

Part D

Steelmaking

- Physical Chemistry of Primary Steelmaking
- BOF Plant Practice
- Metallurgical Features of Oxygen Steelmaking
- Process Control for Basic Oxygen Steelmaking
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- Secondary Steelmaking
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Physical Chemistry of Primary Steelmaking

15.1 INTRODUCTION

Chapter 1 contained a broad overview of ironmaking and steelmaking. Chapter 3 presented an outline of modern steelmaking. From those chapters, the following can be noted.

- A modern steel melting shop has three broad groups of facilities, viz. *primary steelmaking*, *secondary steelmaking*, and *casting of liquid steel*.
- Primary steelmaking is dominantly carried out in top-blown *Basic Oxygen Furnaces* (BOFs). The process has several variants, as already enumerated in Chapter 3. Another category of oxygen-based steelmaking processes rely on bottom-blowing of oxygen through special tuyeres. All these latter processes can be clubbed together under the generic category of Basic Oxygen Steelmaking (BOS) processes.

Electric Arc Furnace (EAF) steelmaking is in addition to BOF and BOS, i.e. there are three broad methods of making steel. These three groups of processes together account for almost the entire liquid steel production in the world today.

Chapters 16 to 18 will cover various aspects of BOF steelmaking, along with a very brief discussion of BOS processes like OBM, etc. (in Chapter 17) while Chapter 19 will deal with EAF steelmaking. Since the open-hearth process of steelmaking has been phased out and is virtually non-existent today, only a very brief discussion of open-hearth steelmaking is included in Chapter 19.

The present chapter is concerned with some relevant physicochemical aspects of steelmaking, that are applicable to all the primary steelmaking processes. These fundamentals also constitute the basics of secondary steelmaking processes. However, BOF/BOS is the principal focus of this chapter.

Primary steelmaking is a process of oxidation. The principal oxidising agent is gaseous oxygen, along with iron oxide (added as iron ore). The extent of refining in oxygen steelmaking processes is substantial since the principal metallic feed is blast furnace hot metal containing

high percentages of carbon, silicon, phosphorus and manganese. In EAF steelmaking, the extent of refining is far less since a large proportion of the metallic feed is in the form of steel scrap containing low levels of impurities.

The oxidation reactions are exothermic and constitute the source of heat in BOF and BOS processes, leading to an increase in the bath temperature to 1600–1650°C at the end of refining, from an initial temperature of 1250–1300°C. On the other hand, in EAF steelmaking the major heat source is electrical power.

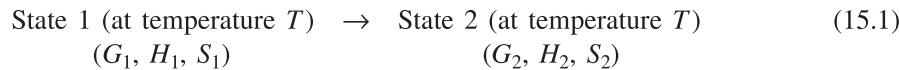
Oxidation of Si, Fe, Mn, P (and sometimes small amounts of Ti) leads to the formation of SiO_2 , FeO , MnO , P_2O_5 (and TiO_2). These oxides combine with the fluxing agents added (principally lime, sometimes along with fluorspar, ilmenite, dolomite, etc.) to form a basic molten slag, which helps in refining. Carbon is oxidised in the form of gaseous carbon monoxide.

15.2 REACTIONS AND HEAT EFFECTS

Chapter 6, Section 6.1.1 has briefly dealt with the basic procedure of mass and heat balance with specific reference to blast furnace ironmaking. A similar procedure is to be adopted to predict the temperature rise during steelmaking, which will be taken up in Chapter 18. This section will briefly present the *thermochemical aspects of enthalpy changes*.

Chapter 4 has reviewed the fundamentals of thermodynamics for the application of Gibbs free energy (ΔG) criterion for process calculations. As discussed there, only *isothermal* reactions and processes can be handled using this approach. The reactions can be *reversible* or *irreversible*; the only stipulation is that the initial and final temperatures should be the same.

Consider the process:



$$\begin{aligned} \Delta G &= G_2 - G_1 \\ &= (H_2 - TS_2) - (H_1 - TS_1) \\ &= (H_2 - H_1) - T(S_2 - S_1) \\ &= \Delta H - T\Delta S \end{aligned} \quad (15.2)$$

As mentioned in Chapter 4, Section 4.2.3, the variation of the *standard free energy of formation* of a compound (ΔG_f^0) as a function of temperature is approximately linear. Therefore, for practical purposes, the simplest form of the equation (Eq. (4.22)) viz.

$$\Delta G_f^0 = AT + B$$

is employed in which A and B are empirical constants.

