasification of Carbon by CO_2

Blast furnace coke has 80–90% carbon, the rest is ash, which consists of various inorganic oxides. The gasification reaction is also of significant interest in carbothermic reduction of some other metals as well as in several chemical industries. Therefore, the kinetics of this reaction has been a subject of intense study from as early as the 1920s, initially by physical chemists, and later by chemical/metallurgical engineers and fuel technologists. A large amount of literature is available on this topic.

The degree of gasification of carbon (F_C) is given as

$$F_C = \frac{\text{mass loss of carbon in the sample}}{\text{total mass of carbon in the sample}} \quad (5.22)$$

The term Reactivity is commonly used to denote the speed of the gasification reaction. The higher the reactivity of the sample, the faster is the gasification. The reactivity (r_C) can be defined as

$$r_C = \frac{dF_C}{dt} \quad (5.23)$$

where t is the time of reaction. In contrast to ore reduction, F_C has been found to vary approximately linearly with t , up to about $F_C = 0.3$ to 0.4 . In this region, therefore, r_C is a constant.

The kinetic steps involved in the gasification of a piece of carbon are:

- Transfer of CO_2 across the gas boundary layer to the surface of the particle
- Inward diffusion of CO_2 through the pores
- Chemical reaction on the pore surfaces
- Outward diffusion of CO through the pores
- Transfer of CO into the bulk gas by mass transfer across the boundary layer.

Laboratory experiments have demonstrated that the chemical reaction is much slower compared with the other steps; hence it constitutes the principal rate controlling step. Such a conclusion has been arrived at on the basis of the large activation energy involved, strong retarding influence of CO on the rate, significant catalytic enhancement of the rate in the presence of metallic iron, alkalis, etc., and retardation by sulphides.

Since the chemical reaction is the rate controlling step, the reaction occurs internally as in Figure 5.6(a). Therefore, the rate increases with increase in pore surface area (S). It so happens that S varies from $0.1 \text{ m}^2 \cdot \text{g}^{-1}$ to $10^3 \text{ m}^2 \cdot \text{g}^{-1}$, depending on the nature of carbon. Therefore, the rate of gasification is strongly dependent on the nature and source of carbon as indicated in Figure 5.7 (Turkdogan et al. 1970).

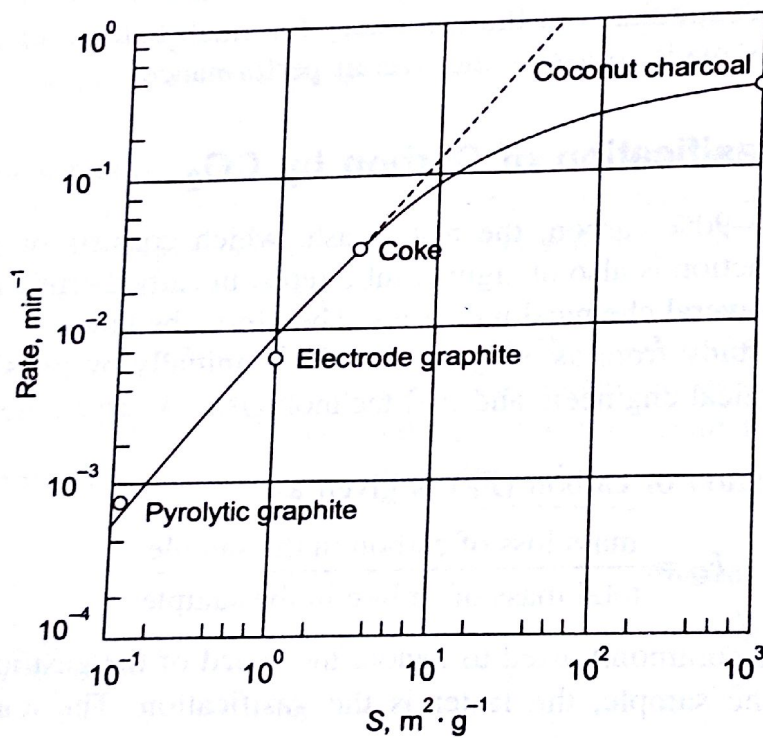


Figure 5.7 Rate of oxidation of carbon samples in CO_2 at 1100°C as a function of internal pore surface area.

5.3.3 Kinetics of Reduction of FeO by Carbon

As discussed in Section 5.2.2, reduction actually occurs via the gas phase through coupling of reaction (5.5), i.e. gasification of carbon with reaction (5.11), which is the reduction of FeO by CO . Laboratory experiments have confirmed that the net rate of this reaction is primarily

controlled by the rate of the gasification reaction. As in the case of the gasification reaction, it is characterised by large activation energy and is catalysed/inhibited by the reagents which influence the gasification reaction in a similar way.

When the molar rates of reactions (5.5) and (5.11) become equal, then, reaction (5.12) takes place stoichiometrically. This equality is expressed as $\text{FeO} + \text{C} = \text{Fe} + \text{CO}$

$$\begin{aligned} & \text{mass of ore} \times \text{fraction of oxygen in ore} \times r_{\text{O}} \times \frac{1}{16} \\ & = \text{mass of coke} \times \text{fraction of carbon in coke} \times r_{\text{C}} \times \frac{1}{12} \end{aligned} \quad (5.24)$$

The factors 16 and 12 denote the atomic masses of oxygen and carbon respectively.

The calculated rates of generation of CO by gasification and consumption of CO by the reduction reaction as a function of temperature for a sample of 1500 kg ore and 500 kg coke are plotted in Figure 5.8 (Turkdogan 1978). At lower temperature, the gasification rate is much lower than the reduction rate, but with the increasing temperature, they tend to equalise. This happens because the rate of the gasification reaction increases rapidly with the increase in temperature because of large activation energy. That is why direct reduction in a blast furnace takes place only in the bosh and lower stack regions.

