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POTENTIAL-EQUIVALENCE IONIC COMPOSITION FOR MOLTEN SALTS AND SLAGS

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Synopsis: Both Temkin's theory and Flood's model concerning ionic nature of molten salts and slags were examined and a new approach was formulated to further develop these concepts. Electrically equivalent ionic fraction was introduced in Flood's model to represent stoichiometry of the binary reactions. To further develop Temkin's theory, a new ionic composition, the potential equivalence ionic composition was proposed.

The newly defined ionic composition was applied to Flood's model and the following final relationship was obtained based on the authors' experimental data of steel dephosphorization with basic slags:

$$\log \frac{(N''_{PO_4^{3-}})^2}{(N''_{O^{2-}})^3 a_{[P]}^2 a_{[O]}^5} = \Sigma N'_{M_i^{i+}} + \log K_{M_i^{i+}} = 12.23N'_{Ca^{2+}} + 6.27N'_{Mg^{2+}} - 0.14N'_{Fe^{2+}}$$

where N' is the electrically equivalent ionic fraction. The equilibrium constants of the binary reactions for Ca^{2+} and Mg^{2+} were calculated from the latest available data in the literature, and that for Fe^{2+} was obtained by fitting the experimental data to the equation. A better accordance was obtained when compared with the earlier published results.

Key words: slags, slag theory, thermodynamics, dephosphorization.

1. Introduction

Since a molten slag consists of ions rather than molecules, any rigorous discussion on the reaction thermodynamics between slag and metal can only be made based on the physicochemical background of ionic solution. Considering ionic structure of molten slags, there have been a few theories, such as by Temkin[1], Flood[2] and Masson[3], among which Temkin's theory can be considered as the most feasible one for highly basic slags where complete dissociation of compounds into ions is presumable.

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None of the theories, however, have taken into consideration charge number and size of different ion species. The aim of the present study is, therefore, trying to work out a proper way for taking into account the charge number and size of different ion species.

2. Examination of Temkin's theory and Flood's model

In Temkin's theory, a molten slag is considered to be a solution which is completely dissociated into simple ions. The arrangement of ions in the slag is similar to that in a crystal lattice, so that each cation is always surrounded by anions, and vice versa. There is no interaction between ions of the same charge sign, the state being that of complete randomness. Therefore, the slag is composed as if by mixing two independent ideal solutions, one being cations, i+, and the other being anions, j-. The enthalpy of mixing is nil and the entropy of mixing is the sum of the two mixing entropies when the cations and anions are mixed independently. Accepting these hypotheses, the following two equations can be derived:

$$a_{i+} = N_{i+} = n_{i+} / \Sigma n_{i+} \tag{1}$$

$$a_{j-} = N_{j-} = n_{j-} / \Sigma n_{j-} \tag{2}$$

where a is activity, N is mole fraction and n is mole number of ions.

To define the standard state of a component ij of this solution, the following equilibrium is considered

$$ij = i_+ + j_- \tag{3}$$

If a pure component in equilibrium with its ions is taken as the standard state, the standard free energy will be nil and thus the following equation is obtained.

$$K = \frac{a_{i+} a_{j-}}{a_{ij}} \tag{4}$$

Or according to Eqs. (1) and (2), we get the following relation:

$$a_{ij} = N_{i+} N_{j-} \tag{5}$$

According to the hypotheses of Temkin's theory, it is presumed that this relation holds whatever the molar fraction of the component ij in solution.

Based on Temkin's theory, Flood and Grjotheim (FG)[2] presented in 1952 a relationship between the equilibrium quotient of a slag-metal exchange reaction and the ionic composition of the basic slag, by using a thermodynamically reversible cycle. This treatment has often been called Flood's theory and was further detailed in 1977 by Forland and Grjotheim (FOG)[4]. In 1975, Elliot, Lynch and Braun (ELB)[5] examined the original FG treatment and employed revised thermodynamic cycle to obtain their own relationship. They also represented the activity coefficient term as a function of slag composition. More recently, in 1984, Guo[6,7] developed a new treatment to obtain the relationship by using a more strictly defined cycle and to represent the activity coefficient term as a function of slag composition by applying Taylor series. Taking the dephosphorization reaction as an example, all the above treatments arrive at an essentially same final correlationship, i.e. a linear part and an activity coefficient term as shown by the following equation:

$$\log \frac{(N_{PO_4^{3-}})^2}{(N_{O^{2-}})^3\, a_{[P]}^2 a_{[O]}^5} = \Sigma N'_{M_i^{i+}} + \log K_{M_i^{i+}} + f(\gamma) \tag{6}$$

Where N is Temkin's ionic fraction, a is activity, N' is Flood's ionic fraction, and f(γ) is a complex function of concerned activity coefficients.

