

Early Models of the Thermodynamic Behavior of Slags and Salts

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Abstract

The ability to optimize the values of the large numbers of parameters used in thermodynamic models of multicomponent slags has increased immensely in the twenty years that have passed since Charles Masson organized his very successful "International Symposium on Metallurgical Slags" in Halifax, Nova Scotia. In view of this high level of computer sophistication it is useful to look back at the origins of the theories and models of slag behavior, and this paper is an attempt to provide such a review. The earliest models assumed the formation of complex molecular oxides, the dissociation constants for which were determined by the Law of Mass Action using the active concentrations (weight percentages) of the various free and complex molecular oxides, and the dependencies of the dissociation constants on temperature were determined by complex mathematical manipulation to reproduce works data. Eventually the mathematical complexity was such that the models, and the application of the Law of Mass Action, offered no advantage over calculating the activity coefficients of the components of the slag. The early ionic models made assumptions as to the natures of the ions occurring in slags and to the influence of the interactions among these ions, and their entropies of mixing, on the free energies of formation of the slags. This activity continued into the 1980's and it is interesting to note that a theoretical model, published in 1953 and 1954, led to a spirited controversy during the period 1975-78. This model is revisited.

The Early Molecular Models of Slags

The earliest theories of the constitution of slags were developed as a result of mineralogical examination of the constituents of solidified slags. However, in 1923, Colclough pointed out that, as the phases occurring in the solid state are formed by selective crystallization from the melt, mineralogical examination cannot provide evidence that the compounds, observed in the solid state, had existed in the liquid⁽¹⁾. Colclough studied the effects of slags of various compositions on the refining reactions occurring in a 60-ton open hearth furnace, and the following is an account of the conclusions which were drawn from his study. Chemical analysis of the slags led to the suggestion that, in a melting slag, each molecule of P_2O_5 is associated with four molecules of CaO and each molecule of SiO_2 is associated with two molecules of basic oxide RO, where RO is CaO, MnO, MgO and, to a small extent, FeO. Thus Colclough considered what he termed a "true melting slag" to be a molecular solution of $4CaO.P_2O_5$, $2RO.SiO_2$ and some uncombined FeO and Fe_2O_3 . During melting, oxidation of iron, silicon and manganese in the charge produces a slag containing molecules of $2FeO.SiO_2$ and $2MnO.SiO_2$ and, as the charged lime dissolves in the slag it displaces FeO and MnO from their orthosilicates to produce the more stable $2CaO.SiO_2$. When the silicon content of the metal bath has been decreased to a trace, the dissolving CaO is available to form $4CaO.P_2O_5$ as the product of oxidation of phosphorus in the bath. A true melting slag thus has a critical composition; no free molecular oxides, other than FeO, exist and the slag is saturated with phosphorus. Consequently, the extent to which phosphorus can be removed from the metal is determined by the silicon content of the metal charge and by the amount of lime charged.

The addition of iron oxides to a slag of this critical composition does not cause any change in its constitution; the iron oxides simply dissolve in the slag where they become available for the oxidation of carbon in the metal. However, the addition of lime does cause a fundamental change in the constitution. It appeared that some fraction of the added lime displaces FeO and MnO from their orthosilicates and that these liberated molecules oxidize more phosphorus from the metal bath, which, in turn, is stabilized in the slag by combination with the remaining added CaO to form more $4\text{CaO} \cdot \text{P}_2\text{O}_5$. During this period of solution of the added lime it was observed that oxidation of carbon from the bath ceases, indicating that the liberated basic oxides are being consumed completely by the preferred oxidation of phosphorus.

Colclough considered that desulfurization of the metal, which was observed to occur during this period of lime solution, was only indirectly caused by the CaO. The manganese, produced in the metal as the product of the oxidation of phosphorus by the liberated MnO, combines with sulfur to form molecules of MnS which dissolve in the slag. At the slag-gas interface this MnS is oxidized by the furnace atmosphere to MnO and gaseous SO_2 and the regenerated MnO is then available for further oxidation of phosphorus and reduction of sulfur from the bath. When solution of the added lime is complete the slag has again acquired its critical composition. It was observed that the addition of silica to this slag caused a stoichiometric reversion of phosphorus to the metal due to the SiO_2 displacing P_2O_5 from $4\text{CaO} \cdot \text{P}_2\text{O}_5$ and the unstable freed P_2O_5 being reduced by manganese, carbon or iron in the melt.

With the continued addition of lime, the phosphorus is virtually eliminated from the melt and, eventually, a second critical slag composition is reached in which the CaO content is sufficient to combine with all the P_2O_5 and all the SiO_2 . This slag thus contains the molecular species $4\text{CaO} \cdot \text{P}_2\text{O}_5$, $2\text{CaO} \cdot \text{SiO}_2$ and free molecules of MgO, MnO, FeO and Fe_2O_3 . Colclough considered that the increase in the Fe_2O_3 content, which is caused by the addition of CaO beyond that level required for achieving the second critical composition, is due to formation of molecular $x\text{CaO} \cdot \text{Fe}_2\text{O}_3$. He further considered that CaF_2 , added as a flux, reacts to form the molecular species $\text{CaF}_2 \cdot 3\text{CaO} \cdot \text{P}_2\text{O}_5$ which, consequently increases the solubility of CaO in the slag and decreases the amount of CaO required to neutralize the P_2O_5 .

Although this model of the constitution of steelmaking slags provided an adequate explanation of the dependence, on the slag composition, of the order in which solutes are eliminated from the metal bath, it was not amenable to a consideration of slag-metal equilibrium. For example, as the reversion of silicon from the slag to the metal was never observed, Colclough considered that the reaction



is irreversible⁽²⁾. Also, if sufficient CaO is present in the slag it was considered that the reaction



is irreversible. As neither free molecular SiO_2 nor free molecular P_2O_5 could exist in the slag, it appeared that the Law of Mass Action could not be applied to the reactions given by Eqs. (1) and (2). On the other hand Colclough considered that the reaction



is reversible, and, from the total weight percentages of FeO and MnO in clear melting slags, he calculated

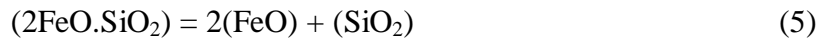
$$K_{\text{Mn}} = \frac{(\text{wt}\% \text{FeO}) \cdot [\text{wt}\% \text{Mn}]}{(\text{wt}\% \text{MnO})} = 10.8 \times 10^{-4} \quad (4)$$

at an unspecified temperature.

The concept of thermodynamic equilibrium, as it pertains to slag-metal reactions was emphasized by Schenck⁽³⁾, who stated that, irrespective of the quantities added to a system, each reaction only proceeds to a certain limit at which point the reaction equilibrium is established. Thus reactions, by means of which complex molecular oxides are formed in slags, do not proceed to the point of total consumption of one of the reacting species. Of the more than 40 complex oxides which could form in steelmaking slags, Schenck considered that only $2\text{FeO} \cdot \text{SiO}_2$, $2\text{MnO} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{SiO}_2$, $4\text{CaO} \cdot \text{P}_2\text{O}_5$ and $3\text{CaO} \cdot \text{Fe}_3\text{O}_4$ are important; all other complex oxide species are dissociated to an extent that renders their concentrations negligibly small. The molecular constitution of a slag is thus determined by four dissociation constants,

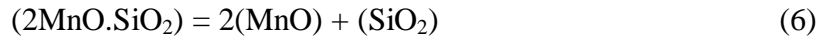
$$D_{2\text{FeO} \cdot \text{SiO}_2} = \frac{(\text{wt}\% \text{FeO})^2 \cdot (\text{wt}\% \text{SiO}_2)}{(\text{wt}\% 2\text{FeO} \cdot \text{SiO}_2)}$$

for the equilibrium



$$D_{2\text{MnO} \cdot \text{SiO}_2} = \frac{(\text{wt}\% \text{MnO})^2 \cdot (\text{wt}\% \text{SiO}_2)}{(\text{wt}\% 2\text{MnO} \cdot \text{SiO}_2)}$$

for the equilibrium



$$D_{\text{CaO} \cdot \text{SiO}_2} = \frac{(\text{wt}\% \text{CaO}) \cdot (\text{wt}\% \text{SiO}_2)}{(\text{wt}\% \text{CaO} \cdot \text{SiO}_2)}$$

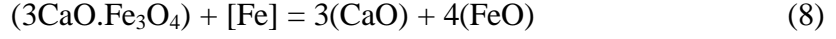
for the equilibrium



and

$$K_{\text{Fe/CaO}} = \frac{(\text{wt\%CaO})^3 \cdot (\text{wt\%FeO})^4}{(\text{wt\%3CaO.Fe}_3\text{O}_4)}$$

for the equilibrium



These expressions contain the weight percentages of the various free and complex molecular oxides as they occur at equilibrium in the slag. The extent of dissociation of $4\text{CaO.P}_2\text{O}_5$ was considered to be negligible and, at the levels at which they occur in steelmaking slags, the constituents Al_2O_3 , MgO and CaF_2 were considered to behave as simple neutral diluents. Schenck noted that his choice of a limited number of compounds left his model open to criticism on purely theoretical grounds, but added that, from the point of view of applied theoretical metallurgy, the justification for certain assumptions and omissions depends on whether the remaining mathematical data are sufficient to confirm works experience and permit systematic control of chemical reactions.

The dissociation constant $D_{2\text{FeO.SiO}_2}$ was evaluated in the following manner. The distribution of silicon between liquid iron and FeO-SiO_2 melts, expressed as



is determined, via the Law of Mass Action, by the equilibrium constant K_{Si} , where

$$K_{\text{Si}} = \frac{(\text{wt\%FeO})^2 \cdot [\text{wt\%Si}]}{(\text{wt\%SiO}_2)} \quad (10)$$

where (wt\%FeO) and (wt\%SiO_2) are the percentages by weight of free molecular FeO and SiO_2 in the slag. By means of trial and error analysis of experimental data for the distribution of silicon between liquid iron and FeO-SiO_2 slags, and the requirement that $(\text{wt\%FeO}) + (\text{wt\%SiO}_2) + (\text{wt\%2FeO.SiO}_2) = 100$, Schenck extracted

$$\log D_{2\text{FeO.SiO}_2} = - 11,230/T + 7.76 \quad (11)$$

and

$$\log K_{\text{Si}} = - 11,106/T + 4.5 \quad (12)$$

The theoretical molecular constitution of iron silicates, as given by Eq. (11) at 1600°C is shown in Fig. 1.

The dissociation constant $D_{2\text{MnO.SiO}_2}$ was evaluated in a similar manner by considering the distribution of manganese and silicon between liquid iron and FeO-MnO-SiO₂ melts. In this case the equilibria given by Eqs. (5), (6) and (9), together with the equilibrium



are of interest. Again, from trial and error analysis of the experimental data using the previously-determined values of K_{Si} and $D_{2\text{MnO.SiO}_2}$ and the requirement that the sum of the weight percentages of the five molecular species in the slag be 100, Schenck extracted

$$\log D_{2\text{MnO.SiO}_2} = - 18,880/T + 10.77 \quad (14)$$

and

$$\log K_{\text{Mn}} = - 6,234/T + 3.026 \quad (15)$$

where

$$K_{\text{Mn}} = \frac{(\text{wt}\% \text{FeO}) \cdot [\text{wt}\% \text{Mn}]}{(\text{wt}\% \text{MnO})} \quad (16)$$

The theoretical molecular constitution of manganese melts at 1600°C, as given by Eq. (14) is shown in Fig. 2 and the theoretical weight percentages of free FeO in FeO-MnO-SiO₂ melts at 1527°C are shown in Fig. 3. The constancy of Colclough's K_{Mn} in Eq. (4) suggests that, in clear melts, the weight percentages of free MnO and free FeO are proportional, respectively, to the total weight percentages of MnO and FeO.

From analysis of works data for basic open hearth furnaces and Thomas converters, Schenck obtained $D_{\text{CaO.SiO}_2}$ and $K_{\text{Fe/CaO}}$ as

$$\log D_{\text{CaO.SiO}_2} = - 3,186/T + 2.61 \quad (17)$$

and

$$\log K_{\text{Fe/CaO}} = - 39,684/T + 27.26 \quad (18)$$

The theoretical constitution of CaO-SiO₂ melts, as given by Eq. (17) at 1600°C, is shown in Fig. 4.

The relationship between the theoretical equilibrium concentrations of free and complex oxides and the gross composition of the slag, obtained by chemical analysis as (\square wt%Fe), (\square wt%SiO₂), (\square wt%CaO) and (\square wt%MnO), the total weight percentages of Fe, SiO₂, CaO and MnO in the slag are thus

$$(\square \text{ wt}\% \text{Fe}) = 0.77(\text{wt}\% \text{Fe}) + 0.548(\text{wt}\% 2\text{FeO.SiO}_2) + 0.419(\text{wt}\% 3\text{CaO.Fe}_3\text{O}_4) \quad (19)$$

$$(\square \text{wt\%SiO}_2) = (\text{wt\%SiO}_2) + 0.295(\text{wt\%2FeO.SiO}_2) + 0.517(\text{wt\%CaO.SiO}_2) + 0.298(\text{wt\%2MnO.SiO}_2) \quad (20)$$

$$(\square \text{wt\%CaO}) = (\text{wt\%CaO}) + 0.421(\text{wt\%3CaO.Fe}_3\text{O}_4) + 0.483(\text{wt\%CaO.SiO}_2) + 0.612(\text{wt\%4CaO.P}_2\text{O}_5) \quad (21)$$

$$(\square \text{wt\%MnO}) = (\text{wt\%MnO}) + 0.702(\text{wt\%2MnO.SiO}_2) \quad (22)$$

Although calculation of the gross composition of a steelmaking slag from knowledge of the concentrations of the various free and complex oxides species is simple, the reverse calculation is by no means straight forward. The difficulties with the latter type of calculation are such that Schenck presented the results of his calculations in graphical form as a series of isothermal 2-dimensional sections of the pseudo-quaternary system Fe-SiO₂-CaO-MnO. Figs. 5(a) – (d) show such a section using, as ordinates, ($\square \text{wt\%SiO}_2$) and ($\square \text{wt\%CaO}$)', where ($\square \text{wt\%CaO}$)' = ($\square \text{wt\%CaO}$) – 1.57($\square \text{wt\%P}_2\text{O}_5$), for the conditions $T = 1627^\circ\text{C}$, ($\square \text{wt\%Fe}$) = 10 and ($\square \text{wt\%MnO}$) = 5. Figs. 5(a) – (d) show, respectively, the theoretical variations of (wt%FeO) and (wt%CaO) and the theoretical variations of [wt%Mn] and [wt%Si] with slag composition.

Consideration of the equilibria given by Eqs. (5), (7) and (8) indicates that the addition of SiO₂ to a slag causes equilibrium (5) to shift to the left and equilibrium (8) to shift to the right. Thus, whether or not (wt%FeO) is thereby decreased depends on whether the increased formation of 2FeO.SiO₂ or the increased extent of dissociation of 3CaO.Fe₃O₄ predominates. Fig. 5(a) shows that when SiO₂ is added to a slag of high CaO content, (arrow *a*), (wt%FeO) increases due to the predominance of the dissociation of 3CaO.Fe₃O₄, whereas the addition of SiO₂ to a slag of low CaO content, (arrow *b*), causes a decrease in (wt%FeO) due to the predominance of the formation of 2FeO.SiO₂. Similarly, the addition of CaO to a slag causes equilibrium (7) to shift to the left and equilibrium (5) to shift to the right. Fig. 5(a) shows that the addition of CaO to a slag of low SiO₂ content, (arrow *c*) causes an decrease in (wt%FeO) whereas the addition of CaO to a slag of higher SiO₂ content, (arrow *d*), causes an increase in (wt%FeO). Thus along composition paths of (wt%CaO)' + (wt%SiO₂) = constant, (wt%FeO) passes through a maximum. This is shown in Figs. 6(a) and (b), which are drawn for (wt%CaO)' + (wt%SiO₂) = 50 at 1627°C and 1527°C respectively. The theoretical constitution of a slag can be determined from sections such as given by Figs. 5(a) – (d). Consider the composition ($\square \text{wt\%CaO}$)' = 20, ($\square \text{wt\%SiO}_2$) = 50. Figs. 5(a) – (d), respectively, indicate that, at this composition (wt%FeO) = 5.1, (wt%CaO) = 7.5, and, in the metal, [wt%Mn] = 0.12 and [wt%Si] = 0.055. Thus, from Eq.(12), (wt%SiO₂) = 31.7, from Eq. (15) (wt%MnO) = 1.1, from Eq. (11) (wt%2FeO.SiO₂) = 11.7, from Eq. (14) (wt%2MnO.SiO₂) = 5.6, from Eq. (17) (wt%CaO.SiO₂) = 21.7 and from Eq. (18) (wt%3CaO.Fe₃O₄) = 0.1.

An alternative approach to consideration of the behavior of Mn and S in the open hearth was taken by Darken and Larsen⁽⁴⁾ who used equilibrium constants, calculated from the results of laboratory investigations of reactions between metal and simple slags, to calculate the equilibrium distribution of Mn and S between liquid steel and open hearth slags over a wide range of operating condition. In order to attempt this application Darken and Larsen were forced to make some simplifying assumptions as to the constitution of the slag. These were

- i. all of the Mn in the slag exists as free MnO,
- i. all of the Mn in the slag exists as free MnO,
- ii. all of the Fe in the slag is present as either free FeO or free Fe₂O₃,
- iii. all of the Fe₂O₃ is reduced to FeO at the slag-metal interface according to (Fe₂O₃) + [Fe] = 3(FeO) so that each mole of Fe₂O₃ determined by chemical analysis is equivalent to three moles of FeO,
- iv. all of the P₂O₅ occurs as molecular 4CaO.P₂O₅,
- v. the concentration of free SiO₂ molecules is vanishingly small and the silicates, which are mainly of the form 2MO.SiO₂ and 3MO.SiO₂, contain only one molecule of SiO₂ per mole of silicate, such that the number of moles of silicates is equal to the number of mole of SiO₂ as determined by chemical analysis,
- vi. compounds of the form MO.M₂O₃ dot not occur,
- vii. the solubility of MgO in the more basic slags is negligibly small and
- viii. the influence of CaO is characterized by the ratio

$$L = \frac{(\text{CaO}) - 4(\text{P}_2\text{O}_5)}{(\text{SiO}_2)} \quad (23)$$

which is a measure of the number of moles of CaO in the slag which are available for combination with SiO₂ to form calcium silicates.