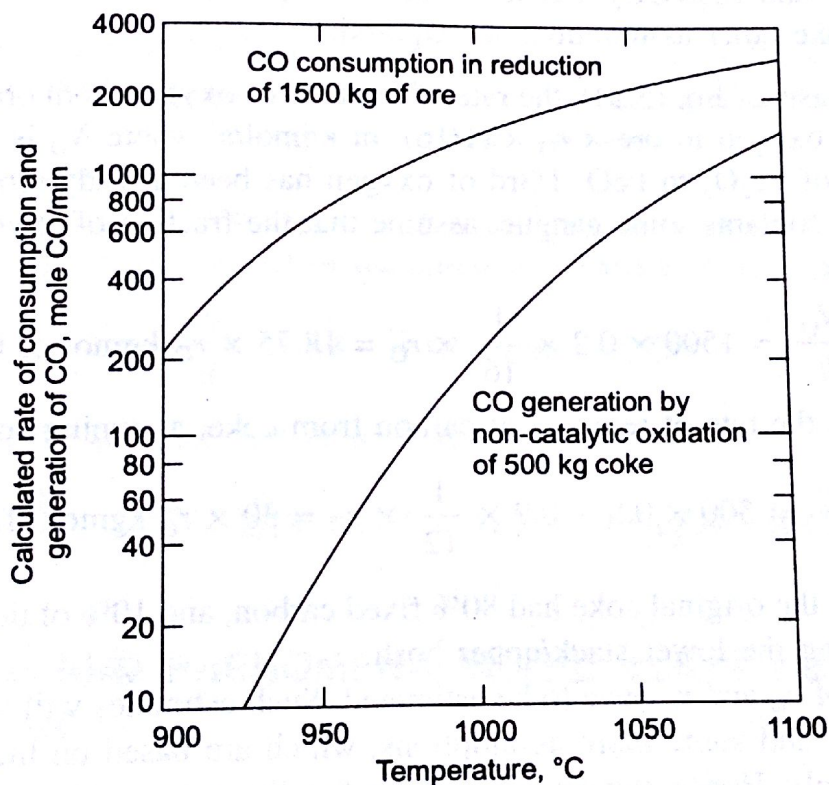


Figure 5.8 Rates of reduction of lump haematite ore (1500 kg, 1 cm dia.) and non-catalytic internal oxidation of coke (500 kg) at simulated blast furnace gas composition and pressure.

5.3.4 Direct and Indirect Reduction in the Blast Furnace

The carbon in coke charged into a blast furnace has two functions, namely *chemical* (i.e. as a reducing agent) and *thermal* (i.e. as a provider of heat).

When the carbon burns at the tuyeres and generates CO, the gas reduces iron oxide by indirect reduction, and only one oxygen atom of the oxide is removed by one atom of carbon. On the other hand, if the oxide is also reduced directly by carbon in the lower part of the furnace, the resulting CO again reduces the oxide. Thus, one carbon atom removes two atoms of oxygen from the ore. Therefore, direct reduction improves the chemical utilisation of carbon. However, since direct reduction is strongly endothermic, it lowers the thermal efficiency. Hence, it is normally desirable that there should be a balance between direct and indirect reduction—about 66% indirect and the remainder direct reduction is considered to be the optimum.

- To achieve this objective, the following are required:
- The reducibility of the iron oxide used should be as high as possible.
 - The reactivity of coke should have an optimum value (opinions vary on what is the optimum).

EXAMPLE 5.3

Calculate the rate of oxygen removal due to reduction of FeO in iron ore by CO, and the rate of gasification of carbon in coke by CO₂, for a situation prevailing at the lower stack/upper bosh of a blast furnace. Assume the temperature as 1100°C, pressure of CO + CO₂ as 0.7 atmosphere, of which 90% is CO and 10% CO₂. Calculate for 1500 kg of original ore before reduction, and 500 kg of coke. Make other assumptions as required.

Solution: On the basis of Eq. (5.24), the rate of removal of oxygen from ore ($-dN_O/dt$) = mass of ore × fraction of oxygen in ore × r_O × (1/16), in kgmol/s, where N_O is kgmol of O.
 After reduction of Fe₂O₃ to FeO, 1/3rd of oxygen has been already removed. Considering this and that the ore contains some gangue, assume that the fraction of oxygen remaining with the ore is 0.2. Hence,

$$-\frac{dN_O}{dt} = 1500 \times 0.2 \times \frac{1}{16} \times r_O = 18.75 \times r_O \text{ kgmol of O/s} \quad (\text{Ex. 5.4})$$

Proceeding similarly, the rate of removal of carbon from coke, assuming coke to have 80% C,

$$-\frac{dN_C}{dt} = 500 \times 0.8 \times 0.9 \times \frac{1}{12} \times r_C = 30 \times r_C \text{ kgmol of C/s} \quad (\text{Ex. 5.5})$$

This assumes that the original coke had 80% fixed carbon, and 10% of that has been gasified already before reaching the lower stack/upper bosh.

Now, the values of r_O and r_C have to be estimated. Such estimates will be done on the basis of data in this chapter and some more assumptions, which are based on literatures in this area and are approximate only. Hence, the calculations are for illustration only and are not necessarily representative of a real blast furnace.

Estimation of r_O

From Eq. (5.20), $r_O = (dF_O/dt)$. Figure 5.4 presents F_O vs. t curves for reduction by H₂ at 900°C for two ores. Let us take ore A. The curve is approximately linear in the middle ranges. The values of F_O after 10 and 20 minutes from the start of reduction are 0.24 and 0.6 respectively. This gives

$$r_O = \frac{0.6 - 0.24}{20 - 10} \times \frac{1}{60} = 6 \times 10^{-4} \text{ s}^{-1}$$

On an average, reduction by CO is lower by a factor of 6 than that by H₂. This gives a value of 10^{-4} s^{-1} for reduction by pure CO at 900°C.

Taking an approximate value of activation energy of reduction as 30 kJ/mol, calculations give r_O for pure CO = $1.57 \times 10^{-4} \text{ s}^{-1}$. The influence of gas composition on rate is

$$\text{for reduction of FeO by CO-CO}_2 \text{ mixture, } r_O = k_C \left(p_{\text{CO}} - \frac{p_{\text{CO}_2}}{K_{11}} \right) \quad (5.20)$$

From data provided, p_{CO} and p_{CO_2} are 0.63 and 0.07 atmosphere respectively. At 1100°C, $K_{11} = 0.4$.

Substituting the values in Eq. (5.20), $r_O = 0.714 \times 10^{-4} \text{ s}^{-1}$.

Estimation of r_C

From Eq. (5.23), $r_C = dF_C/dt$. Figure 5.7 presents the values of r_C for some carbonaceous materials at 1100°C in pure CO₂. For coke, the value is $3.2 \times 10^{-2} \text{ min}^{-1}$, i.e. $5.33 \times 10^{-4} \text{ s}^{-1}$.