Again, from Eq. (15.2),

$$\Delta G_f^0 = \Delta H_f^0 - T\Delta S_f^0 \quad (15.3)$$

where ΔH_f^0 and ΔS_f^0 are *standard enthalpy* and *entropy of formation* of the compound respectively.

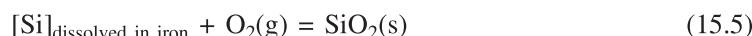
A comparison of Eq. (15.3) and Eq. (4.22) shows that $A = \Delta H_f^0$ and $B = -\Delta S_f^0$, and these have been assumed to be independent of temperature. Table 4.1 has presented the values of A and B for the formation of some oxides. Hence, A is to be taken as ΔH_f^0 .

Table 4.2 contained values of the *free energy of mixing* of some elements at 1 wt% standard state in liquid iron (\bar{G}_i^m) as a function of temperature as

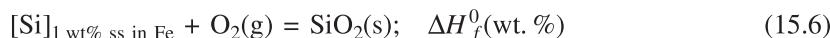
$$\bar{G}_i^m = C + DT \quad (15.4)$$

Again, from the above analysis, it is possible to take $C = \bar{H}_i^m$ and $D = -\bar{S}_i^m$.

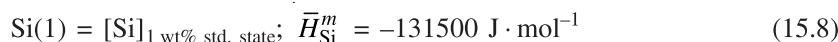
Primary steelmaking is concerned with the oxidation of solutes dissolved in liquid iron. For example, the oxidation of silicon may be written as



At 1 wt.% standard state, it may be written as



From Tables 4.1 and 4.2,



Subtracting Eq. (15.8) from Eq. (15.7), Eq. (15.6) is obtained. Hence,



On the basis of the above, the ΔH_f^0 (wt. %) values (except for Fe, because it is the solvent) have been listed in Table 15.1. For convenience, these have been reported as ΔH_f^0 in kilojoules per mole with the values rounded-off to 4 digits. The table also includes values of ΔS_f^0 in $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

Table 15.1 Standard enthalpies and entropies of formation of some oxides from elements dissolved in liquid iron

| Reaction | $\Delta H_f^0, \text{kJ} \cdot \text{mol}^{-1}$ | $\Delta S_f^0, \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ |
|--|---|--|
| $\text{Fe}(\text{l}) + (1/2) \text{O}_2(\text{g}) = \text{FeO}(\text{l})$ | -259.6 | -62.55 |
| $[\text{C}] + (1/2) \text{O}_2(\text{g}) = \text{CO}(\text{g})$ | -134.3 | 129.9 |
| $[\text{C}] + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$ | -416.7 | 43.1 |
| $[\text{Cr}] + (3/4) \text{O}_2(\text{g}) = (1/2) \text{Cr}_2\text{O}_3(\text{s})$ | -585.2 | -175.3 |
| $[\text{Mn}] + (1/2) \text{O}_2(\text{g}) = \text{MnO}(\text{s})$ | -412.2 | -126.9 |
| $[\text{P}] + (5/4) \text{O}_2(\text{g}) = (1/2) \text{P}_2\text{O}_5(\text{g})$ | -663.0 | -260.5 |
| $[\text{Si}] + \text{O}_2(\text{g}) = \text{SiO}_2(\text{s})$ | -816.2 | -216.0 |
| $[\text{Si}] + \text{O}_2(\text{g}) = \text{SiO}_2(\text{l})$ | -804.9 | -210.0 |
| $[\text{Ti}] + \text{O}_2(\text{g}) = \text{TiO}_2(\text{s})$ | -889.1 | -218.8 |

Note: For Fe, pure iron is the standard state; for others, values correspond to those for 1 wt.% standard state in liquid iron.

All these reactions involving the oxidation of metalloids are *highly exothermic*. Among them in BOF/BOS steelmaking, the major heat producing reactions are oxidation of Si, C, and Fe, since large quantities of these species are present. The *endothermic steps* include heating-up of the inputs and the additions made during the blow to steelmaking temperatures. The principal inputs are: molten hot metal at around 1250–1300°C, and scrap, lime (and other fluxes), iron ore, pig iron all at room temperature. Sometimes, other minor additions are made depending on the practice adopted; however, they can be ignored in this general analysis.