Darken and Larsen considered the equilibrium



for which

$$[\% \text{Mn}] = \frac{1}{K_{\text{Mn}}} \cdot \frac{(\text{MnO})}{(\text{FeO})}$$

where (MnO) and (FeO) are, respectively, the numbers of moles of MnO and FeO existing as simple molecules per unit weight of slag and K_{Mn} , given as

$$\log K_{\text{Mn}} = \frac{5950}{T} - 2.877$$

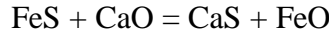
is the equilibrium constant obtained in laboratory experiments by Korber⁽⁵⁾. Analysis of a large number of laboratory studies and open-hearth data gave the variation of R , the ratio of the observed [%Mn] to the calculated value, with L as shown in Fig. 7. With $L > 2.4$ the equilibrium manganese content is accurately evaluated using the specific assumptions, i.e. the result indicate that when $L > 2.4$, FeO and MnO exist as free molecular oxides exhibiting ideal behavior. With decreasing values of L , the concentrations of free FeO and free MnO are decreased due to the formation of 2FeO.SiO₂ and 2MnO.SiO₂. The decrease in R with decreasing L was taken as indicating that 2MnO.SiO₂ forms to a greater extent than does 2FeO.SiO₂, with consequence that the concentration of free MnO is decreased to a greater extent than is that of free FeO. This

behavior was also interpreted as indicating that the orthosilicate molecules are fairly stable at steelmaking temperatures.

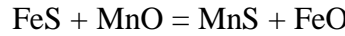
In the case of sulfur equilibrium Darken and Larsen derived an expression for the ratio of (S), the number of moles of sulfur per unit weight of equilibrated slag, to [S], the number of moles of sulfur per unit weight of equilibrated metal. By considering sulfur to exist in the slag as molecular FeS, MnS and CaS, the ratio (S)/[S] can be written as

$$\frac{(S)}{[S]} = \frac{(FeS) + (MnS) + (CaS)}{[S]} \quad (25)$$

the value of which is determined by the activities of the three sulfide species in the slag. Consideration of the virtual equilibrium



and



in the slag allows (CaS) and (MnS) to be evaluated as

$$(CaS) = B'' \cdot \frac{(CaO)_f \cdot (FeS)}{(FeO)}$$

and

$$(MnS) = C'' \cdot \frac{(MnO) \cdot (FeS)}{(FeO)}$$

where (CaO)_f is the number of moles of free molecular CaO per unit weight of slag. Substitution into Eq. (25) gives

$$\frac{(S)}{[S]} = \frac{(FeS)}{[S]} \left[1 + B'' \cdot \frac{(CaO)_f}{(FeO)} + C'' \cdot \frac{(MnO)}{(FeO)} \right] \quad (26)$$

Multiplying both sides of Eq. (26) by N_m/N_s , the ratio of the number of moles of components in the metal phase per unit weight of metal to the number of moles of molecular species in the slag per unit weight, and noting that

$$\frac{(FeS)}{[S]} \cdot \frac{N_m}{N_s} = A'$$

where A' is the equilibrium constant for

$$[\text{FeS}] = (\text{FeS})$$

gives

$$\frac{(\text{S})}{[\text{S}]} \cdot \frac{N_m}{N_s} = A' \left[1 + B' \frac{(\text{CaO})_f}{(\text{FeO})} + C' \frac{(\text{MnO})}{(\text{FeO})} \right] \quad (27)$$

Finally, as N_m is more or less constant and (S) and [S] are proportional to the weight percentages of sulfur in the slag and metal, respectively,

$$\frac{(\% \text{S})}{[\% \text{S}]} = N_s \left[A + B' \frac{(\text{CaO})_f}{(\text{FeO})} + C' \frac{(\text{MnO})}{(\text{FeO})} \right] \quad (28)$$

or, by substituting Eq. (24),

$$\frac{(\% \text{S})}{[\% \text{S}]} = N_s \left[A + B' \frac{(\text{CaO})_f}{(\text{FeO})} + C[\% \text{Mn}] \right] \quad (29)$$

From available laboratory data Darken and Larsen selected $A = 2.6$, $C = 11.0$ and $B' = 7.7$. Under the assumptions as to the molecular constitution of slags of $L > 2$, the number of moles of molecular components per unit weight of slag is

$$N_s = (\text{FeO}) + (\text{MnO}) + (\text{SiO}_2) + (\text{P}_2\text{O}_5) + (\text{CaO})_f \quad (30)$$

$(\text{CaO})_f$ was estimated by substituting Eq. (30) into Eq. (29) and, with the aid of laboratory and open hearth plant data for the ratio $(\% \text{S})/[\% \text{S}]$, plotting the thereby-calculated ratio $(\text{CaO})_f/(\text{CaO})'$, as a function of L . This variation is shown in Fig. 8.

With $L > 2$ the variation is adequately reproduced by

$$\frac{(\text{CaO})_f}{(\text{CaO})'} = 0.21(L - 2) \quad (31)$$

which indicates that, in essence, the free CaO contents of slags of $L < 2.0$ are zero, i.e. the extent of dissociation of the molecular species $2\text{CaO} \cdot \text{SiO}_2$ is negligible. Substitution of Eq. (31) into Eq. (29) and Eq. (30) gives

$$\frac{(\% \text{S})}{[\% \text{S}]} = N_s \left[2.6 + \frac{1.6(\text{CaO})'(L - 2)}{(\text{FeO})} + 11.0[\% \text{Mn}] \right] \quad (32)$$

and

$$N_s = (\text{FeO}) + (\text{MnO}) + (\text{SiO}_2) + (\text{P}_2\text{O}_5) + 0.21(L-2)(\text{CaO})' \quad (33)$$

After estimating the influence of carbon and manganese on the activity coefficient of sulfur in the metal Darken and Larsen plotted $(\%S)/[\%S]$, calculated from Eq. (32), against the sulfur ratios observed in the corresponding slag-metal couples. This variation is shown in Fig. 9.

With respect to the influence of the molecular constitution of the slag on the partitioning of sulfur, the following points were noted.

- (i) The ratio decreases with decreasing N_s and thus an increased concentration of SiO_2 leads to formation of complex silicate molecules, with a consequent decrease in N_s , which, in turn, decreases the extent of desulfurization.
- (ii) The sulfur ratio decreases with increasing L as SiO_2 , by combining with CaO to form calcium silicates, decreases the concentration of free CaO and, hence, the equilibrium concentration of CaS .

Fig. 8 provides a definite indication of the stability of $2\text{CaO}.\text{SiO}_2$ and an indication of the presence of molecules of $3\text{CaO}.\text{SiO}_2$. Darken and Larsen considered the extent of dissociation



for which

$$K = \frac{(\text{CaO}).(2\text{CaO}.\text{SiO}_2)}{N_s(3\text{CaO}.\text{SiO}_2)} \quad (34)$$

From the stoichiometry requirements

$$(\text{CaO})' = (\text{CaO}) + 2(2\text{CaO}.\text{SiO}_2) + 3(3\text{CaO}.\text{SiO}_2)$$

and

$$(\text{SiO}_2) = (2\text{CaO}.\text{SiO}_2) + (3\text{CaO}.\text{SiO}_2)$$

Eq. (34) can be written as

$$K = \frac{(\text{CaO}).(3\text{SiO}_2 - \text{CaO}' + \text{CaO})}{N_s(\text{CaO}' - 2\text{SiO}_2 - \text{CaO})}$$

in which case

$$(\text{SiO}_2) = \frac{[KN_s + (\text{CaO})].[(\text{CaO})' - (\text{CaO})]}{[3(\text{CaO}) + 2KN_s]}$$

and hence

$$L = \frac{\frac{3(\text{CaO})}{(\text{CaO})'} + 2KN_s}{[1 - \frac{(\text{CaO})}{(\text{CaO})'}][KN_s + \frac{(\text{CaO})}{(\text{CaO})'}]} \quad (35)$$

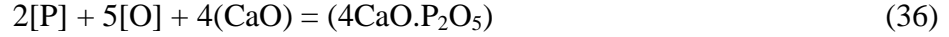
The variations of $(\text{CaO})/(\text{CaO})'$ with L for various values of K are shown in Fig. 8. The extremes are $K = \infty$ and $K = 0$, corresponding, respectively, to complete dissociation and no dissociation of $3\text{CaO} \cdot \text{SiO}_2$. The experimental points are best fitted with $K \sim 0.25$ which indicates that approximately half of the $3\text{CaO} \cdot \text{SiO}_2$ is dissociated.

In spite of this analysis Darken and Larsen concluded that their picture of the constitution of the liquid slag was sketchy and incomplete; that more information was required on such details as the solubilities of MgO and $2\text{CaO} \cdot \text{SiO}_2$, the dissociation of phosphates, silicates and ferrites and the forms assumed by Al_2O_3 , MgO and CaF_2 in the liquid slag.

In the foregoing approaches correlation of operating and laboratory data for the distribution of solutes between slag and metal was made possible by assuming molecular constitutions of the slags which produced Raoultian mixture of the molecular species. Feters and Chipman noted that, from a thermodynamic viewpoint, such assumptions are merely useful dodges which enable guesses to be made as to the magnitudes of the fundamental quantities such as chemical potentials and activities of the components of the slag. Consequently Chipman and his coworkers took the alternative approach of measuring fundamental thermodynamic quantities in laboratory experiments. Fig. 10 shows the variation of the measured activity of iron oxide with composition in the system $(\text{CaO} + \text{MgO})\text{-FeO-T-SiO}_2$ at $1600^\circ\text{C}^{(6,7)}$. In this study the activity of iron oxide was measured as the ratio of the oxygen content of liquid iron in equilibrium with a given slag to the oxygen content of liquid iron in equilibrium with “pure” liquid iron oxide. Chipman then attempted to deduce the molecular constitution of the slags from this measured behavior. Firstly, the symmetrical variation of a_{FeO} with composition about the section $(\text{Ca}, \text{Mg})_2\text{SiO}_4\text{-FeO}$ suggested that $(\text{Ca}, \text{Mg})_2\text{SiO}_4$ may be one of the more important molecular aggregates in the slag. The deviation of a_{FeO} from Raoultian ideality in the pseudo-binary $(\text{Ca}, \text{Mg})_2\text{SiO}_4\text{-FeO}$ (considered to comprise melts containing the molecular species Ca_2SiO_4 and FeO)⁽⁶⁾ was almost entirely eliminated by choosing the molecular species to be FeO and the double molecule $4\text{CaO} \cdot 2\text{SiO}_2$ ⁽⁷⁾. The effect of this change in the selection of the molecular species is shown in Fig. 11, in which the measured activity is plotted as a function of the molecular fraction of FeO , N_{FeO} , in the hypothetical melts. The negative deviations from Raoultian ideality observed in the system CaO-FeO were taken as being due to the formation of stable calcium ferrites in the slag. Taylor and Chipman considered that the iso-activity lines in Fig. 10 could be reasonably extrapolated to terminal points in the FeO-SiO_2 binary at which $a_{\text{FeO}} = N_{\text{FeO}}$, which, consequently, could be taken as indicating that any compound of FeO and SiO_2 is completely dissociated at 1600°C . The broken lines in Fig. 10 are drawn on the assumption that the melts are Raoultian mixtures of the molecular species $4\text{CaO} \cdot 2\text{SiO}_2$, FeO and SiO_2 . In highly basic melts, (of $\text{wt}\% \text{CaO}/\text{wt}\% \text{SiO}_2 > 4.6$), the measured activity of FeO shows significant negative deviation from that calculated assuming $4\text{CaO} \cdot 2\text{SiO}_2$, CaO and FeO as the only molecular species. This deviation was eliminated by considering the chemically-analysed Fe_2O_3 to occur in the melts as molecules of $\text{CaO} \cdot \text{Fe}_3\text{O}_4$. The variation of the measured a_{FeO} with

molecular fraction of FeO in melts of wt%CaO/wt%SiO₂ > 4.6, in which the assumed molecular species are 4CaO.2SiO₂, CaO.Fe₃O₄, CaO and FeO is shown in Fig. 12.

Analysis of the results of a subsequent study of the equilibrium distribution of phosphorus between liquid iron and basic slags force Winkler and Chipman to make further speculation as to the molecular constitution of slag⁽⁸⁾. Winkler and Chipman considered the equilibrium



for which

$$K_P = \frac{(a_{4CaO.P_2O_5})}{[a_P]^2 [a_O]^5 (a_{CaO})^4} = \frac{N'_{4CaO.P_2O_5}}{[%P]^2 [%O]^5 (N'_{CaO})} \quad (37)$$

where N'_i is the molecular fraction of the species i in the melt. According to the theories of slag constitution which assume no dissociation of complex molecules, the molecular fraction of free CaO, N'_{CaO} , is zero in slags of $N_{CaO}/N_{SiO_2} < 2$, and hence, it would be expected that such slags would not effect any dephosphorization of liquid iron. However, as Winkler and Chipman observed that phosphorus is absorbed by slags of $N_{CaO}/N_{SiO_2} < 2$, it appeared that calcium orthosilicate was not as stable as, hitherto, had been proposed. Winkler and Chipman assumed that calcium orthosilicate dissociates according to



for which

$$K_D = \frac{(N'_{2CaO.2SiO_2})(N'_{CaO})^2}{(N'_{4CaO.2SiO_2})} \quad (39)$$

such that, in acid slags, the phosphorus equilibrium could be written as



for which

$$K'_P = \frac{(N'_{4CaO.P_2O_5})(N'_{2CaO.2SiO_2})^2}{[%P]^2 [%O]^5 (N'_{4CaO.2SiO_2})} \quad (41)$$

Winkler and Chipman assumed the slags to be Raoultian mixtures of the molecular species 4CaO.2SiO₂, 2CaO.2SiO₂, CaO, 4CaO.P₂O₅, FeO, CaO.Fe₂O₃ and 4CaO.P₂O₅.CaF₂ and assumed that the chemical behavior of MnO and MgO is identical with that of CaO. In a series of successive approximations they sought the value of K_D which, in conjunction with the experimentally-determined values of [%P], [%O] and (%P₂O₅), would give constant values of K_P

and K'_P , and meet the requirement that $(K'_P/K_P)^{1/2} = K_D$. These iterations yielded a temperature-independent value of 0.01 for K_D and the variation of K_P with temperature shown in Fig. 13. An additional check on the internal consistency of the model was provided by comparing the calculated molecular fraction of FeO, N_{FeO} , in the hypothetical melts with the measured activities of FeO. This comparison is shown in Fig. 14 for melts in the pseudo-ternary system (CaO+MgO+MnO)-(SiO₂+2P₂O₅+1/2Fe₂O₃+1/2Al₂O₃)-FeO.

The natures of the approaches made by the various workers towards the determination of the molecular constitution of steelmaking slags are essentially identical; in each case a model was juggled to give agreement with observation. Thus, rather than the constitution of the slag being deduced from the observed behavior, a set of arbitrary assumptions was manipulated to reproduce the observed behavior. Comparison among the approaches of Schenck, Darken and Larsen and Chipman shows that the degree of success of any model in giving the required reproduction is not sensitive to the finer details of the assumed constitution or to the internal thermodynamic consistency of the model.

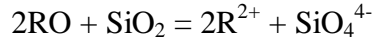
In discussing his model, Schenck noted that an applied science ought not to be afraid of assumptions, conjectures and certain limitations if it wants to attain the aim it has set for itself, namely, the elucidation of the process to such a degree that a technical need requires. Thus Schenck's stated primary goal was to formulate laws for metallurgical reactions which could be used satisfactorily under the most diverse works conditions. Similarly, although initially, Chipman considered assumptions as to the molecular constitution of slags to be merely useful dodges, he later expressed the opinion that the concept of a simple liquid slag, in which all the molecular species obey Raoult's law, offers advantages of simplicity in numerical calculation even if it requires the use of fictitious or improbable chemical formulae. Thus although definite compounds may not exist in the liquid state, the assumption of their formation at least affords a logical pattern for the attractions between slag components, which, in order to account for slag-metal reactions, must exist; the immediate usefulness of an assumption is not dependent on its ultimate truth.

The immediate usefulness of the assumptions was greatly appreciated by practical steelmakers who used the models as book-keeping systems for works practice. However, despite the simplicity of the concept of slags being Raoultian molecular solutions, the arithmetic complexity of the models, which, in the case of Schenck's model, required graphical presentation, led eventually to abandonment. (The arithmetic complexity can be appreciated by attempting to convert the data presented in Fig. 14 to the form of Fig. 5). In effect this arithmetic complexity was such that the models eventually offered no advantage over calculating and recording the activity coefficients of the components of the slag.

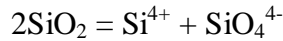
Early Ionic Models

In discussing his molecular model, Schenck noted that its theoretical value was decreased by the fact that electrolytic dissociation of the slag components was ignored. X-ray studies had shown that most metal oxides, salts and silicate consist of ions situated on well-defined lattice points and the existence of ions in the liquid state had been demonstrated in 1923 by Sauerwald and Neuendorff⁽⁹⁾ who successfully electrolyzed iron silicate melts, and in 1924 by Farup et

al.⁽¹⁰⁾ who measured the conductivities of melts in the systems CaO-SiO₂ and CaO-Al₂O₃-SiO₂. The assumption of electrolytic dissociation in metallurgical slags was first made in 1931 by Tamman⁽¹¹⁾ and the first application of an ionic theory of slags to the treatment of slag-metal equilibria was made in 1938 by Herasymenko⁽¹²⁾. In analyzing works data for the distribution of Mn and Si between steel and acid open-hearth slags, Herasymenko assumed that the slags were mixtures of Fe²⁺, Mn²⁺, Ca²⁺, Al³⁺ and SiO₄⁴⁻, and, for the purpose of calculating the ionic constitution, assumed that the SiO₂ occurring in excess of the requirement for



dissociated completely according to



In this electrochemical theory the activities of MnO, FeO and SiO₂ were taken as the fractions of all the ions occurring as Mn²⁺, Fe²⁺ and Si⁴⁺ respectively. The apparent success of this application of his theory was solely due to the fact that all of the slags were saturated with SiO₂ and that they varied very little in composition.