In CO-CO₂ atmosphere, the rate of reaction can be expressed as

$$r_C = r_C \text{ in pure CO}_2 \times [p_{\text{CO}_2} - (p_{\text{CO}_2})_{\text{eq}}] \quad (\text{Ex. 5.6})$$

where the equilibrium refers to reaction (5.5), for which K is given in Eq. (5.7). At 1100°C, i.e. 1373 K, $K = 6.0$. At the given gas composition, and for total pressure of CO + CO₂ = 0.7 atmosphere, calculations give the value of partial pressure of CO₂ at equilibrium with $p_{\text{CO}} = 0.63$, as 0.066 atmosphere.

Inserting values in Eq. (Ex. 5.6), $r_C = 5.33 \times 10^{-4}(0.07 - 0.066) = 2.13 \times 10^{-6} \text{ s}^{-1}$

Therefore, from Eq. (Ex. 5.4), the rate of reduction of 1500 kg of ore,

$$-\frac{dN_O}{dt} = 13.4 \times 10^{-4} \text{ kgmol of O/s}$$

and rate of carbon gasification of 500 kg of coke,

$$-\frac{dN_C}{dt} = 30 \times 2.13 \times 10^{-6} = 0.63 \times 10^{-4} \text{ kgmol of C/s}$$

5.4 REACTIONS AND PHENOMENA IN THE BLAST FURNACE BOSH AND HEARTH

The composition of hot metal produced in blast furnaces operating around the world lies within the following overall range (weight percent): Carbon: 3.5–4.3, Silicon: 0.2–1.5, Sulphur: 0.020–0.050, Phosphorus: 0.1–2.0, Manganese: 0.2–1.5, Titanium: 0.15 maximum. The composition differs from country to country and even from region to region in the same country because of the compositions of raw materials used and the ironmaking practice adopted.

As far as hot metal composition control in the blast furnace is concerned, the following need to be noted.

- Some amount of manganese is desirable in hot metal.
- Control of carbon, phosphorus and titanium are not possible.
- Sulphur and silicon can be and should be controlled. Silicon should be maintained below 0.6%, if possible. However, this is not always possible on account of raw materials normally speaking, it should be as low as possible, often when going in for increased productivity, the sulphur content is allowed to increase, since external desulphurisation of hot metal (Chapter 16) is now a standard practice.

In view of the above, no further discussion on carbon and phosphorus is included. The formation of a slag of desirable properties is of considerable importance in order to:

- Control the hot metal composition
- Obtain sufficiently fluid slag at as low a temperature as possible
- Make the slag suitable for use in cement-making.

The subsequent sections shall briefly discuss some of these issues.

5.4.1 Blast Furnace Slag—Composition and Viscosity

In Section 4.4.1 the properties of liquid iron and steel have been presented. In a blast furnace, metallic iron starts absorbing carbon in the lower part of the stack owing to the presence of coke, and it becomes liquid at as low a temperature as approximately 1300°C. In the hearth, molten hot metal contains about 4% C with a liquidus temperature lower than 1200°C (see Section 4.4.1).

The structure and physicochemical properties of slag melts have already been dealt with in Section 4.4.2. The major constituents of blast furnace slag are CaO, Al₂O₃, SiO₂, and in most cases, some amount of MgO is also present. The minor constituents are: MnO, TiO₂, FeO, alkali oxides, etc. SiO₂ and Al₂O₃ come from the gangue contained in iron ore and from the coke ash, while CaO and MgO come from the fluxes (limestone and dolomite).

Figure 4.3 has presented the iso-activity lines of SiO₂ in the liquid field of the ternary CaO-SiO₂-Al₂O₃ system at 1550°C (1823 K). It will be noted that the liquid field is fairly large; however, with decreasing temperature, it becomes smaller and smaller, and disappears completely at around 1250°C. It has also been mentioned in Section 4.4.2 that liquid slag is much more viscous than liquid iron. Furthermore, the viscosity varies by orders of magnitude depending on the composition and temperature. In Figure 4.8, the iso-viscosity lines for CaO-SiO₂-Al₂O₃ slags at 1500°C have been shown. The overall variation is from 2.5 to 2000 poise (i.e. 0.25 to 200 kg·m⁻¹·s⁻¹).

For proper furnace operation, the liquid slag should have as low a viscosity as possible, preferably lower than 2 poise. Viscous slags:

- Pose difficulties during slag-metal separation in the hearth
- Slowdown the rates of slag-metal reactions
- Do not flow down properly from the bosh to the hearth
- Hinder smooth upward flow of gas through the burden.

Extensive viscosity measurements have been carried out in the laboratory for 'synthetic' blast furnace liquid slags, and enough data are available on this subject.

Slag basicity is another important parameter (see Section 4.4.3). Acceptable levels of transfer of both sulphur and silicon from the metal to slag are facilitated if the slag is basic. But, highly basic slags have higher viscosity as well. These two contradictory requirements are met in the blast furnace by maintaining a V-Ratio (see Eq. (4.46)) of the *Hearth slag* between 1.0 and 1.25.

Nowadays it has become a standard practice to use slags containing 4–10% MgO in the blast furnace since MgO lowers both the liquidus temperature as well as the viscosity. The gangue of Indian iron ore has high $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios, resulting in high Al_2O_3 in blast furnace slag in Indian furnaces. In this situation, addition of larger amounts of MgO to arrive at a hearth slag composition of about 30–32% CaO, 30% SiO_2 , 25–30% Al_2O_3 and 7–10% MgO is resorted to.

At any given composition of slag, its viscosity decreases with increasing temperature. Figure 5.9 (Coudurier et al., 1985) shows viscosity (η) vs. temperature (T) curves for blast furnace-type slags at three different basicity ratios. To obtain a fluid, free-running slag, a minimum hearth temperature is required. This is known as the *Critical Hearth Temperature*. It should be as low as possible in order to cut down the heat requirement as well as to increase the hearth lining life. Typically, it is maintained at 1400–1450°C. At this temperature CaO– SiO_2 – Al_2O_3 –MgO containing slags become sufficiently fluid owing to the presence of the minor constituents (MnO, TiO_2 , alkali oxides, etc.).