Although the treatments above differ in details they are based on the same physicochemical background, i.e. Temkin's ionic theory. The electrically equivalent ionic fraction introduced by these treatments takes into consideration the reaction stoichiometry e.g. in dephosphorization it indicates, that 3 moles Ca^{2+} of CaO is needed for the reaction with P_2O_5 to form two moles phosphate anions while 6 moles Na^+ of Na_2O is required for the corresponding reaction. The electrically equivalent ionic fractions do not give any relations between component activities and the slag composition. The essential of Flood's pioneer work was a correlationship between the equilibrium constant of a metal-slag exchange reaction and the slag composition derived by using a thermodynamically reversible cycle. The succeeding works may be considered as different modifications of Flood's model.

When endeavouring to further develop ionic slag theories Temkin's model can be taken as a start point. In Temkin's theory, all the ions of the same charge sign are considered identical and thus the interactions among ions of same charge sign are considered equal irrespective of ion species. This is not the situation in complex molten slags and may be considered as one of the main reasons for the inconsistency between the measured activity values of slag components and the calculated ones by Temkin's theory. Indeed, the cations or anions in a commonly-encountered metallurgical slag greatly differ in size and charge number. The effect of these differences on the states of respective ions should be taken into account.

3. Definition of the potential-equivalence ionic composition

The electrostatic state of an ion in solution is determined by both size and charge number of itself as well as those of its surrounding ions of the opposite charge sign. For example, in the ionic solution of CaO+MgO, although both Ca^{2+} and Mg^{2+} are surrounded by the same O^{2-}, they can not be considered identical because the attraction between Ca^{2+} and O^{2-} is weaker than that between Mg^{2+} and O^{2-} because of larger size of Ca^{2+} than that of Mg^{2+}. On the other hand, the oxygen ions surrounded by Ca^{2+} can not be considered equivalent to those surrounded by Mg^{2+} for the same reason. In Temkin's theory, the interaction between ions of different charge sign has been mostly taken into account by the assignment that each ion is always surrounded by ions of opposite charge sign, but not the interactions among ions of the same charge sign. For a slag containing n_{C1}, n_{C2}, n_{C3}, ... moles of cations c1, c2, c3, ... with their cationic fractions N_{C1}, N_{C2}, N_{C3}, ... and n_{a1}, n_{a2}, n_{a3}, ...moles of anions a1, a2, a3, ... with their anion fractions N_{a1}, N_{a2}, N_{a3}, considering that the potential, or strength, of an ion species is determined by the ratio of its charge number to its radius, the interactions among ions of the same charge sign but different charge number may be taken into consideration by calculating the ionic composition in the following way.

$$N''_{ci} = \frac{n_{ci} z_{ci} / r_{ci}}{\Sigma n_{ci} z_{ci} / r_{ci}} \tag{7}$$

$$N''_{aj} = \frac{n_{aj} z_{aj} / r_{aj}}{\Sigma n_{aj} Z_{aj} / r_{aj}} \tag{8}$$

Where n, z and r denote mole number, charge number and radius respectively. In this way, the concentration of an ion species is calculated on the basis of potential equivalence whereby both the size and charge number are taken into account. Accordingly, the N" in the above equations may be called the potential-equivalence ionic fraction.

4. Application of the newly defined ionic composition

The application of the potential-equivalence ionic fraction to Flood's model is simple, i.e. just substituting the Temkin's ionic fractions (not the electrically equivalent ionic fractions) by their corresponding potential-equivalence ionic fractions. If the hypotheses of Temkin's theory hold true, it can be understood that the deviation of the ionic solution from ideality arises only from the assumption that all the ions of the same charge sign are identical. Or in other words, the reason for that the activity coefficients appear in Flood's model is that the size and charge number are not taken into account in the calculation of the ionic composition of the slag. Now that the size and charge number of different ion species can be taken into account by substituting the potential-equivalence ionic fractions for Temkin's ionic fraction in the model, it may be expected that those activity coefficients may disappear once the substitution is made, arriving at the following equation.