The first major advance in the application of ionic theory to thermodynamic analysis of slag-metal behavior was made by Temkin⁽¹³⁾ who considered that the electrostatic forces of ionic interaction in a mixture of fused salts are sufficiently strong that the arrangement of ions in the pure fused salts and in mixtures of salts are similar to those in the crystalline state, i.e. that cations are co-ordinated by anions and vice versa. Temkin thus defined an ideal mixture of fused salts as one in which the heat of mixing is zero and the free energy decrease accompanying mixing is due solely to the random mixing of cations on “cation sites” and anions on “anion sites”. As an example Temkin considered a mixture of n_1 moles of CaO, n_2 moles of FeO, n_3 moles of CaS and n_4 moles of FeS, which thus contains $(n_1 + n_3)$ moles of Ca²⁺, $(n_2 + n_4)$ moles of Fe²⁺, $(n_1 + n_2)$ moles of O²⁻ and $(n_3 + n_4)$ moles of S²⁻. With N_A denoting Avogadro's Number, the number of configurations available to the $(n_1 + n_2 + n_3 + n_4)$ moles of cations is

$$W_+ = \frac{[N_A(n_1 + n_2 + n_3 + n_4)]!}{[N_A(n_1 + n_3)]![N_A(n_2 + n_4)]!}$$

and the number of configurations available to the $(n_1 + n_2 + n_3 + n_4)$ moles of anions is

$$W_- = \frac{[N_A(n_1 + n_2 + n_3 + n_4)]!}{[N_A(n_1 + n_2)]![N_A(n_3 + n_4)]!}$$

Thus the configurations entropy of mixing, ΔS_{mix} , is

$$\Delta S_{\text{mix}} = k \ln W_+ W_-$$

which, with $\Delta H_{\text{mix}} = 0$, gives

$$\Delta G_{\text{mix}} = -T\Delta\Delta_{\text{mix}} = RT[n_1 \ln N_{\text{Ca}^{2+}} \cdot N_{\text{O}^{2-}} + n_2 \ln N_{\text{Fe}^{2+}} \cdot N_{\text{O}^{2-}} + n_3 \ln N_{\text{Ca}^{2+}} \cdot N_{\text{S}^{2-}} + n_4 \ln N_{\text{Fe}^{2+}} \cdot N_{\text{S}^{2-}}]$$

Thus, in a Temkin mixture of fused salts, the activity of a component salt, with respect to the pure fused salt is given by the product of the ion fractions of the ions into which it is presumed that the salt dissociates. The activity of the salt $A_a X_x$ in a Temkin mixture is thus

$$a_{A_a X_x} = N_{A^{z+}}^a \cdot N_{X^{z-}}^x \quad (42)$$

where $N_{A^{z+}}$ is the cation fraction of A^{z+} and $N_{X^{z-}}$ is the anion fraction of X^{z-} . In comparison with the expression for the activity of an electrolyte which, in aqueous solution, dissociates to yield \square_+ cations and \square_- anions, i.e.

$$a = a_+^{v_+} \cdot a_-^{v_-}$$

a Temkin mixture of fused salts is one in which $a_+ = N_+$ and $a_- = N_-$. However, there is no fixed standard state for an ion in a mixture of fused salts and thus, if the mixture does not exhibit Temkin ideality, only the product of the activities of the individual ions has physical significance. Temkin proposed that a definite significance can be assigned to the ratio of the activities of ions of the same sign, e.g. in the CaO-FeO-CaS-FeS mixture

$$\frac{a_{\text{O}^{2-}}}{a_{\text{S}^{2-}}} = \frac{a_{\text{O}^{2-}} \cdot a_{\text{Fe}^{2+}}}{a_{\text{S}^{2-}} \cdot a_{\text{Fe}^{2+}}} = \frac{a_{\text{FeO}}}{a_{\text{FeS}}} \quad (43)$$

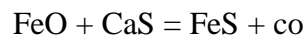
or

$$\frac{a_{\text{O}^{2-}}}{a_{\text{S}^{2-}}} = \frac{a_{\text{O}^{2-}} \cdot a_{\text{Ca}^{2+}}}{a_{\text{S}^{2-}} \cdot a_{\text{Ca}^{2+}}} = \frac{a_{\text{CaO}}}{a_{\text{CaS}}} \quad (44)$$

In aqueous solutions the definition of the activity of an electrolyte is based on the properties of infinitely dilution solutions, such that, for example, in infinitely dilute solutions of FeSO_4 and FeCl_2 the Fe^{2+} ion exists in the same state. However the Fe^{2+} ion in pure fused FeSO_4 is not in the same state as the Fe^{2+} ion in pure fused FeCl_2 . Thus the ionic activities of Fe^{2+} and Ca^{2+} cannot be cancelled, respectively, in Eqs. (43) and (44). Instead, the ratio of the activity of Fe^{2+} in a mixture relative to Fe^{2+} in pure FeO, to the activity of Fe^{2+} in the mixture relative to Fe^{2+} in pure FeS is some undeterminable constant, in which case Eqs. (43) and (44) must be written as

$$\frac{a_{\text{O}^{2-}}}{a_{\text{S}^{2-}}} \propto \frac{a_{\text{FeO}}}{a_{\text{FeS}}} \propto \frac{a_{\text{CaO}}}{a_{\text{CaS}}}$$

Consideration of the exchange reaction



For which the standard free energy change is ΔG° , gives $\exp(\Delta G^\circ/RT)$ as the proportionality constant between $a_{\text{FeO}}/a_{\text{FeS}}$ and $a_{\text{CaO}}/a_{\text{CaS}}$, i.e.

$$\frac{a_{\text{FeO}}}{a_{\text{FeS}}} = \frac{a_{\text{CaO}}}{a_{\text{CaS}}} \cdot \exp\left(\frac{\Delta G^\circ}{RT}\right)$$

Temkin defined the ionic activity coefficients as $\gamma_+ = \frac{a_+}{N_+}$ and $\gamma_- = \frac{a_-}{N_-}$, and, considering the normal definition of the activity coefficient of an electrolyte,

$$\gamma = (\gamma_+^{v_+} \cdot \gamma_-^{v_-})^{\frac{1}{v_+ + v_-}}$$

suggested the use of

$$\gamma = \frac{(a_+^{v_+} \cdot a_-^{v_-})^{\frac{1}{v_+ + v_-}}}{(N_+^{v_+} \cdot N_-^{v_-})^{\frac{1}{v_+ + v_-}}} = \frac{a^{\frac{1}{v_+ + v_-}}}{(N_+^{v_+} \cdot N_-^{v_-})^{\frac{1}{v_+ + v_-}}}$$

instead of

$$\gamma = \frac{a}{N_+^{v_+} \cdot N_-^{v_-}}$$

The assignment of a numerical value to an individual ionic activity or activity coefficient presumes that the energy of interaction between neighboring ions of different sign can be divided into a part which can be assigned to the cation and a part which can be assigned to the anion. Much confusion has arisen in the literature as a result of misuse of ionic activities and ionic activity coefficients.

The first application of Temkin's theory to slag-metal equilibrium was made by Samarin, Temkin and Scharzman⁽¹⁴⁾ who examined the results of six independent investigations of the distribution of sulfur between slag and metal. Assuming SiO_4^{4-} to be the only silicate ion occurring in CaO-FeO-SiO_2 melts of $(N_{\text{CaO}} + N_{\text{FeO}})/N_{\text{SiO}_2} > 2$, one mole of melt contains N_{FeO} moles of Fe^{2+} , N_{CaO} moles of Ca^{2+} , N_{SiO_2} moles of SiO_4^{4-} and $N_{\text{FeO}} + N_{\text{CaO}} - 2N_{\text{SiO}_2}$ moles of O^{2-} such that

$$N_{\text{Ca}^{2+}} = \frac{N_{\text{CaO}}}{N_{\text{CaO}} + N_{\text{FeO}}}, N_{\text{Fe}^{2+}} = \frac{N_{\text{FeO}}}{N_{\text{FeO}} + N_{\text{CaO}}}$$

$$N_{O^{2-}} = \frac{N_{CaO} + N_{FeO} - 2N_{SiO_2}}{N_{CaO} + N_{FeO} - N_{SiO_2}}, N_{SiO_4^{4-}} = \frac{N_{SiO_2}}{N_{CaO} + N_{FeO} - N_{SiO_2}}$$

The theoretical variations, with composition, of $a_{FeO} = N_{Fe^{2+}} \cdot N_{O^{2-}}$ and $a_{Ca_2SiO_4} = N_{Ca^{2+}}^2 \cdot N_{SiO_4^{4-}}$ are shown in Fig. 15, and it can be noted that the iso-activity lines for $a_{CaO} = N_{Ca^{2+}} \cdot N_{O^{2-}}$ and $a_{Fe_2SiO_4} = N_{Fe^{2+}}^2 \cdot N_{SiO_4^{4-}}$ are, respectively, the mirror images of the theoretical iso-activity lines of FeO and Ca_2SiO_4 about the line $N_{FeO}/N_{CaO} = 1$. Samarin et al. Considered the distribution of sulfur and metal by writing the equilibrium as

$$[FeS]_{metal} = (FeS)_{slag}$$

for which

$$K_s = \frac{(a_{FeS})}{[a_{FeS}]} = \frac{a_{Fe^{2+}} \cdot a_{S^{2-}}}{[a_{FeS}]} \quad (45)$$

and

$$[FeO]_{metal} = (FeO)_{slag}$$

for which

$$K_o = \frac{(a_{FeO})}{[a_{FeO}]} = \frac{a_{Fe^{2+}} \cdot a_{O^{2-}}}{[a_{FeO}]} \quad (46)$$

Dividing Eq. (45) by Eq. (46) and canceling the activity of Fe^{2+} gives

$$\frac{K_s}{K_o} = \frac{a_{S^{2-}}}{a_{O^{2-}}} \cdot \frac{[a_{FeO}]}{[a_{FeS}]}$$

and assuming Henrian behavior of the solutes in the metal phase and Temkin behavior of the slag phase gives

$$\frac{K_s}{K_o} = \frac{N_{S^{2-}}}{N_{O^{2-}}} \cdot \frac{[wt\%O]}{[wt\%S]}$$

Fetters and Chipman⁽⁶⁾ had determined that the oxygen content of liquid iron in equilibrium with liquid iron oxide at 1600°C is 0.23 wt %, and thus, with $K_o = 0.23$,

$$K_s = \frac{1}{0.23} \cdot \frac{N_{S^{2-}}}{N_{O^{2-}}} \cdot \frac{[wt\%O]}{[wt\%S]} \quad (47)$$

Samarin et al. divided the slag compositions studied by Fетters and Chipman into two groups; one in which $N_{\text{CaO}}/N_{\text{SiO}_2} > 3$ and, hence, in which it is fairly certain that silicon occurs exclusively as the SiO_4^{4-} ion, and one in which $N_{\text{CaO}}/N_{\text{SiO}_2} < 3$ and, hence, in which the assumption of SiO_4^{4-} as the sole silicate ion is less certain. In the former group, the application of Eq.(47) to the experimental data for 10 slag-metal equilibrations gave $K_S = 0.069 \pm 0.009$. Having thus calculated K_S from the distribution of oxygen and sulfur between metal and slag, Samarin et al. calculated K_S from the results of 4 independent investigations of the distribution of sulfur between slag and metal as

$$K_S = \frac{N_{\text{Fe}^{2+}} \cdot N_{\text{S}^{2-}}}{[\text{wt}\% \text{S}]}$$

and obtained values of 0.068, 0.078, 0.052 and 0.071. However, with slags of $(\text{wt}\% \text{SiO}_2) > 30$, the calculated values of K_S were considerably lower.

Comparison between the values of a_{FeO} in slags measured by Fетters and Chipman and the theoretical Temkin activities given by $N_{\text{Fe}^{2+}} \cdot N_{\text{O}^{2-}}$ is shown in Fig. 16.

Reciprocal Salt Mixtures

Consider mixing in the system FeO-CaS, for which the standard free energy change, G° , for the exchange reaction



is not zero. The mixing of N moles of FeO and $(1-N)$ moles of CaS produces a reciprocal salt mixture in which

$$N_{\text{FeO}} = N_{\text{Fe}^{2+}} \cdot N_{\text{O}^{2-}} = N^2$$

$$N_{\text{CaS}} = N_{\text{Ca}^{2+}} \cdot N_{\text{S}^{2-}} = (1-N)^2$$

$$N_{\text{FeS}} = N_{\text{Fe}^{2+}} \cdot N_{\text{S}^{2-}} = N(1-N)$$

and

$$N_{\text{CaO}} = N_{\text{Ca}^{2+}} \cdot N_{\text{O}^{2-}} = N(1-N)$$

Fig. 17. shows the variations, with N , of the mole fractions of the four species in the reciprocal salt mixture. Thus, if it is considered that, on mixing, N moles of FeO and $(1-N)$ moles of CaS “react” to form $N(1-N)$ moles each of FeS and CaO in accordance with Eq. (48), the nonconfigurational contribution to the molar free energy of mixing is $N(1-N) G^\circ$. If it is

considered further that random mixing of the cations and anions on their respective sub-lattices occurs, the configurational contribution to the free energy of mixing is

$$RT[N^2 \ln N^2 + (1-N)^2 \ln(1-N)^2 + 2N(1-N) \ln N(1-N)]$$

giving, thus, as the total molar free energy of mixing

$$\begin{aligned} \Delta G^M &= N(1-N)\Delta^\circ + 2RT[N^2 \ln N + (1-N)^2 \ln(1-N) + (N(1-N) \ln N(1-N))] \\ &= N(1-N)\Delta^\circ + 2RT[N \ln N + (1-N) \ln(1-N)] \end{aligned} \quad (49)$$

For a system in which G° is positive, Eq. (49) indicates that liquid immiscibility occurs when $G^\circ > 4RT$. From Eq.(49),

$$\begin{aligned} \Delta \bar{G}_{FeO}^M &= RT \ln a_{FeO} = \Delta G^M + (1-N) \frac{\partial \Delta G^M}{\partial N} \\ &= (1-N)^2 \Delta G^\circ + RT \ln N^2 \end{aligned}$$

or

$$a_{FeO} = N^2 \exp[(1-N)^2 \frac{\Delta G^\circ}{RT}] \quad (50)$$

$$= N_{Fe^{2+}} \cdot N_{O^{2-}} \cdot \exp[N_{Ca^{2+}} \cdot N_{S^{2-}} \cdot \frac{\Delta G^\circ}{RT}] \quad (51)$$

and similarly,

$$\begin{aligned} \Delta \bar{G}_{CaS}^M &= RT \ln a_{CaS} = \Delta G^M - N \frac{\partial \Delta G^M}{\partial N} \\ &= N^2 \Delta G^\circ + RT \ln(1-N)^2 \end{aligned}$$

or

$$a_{CaS} = (1-N)^2 \exp[N^2 \cdot \frac{\Delta G^\circ}{RT}] \quad (52)$$

$$= N_{Ca^{2+}} \cdot N_{S^{2-}} \cdot \exp[N_{Fe^{2+}} \cdot N_{O^{2-}} \cdot \frac{\Delta G^\circ}{RT}] \quad (53)$$

Furthermore, from Eq. (49),

$$\frac{a_{CaS} \cdot a_{FeS}}{a_{FeO} \cdot a_{CaS}} = \exp[-\frac{\Delta G^\circ}{RT}]$$

and substitution from Eqs. (50) and (51) gives

$$a_{\text{CaS}} \cdot a_{\text{FeS}} = N^2 (1 - N)^2 \exp[-2N(1 - N) \frac{\Delta G^0}{RT}]$$

and hence

$$a_{\text{CaO}} = a_{\text{FeS}} = N(1 - N) \exp[-N(1 - N) \frac{\Delta G^0}{RT}] \quad (54)$$

Eqs. (51), (53) and (54) were first derived by Flood, Forland and Grjotheim^(15,16).

In considering ionic mixtures containing ions of differing charge, Flood et al. introduced the concept of electrically-equivalent ion fractions. In a mixture of A^+ , B^{2+} , C^{3+} , X^- , Y^{2-} , Z^{3-} , the electrically-equivalent ion fractions, N'_i , are

$$N'_{A^+} = \frac{n_{A^+}}{n_{A^+} + 2n_{B^{2+}} + 3n_{C^{3+}}}$$

$$N'_{B^{2+}} = \frac{2n_{B^{2+}}}{n_{A^+} + 2n_{B^{2+}} + 3n_{C^{3+}}}$$

$$N'_{X^-} = \frac{n_{X^-}}{n_{X^-} + 2n_{Y^{2-}} + 3n_{Z^{3-}}}$$

$$N'_{Z^{3-}} = \frac{3n_{Z^{3-}}}{n_{X^-} + 2n_{Y^{2-}} + 3n_{Z^{3-}}}$$

etc. and the equivalent fraction of the component AX is

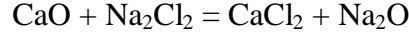
$$N'_{AX} = N'_{A^+} \cdot N'_{X^-}$$

Thus, in a mixture of N moles of CaCl_2 and $(1-N)$ moles of NaCl , the equivalent fraction of CaCl_2 is

$$N'_{\text{CaCl}_2} = N'_{\text{Ca}^{2+}} \cdot N'_{\text{Cl}^-} = \frac{2N}{1 + N}$$

However, if the binary components were chosen as $\text{Ca}_{0.5}\text{Cl}$ and NaCl , the melt would contain $2N$ moles of $\text{Ca}_{0.5}\text{Cl}$ and $(1-N)$ moles of NaCl , and the mole fraction of $\text{Ca}_{0.5}\text{Cl}$ would be $2N/(1+N)$. Thus, the equivalent fractions of CaCl_2 and NaCl in the system $\text{CaCl}_2\text{-NaCl}$ are simply the mole fractions of $\text{Ca}_{0.5}\text{Cl}$ and NaCl in the system $\text{Ca}_{0.5}\text{Cl-NaCl}$.