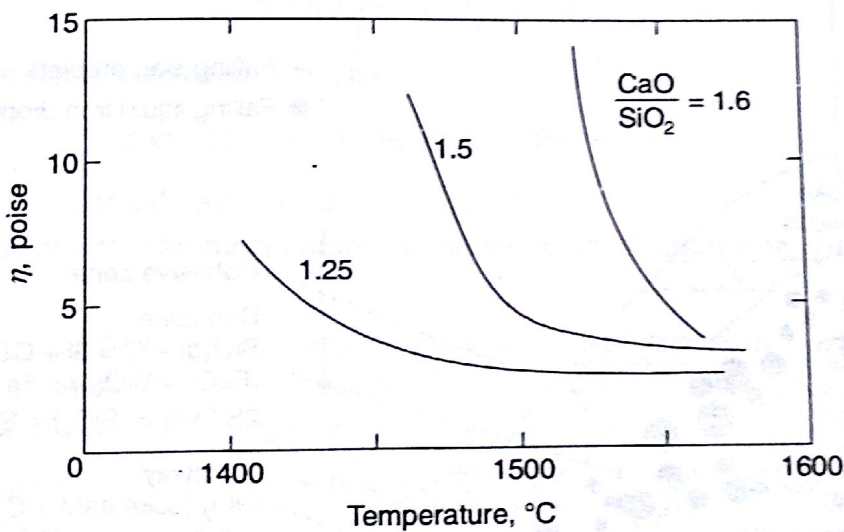


Figure 5.9 The relationship between viscosity and temperature for basic blast furnace slags.

In modern blast furnaces, *prepared sinter* constitutes a large percentage of the iron oxide burden. The sinter may be acid sinter, self-fluxed sinter, or super-fluxed sinter, having CaO/SiO₂ ratios less than 1, approximately equal to 1 and above 2, respectively. The first slag that forms in the belly region at around 1200–1300°C may or may not contain any CaO. As stated in Section 4.4.2, melting at such a low temperature is only possible because of the formation of FeO–SiO₂ compounds in large amounts. These compounds have very low liquidus temperatures when they react with the reduced FeO to form what is known as the *primary slag*.

As the primary slag trickles down through the bed of solids, its temperature rises. Moreover, FeO gets reduced and the slag dissolves more CaO. At the tuyere level, the coke burns thereby releasing coke ash consisting of SiO₂ and Al₂O₃. This makes the slag at the tuyere level high in SiO₂ (acid slag). The slag at the bosh region is known as *Bosh slag*. Final composition adjustments occur during the passage of the bosh slag into the hearth, during which the FeO content becomes very low.

5.4.2 Reaction of Silicon

Reaction in raceway and bosh

Figure 5.10 schematically shows the mechanism of reduction of SiO₂, pick up of metallic Si by liquid iron, etc. in the blast furnace raceway, bosh and hearth. The coke burns in the blast furnace raceway in front of the tuyeres, thus releasing coke ash containing SiO₂. Some molten slag

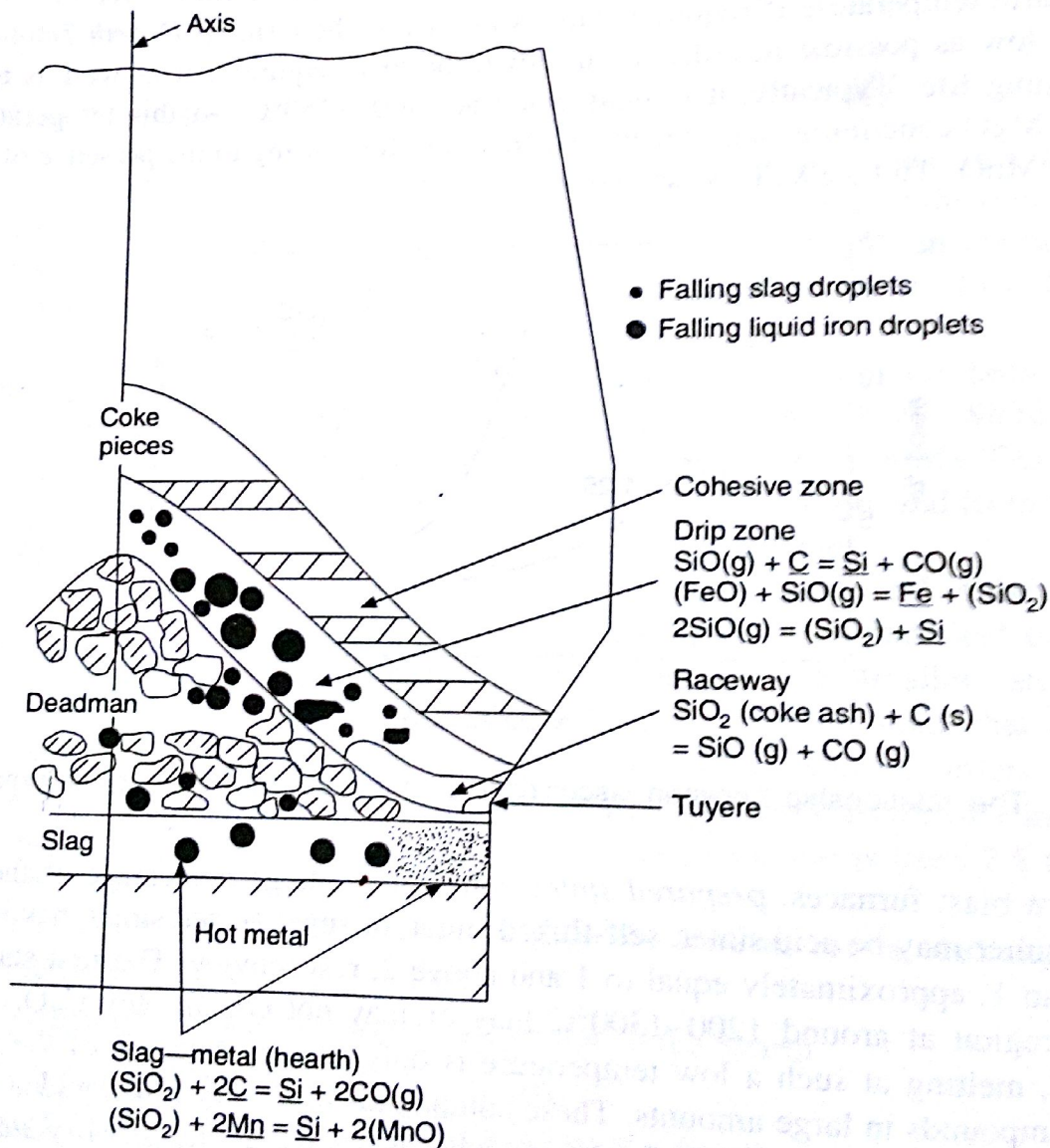
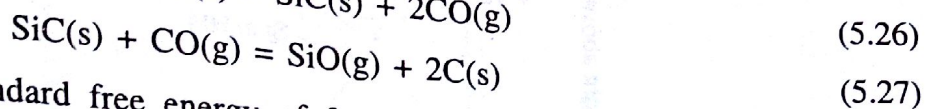
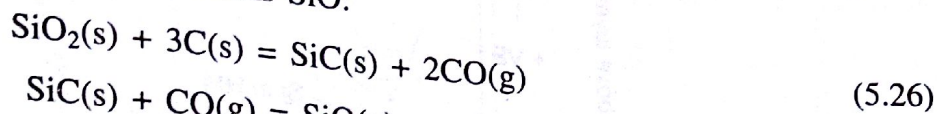
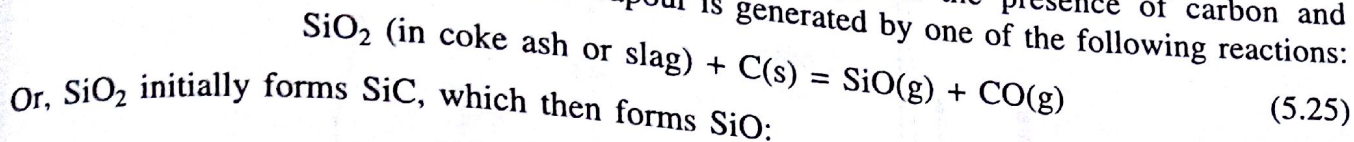