$$\log \frac{(N''_{PO_4^{3-}})^2}{(N''_{O^{2-}})^3 a_{[P]}^2 a_{[O]}^5} = \Sigma N'_{M_i^{i+}} + \log K_{M_i^{i+}} \qquad (9)$$

In order to calculate the potential-equivalence ionic fraction, the radii of all the ion species present in the slag must be known. For simple elementary ions such as F^{1-}, O^{2-}, Ca^{2+}, Mg^{2+}, etc., the data of their radii are readily available. For more complex anions such as SiO_4^{4-}, PO_4^{3-} and FeO_4^{5-}, however, there are no available data in the literature. Fortunately, the chemistry of ionic crystals can lend us a temporary expedient to solve this problem. According to the chemistry of ionic crystals, the so called thermochemical radii of complex ions can be determined by using Kapuatinskii's equation if the lattice energy of the crystal containing this ion species is known from thermochemical cycles. This has been done for various tetrahedral anions and the tabulated data are available in the text book by Greenwood[8]. The thermochemical radii of complex ions obtained in this way are not necessarily the same as their stereochemical radii. Considering that the structure of a molten slag is more similar to its solid state rather than to its gaseous state, however, the thermochemical radii can be accepted as a first approximation of the stereochemical radii. Besides, there are no other available data.

For FeO_4^{5-}, however, there are no available data of even thermochemical radii. By examining the tabulated data for tetrahedral oxy-anions, it is found that the logarithmic radius values of various tetrahedral oxy-anions with the same valency can be approximately related to the corresponding logarithmic $z_C z_{O2-}/(r_C+r_{O2-})^2$ values by a simple linear function. Therefore, extrapolating this relationship, the thermochemical radius of FeO_4^{5-} is estimated. Together with its estimated value, the tabulated radius data for various ions from Greenwood's text book are listed in the following Table 1.

Table 1 Ionic Radii (A)

Cations					Anions				
Na^{1+}	Ba^{2+}	Ca^{2+}	Mg^{2+}	Fe^{2+}	F^{1-}	O^{2-}	SiO_4^{4-}	PO_4^{3-}	FeO_4^{5-}
0.95	1.35	0.99	0.65	0.76	1.36	1.40	2.40	2.38	2.65*

* Estimated

Considering the equilibrium constants for the binary dephosphorization reactions in Flood's model, various data have been reported in the literature, which differ greatly from each others as shown in Table 2. It is difficult to say which of the data are the most correct. Therefore, it was decided to derive K_{Ca} and K_{Mg} again based on the available thermodynamic data. The standard free energies of formation for $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$, the standard free energy changes of fusion for CaO and $Mg_3(PO_4)_2$ and the melting point of

$Ca_3(PO_4)_2$ were all taken from Turkdogan's monograph[9]. The melting point and enthalpy for MgO were taken from Barin and Knacke's handbook[10] while the standard Gibbs energy changes of dissolution for oxygen and phosphorus into liquid steel are the original data by Dastur and Chipman[11, 12] and Bookey[13] respectively. Since there are no available data for the fusion enthalpy of $Ca_3(PO_4)_2$, it was assumed to be the same as that of $Mg_3(PO_4)_2$ as proposed by Suito et al.[14]. Based on these data, K_{Ca} and K_{Mg} were derived and the following expressions were obtained.

$$\log K_{Ca} = 82176/T - 31.646 \tag{10}$$
$$\log K_{Mg} = 66587/T - 29.284 \tag{11}$$

Table 2 Values of $\log K_{M_i}{}^{i+}$ at 1600°C

Reference	$\log K_{Ca}{}^{2+}$	$\log K_{Mg}{}^{2+}$	$\log K_{Fe}{}^{2+}$	$\log K_{Mn}{}^{2+}$
Flood et al [2] *1	10.20	7.16	1.16	—
Elliot et al [5] *2	9.68	11.85	-2.24	-0.05
Suito et al [4] *3	11.10	5.29	0.96	—
Guo et al [6] *4	9.68	4.23	-0.76	—
Present Work	12.23	6.27	-0.14	-0.05

*1 Extrapolation of the first approximation of Flood's model
*2 Based on selected thermodynamic data
*3 Multiple linear regression for the first approximation of Flood's model
*4 Based on selected thermodynamic data except $\log K_{Fe}{}^{2+}$ for which the method was not given

The values of these expressions at 1600°C are listed in Table 2. For K_{Fe}, however, there are not sufficient data for the derivation. If Temkin's hypotheses are supposed true and the introduction of the potential-equivalence ionic composition will fully take into account the effect of size and charge number of different ion species, the activity coefficient term in Flood's model will then disappear. Therefore, adopting the newly derived $\log K_{Ca}$ and $\log K_{Mg}$, the value of $\log K_{Fe}$ at 1600°C can be evaluated by fitting the experimental data from the present authors' previous work[15] to Flood's model.