Equation (6.5) of Section 6.1.1, gives the general equations for *sensible heat* ($H_T - H_{298}$) of a substance as a function of temperature. As a simplification, hot metal, pig iron and scrap may all be assumed to be pure iron. Similarly, iron ore may be assumed to be either pure Fe_2O_3 or pure Fe_3O_4 . Table 15.2 (Kelley 1960) lists the ($H_T - H_{298}$) values on this basis. The range of temperature at which they are valid are also shown.

Table 15.2 Sensible heats of some substances as function of temperature

| Substance | $H_T - H_{298}, \text{ J} \cdot \text{mol}^{-1}$ | Temperature range, K |
|---------------------------------|--|----------------------|
| Fe(l) | $40.9T + 0.837 \times 10^{-3}T^2 - 2805$ | 1812–3000 |
| CaO(s) | $48.85T + 2.26 \times 10^{-3}T^2 + 6.53 \times 10^5T^{-1} - 16957$ | 298–2000 |
| $\text{Fe}_2\text{O}_3(\gamma)$ | $132.7T + 36.84 \times 10^{-3}T^2 - 35355$ | 1050–1800 |
| $\text{Fe}_3\text{O}_4(\beta)$ | $200.9T - 52953$ | 900–1800 |

Other thermochemical data required for thermal calculations are enthalpies of dissolution (i.e. *heats of mixing*) in liquid metal and slag. These are smaller quantities in comparison with the exothermic oxidation reactions and sensible heats, and may be ignored for approximate calculations.

As discussed earlier, for liquid iron solution, data have already been provided in Table 4.2. Steelmaking slag may be considered as a mixture of dicalcium ferrite, dicalcium silicate and calcium phosphates, for which the heats of formation data are noted in Table 15.3 ((1) Ward 1962; (2) Bogdandy and Engells, 1971).

Table 15.3 Heats of formation of some double compounds of oxides at steelmaking temperatures (approximate values)

| Source | Formation reaction | $\Delta H_f^\circ, \text{ kJ} \cdot \text{mol}^{-1}$ |
|--------|--|--|
| (1) | $2\text{CaO}(s) + \text{SiO}_2(s) = 2\text{CaO} \cdot \text{SiO}_2(s)$ | -124 |
| (1) | $3\text{CaO}(s) + \text{SiO}_2(s) = 3\text{CaO} \cdot \text{SiO}_2(s)$ | -123 |
| (2) | $2\text{CaO}(s) + \text{Fe}_2\text{O}_3 = 2\text{CaO} \cdot \text{Fe}_2\text{O}_3(l)$ | -109 |
| (1) | $3\text{CaO}(s) + \text{P}_2\text{O}_5(g) = 3\text{CaO} \cdot \text{P}_2\text{O}_5(s)$ | -1697 |
| (1) | $4\text{CaO}(s) + \text{P}_2\text{O}_5(g) = 4\text{CaO} \cdot \text{P}_2\text{O}_5(s)$ | -1740 |

EXAMPLE 15.1

For a BOF heat, the following data are given.

- (i) Hot metal contains 1% Si, 0.15% P, 0.25% Mn and 3.5% C.
- (ii) Weight of scrap is 10% of hot metal.
- (iii) Steel at tap contains 0.2% C.
- (iv) Slag has 54% CaO, 18% FeO, 2.5% MgO, 2.5% MnO, and CaO/SiO₂ ratio = 3.2.

Calculate the following per tonne (i.e. 1000 kg) of steel.

- (a) Weight of hot metal charge
- (b) Weight of slag produced
- (c) Quantity of lime required.

Solution: The procedure is to be iterative.

$$\text{Si-balance: Si in hot metal} = \text{Si as SiO}_2 \text{ in slag} \quad (\text{Ex.15.1})$$

Assuming weight of hot metal (W_{HM}) as 1 tonne as first approximation, and noting that wt. % SiO₂ in slag = 54/3.2 = 16.9%,

$$1000 \times 0.01 = W_{\text{slag}} \times 0.169 \times 28/60, \text{ giving } W_{\text{slag}} = 127 \text{ kg as first approximation.}$$

$$\text{Fe-balance: Fe in HM + Fe in scrap} = \text{Fe in steel + Fe in slag} \quad (\text{Ex.15.2})$$

Assuming scrap as pure iron, and noting that wt. % Fe in HM = 94.10%, wt. % Fe in slag = $18 \times \frac{56}{72} = 14\%$, scrap wt. is 10% of W_{HM} , and steel has 99.8% Fe,

$$\text{Fe-balance: } W_{\text{HM}}(0.9410 + 0.1) = 0.998 + 0.127 \times \frac{14}{100}, \text{ giving } W_{\text{HM}} = 975 \text{ kg}$$

Using this value of W_{HM} in Si-balance, the revised value of slag weight is 130 kg.

$$\text{CaO-balance: CaO to be added} = \text{CaO in slag} = W_{\text{slag}} \times \frac{54}{100} = 70.2 \text{ kg}$$

EXAMPLE 15.2

For the heat in Example 15.1, calculate the quantity of oxygen required per tonne of steel. Assume that the exit gas of the converter contains 10% CO₂ and 90% CO as average of the entire heat.