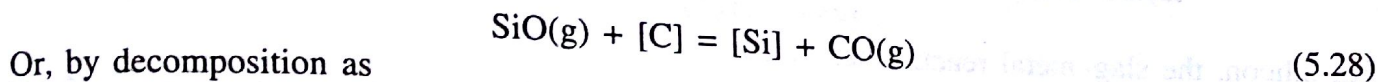
Figure 5.10 Schematic representation of the mechanism of silicon reaction in a blast furnace.

containing high SiO_2 and FeO also drips down through the raceway. The temperature in the raceway zone is $1900\text{--}2000^\circ\text{C}$ (2200 K approximately). In the presence of carbon and depending on the activity of silica, SiO vapour is generated by one of the following reactions:

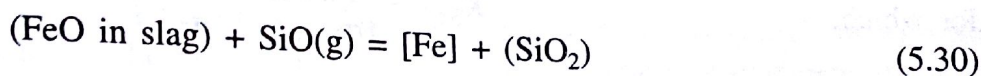


The values of ΔG_f^0 , i.e. standard free energy of formation for CO and SiO_2 are given in Table 4.1. From thermodynamic data sources, ΔG_f^0 for SiO and SiC are -253250 and -7565 J at 2173 K (i.e. 1900°C). At $a_{\text{SiO}_2} = 1$ and $p_{\text{CO}} = 1$ atmosphere, calculations yield $p_{\text{SiO}} = 4.4$ and 0.044 respectively for reaction (5.25) and (5.27). Hence, for SiO formation, the dominant reaction is (5.25).

At 1500°C (1773 K), p_{SiO} at equilibrium with reaction (5.25) is approximately 10^{-4} atmosphere. This makes SiO vapour unstable when it rises upwards in the bosh. Therefore, iron in the following way.



Other reactions have been proposed, such as:



In whichever way it is formed, SiO_2 joins the slag phase.

Recent investigations on the mechanism of the reaction of silicon in the blast furnace have shown that:

- The percentage of Si in liquid metal is as high as $6\text{--}8\%$ within 1 metre of the raceway, decreasing to about zero towards the furnace axis, indicating that large-scale Si absorption by metal takes place in the raceway.
- The percentage of Si in metal increases with increase in *RAFT* (i.e. *Raceway Adiabatic Flame Temperature*).

As early as the 1950s and 1960s, investigators quenched running blast furnaces by using a cold nitrogen blast. This froze the liquids in the bosh and tuyere regions. Samples collected from the frozen metal demonstrated the pattern of variation in Si dissolved in iron which is shown in Figure 5.11. The maximum value was at the tuyere level.

Reactions in hearth

Molten metal droplets react with the slag in hearth while passing through the slag layer. Extensive laboratory and plant investigations have been carried out on several blast furnace reactions in the hearth.

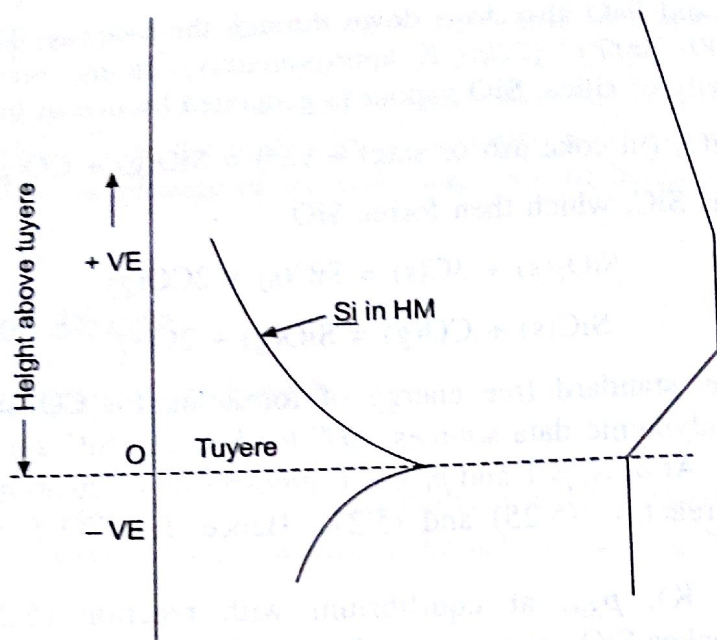
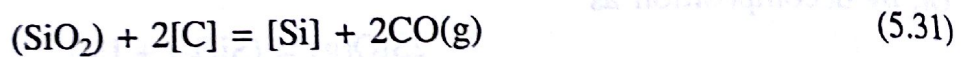


Figure 5.11 Schematic representation of the profile of silicon concentration in liquid iron near the tuyere level.