Consider mixing of M moles of the component CaO and $(1-M)$ moles of the component Na_2Cl_2 , which undergo the exchange reaction



Derivation, as before, gives

$$\overline{G}_{\text{CaO}}^{\text{xs}} = (1 - M)^2 \Delta G^\circ \quad (55)$$

M moles of CaO and $(1-M)$ moles of Na_2Cl_2 are equivalent to a mixture of the components CaO and NaCl in which N_{CaO} , the mole fraction of CaO, is $M/(2-M)$ and N_{NaCl} , the mole fraction of NaCl, is $(2-2M)/(2-M)$. Thus

$$M = \frac{2N_{\text{CaO}}}{1 + N_{\text{CaO}}}$$

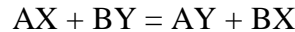
and the term $(1-M)^2$ in Eq. (55) becomes $[(1-N)/(1+N)]^2$, which is the equivalent fraction of NaCl in the CaO-NaCl- CaCl_2 - Na_2O reciprocal mixture. Thus, in a mixture of N moles of CaO and $(1-N)$ moles of NaCl,

$$\overline{G}_{\text{CaO}}^{\text{xs}} = N'_{\text{Na}^+} \cdot N'_{\text{Cl}^-} \cdot \Delta \Delta^\circ$$

and hence

$$a_{\text{CaO}} = N_{\text{Ca}^{2+}} \cdot N_{\text{O}^{2-}} \cdot \exp[N'_{\text{Na}^+} \cdot N'_{\text{Cl}^-} \cdot \exp \frac{\Delta G^\circ}{RT}]$$

Generally, in a reciprocal salt mixture which undergoes the exchange reaction



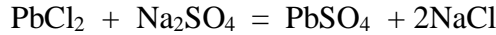
$$a_{\text{AX}} = N_{\text{A}^{z+}} \cdot N_{\text{X}^{z-}} \cdot \exp[N'_{\text{B}^{z+}} \cdot N'_{\text{Y}^{z-}} \cdot \exp \frac{\Delta G^\circ}{RT}] \quad (56)$$

Non-ideal behavior was accounted for by Flood et al. by the inclusion of the activity coefficients γ_{A} and γ_{X} in Eq. (54). These activity coefficients are obtained from consideration of the behavior in the pseudo-binary system $\text{A}(\text{X}, \text{Y}) - \text{B}(\text{X}, \text{Y})$, i.e. a mixture in which the ratio $N_{\text{X}}/N_{\text{Y}}$ is constant, and $(\text{A}, \text{B})\text{X} - (\text{A}, \text{B})\text{Y}$, i.e. a mixture in which the ratio $N_{\text{A}}/N_{\text{B}}$ is constant. The activity coefficient γ_{A} is the activity coefficient of the component $\text{A}(\text{X}, \text{Y})$ in the pseudo-binary $\text{A}(\text{X}, \text{Y}) - \text{B}(\text{X}, \text{Y})$ and γ_{X} is the activity coefficient of the component $(\text{A}, \text{B})\text{X}$ in the pseudo-binary $(\text{A}, \text{B})\text{X} - (\text{A}, \text{B})\text{Y}$.

In analyzing their experimental data for the activity of PbCl_2 in the reciprocal salt system $\text{PbCl}_2 - \text{Na}_2\text{SO}_4$, Bloom and Welch⁽¹⁷⁾ arbitrarily wrote Eq. (56) as

$$a_{\text{PbCl}_2} = N_{\text{Pb}^{2+}} \cdot N_{\text{Cl}^-}^2 \cdot \gamma_{\text{Pb}^{2+}} \cdot \gamma_{\text{Cl}^-}^2 \cdot \exp\left[N'_{\text{Na}^+} \cdot N'_{\text{SO}_4^{2-}} \cdot \frac{\Delta G^\circ}{RT}\right] \quad (57)$$

i.e. substituted individual activity ionic activity coefficients for the activity coefficients of the pseudo-binary components of Flood et al. At their experimental temperature of 1003 K, ΔG° for the reaction



is 20 kJ, and, hence, in a mixture of N moles of PbCl_2 and $(1-N)$ moles of Na_2SO_4 , Eq. (56) gives

$$a_{\text{PbCl}_2} = \left(\frac{N}{2-N}\right)\left(\frac{2N}{1+N}\right)\exp[2.4(1-N)^2] \quad (58)$$

which is shown in comparison with the experimentally-measured variation of the activity of PbCl_2 in Fig. 18. As Bloom and Welch considered the discrepancy between the theoretical and the measured behavior to be beyond the limits of experimental error, they ascribed the discrepancy to incomplete formulation of Eq. (56) by Flood et al. They pointed out that although Flood et al. assumed the non-configurational contribution to the free energy of mixing to be due entirely to the exchange reaction, Hildebrand and Salstrom⁽¹⁸⁾ had observed regular solution behavior in the systems $\text{AgBr}-\text{Alk Br}$ where $\text{Alk} = \text{Li}, \text{Na}$ and K , i.e. in fused salt mixtures containing a common anion and, hence, in which an exchange reaction could not occur. Bloom and Welch thus suggested that regular solution behavior in mixtures of AX and BX could be described by

$$RT \ln \gamma_{A^{z+}} = b N_{B^{z+}}^2 \quad (59)$$

where $\gamma_{A^{z+}}$ is the activity coefficient of A^{z+} and b is a constant for the system, which is independent of temperature. Similarly, regular solution behavior in the system $\text{AX}-\text{AY}$ could be described by

$$RT \ln \gamma_{X^{z-}} = b' N_{Y^{z-}}^2 \quad (60)$$

Thus, assuming a “regular solution” interaction in reciprocal salt solutions between the two types of cation and between the two types of anion, Bloom and Welch substituted Eqs. (59) and (60) into Eq. (57) to give

$$a_{\text{PbCl}_2} = N_{\text{Pb}^{2+}} \cdot N_{\text{Cl}^-}^2 \cdot \exp\left[\frac{\Delta G^\circ \cdot N'_{\text{Na}^+} \cdot N'_{\text{SO}_4^{2-}} + b N_{\text{Na}^+}^2 + 2b' N_{\text{SO}_4^{2-}}^2}{RT}\right] \quad (61)$$

By curve-fitting with their experimental data they derived $b = 50$ and $b' = 500$ to give the fit shown in Fig. 18. As is seen, the difference between Eq. (58) and Eq. (61) is insignificant. Fig. 19 shows the activity of PbCl_2 in the system $\text{NaCl} - \text{PbSO}_4$ at 1003 K along with the theoretical curves and, in this system Eq. (58) actually provides a better fit to the data than does Eq. (61).

The activity of CdCl_2 in the system $\text{CdCl}_2-\text{Na}_2\text{SO}_4$, measured at 1003 K by Bloom and

Welch is shown in Fig. 20. In this system the free energy change for the exchange reaction is + 46 kJ and Bloom and Welch showed that the data are fairly closely reproduced by Eq.(59) with $b' = +500$ (the value for anion mixing in the system $\text{PbCl}_2\text{-Na}_2\text{SO}_4$) and $b = -4000$.

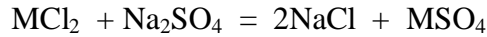
In considering mixing in reciprocal systems in which G° is not zero Eq (49) shows that the excess molar free energy of mixing, G^{xs} , given by $G^{xs} = N(1-N) G^\circ$ has the parabolic form characteristic of regular solution behavior. Consequently, the activity coefficients in a system such as $\text{MCl}_2 - \text{Na}_2\text{SO}_4$ are given as

$$\ln \gamma_{\text{MCl}_2} = (1 - N)^2 \frac{\Delta G^\circ}{RT}$$

and

$$\ln \gamma_{\text{Na}_2\text{SO}_4} = N^2 \frac{\Delta G^\circ}{RT}$$

and the term G°/RT can be formally identifies as a regular solution interaction parameter. As random mixing of the cations and anions is the underlying assumption in all of the ionic models, the validity of the theoretical assumptions decreases as the magnitude of G°/RT increases. With a positive value of G° for an exchange reaction of the type



the preferred ionic associations in the melt are M^{2+} with the Cl^- and Na^+ with the SO_4^{2-} . The activity coefficients of MCl_2 and Na_2SO_4 become greater than unity and the activity coefficients of NaCl and MSO_4 , given by Eq. (54) as

$$\ln \gamma_{\text{NaCl}} = \ln \gamma_{\text{MSO}_4} = -N(1 - N) \frac{\Delta G^\circ}{RT}$$

become less than unity. With an exchange free energy of 46 kJ at 1003 K it is not to be expected that the measured behavior could be reproduced by a model in which random mixing is assumed. Furthermore, the inclusion of additional regular solution parameters, as in Eq. (61), gives theoretical activities of MCl_2 and Na_2SO_4 which obey the Gibbs-Duhem relationship only when $b = b' = 0$.

As $\Delta G^\circ > 4RT$ in the system $\text{CdCl}_2 - \text{Na}_2\text{SO}_4$, the equation of Flood et al. predicts a liquid immiscibility gap as shown in Fig. 20. Also, as is seen in Fig. 20, the experimental data are reasonably approximated by assuming simple Temkin mixing.

Flood and Grjotheim's Treatment of Slag-Metal Equilibria

Flood and Grjotheim's treatment of slag-metal equilibria⁽¹⁹⁾ was developed as an application of an earlier theoretical treatment by Flood and Muan⁽²⁰⁾, of the relationship between an anion exchange equilibrium quotient and the cation composition of a molten salt. The original

treatment of slag-metal equilibria has been criticized⁽²¹⁾ and supported⁽²³⁻²⁵⁾. As the criticism arose, in part, from possible ambiguities in word usage in the original publication, an attempt is made to eliminate these ambiguities in the following derivation.

Consider the distribution of Mn between liquid iron and a melt in the system FeO-MnO-SiO₂. If it is assumed that O²⁻ and SiO₄⁴⁻ are the only anionic species occurring in the melts consideration is restricted to melts of $N_{\text{SiO}_2} \leq 1/3$, in which case it is convenient to consider that the melt exists in the reciprocal system FeO-Mn(SiO₄)_{0.5}–MnO-Fe(SiO₄)_{0.5}. Any melt in the reciprocal system can be considered as a pseudo-binary mixture of the components Fe(A) and Mn(A) and the slag-metal equilibrium of interest can be written as



Flood and Grjotheim's treatment consists of consideration of the following cycle.

- (1) With the slag and metal at equilibrium, one mole of Fe is reversibly transferred from the slag to the metal and one mole of Mn is reversibly transferred in the reverse direction in accordance with Eq. (62). The quantities of slag and metal considered are sufficiently large that this transfer reaction does not measurably change the composition of either phase.
- (2) One mole of the pseudo-binary component Mn(A) is reversibly extracted from the large quantity of Fe(A)-Mn(A) pseudo-binary mixture.
- (3) The mole of Mn(A) is reversibly unmixed to produce its components pure MnO and pure Mn(SiO₄)_{0.5}.
- (4) One mole of Fe is reversibly extracted from the large quantity of metal phase.
- (5) The unmixed pure MnO is reacted with the stoichiometric amount of pure unmixed Fe to produce pure FeO and Mn (in the 1wt% standard state in Fe), and the unmixed Mn(SiO₄)_{0.5} is reacted with the stoichiometric amount of pure unmixed Fe to produce pure Fe(SiO₄)_{0.5} and Mn (in the 1 wt% standard state in Fe).
- (6) The pure FeO and Fe(SiO₄)_{0.5}, formed in step 5, are reversibly mixed to form one mole of Fe(A).
- (7) The mole of Fe(A), formed in step 6, is reversibly added to the large quantity of Fe(A)-Mn(A) pseudo-binary mixture.
- (8) The mole of Mn, formed in step 5, is transferred from the 1 wt% standard state in Fe to its equilibrium concentration in the large quantity of metal phase.

As steps 1-8 represent a cycle, the overall change in free energy is zero.

Step 1. As the reaction is conducted reversibly at reaction equilibrium, $G_1 = 0$.

Step 2. The free energy change is the negative of the partial molar free energy of mixing of Mn(A) in the pseudo-binary mixture Fe(A)-Mn(A).

$$\Delta G_2 = -\Delta \bar{G}_{\text{Mn(A)}}^{\text{M}} = -RT \ln a_{\text{Mn(A)}}$$

As the anion constitution of (A) is constant in the pseudo-binary system, the mole fraction of Mn(A) equals $N_{\text{Mn}^{2+}}$ in the pseudo-binary mixture, and, with $a_{\text{Mn(A)}}$ being the activity coefficient of Mn(A) in the pseudo-binary mixture with reference to pure Mn(A) as the standard state

$$\Delta G_2 = -RT \ln N_{\text{Mn}^{2+}} \cdot \gamma_{\text{Mn(A)}}$$

Step 3. The free energy change is the negative of the molar free energy of formation of Mn(A) from its components MnO and Mn(SiO₄)_{0.5}. From the relationship between mole fractions and electrically-equivalent ion fractions, as Mn²⁺ is the sole cation species and it is assumed that O²⁻ and SiO₄⁴⁻ are the sole anionic species,

$$N_{\text{MnO}} = N'_{\text{O}^{2-}}$$

and

$$N_{\text{Mn(SiO}_4\text{)}_{0.5}} = N'_{\text{SiO}_4^{4-}}$$

Thus

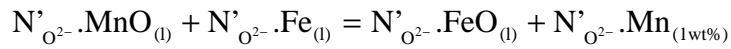
$$\begin{aligned} \Delta G_3 &= -RT [N'_{\text{O}^{2-}} \cdot \ln a_{\text{MnO}} + N'_{\text{SiO}_4^{4-}} \cdot \ln a_{\text{Mn(SiO}_4\text{)}_{0.5}}] \\ &= -RT [N'_{\text{O}^{2-}} \cdot \ln a_{\text{Mn}^{2+}} \cdot a_{\text{O}^{2-}} + N'_{\text{SiO}_4^{4-}} \cdot \ln a_{\text{Mn}^{2+}} \cdot a_{\text{SiO}_4^{4-}}^{0.5}] \\ &= -RT [N'_{\text{O}^{2-}} \cdot \ln N_{\text{O}^{2-}} \cdot \gamma_{\text{MnO}}^* + N'_{\text{SiO}_4^{4-}} \cdot \ln N_{\text{SiO}_4^{4-}}^{0.5} \cdot \gamma_{\text{Mn(SiO}_4\text{)}_{0.5}}^*] \end{aligned}$$

where γ_{MnO}^* is the activity coefficient of MnO in Mn(A) relative to pure MnO as the standard state and $\gamma_{\text{Mn(SiO}_4\text{)}_{0.5}}^*$ is the activity coefficient for Mn(SiO₄)_{0.5} in Mn(A) relative to pure Mn(SiO₄)_{0.5} as the standard state.

Step 4. The free energy change is the negative of the partial molar free energy of mixing of Fe in the metal phase.

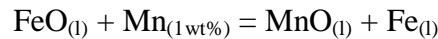
$$\Delta G_4 = -\Delta \bar{G}_{\text{Fe}}^{\text{M}} = -RT \ln a_{\text{Fe}}$$

Step 5. For the reaction

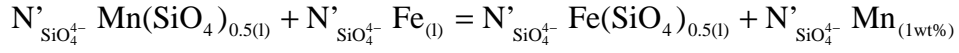


$$\Delta G = -N'_{\text{O}^{2-}} \cdot \Delta \Delta_{\text{O}}^{\circ} = -RT \ln K_{\text{O}}$$

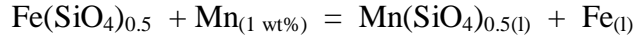
where $\Delta G_{\text{O}}^{\circ}$ and K_{O} are, respectively, the standard free energy change and the equilibrium constant for the reaction



Similarly for



where $\Delta G_{\text{SiO}_4}^o$ and K_{SiO_4} are, respectively, the standard free energy change and the equilibrium constant for the reaction



Thus

$$\Delta G_5 = N'_{\text{O}^{2-}} \cdot RT \ln K_{\text{O}} + N'_{\text{SiO}_4^{4-}} \cdot RT \ln K_{\text{SiO}_4}$$

Step 6 The free energy change is the molar free energy of formation of Fe(A) from its components FeO and $\text{Fe}(\text{SiO}_4)_{0.5}$.

$$\begin{aligned} \Delta G_6 &= RT [N'_{\text{O}^{2-}} \cdot \ln a_{\text{FeO}} + N'_{\text{SiO}_4^{4-}} \cdot \ln a_{\text{Fe}(\text{SiO}_4)_{0.5}}] \\ &= RT [N'_{\text{O}^{2-}} \cdot \ln N_{\text{O}^{2-}} \cdot \gamma_{\text{FeO}}^* + N'_{\text{SiO}_4^{4-}} \cdot \ln N_{\text{SiO}_4^{4-}}^{0.5} \cdot \gamma_{\text{Fe}(\text{SiO}_4)_{0.5}}^*] \end{aligned}$$

Step 7. The free energy change is the partial molar free energy of mixing of Fe(A) in the pseudo-binary mixture Fe(A)-Mn(A)

$$\Delta G_7 = RT \ln a_{\text{Fe(A)}} = RT \ln N_{\text{Fe}^{2+}} \cdot \gamma_{\text{Fe(A)}}$$

Step 8. The free energy change is that for the transfer of 1 mole of Mn from the 1 wt% standard state in Fe to the activity h_{Mn} at which it is in equilibrium with the given slag.

$$\Delta G_8 = RT \ln h_{\text{Mn}}$$

The sum of the free energy changes is zero and rearrangement gives

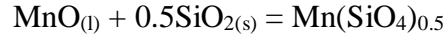
$$\ln \frac{N_{\text{Mn}^{2+}} \cdot a_{\text{Fe}}}{N_{\text{Fe}^{2+}} \cdot h_{\text{Mn}}} = N'_{\text{O}^{2-}} \cdot \ln K_{\text{O}} + N'_{\text{SiO}_4^{4-}} \cdot \ln K_{\text{SiO}_4} + N'_{\text{O}^{2-}} \cdot \ln \frac{\gamma_{\text{FeO}}^*}{\gamma_{\text{MnO}}} + N'_{\text{SiO}_4^{4-}} \cdot \ln \frac{\gamma_{\text{Fe}(\text{SiO}_4)_{0.5}}^*}{\gamma_{\text{Mn}(\text{SiO}_4)_{0.5}}} + \ln \frac{\gamma_{\text{Fe(A)}}}{\gamma_{\text{Mn(A)}}} \quad (63)$$

as the variation of h_{Mn} , and hence [wt% Mn], with slag composition. If all of the binary and pseudo-binary system considered are Temkin ideal mixtures, all of the activity coefficients are zero and Eq. (63) indicates that the distribution of Mn and Fe (which exist as cation in the slag) between the slag and metal is determined solely by the anion composition as quantified by $N'_{\text{O}^{2-}}$ and $N'_{\text{SiO}_4^{4-}}$.

