Figure 4.1 has presented the variation in ΔG_f^0 as a function of temperature for some oxides. It may be seen that the chemical potentials of oxygen follow the following order at steelmaking temperatures: μ_{O_2} (Fe−FeO) > μ_{O_2} (Si−SiO$_2$) > μ_{O_2} (Ca−CaO).

Since Fe−FeO has highest μ_{O_2}, its concentration determines the chemical potential of O$_2$ in slag. Again, Fe is present as Fe^{2+} and Fe $^{3+}$ ions in slag. Actually, μ_{O_2} in the slag is governed by the equilibrium of the reaction:

$$4 \text{ (FeO)} + O_2(g) = 2(Fe_2O_3) \tag{15.10}$$

The Fe^{3+}/Fe^{2+} ratio varies to a very major extent during steelmaking. It is also not measured for all heats on a regular basis because of difficulties in taking representative samples. Therefore, the standard practice is to determine the metallic Fe concentration in the slag and report it as FeO. This is represented as either FeO (total) or 'FeO'.

The ternary CaO–SiO$_2$–FeO (or Fe$_2$O$_3$) constitutes the basic phase diagram in primary steelmaking. Figure 15.1 (Muan and Osborn, 1965) shows the isothermal sections at 1600°C, in contact with metallic iron, as well as in contact with air. The liquid fields are shown along with the solid compounds at equilibrium with various liquid field boundaries. The solid circle corresponds to the nominal turndown slag composition (assuming CaO + SiO$_2$ + FeO (or Fe$_2$O$_3$) = 100%). Of course, the actual compositions lie over a range around this region. It may be noted that the solids, which are likely to coexist with the primary steelmaking slag are 2CaO · SiO$_2$, 3CaO · SiO$_2$ and CaO.
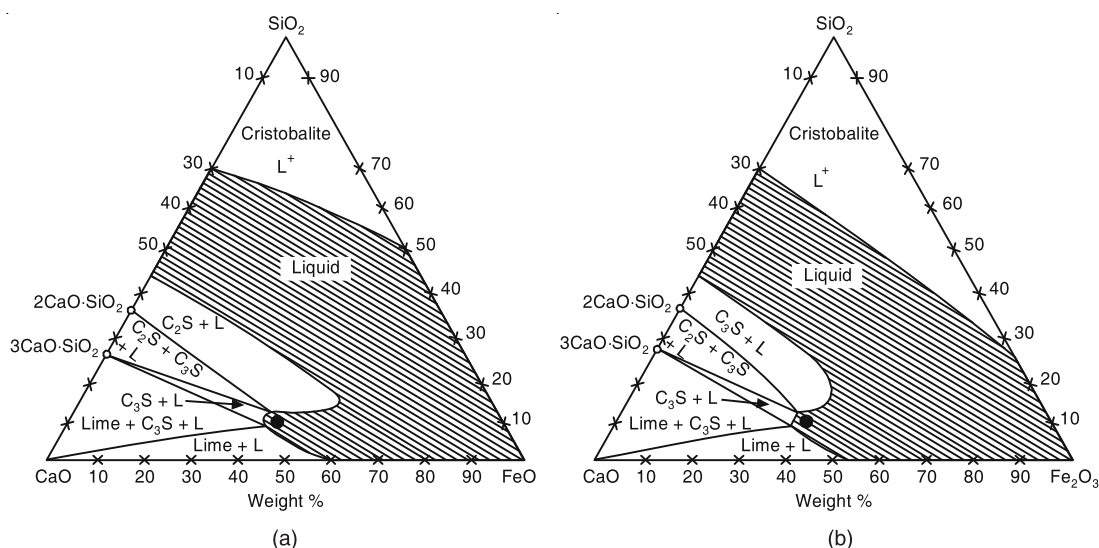

Figure 15.1   Isothermal sections at 1600°C (i.e. 1873 K) in the system CaO–iron oxide–SiO$_2$, in contact with (left) metallic iron, (right) air.