For silicon, the slag–metal reaction is:



for which,

$$K_{31} = \frac{[\% \text{Si}][f_{\text{Si}}]}{(a_{\text{SiO}_2})} \left(\frac{p_{\text{CO}}}{a_{\text{C}}} \right)^2 \quad (5.32)$$

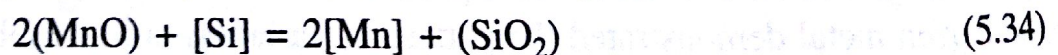
and

$$\log K_{31} = -\frac{30,935}{T} + 20.455 \quad (5.33)$$

(Note: [%Si] is another way of representing wt. % Si dissolved in metal. It is used in most of the books; but in this book, the symbol [W_{Si}] has been chosen. However, the symbol chosen is inconsequential.)

Based on the above as well as the empirical relations of a_{SiO_2} in slag with slag composition, an empirical correlation can be obtained, as illustrated in Figure 5.12 (Fruehan (Ed.) 1998). The assumption in all such cases is that the hot metal is saturated with graphite (i.e. $a_{\text{C}} = 1$).

It has been further observed that the Si–Mn reaction, which is a slag–metal reaction, also occurs in blast furnace hearth, i.e.



It has been proposed that the experimental data for graphite saturated melts at 1400–1600°C may be represented by the following equation:

$$\log K_{34} = 2.8 \left(\frac{\% \text{CaO} + \% \text{MgO}}{\% \text{SiO}_2} \right)_{\text{in slag}} - 1.16 \quad (5.35)$$

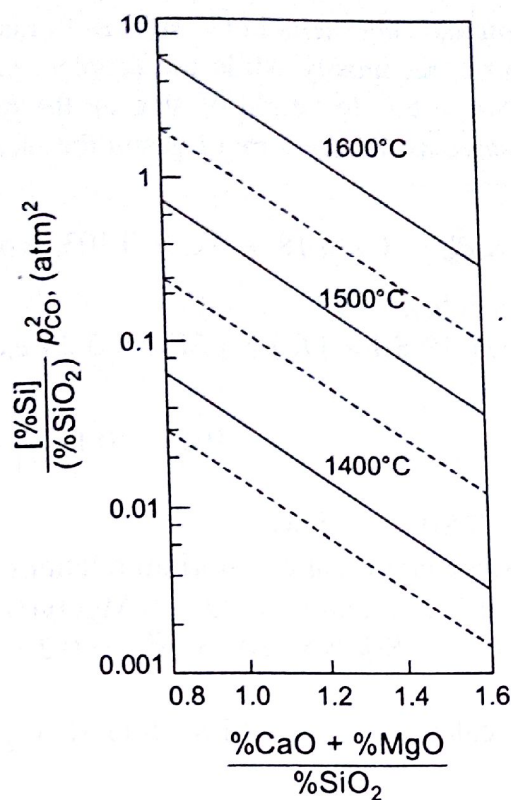


Figure 5.12 Silicon distribution ratio for graphite-saturated melts for blast furnace type slags containing about 10% MgO and 10% Al₂O₃.

Controversies exist as to whether reactions of Si-SiO₂ with carbon (Eq. (5.31)) or with Mn (Eq. (5.34)) attain equilibrium in the blast furnace hearth. From a variety of evidence, it can be concluded that equilibrium is not attained. The actual silicon content of hot metal is a few times higher than that predicted by the slag-metal equilibria. This is in conformity with Figure 5.11, which indicates that Si content of metal decreases from the tuyere to the hearth level.

EXAMPLE 5.4

For the reaction (5.31), i.e. (SiO₂) + 2[C] = [Si] + 2CO(g), calculate the weight percent Si in liquid iron at equilibrium with the slag in a blast furnace hearth at 1500°C. Assume that the iron contains 4% carbon besides Si, and the slag consists of 49 wt. % CaO, 42 wt. % SiO₂, and 9 wt. % Al₂O₃. Make other assumptions as necessary.

Solution: The equilibrium relation for reaction (5.31) is given as

$$K_{31} = \frac{[\%Si][f_{Si}]}{(a_{SiO_2})} \left(\frac{p_{CO}}{a_C} \right)^2 \quad (5.32)$$

Here a_C may be taken as 1, since the liquid iron may be assumed to be saturated with graphite.

The activity of SiO₂ in slag may be found out from Figure 4.3, Chapter 4. Although the figure is for 1550°C, it is approximately valid for 1500°C as well. For this the conversion of wt. % into mole fractions is required. It can be done using Eq. (4.26) in Chapter 4. Calculations give the values of mole fractions (X) of CaO, SiO₂ and AlO_{1.5} as 0.50, 0.40 and 0.15 respectively. From Figure 4.3, $a_{SiO_2} = 0.1$. From Eq. (5.33), $K_{31} = 1017$.

The gas bubbles inside iron and slag melts in the BF hearth may be assumed to be pure CO. Since the slag-metal reaction occurs mostly while the droplets of liquid iron are going down through the slag melt, the pressure due to height of slag on the bubbles may be ignored. This makes p_{CO} approximately the same as the pressure of gas in the raceway. On this basis, p_{CO} may be taken as 3 atmosphere.

$$\log f_{Si} = W_C \times e_{Si}^C + W_{Si} \times e_{Si}^{Si} = 4 \times 0.18 + W_{Si} \times 0.103, \text{ where } W \text{ is same as wt. \%}$$

Hence, $f_{Si} = 5.25 \exp(0.103 \times \%Si)$.

Substituting values in Eq. (5.33), $[\%Si] \times [f_{Si}] = [\%Si] \times 5.25 \exp(0.103 \times \%Si)$

$$= 1017 \times 0.1 \times \left(\frac{1}{3}\right)^2 = 11.3$$

Trial and error solution gives, $[\%Si] = 1.75 \text{ wt. \%}$

Figure 5.12 has presented some empirical equilibrium relations for the above reaction based on many experimental data. In this problem $(\%CaO + \%MgO)/(\%SiO_2)$ in slag is 1.117. For this slag composition, at 1500°C , $\{[\%Si]/(\%SiO_2)\} \times p_{CO}^2 = 0.25 - 0.3$, an approximate range obtained from Figure 5.12.