The application of Eq. (63) can be illustrated as follows. Consider an FeO-MnO-SiO₂ slag in which $N'_{O^{2-}} = N'_{SiO_4^{4-}} = 0.5$, i.e. Fe(A) is the melt in the system FeO-Fe(SiO₄)_{0.5} of $N_{FeO} = N_{Fe(SiO_4)_{0.5}} = 0.5$ and Mn(A) is the melt in the system MnO-Mn(SiO₄)_{0.5} of $N_{MnO} = N_{Mn(SiO_4)_{0.5}} = 0.5$. Fe(A) thus contains FeO and SiO₂ in the molar ratio 1/0.25 and thus is the composition $N_{FeO} = 0.8$, $N_{SiO_2} = 0.2$ in the system FeO-SiO₂. Similarly Mn(A) is the composition $N_{MnO} = 0.8$, $N_{SiO_2} = 0.2$ in the system MnO-SiO₂. In the system MnO-SiO₂ at 1600°C, at $N_{MnO} = 2/3$ ⁽²⁶⁾, a_{MnO} (relative to liquid MnO) = 0.31 and a_{SiO_2} (relative to solid SiO₂) = 0.16. Therefore, the molar free energy of formation of a manganese silicate melt of orthosilicate composition from liquid MnO and solid SiO₂ is

$$\Delta G^M = 8.3144 \times 1873 [0.667 \ln 0.31 + 0.333 \ln 0.16] = -21,670 J = \frac{1}{3} \Delta G_{Mn_2SiO_4}^o = \frac{2}{3} \Delta G_{Mn(SiO_4)_{0.5}}^o$$

Thus, for the reaction

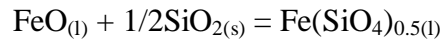


$$\Delta G_{Mn(SiO_4)_{0.5}}^o (1873K) = -32,500J \quad (64)$$

In the system FeO-SiO₂ at 1600°C, at $N_{FeO} = 2/3$ ⁽²⁷⁾, a_{FeO} (relative to Fe-saturated liquid FeO) = 0.59 and a_{SiO_2} (relative to solid SiO₂) = 0.51. Therefore the molar free energy of formation of an iron silicate melt of orthosilicate composition from liquid FeO and solid SiO₂ is

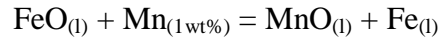
$$\Delta G^M = -8,900J = \frac{2}{3} \Delta G_{Fe(SiO_4)_{0.5}}^o$$

such that, for the reaction



$$\Delta G_{Fe(SiO_4)_{0.5}}^o (1873K) = -13,460J \quad (65)$$

For the reaction



$$\Delta G_o^o (1873K) = -22,700J \quad (66)$$

and combination of Eqs. (64), (65) and (66) gives

$$\Delta G_{SiO_4}^o (1873K) = -41,700J$$

Thus

$$\ln K_o(1873K) = 1.46$$

and

$$\ln K_{SiO_4}(1873K) = 2.68$$

In the system MnO-SiO₂ at 1600°C and $N_{MnO} = 0.8^{(26)}$, a_{MnO} (relative to liquid MnO) = 0.66 and a_{SiO_2} (relative to solid SiO₂) = 0.025. Thus, in this melt

$$a_{Mn(SiO_4)_{0.5}} = \frac{a_{MnO} \cdot a_{SiO_2}^{0.5} (at N_{MnO} = 0.8)}{a_{MnO} \cdot a_{SiO_2}^{0.5} (at N_{MnO} = 2/3)} = \frac{0.66}{0.31} \left(\frac{0.025}{0.16} \right)^{0.5} = 0.84$$

One mole of this melt contains 0.8 moles of MnO and 0.2 moles of SiO₂. Assuming that O²⁻ and SiO₄⁴⁻ are the sole anionic specie, the mole of melt contains 0.4 moles of O²⁻ and 0.2 moles of SiO₄⁴⁻, in which case $N_{O^{2-}} = 2/3$ and $N_{SiO_4^{4-}} = 1/3$ with $N'_{O^{2-}} = 0.5$ and $N'_{SiO_4^{4-}} = 0.5$. Thus, in the melt Mn(A)

$$a_{MnO} = 0.66 = N_{O^{2-}} \cdot \gamma_{MnO}^*$$

such that

$$\gamma_{MnO}^* = 1.5 \times 0.66 = 0.99$$

and

$$a_{Mn(SiO_4)_{0.5}} = 0.84 = N_{SiO_4}^{0.5} \cdot \gamma_{Mn(SiO_4)_{0.5}}^*$$

such that

$$\gamma_{Mn(SiO_4)_{0.5}}^* = \sqrt{3} \times 0.84 = 1.45$$

In the system FeO-SiO₂ at 1600°C and $N_{FeO} = 0.8^{(27)}$ a_{FeO} (relative to Fe-saturated liquid FeO) = 0.82 and a_{SiO_2} (relative to solid SiO₂) = 0.2. In this melt,

$$a_{Fe(SiO_4)_{0.5}} = \frac{0.82}{0.59} \left(\frac{0.2}{0.51} \right)^{0.5} = 0.87$$

and thus

$$\gamma_{FeO}^* = 1.5 \times 0.82 = 1.23$$

and

$$\gamma_{Fe(SiO_4)_{0.5}}^* = \sqrt{3} \times 0.87 = 1.51$$

It has been determined experimentally^(28,29) that melts in the system $MnO.ySiO_2$ - $FeO.ySiO_2$ are ideal solutions of the pseudo-binary components and hence $\gamma_{Fe(A)}$ and $\gamma_{Mn(A)}$ are unity. Therefore, in Eq. (61)

$$\ln \frac{N_{Mn^{2+}} \cdot a_{Fe}}{N_{Fe^{2+}} \cdot h_{Mn}} = (0.5 \times 1.46) + (0.5 \times 2.68) + (0.5 \ln \frac{1.23}{0.99}) + (0.5 \ln \frac{1.51}{1.45}) = 2.2$$

For an equimolar Fe(A)-Mn(A) melt, i.e. $N_{FeO} = N_{MnO} = 0.4$, $N_{SiO_2} = 0.2$ and $a_{Fe} \sim 1$ this gives

$$h_{Mn} = [wt\% Mn] = 0.11$$

and if Temkin mixing were assumed in all of the binary slag systems, $[wt\% Mn]$ would be calculated as 0.13. The experimentally-determined values at 1500°C and 1560°C are, respectively, 0.15⁽²⁸⁾ and 0.14⁽²⁹⁾.

If cationic species other than Fe^{2+} and Mn^{2+} are present in the slag, e.g. Ca^{2+} and Mg^{2+} , the slag is no longer a pseudo-binary mixture of Fe(A) and Mn(A). Consequently, steps 2 and 7 in the thermodynamic cycle are omitted and step 3 becomes the reversible extraction of $N'_{O^{2-}}$ moles of MnO and $N'_{SiO_4^{4-}}$ moles of $Mn(SiO_4)_{0.5}$ from the actual slag, for which

$$\Delta G_3 = -RT [N'_{O^{2-}} \ln N_{Mn^{2+}} \cdot N_{O^{2-}} \cdot \gamma_{MnO} + N'_{SiO_4^{4-}} \ln N_{Mn^{2+}} N_{SiO_4^{4-}}^{0.5} \cdot \gamma_{Mn(SiO_4)_{0.5}}]$$

Similarly, step 6 becomes the reversible addition of $N'_{O^{2-}}$ moles of FeO and $N'_{SiO_4^{4-}}$ moles of $Fe(SiO_4)_{0.5}$ to the actual slag, for which

$$\Delta G_6 = RT [N'_{O^{2-}} \ln N_{Fe^{2+}} \cdot N_{O^{2-}} \cdot \gamma_{FeO} + N'_{SiO_4^{4-}} \ln N_{Fe^{2+}} N_{SiO_4^{4-}}^{0.5} \cdot \gamma_{Fe(SiO_4)_{0.5}}]$$

Consequently, Eq. (63) becomes

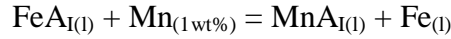
$$\ln \frac{N_{Mn^{2+}} \cdot a_{Fe}}{N_{Fe^{2+}} \cdot [wt\% Mn]} = N'_{O^{2-}} \ln K_O + N'_{SiO_4^{4-}} \ln K_{SiO_4} + N'_{O^{2-}} \cdot \ln \frac{\gamma_{FeO}}{\gamma_{MnO}} + N'_{SiO_4^{4-}} \ln \frac{\gamma_{Fe(SiO_4)_{0.5}}}{\gamma_{Mn(SiO_4)_{0.5}}} \quad (67)$$

in which the activity coefficients are those of the components in the actual slag relative to the pure components as standard states. In the general case of a multicomponent slag containing fluorides, sulfides, phosphates and ferrites, in addition to the oxides and silicates, it is presumed that F^- is the fluoride ion, S^{2-} is the sulfide ion, PO_4^{3-} is the sole phosphate ion and FeO_3^{3-} is the sole ferrite ion. Then, in step 3 of the cycle, N'_{F^-} moles of MnF_2 , $N'_{O^{2-}}$ moles of MnO, $N'_{S^{2-}}$ moles of MnS, $N'_{PO_4^{3-}}$ moles of $Mn(PO_4)_{2/3}$, $N'_{FeO_3^{3-}}$ moles of $Mn(FeO_3)_{2/3}$ and $N'_{SiO_4^{4-}}$ moles of $Mn(SiO_4)_{0.5}$ are reversibly extracted from the slag as pure components, and in step 6 N'_{F^-} moles

of FeF_2 , $N'_{\text{O}^{2-}}$ moles of FeO , etc are reversibly added to the slag. In step 5 the pure manganese compounds are reacted with pure Fe to form the pure iron compounds and Mn in the 1 wt% in Fe standard state. In generalized form, Eq. (67) becomes

$$\ln \frac{N_{\text{Mn}^{2+}} \cdot a_{\text{Fe}}}{N_{\text{Fe}^{2+}} \cdot [\text{wt}\% \text{Mn}]} = \sum N'_{A_i} \ln K_{A_i} + \sum N'_{A_i} \ln \frac{\gamma_{\text{Fe}A_i}}{\gamma_{\text{Mn}A_i}} \quad (68)$$

where N'_{A_i} is the electrically-equivalent fraction of the anion A_i , K_{A_i} is the equilibrium constant for the reaction



And the activity coefficients are for the components $\text{Fe}A_i$ and $\text{Mn}A_i$ in the slag with respect to the pure liquid components as standard states.

Flood and Grjotheim wrote the expression for the distribution of phosphorus between slag and metal as

$$3(\text{M.O}^{2-}) + 5[\text{O}] + 2[\text{P}] = (\text{M}_3(\text{PO}_4)_2)^{3-} \quad (69)$$

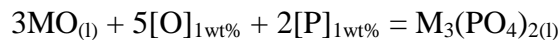
where M represents the cations in the slag, i.e. Fe^{2+} , Mn^{2+} , Ca^{2+} , Mg^{2+} . As before the thermodynamic cycle involves (i) allowing the reaction given by Eq. (67) to proceed reversibly, (ii) the reversible of the pure metal phosphate components, $\text{M}_3(\text{PO}_4)_2$, from the slag, (iii) dissociation of the pure liquid phosphates to produce liquid metal oxides and oxygen and phosphorus at the 1 wt% standard state, (iv) reversible addition of the pure metal oxides to the slag and (v) reversible transfer of the oxygen and phosphorus from the 1 wt% in iron standard states to their respective equilibrium concentrations. As the cations under consideration all have the same charge, their ions fractions and electrically-equivalent fractions are equal. Consequently, in step (ii) a total of one mole of P_2O_5 is extracted in the form of $N_{\text{Fe}^{2+}}$ moles of $\text{Fe}_3(\text{PO}_4)_2$, $N_{\text{Ca}^{2+}}$ moles of $\text{Ca}_3(\text{PO}_4)_2$, $N_{\text{Mn}^{2+}}$ moles of $\text{Mn}_2(\text{PO}_4)_2$ and $N_{\text{Mg}^{2+}}$ moles of $\text{Mg}_2(\text{PO}_4)_2$ and the free energy of unmixing to form to pure liquid phosphates is

$$\Delta G = -RT \sum N_{M^{2+}} \cdot \ln N_{M^{2+}}^3 \cdot N_{\text{PO}_4^{3-}}^2 \cdot \gamma_{\text{M}_3(\text{PO}_4)_2}$$

The free energy change for the step (iii) is

$$\sum N_{M^{2+}} \cdot RT \ln K_M$$

where K_M is the equilibrium constant for the reaction



For step (iv),

$$\Delta G = 3RT \sum N_{M^{2+}} \cdot \ln N_{M^{2+}} \cdot N_{\text{O}^{2-}} \cdot \gamma_{\text{MO}}$$

and for step (v)

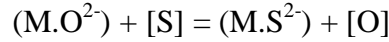
$$\Delta G = 2RT \ln h_p + 5RT \ln h_o$$

As the total change in free energy for the cycle is zero, summation and rearrangement gives

$$\ln \frac{N_{PO_4^{3-}}^2}{N_{O^{2-}}^3 \cdot h_o^5 \cdot h_p^2} = \sum N_{M^{2+}} \ln K_M + \sum N_{M^{2+}} \ln \frac{\gamma_{MO}^3}{\gamma_{M_3(PO_4)_2}} \quad (70)$$

Thus, if the slag were a Temkin ideal mixture, the distribution of phosphorus between slag and metal would be determined solely by the cation composition of the slag.

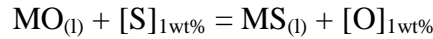
Similarly, in Flood and Grjotheim's treatment, the distribution of sulfur between slag and metal, written as



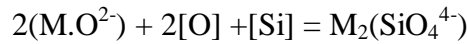
is given as

$$\ln \frac{N_{S^{2-}} \cdot h_o}{N_{O^{2-}} \cdot h_s} = \sum N_{M^{2+}} \ln K_M + \sum N_{M^{2+}} \cdot \ln \frac{\gamma_{MO}}{\gamma_{MS}}$$

where K_M is the equilibrium constant for the reaction



And the distribution of silicon between slag and metal, written as



is given as

$$\ln \frac{N_{SiO_4^{4-}}}{N_{O^{2-}}^2 \cdot h_o^2 \cdot h_{Si}} = \sum N_{M^{2+}} \cdot \ln K_M + \sum N_{M^{2+}} \ln \frac{\gamma_{MO}^2}{\gamma_{M_2SiO_4}}$$

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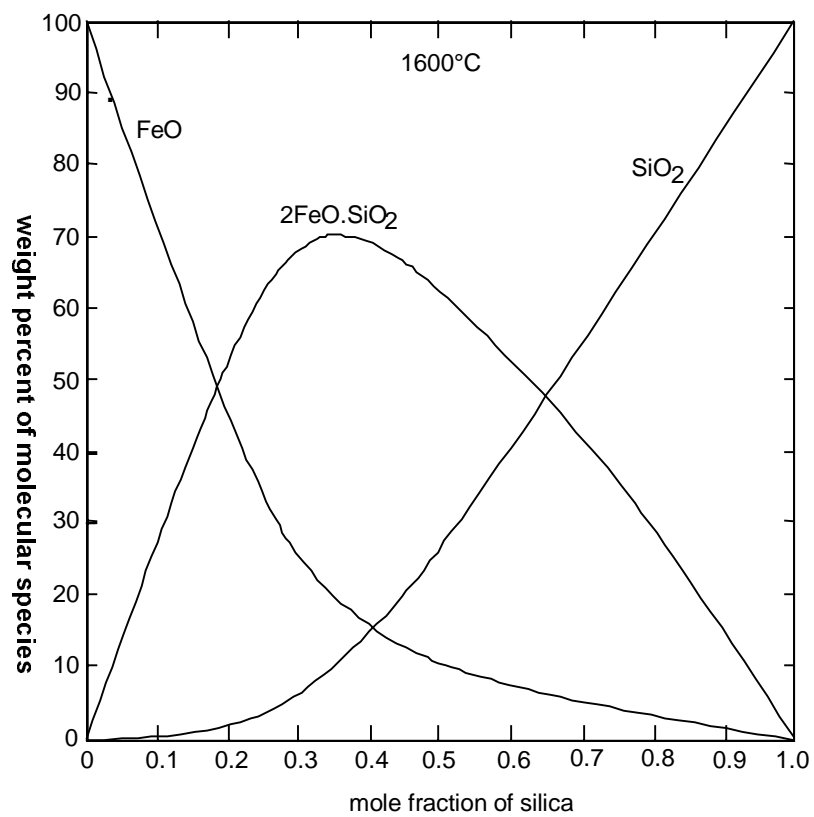


Fig. 1. The molecular constitution of FeO-SiO₂ melts at 1600°C (Ref. 3)

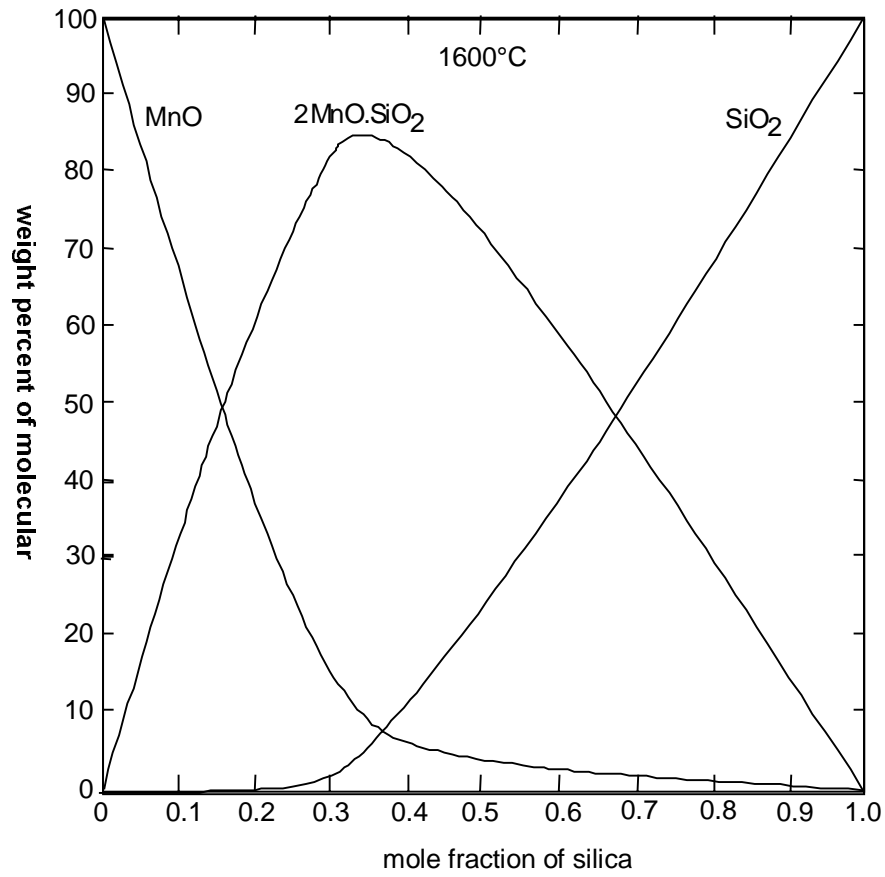


Fig. 2. The molecular constitution of MnO-SiO₂ melts at 1600°C (Ref 3)