However, it has been demonstrated that the effects of other slag components cannot be completely ignored. For this reason, a wider liquid region exists in commercial slags at 1600°C, than what can be inferred from the ternary diagram for pure compounds. The total concentration of CaO, SiO_2 and FeO(t) is in the range of 80–90%, and if the sum of CaO + SiO_2 + FeO(t) is taken as 100% and the phase diagram recalculated, it does not make a major difference. Of course, such recalculations lead to some errors (Walker and Anderson, 1972). Figure 15.2 (Bardenheuer et al. 1968) shows such a diagram.
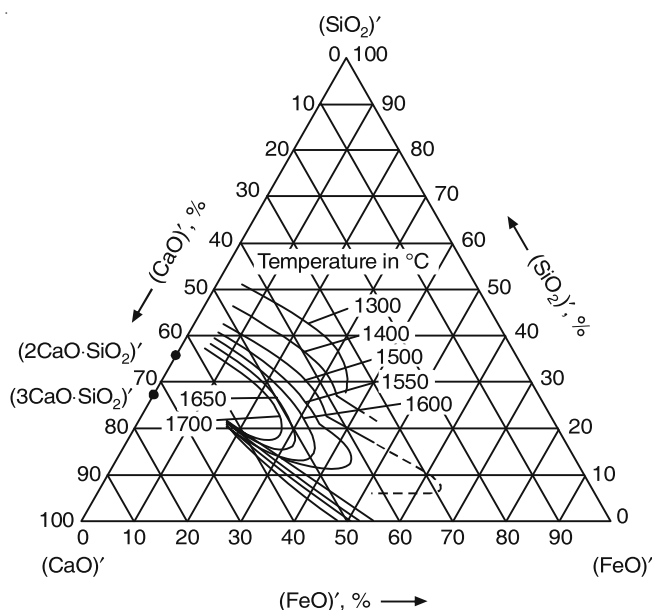
Figure 15.2 Pseudo–ternary system CaO–SiO_2–'FeO'; average CaO + SiO_2 + 'FeO' = 80 wt% in actual slag.

Figure 15.3 (Taylor and Chipman, 1943) presents activity vs. composition diagrams for the CaO–SiO_2–FeO system at 1550°C. Standard state for FeO is liquid and its activity was measured experimentally. Activities of SiO_2 and CaO with respect to the pure solid oxides as standard states were calculated by Gibbs–Duhem integration. If other oxides are to be included in the ternary diagram, an alternative approach would be to lump the other basic oxides (MgO, MnO) with the CaO-corner, SiO_2 + P_2O_5 + Al_2O_3 at the top corner of the triangle.
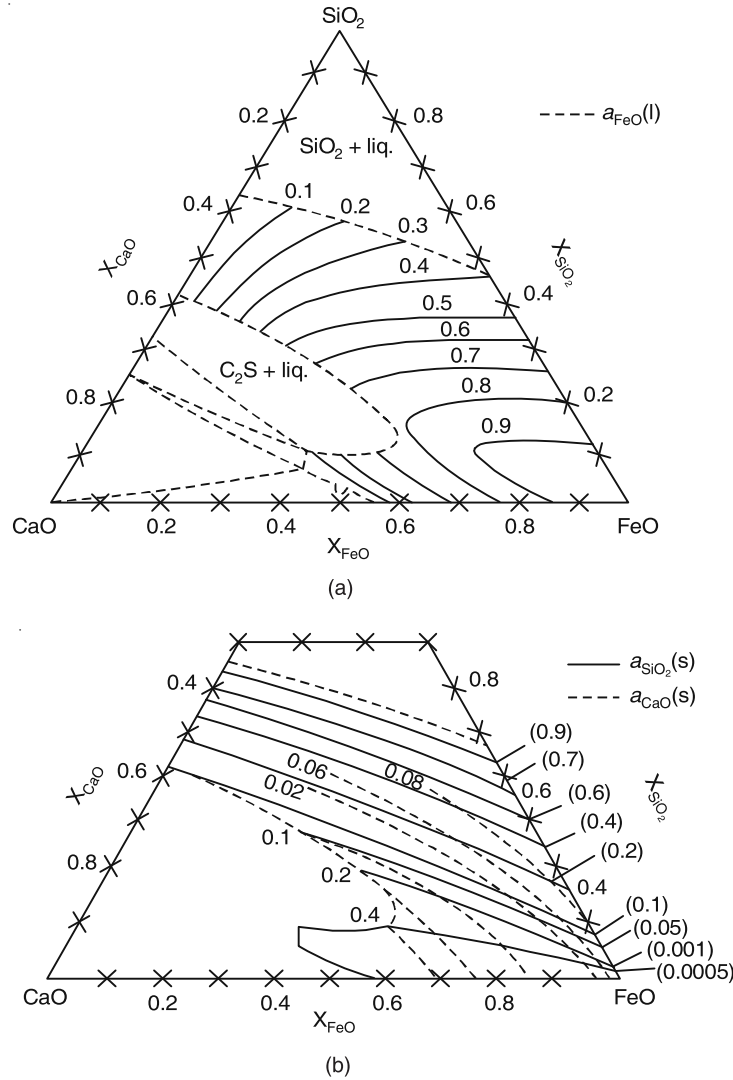
Figure 15.3 Activities of FeO, CaO, SiO$_2$ in CaO–FeO–SiO$_2$ melts in equilibrium with liquid iron at 1550°C (i.e. 1823 K).