Based on our equilibrium calculations, $\{[\%Si]/(\%SiO_2)\} \times p_{CO}^2 = 0.375$. Agreement is therefore fairly good.

Strategy for production of low silicon hot metal

As mentioned earlier, hot metal with a low silicon content is desirable for efficient steelmaking. The strategy for achieving the same can be devised on the basis of the mechanism of silicon reaction, which was discussed in the previous section. The strategy would involve several steps.

1. Decreasing the extent of SiO formation by:
 - Lowering ash in coke, and the coke rate
 - Lowering RAFT
 - Lowering the activity of SiO_2 in coke ash by lime injection through the tuyeres.
2. Decreasing Si absorption by liquid iron in the bosh by enhancing the absorption of SiO_2 by the bosh slag. This can be achieved by:
 - Increasing the bosh slag basicity
 - Lowering the bosh slag viscosity by operating at lower basicities.
3. Removal of Si from metal by slag-metal reaction at the hearth by:
 - Lowering the hearth temperature
 - Producing a slag of optimum basicity and fluidity.

5.4.3 Reaction of Sulphur

Most of the sulphur (say about 80%) enters the blast furnace through coke as CaS and FeS in coke ash as well as in the form of organic sulphur. The remainder comes through the other burden materials. In any blast furnace, about 80–90% of the sulphur input leaves the furnace with the slag, 10–15% reports to flue dust and top gas, while 2–5% gets dissolved in hot metal.

Earlier most steel grades required sulphur contents of less than 0.040%. Subsequent to the adoption of continuous casting, the upper limit was brought down to 0.025%. Earlier all sulphur removal had to be completed within the blast furnace; however, with the current practice of external desulphurisation of hot metal as well as some desulphurisation during secondary steelmaking, blast furnaces have greater flexibility with regard to the final sulphur content in hot metal.

Reactions in raceway and bosh

Figure 5.13 (Biswas 1984) shows the variation of weight percentages of metal sulphur and slag sulphur at various heights from the tuyeres, as measured in different investigations. The behaviour of sulphur is qualitatively similar to that of silicon (Figure 5.11), i.e. the highest sulphur in metal is at the tuyere level.

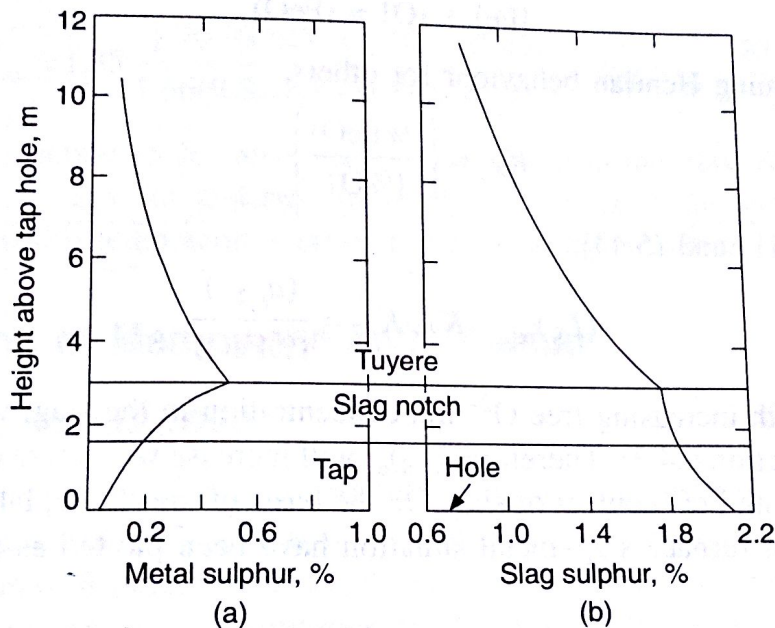
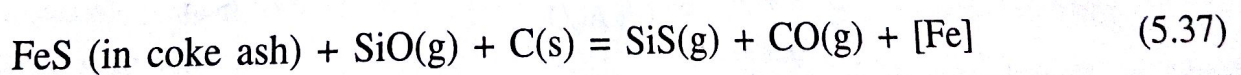
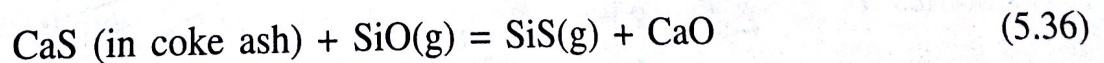


Figure 5.13 Variation of (a) metal sulphur, (b) slag sulphur, above and below the tuyeres.

Recent investigations have established that the dominant mechanism involved in sulphur reactions is broadly similar to that of silicon (Figure 5.10). The sulphur in coke ash undergoes the following reactions in the raceway:



In the bosh and belly regions, SiS decomposes as



Small amounts of sulphur are also absorbed by the bosh slag. It should be mentioned here that sulphur forms some other volatile compounds—COS, CS, which are also carried up into the gas stream and undergo reactions. However, it needs to be emphasised that SiS is the dominant vapour species.

Reactions in hearth

In the hearth, the slag-metal sulphur reaction may be written in general ionic form as



Assuming Henrian behaviour for all species except (O^{2-}) ,

$$K_{39} = \frac{(\%S)[\%O]}{[\%S](a_{O^{2-}})} \tag{5.40}$$

i.e. $(L_S)_{eq}$ = Equilibrium partition coefficient for sulphur

$$= \left(\frac{(\%S)}{[\%S]} \right)_{eq} = K_{39} \frac{(a_{O^{2-}})}{[\%O]} \tag{5.41}$$

Now,



Since $a_{Fe} \approx 1$, assuming Henrian behaviour for others,

$$K_{42} = \left\{ \frac{(\%FeO)}{[\%O]} \right\}_{eq} \tag{5.43}$$

Combining Eqs. (5.41) and (5.43),

$$(L_S)_{eq} = K_{39} \cdot K_{42} = \frac{(a_{O^{2-}})}{(\%FeO)} \tag{5.44}$$

$a_{O^{2-}}$ increases with increasing free O^{2-} ion concentration in the slag, which again increases with slag basicity (Section 4.4.3). Therefore, $(L_S)_{eq}$ will increase with increasing basicity and will decrease with increasing FeO content of slag. On the basis of the above, laboratory experimental data of $(L_S)_{eq}$ for blast furnace slag-metal situation have been plotted as shown in Figure 5.14 (Biswas 1984).