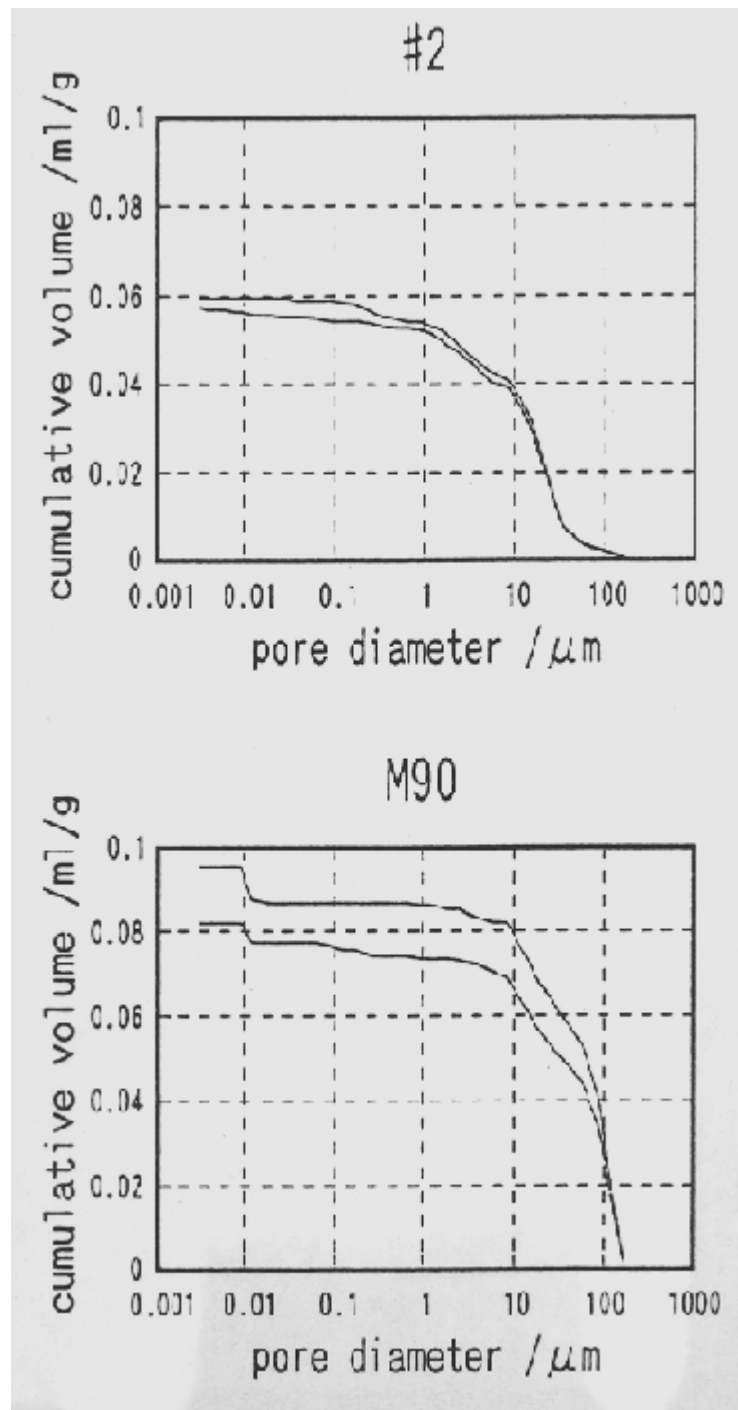


Fig.2 Pore size distribution in the sample A and B.

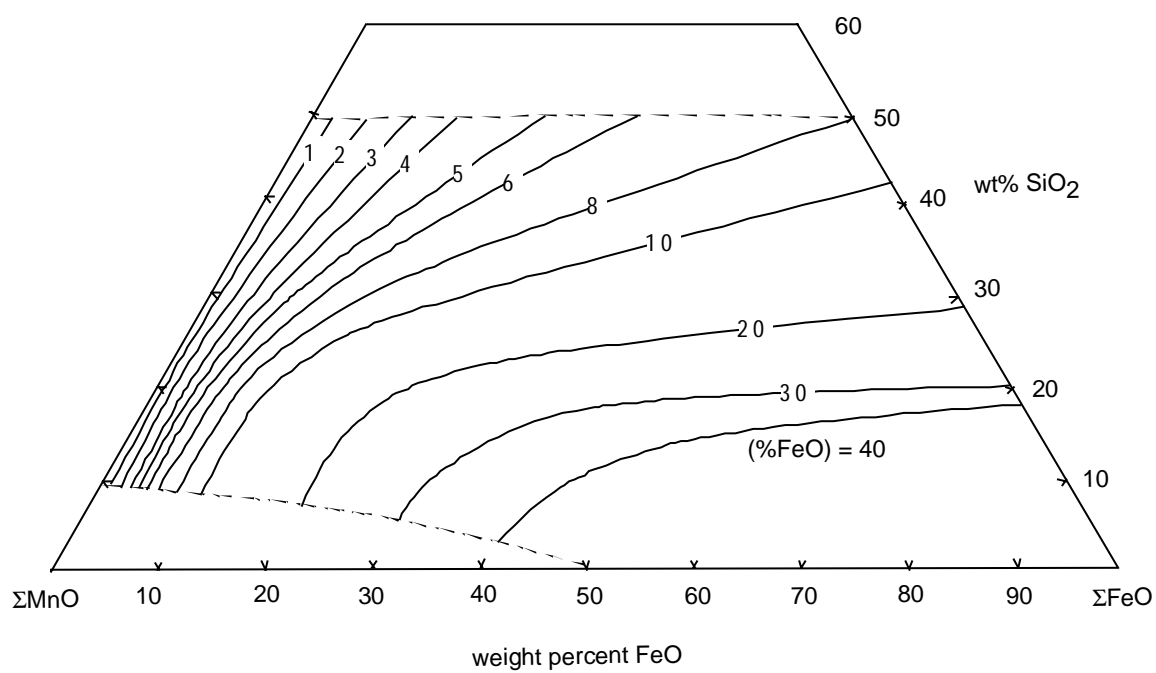


Fig. 3. The weight percentage of free molecular FeO in FeO-MnO-SiO₂ melts at 1600°C (Ref 3)

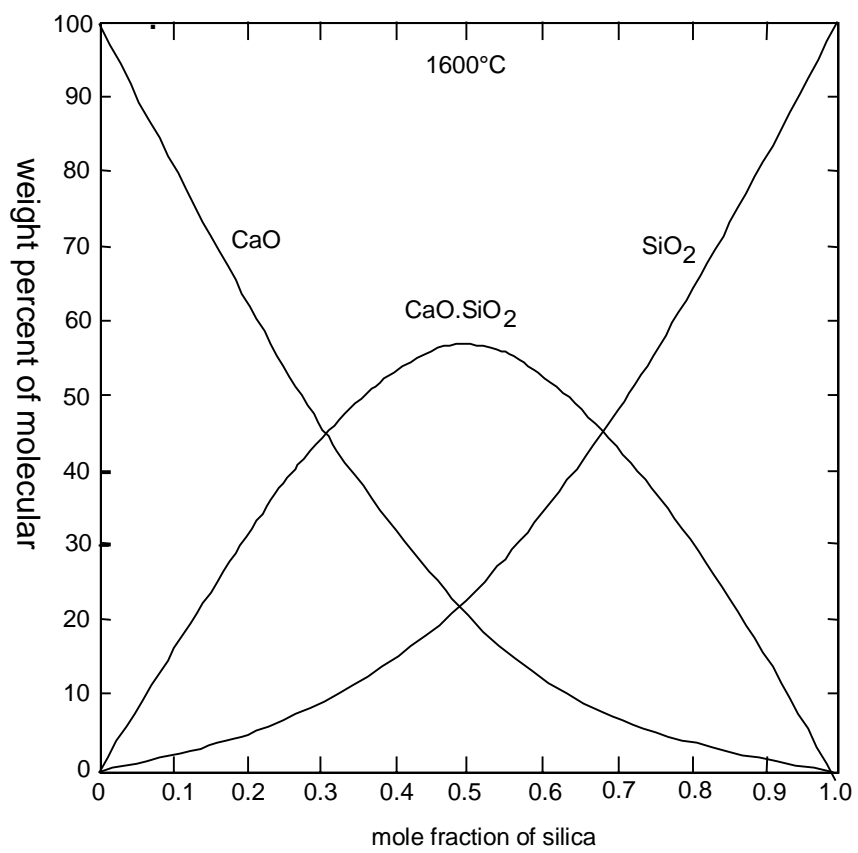


Fig. 4. The molecular constitution of CaO-SiO₂ melts at 1600°C (Ref 3)

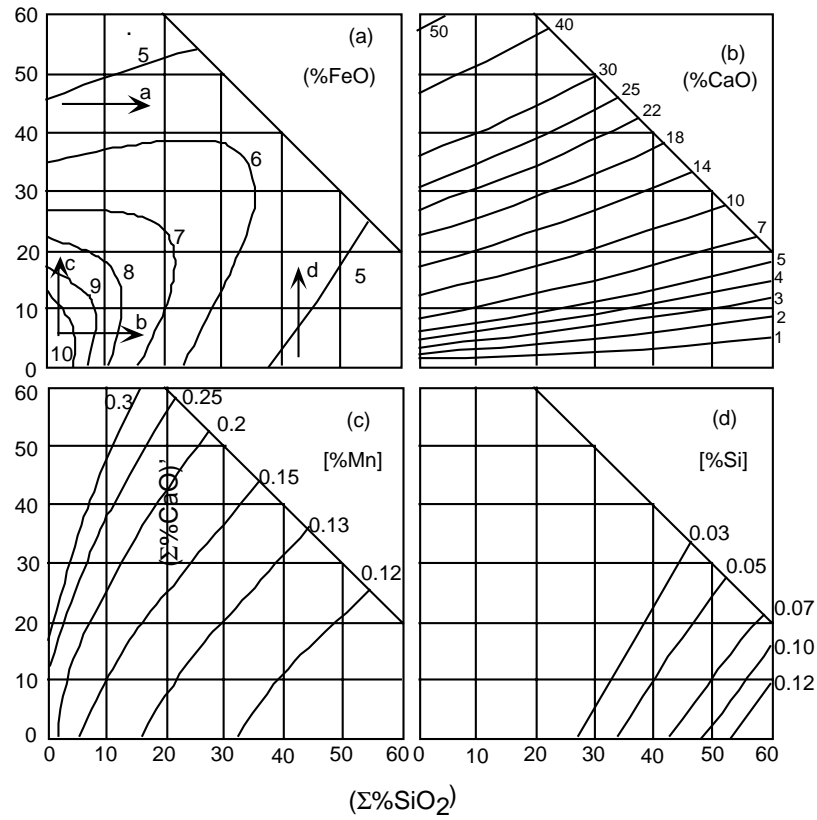


Fig. 5 The weight percentages of free molecular FeO and free CaO in, and the equilibrium percentages of Mn and Si in the metal under, slags of $(\Sigma\%Fe) = 10$ and $(\Sigma\%MnO) = 10$ at $1627^{\circ}C$ (Ref 3)

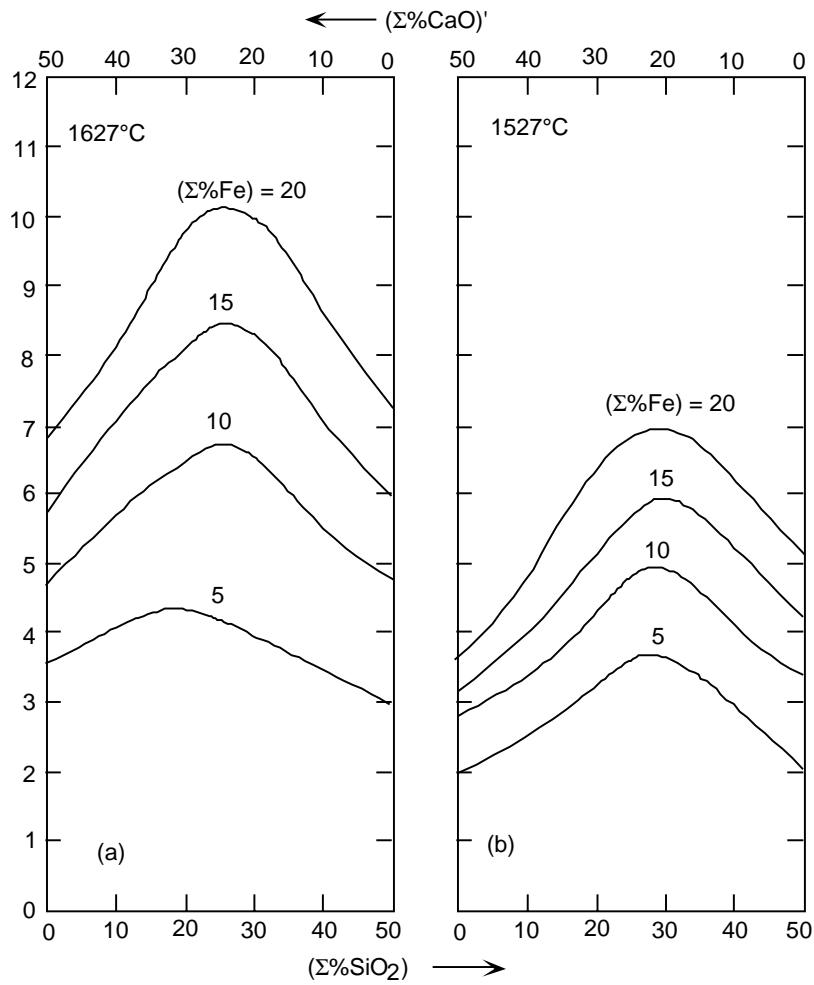


Fig. 6. The variations of (%FeO) with composition in slags of $(\Sigma\%CaO)' + (\Sigma\%SiO_2) = 50$ at 1627°C and 1527°C (Ref 3)

, (%FeO)

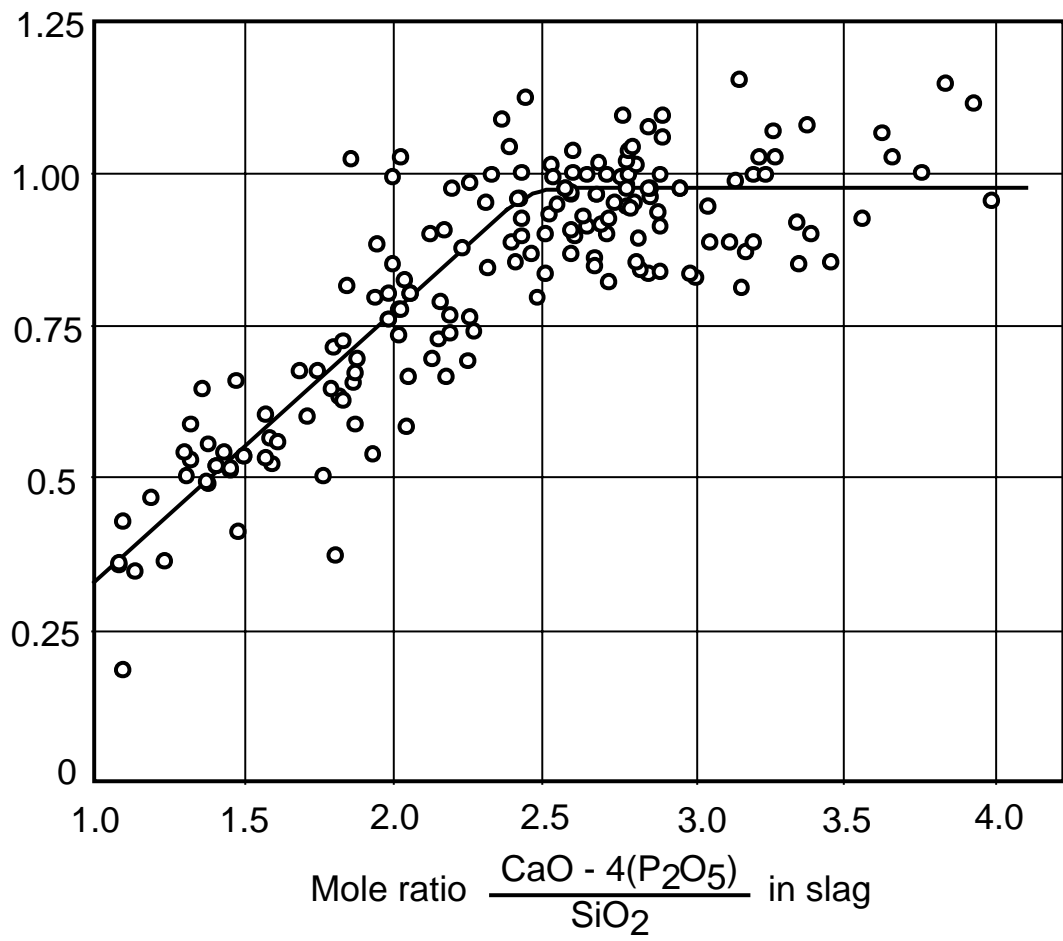


Fig. 7. Variation of the ratio M of observed to calculated residual manganese in open-hearth heats with lime-silica ratio L . (Ref 4)