EXAMPLE 15.3

Calculate the oxygen potential of liquid steel at equilibrium with a molten slag at 1600°C. Given:

  (i) Slag contains CaO, SiO$_2$ and FeO with 0.45, 0.4 and 0.15 mole fractions respectively,
 (ii) [O]$_{wt\%}$ + Fe(l) = FeO (l); K$_1$ = 4.78 at 1600°C from Eq. (15.13),
(iii) O$_2$(g) = 2[O]$_{wt\%}$; K$_2$ = 6.89 × 10^6 at 1600°C.

Solution:
$$\Delta G_f^0 = RT \ln (p_{O_2})_{eq} = [\mu_{O_2}]_{\text{at equilibrium}} \qquad (4.24)$$

Since,
$$K_2 = \frac{[h_O^2]}{p_{O_2}} \text{ at equilibrium,}$$

$$[\mu_{O_2}]_{\text{at equilibrium}} = RT \ln \frac{[h_O^2]}{K_2} \qquad (\text{Ex. } 15.4)$$

h_O can be obtained from the equilibrium of the reaction: $[O]_{wt\%} + Fe(l) = FeO$ (l)
   As steel is almost pure iron, a_{Fe} may be taken as 1, and hence,

$$K_1 = \frac{(a_{FeO})}{[h_O]} \qquad (\text{Ex. } 15.5)$$

From Fig. 15.3(a), at the given composition of slag, $(a_{FeO}) = 0.15$.
From Eq. (Ex. 15.5), therefore, $[h_O] = 0.067$, and $[\mu_{O_2}]_{\text{at equilibrium}} = -329.2$ kJ/mol O_2.

15.3.2   Other Properties of Primary Steelmaking Slags

1. Density (ρ) = 2.46 + 0.018 (%FeO + %MnO)
         = 2.7 to 2.8 $g \cdot cm^{-3}$
2. Viscosity measurement in primary steelmaking slags is very difficult because of the high temperatures involved and the presence of corrosive iron oxide in slag. This makes experimental determinations tedious and consequently, data are very limited and not reliable. Theoretical estimates are also not precise and range from 0.5 poise to 2 poise (i.e. 0.05 to 0.2 $N \cdot sm^{-2}$) for BOF turndown slags.
3. Surface tension data for slags are available in the range of 1400–1450°C. In the CaO–SiO_2–FeO system for the steelmaking composition range, a value of 450–550 $mN \cdot m^{-1}$ seems to be appropriate.

   Molten slags, even at turndown contain undissolved CaO and Ca_2SiO_4 particles to the extent of 5–10 wt.%. This has an influence on slag viscosity as well as on basicity and capacities.

15.4   THE REACTION EQUILIBRIA

15.4.1   Introduction

1. SiO_2, TiO_2 are very stable compounds (see Figure 4.1). Therefore, Si and Ti in hot metal are removed as oxides in the early part of steelmaking, and are of no concern thereafter.
2. Desulphurisation of hot metal occurs to some extent within the blast furnace and subsequently, during hot metal pretreatment. As discussed in Chapter 5, Section 5.4.3, sulphur can be transferred efficiently from metal to slag, only under reducing conditions. Since primary steelmaking slags are highly oxidising in nature, very little sulphur transfer to slag can be achieved in primary steelmaking. Low levels of sulphur required in most steel today and ultra-low sulphur levels in some special steel grades can only be attained through further refining in secondary steelmaking processes. Hence, it is not discussed here.