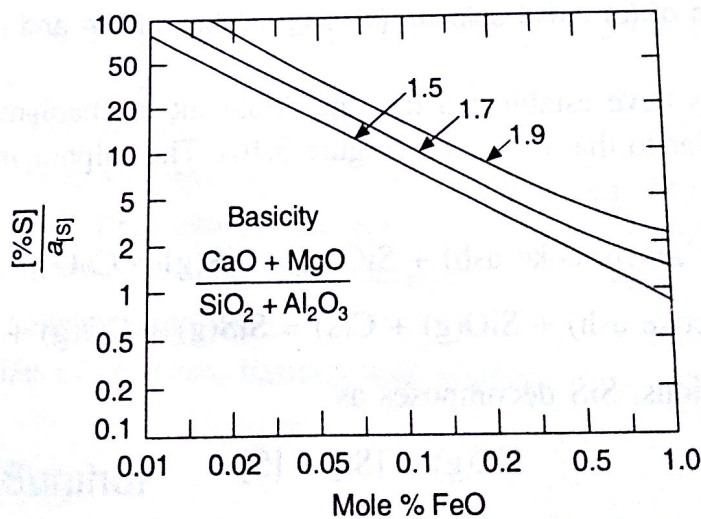


Figure 5.14 Influence of basicity and iron oxide content of slag on equilibrium partition of sulphur between slag and metal in the blast furnace temperature range.

It should be about MgO—about the reaction of Figure 4.1) compounds

On the basis (Gupta)

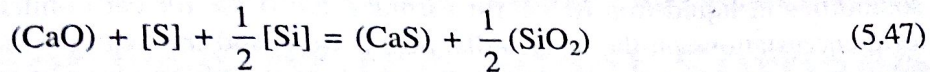
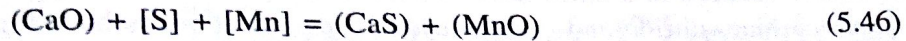
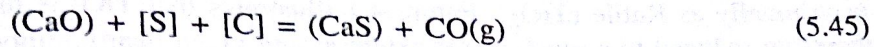
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It should be mentioned that CaO is a much more powerful base and desulphuriser than MgO—about 100 times stronger. It is also to be noted that for adequate desulphurisation, the oxygen content of the metal should be very low. This is achieved in the blast furnace hearth by the reaction of dissolved oxygen in the hot metal with strong oxide formers: C, Si, Mn (reference Figure 4.1) dissolved in liquid metal. On this basis, the following reactions in terms of compounds can be written



On the basis of reaction (5.45), an empirical correlation that has been proposed in Tata Steel (Gupta 1991) is:

$$\log (L_S)_{\text{eq}} = 1.35 \frac{1.79(\% \text{CaO}) + 1.24(\% \text{MgO})}{1.66(\% \text{SiO}_2) + 0.33(\% \text{Al}_2\text{O}_3)} - \log p_{\text{CO}} - \frac{8130}{T} + 4.15 \quad (5.48)$$

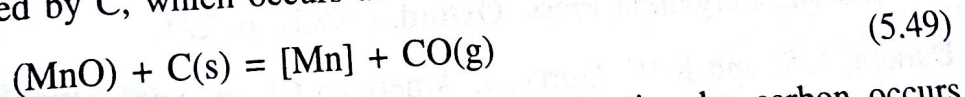
It appears that reaction (5.46) also attains equilibrium in the blast furnace hearth. On the basis of above, the strategy for making low sulphur hot metal is the same as that for silicon, except that higher hearth temperatures promote better desulphurisation.

5.4.4 Reactions of Manganese and Titanium

Reactions of manganese

Whereas the lowest contents of silicon and sulphur in hot metal are desired, it is necessary to maximise manganese recovery in hot metal. Manganese is an input into blast furnaces through iron ore, and sometimes through the deliberate addition of manganese ore. It is present as MnO_2 , which gets reduced to Mn_3O_4 , and subsequently to MnO in the blast furnace stack by indirect reduction.

Figure 4.1 shows that MnO is more stable than FeO, but less stable than SiO_2 . The figure also shows that MnO is reduced by C, which occurs as



This reaction is possible only above 1400°C ; therefore, MnO reduction by carbon occurs primarily in the hearth region, either when the liquid slag containing MnO flows down through the coke bed or during reaction in the hearth between metal and slag.

The earlier sections have already presented Mn–Si coupled reactions as well as Mn–S reaction at the hearth. The manganese content of hot metal ranges between 0.2% and 1.5%, and the MnO content of the slag is also approximately the same.

Recovery of manganese in the hearth can be increased by:

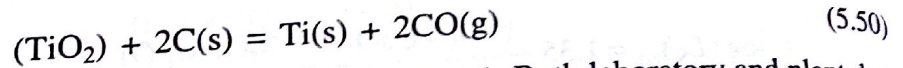
- Increasing γ_{MnO} (i.e. a_{MnO}) in the slag by using higher slag basicity
- Increasing the slag and metal temperatures
- Increasing the silicon content of hot metal.

The typical range of recovery of manganese varies between 60% and 70% for basic slags (i.e. $(\text{CaO}/\text{SiO}_2) > 1$), and between 50% and 60% for acid slags.

Reactions of titanium

Titanium is usually present in blast furnace raw materials as Ilmenite ($\text{FeO}\cdot\text{TiO}_2$) and occasionally as Rutile (TiO_2). Figure 4.1 illustrates that TiO_2 is more stable than SiO_2 , and is therefore reduced to a much lesser extent at any given hearth temperature. Titanium also forms stable carbide, nitride and carbo-nitride. These compounds have high melting points and low solubilities in liquid iron (0.3% for carbides and 0.2% for carbo-nitrides) and they separate to form encrustations on the bosh walls, hearth walls and the hearth bottom, resulting in accretion build-up on the blast furnace bottom region lining. This can often lower the furnace campaign life since the highest temperatures prevail in this region.

For the reaction,



the equilibrium constant can be calculated from data in Table 4.1. Both laboratory and plant data have shown that the Ti content of hot metal increases with greater reduction of SiO_2 and MnO , as expected theoretically. While the wt. % Ti in metal is less than 0.15, the wt. % TiO_2 in slag may be in the range of 0.3–1.

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