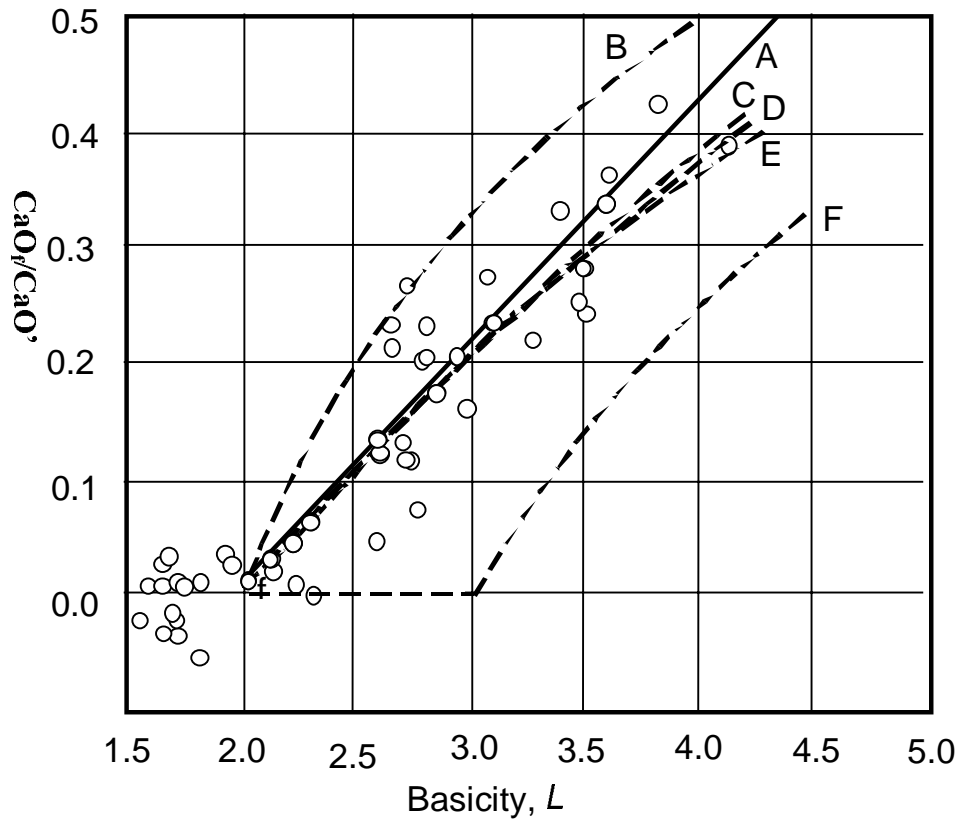


Fig. 8. Open-hearth data showing variation of the ratio CaO_f/CaO' with the lime-silica ratio, A, best straight line through the points. B, theoretical curve for $K' = \infty$. C, theoretical curve with $K' = 0.40$. D, theoretical curve with $K' = 0.35$. E, theoretical curve with $K' = 0.30$. F, theoretical curve with $K' = 0$ (Ref 4)

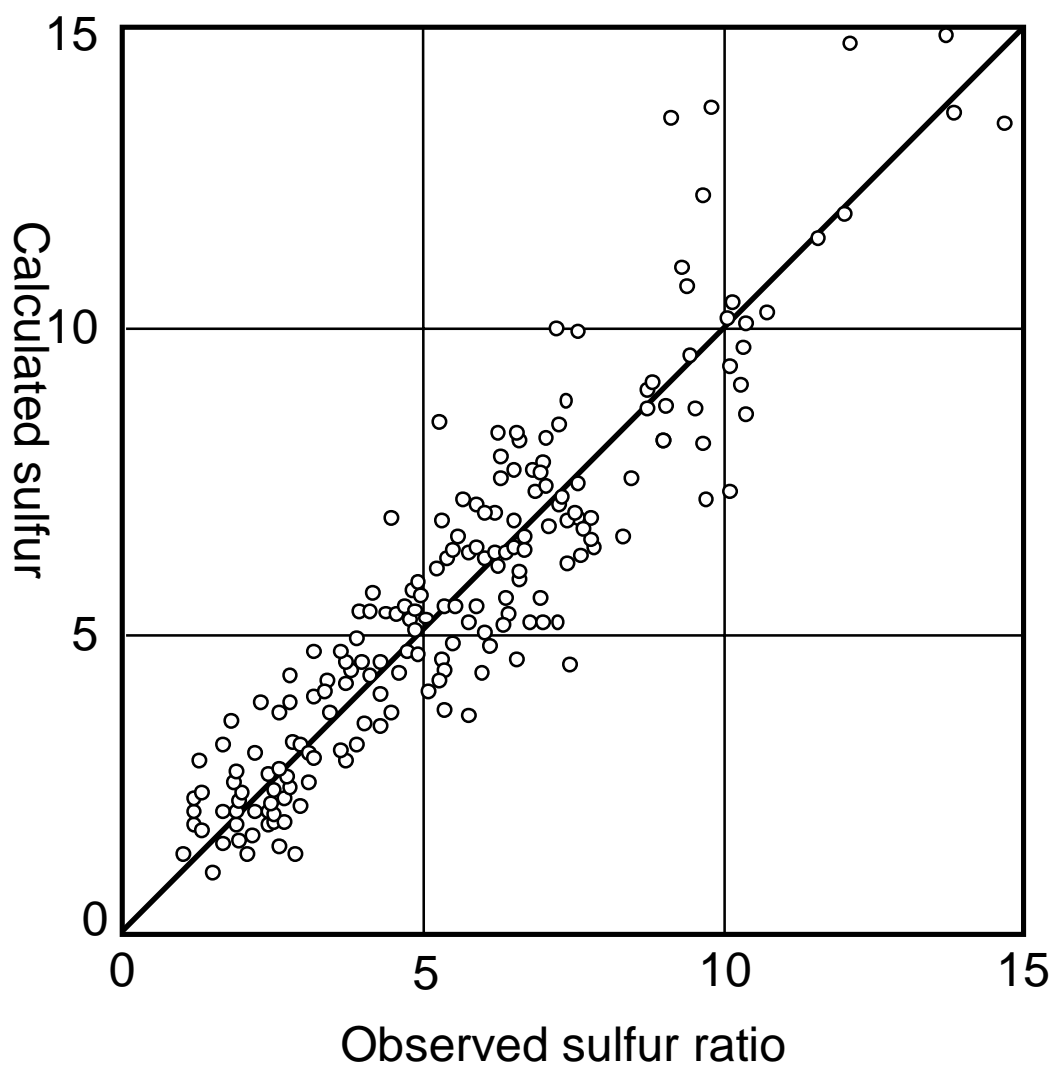


Fig. 9. Comparison between the observed and the calculated values of the sulfur ratio in actual open-hearth heats (Ref 4).

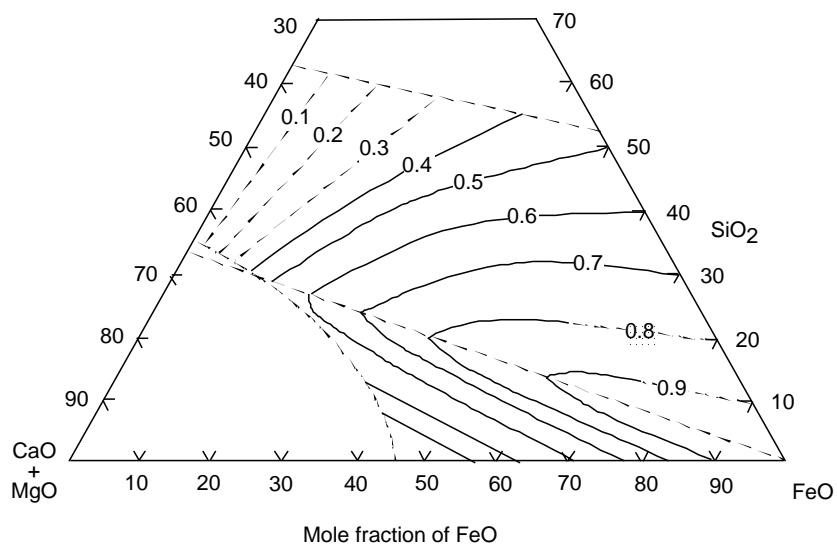


Fig. 10. Isoactivity lines for FeO in the system (CaO-MgO)-FeO-SiO₂ at 1600°C (Refs 6 and 7)

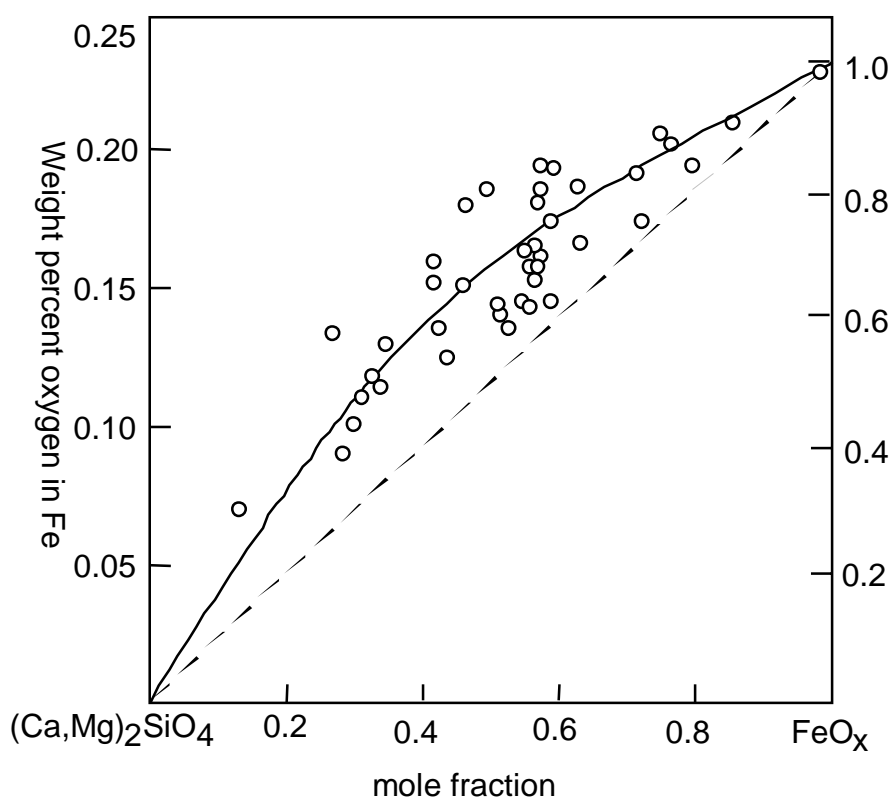


Fig. 11 (a) Oxygen dissolved in liquid Fe as function of slag composition in the system FeO_x-Ca₂SiO₄ at 1600°C (Ref 6)

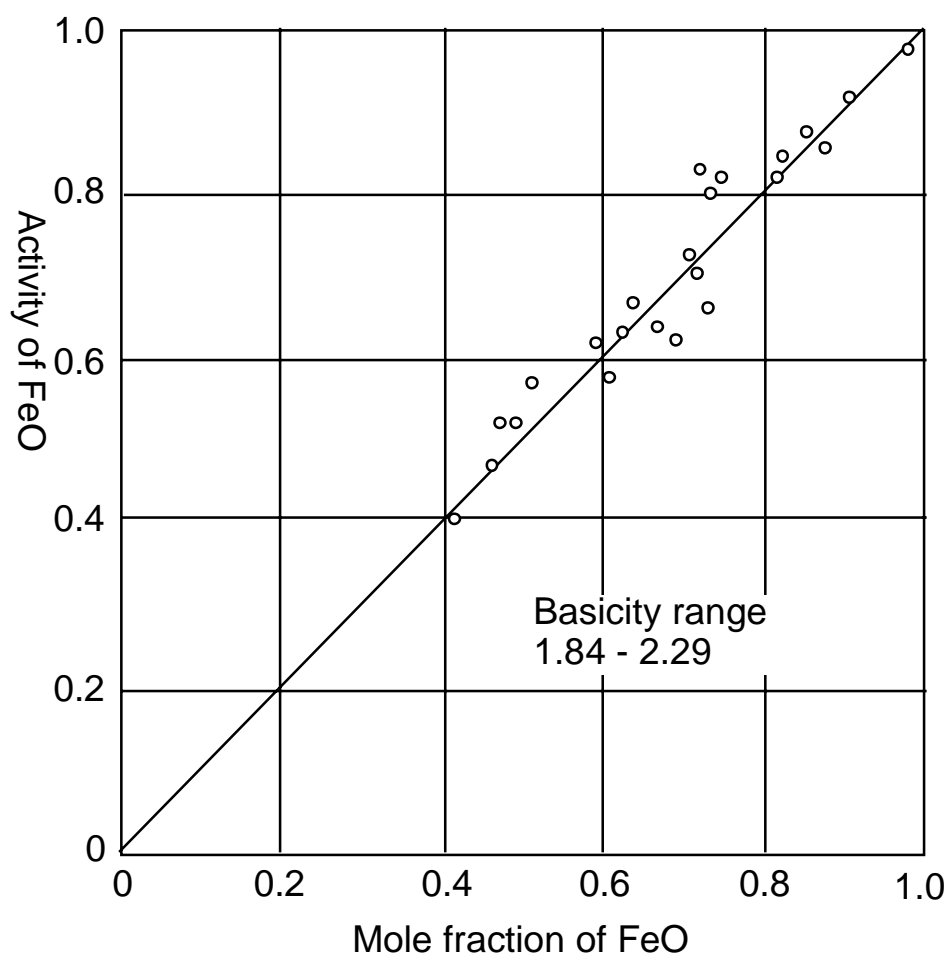


Fig. 11(b). Variation of the activity of FeO with composition assuming the existence of only the molecular species $(2\text{CaO}.\text{SiO}_2)_2$ and FeO (Ref 6)

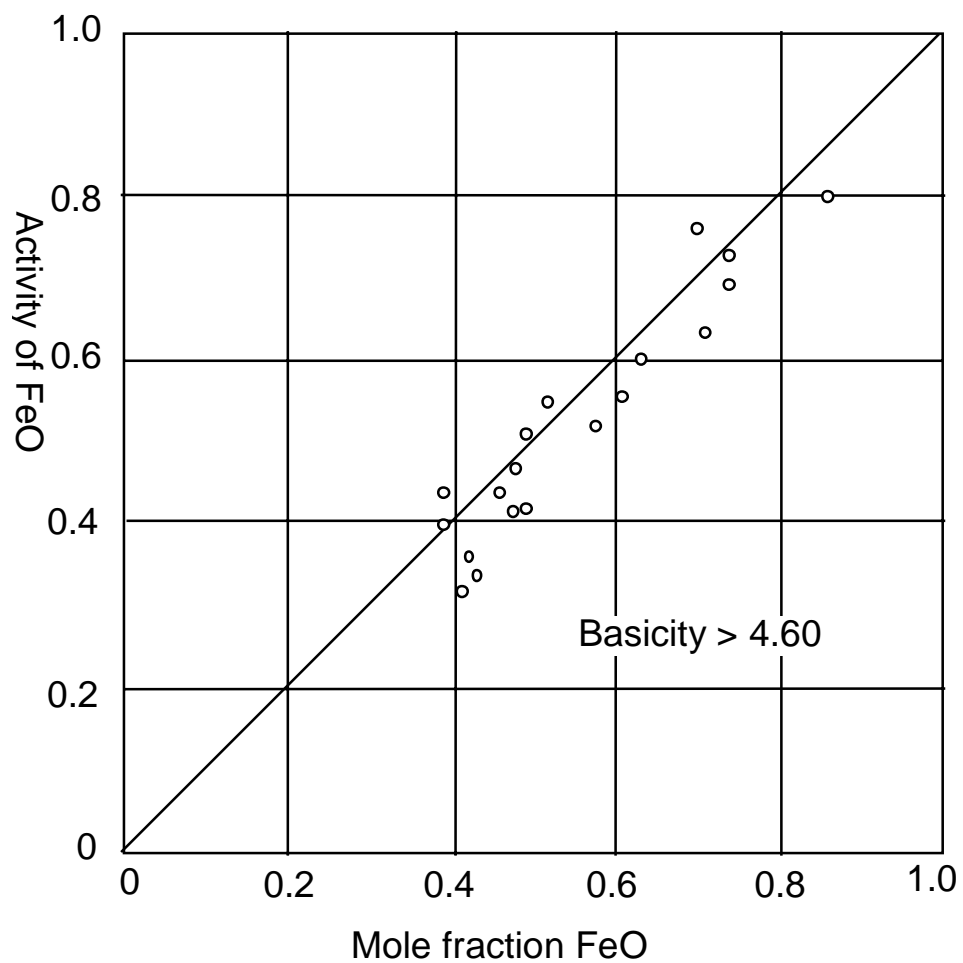


Fig. 12. The activity of FeO as a function of slag composition for basicities > 4.6 assuming the existence of undissociated $(2\text{CaO}.\text{SiO}_2)_2$ and $\text{CaO}.\text{Fe}_3\text{O}_4$ (Ref 7)

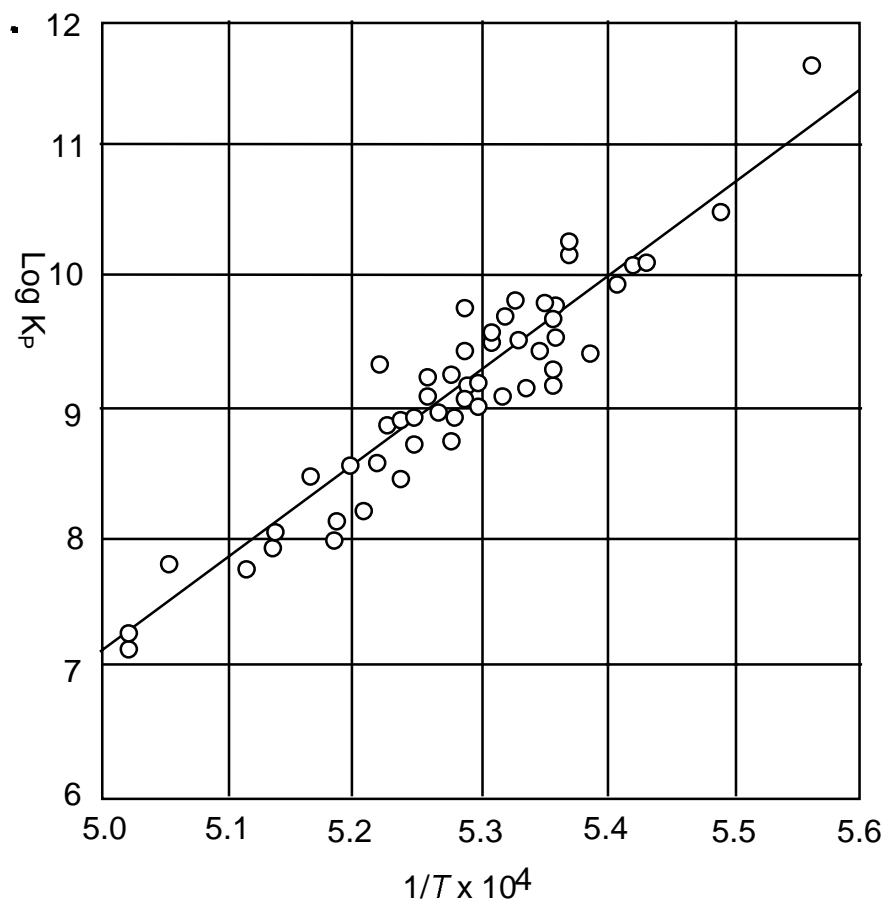


Fig. 13. The influence of temperature on the phosphorus equilibrium constant (Ref 8)