Solution: Noting atomic masses of C, O, Si, P, Mn, Fe as 12, 16, 28, 31, 55 and 56 respectively,

$$\begin{aligned}
 \text{Oxygen required} &= \text{Oxygen to form } (\text{CO} + \text{CO}_2 + \text{SiO}_2 + \text{FeO} + \text{MnO} + \text{P}_2\text{O}_5) \\
 &= \frac{W_{\text{steel}}}{100} \times \left[\text{wt.\% C oxidised} \times \left(0.9 \times \frac{16}{12} + 0.1 \times \frac{32}{12} \right) \right. \\
 &\quad + W_{\text{HM}} \times \left(\text{wt.\% Si} \times \frac{32}{28} + \text{wt.\% Mn} \times \frac{16}{55} + \text{wt.\% P} \times \frac{80}{62} \right) \\
 &\quad \left. + W_{\text{slag}} \times \text{wt.\% FeO in slag} \times \frac{16}{72} \right] \quad (\text{Ex. 15.3})
 \end{aligned}$$

Noting that $W_{\text{steel}} = 1000 \text{ kg}$, $\text{wt.\% C oxidised} = (W_{\text{HM}} \times 3.5 - W_{\text{steel}} \times 0.2)/W_{\text{steel}} = 3.205$, $W_{\text{HM}} = 975 \text{ kg}$, $\text{wt.\% Si} = 1$, $\text{wt.\% Mn} = 0.25$, $\text{wt.\% P} = 0.15$, $W_{\text{slag}} = 130 \text{ kg}$, and $\text{wt.\% FeO in slag} = 18$.

Calculations yield quantity of oxygen required = $59.5 \text{ kg} = 59.5 \times 22.4/32 = 41.7 \text{ Nm}^3$.

15.3 PRIMARY STEELMAKING SLAGS

Chapter 4, Section 4.4.2–4.4.4 has briefly presented the fundamentals of structure, physicochemical properties, activities, basicity and capacity concepts of molten slags, as well as some slag models. In Chapter 5, Section 5.4.1 the salient features and data of blast furnace slags have been covered.

As mentioned, control of carbon, phosphorus and titanium are not possible in blast furnace ironmaking and these impurities have to be removed, to the extent desired, during steelmaking. Out of these impurities, phosphorus removal has received principal attention in primary steelmaking; the details will be discussed later in this chapter. For the time being it will suffice to mention that the removal of phosphorus requires low temperature and a highly basic and oxidising slag containing CaO and FeO as the two major constituents.

For producing carbon and low alloy steels, the composition of slags in primary steelmaking processes varies within the following range, depending on the final carbon content of steel tapped:

40–60% CaO, 10–28% SiO₂, 5–35% FeO (total), 1–3% P₂O₅, 2–8% MgO, 1–8% MnO, 1–2% Al₂O₃, 0–2% CaF₂, 0.1–0.2% sulphur, and minor amounts of other slag constituents.

The composition of turndown BOF slag at Tata Steel, for example, is as follows:

CaO 50–55%, SiO₂ 14–17%, Fe_{total} 14–21%, P₂O₅ 2.8–3.5%, S 0.06–0.2%, MgO 0.7–1.4%, MnO 0.4–0.8%, Al₂O₃ 0.6–1.3%, TiO₂ 0.7–1.0%, Cr₂O₃ 0.25–0.45%.

15.3.1 Phase Diagram and Activity-Composition Diagram

In Chapter 4, Section 4.2.3 the thermodynamics of oxidation-reduction reactions has been discussed. It has been shown that for equilibrium pure M-pure M_xO_y-O₂:

$$\Delta G_f^0 = RT \ln (p_{\text{O}_2})_{\text{eq}} = [\mu_{\text{O}_2}] \text{ at equilibrium} \quad (4.24)$$

where μ_{O_2} is the *chemical potential of oxygen*.