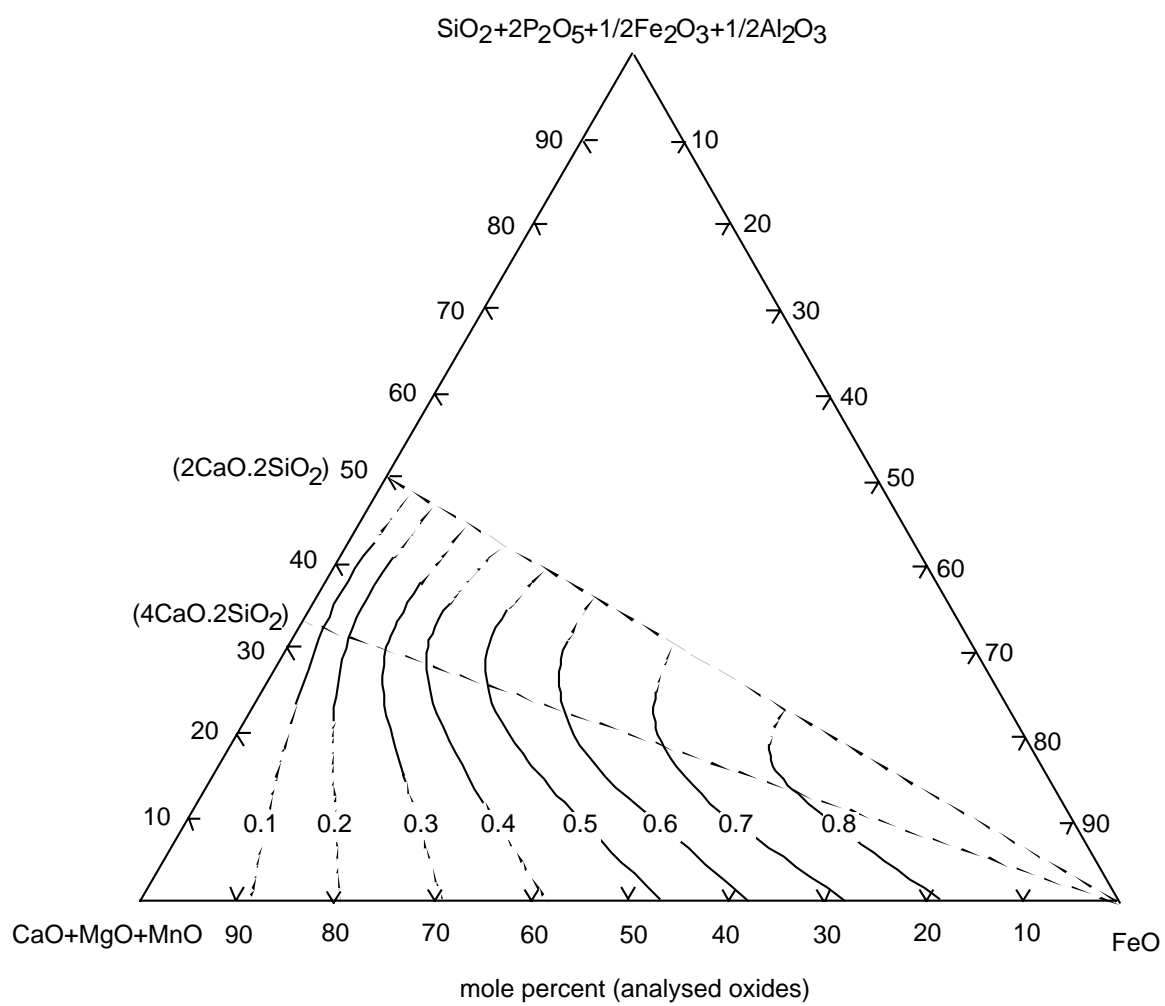


Fig. 14. The activity of iron oxide at 1600°C (Ref 7)

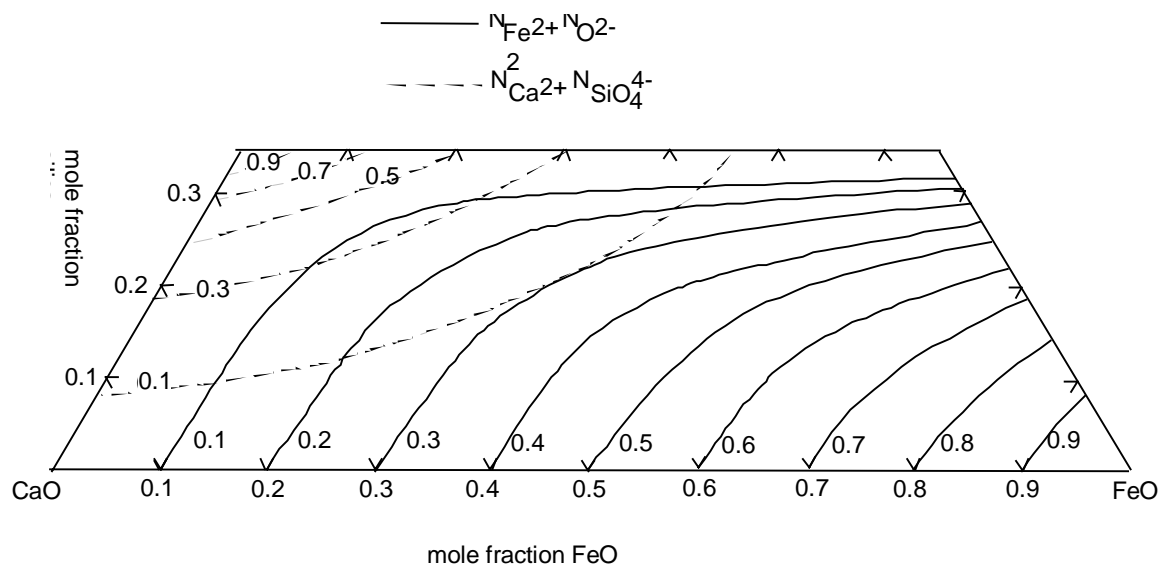


Fig. 15. Iso-activity lines for FeO and Ca_2SiO_4 in the system CaO-FeO-SiO₂ calculated assuming Temkin ideality and the ionic constitution of Fe^{2+} , Ca^{2+} , SiO_4^{4-} , O^{2-} (Ref 14)

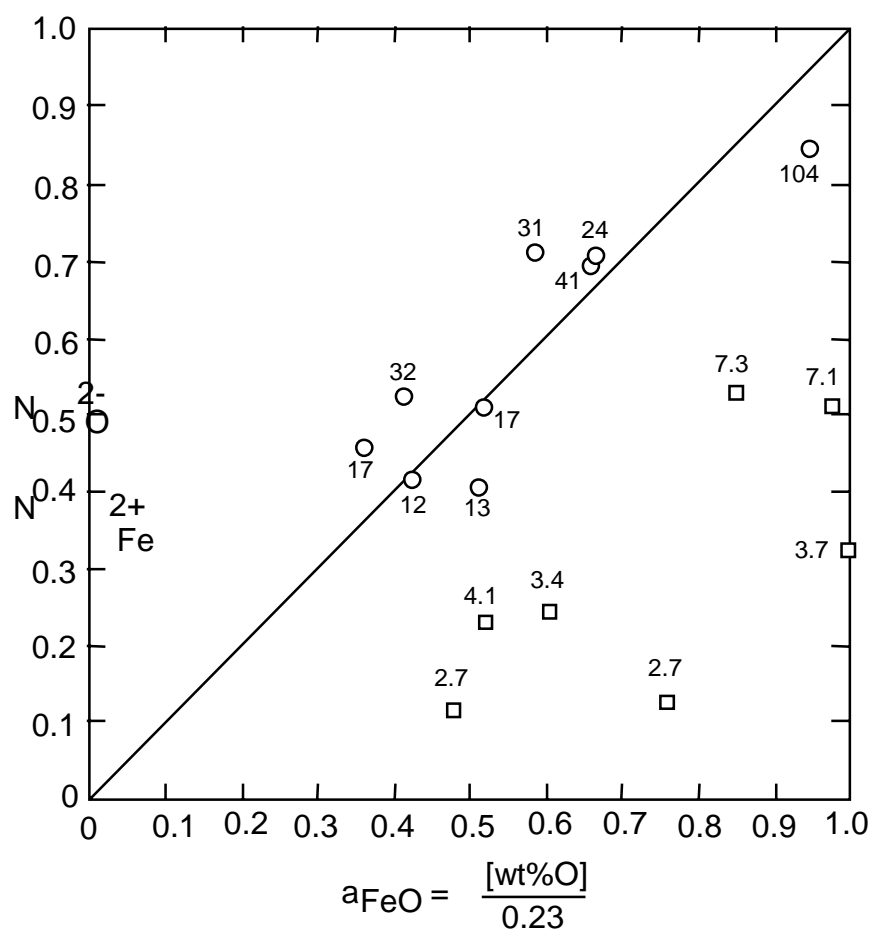


Fig. 16. Correspondance between the activity of FeO assuming Temkin ideality and experimental values in Fetter's and Chipman's slags. Numbers indicate molar ratio of basic oxides (CaO + FeO + MgO) to SiO_2

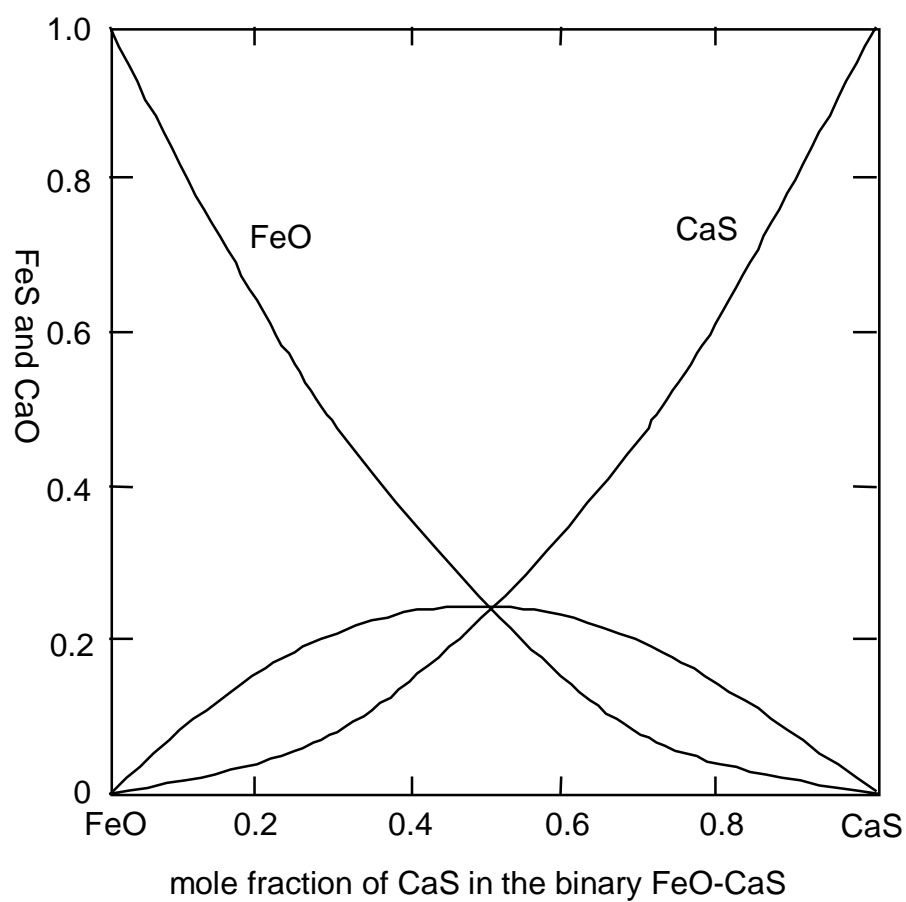


Fig. 17. The mole fractions of species in the reciprocal system FeO-FeS-CaO-CaS as functions of composition in the binary system FeO-CaS. (ref 13)

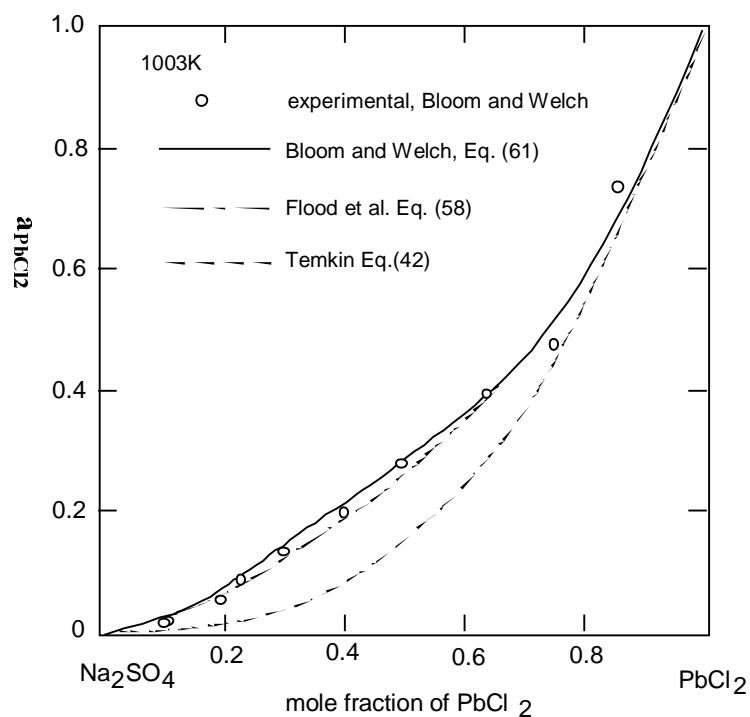


Fig. 18. Experimental and theoretical activities of PbCl_2 in the system Na_2SO_4 - PbCl_2 at 1003K

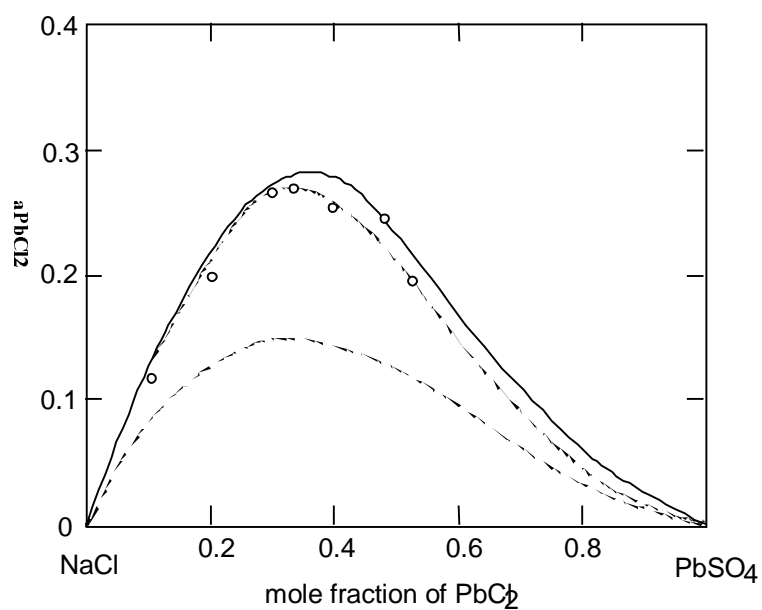


Fig. 19. Experimental and theoretical activities of PbCl_2 in the system NaCl - PbSO_4 at 1003K

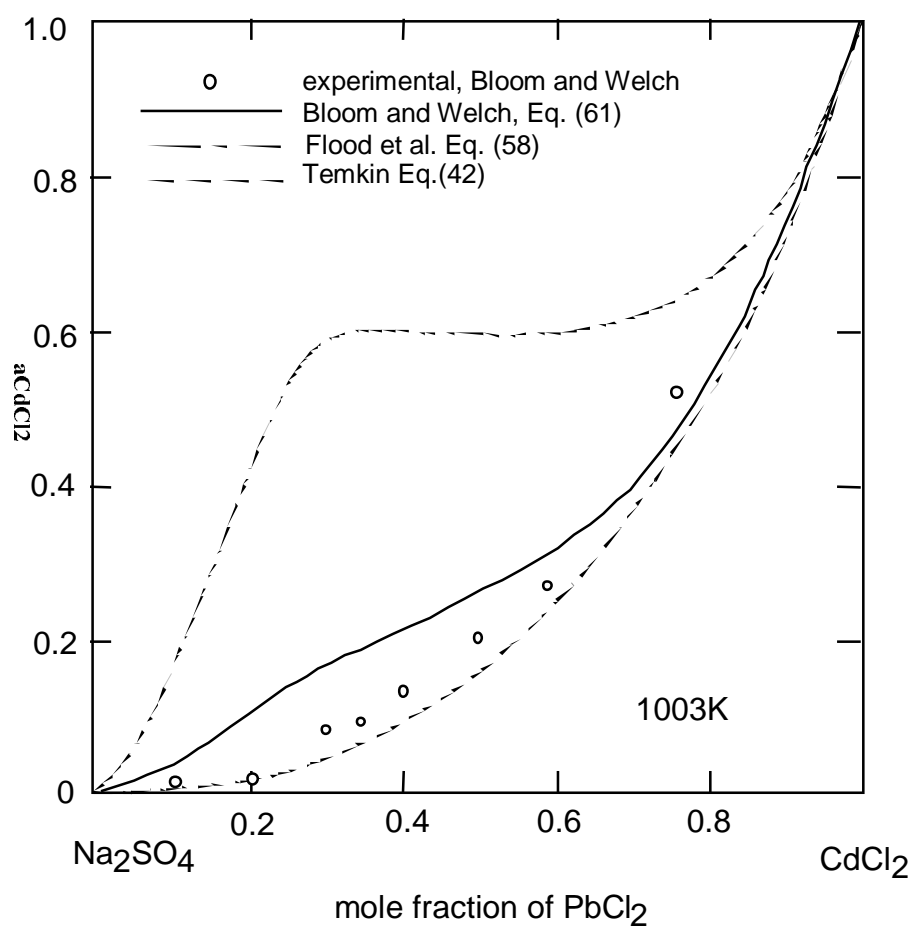


Fig. 20. Experimental and theoretical activities of CdCl_2 in the system Na_2SO_4 - CdCl_2 . at 1003K.