Applying the potential-equivalence ionic composition, the data points for normal CaF_2-containing slags are plotted in Fig.1 by Flood's model with the value of $\log K_{Fe}$ being -0.14 which was determined by using the method of least square.

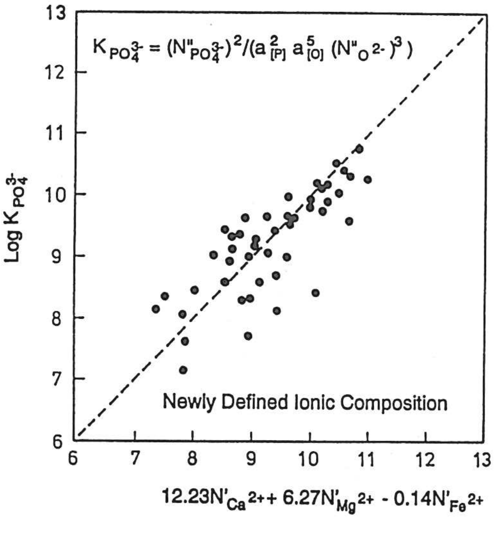

Fig. 1 Dephosphorization data plotted by applying the potential-equivalence ionic composition in Flood's model.

Now this value can be compared with those from the literature (Table 2). There are two positive values, 1.16 and 0.92 which were obtained as the first approximation of Flood's model either by extrapolation or linear regression. It means that they contain the corresponding part of the activity coefficient term. In consequence, the true value of $\log K_{Fe}$ must be smaller than these two values. Both of the two negative values, -2.24 and -0.76 were estimated for $\log K_{Fe}$ with the activity coefficient term taken into account separately. Therefore, they should be better approaches to $\log K_{Fe}$ than the former two positive values. The value, -0.14 by the present authors was obtained based on the potential-equivalence ionic composition. It is comparable with the value, -0.76 by Guo et al[6].

A little more serious evaluation can be made by extrapolating $\log K_{PO_4^{3-}}$ up to the value $(\%Fe_tO)=100$. Based on various data sources, Nagabayashi et.al[16] plotted log((P)/[P]) against $(\%Fe_tO)$ in slag for the slag systems of Fe_tO-P_2O_5-CaO, Fe_tO-P_2O_5-MgO, Fe_tO-P_2O_5-SiO_2 and Fe_tO-P_2O_5. When extrapolated all these slag systems to $(\%Fe_tO)=100$, the same distribution (P)/[P]=0.8 was resulted. Based on this result and applying the potential-equivalence ionic composition, $\log K_{Fe}$ was calculated and it gets a value -0.40 when [P] approaches to zero. In this evaluation, it was assumed that all the iron in the slag exists as Fe^{2+} ions and the value of 0.23% was selected for the oxygen saturation content in liquid iron.
In fact, however, there is always some ferric iron in the slag which generally can be anticipated to decrease the activity of oxygen ions. Moreover, the preferential orientation of Fe^{2+}/O^{2-} caused by the strong polarization between this pair of ions is also believed to decrease the activity of oxygen ions. Therefore, the activity of oxygen ions must be smaller than the calculated value on the assumption that all the iron in slag exists as simple Fe^{2+} ions. Accordingly, the true $\log K_{Fe}$ value must be higher, at least not lower, than the evaluated value -0.40 above. Consequently, the present value -0.14 for $\log K_{Fe}$ is considered most reasonable.

5. Concluding remarks

By scrutinizing Temkin's theory and Flood's model concerning the ionic nature of molten salts and slags, it was concluded that the electrically equivalent ionic fraction in Flood's model merely represents the stoichiometry of the binary reactions but does not take into account electric and ionic characteristics of different cations and anions.

In order to further develop Temkin's theory for basic slags a new ionic composition, the potential-equivalence ionic composition, was defined whereby the interactions among ions of same charge sign but different size and charge number are taken into account. The newly defined ionic composition was successfully applied to Flood's model in the case of steel dephosphorization. The new model also simplifies Flood's treatment by getting rid of the complex activity coefficient term in Flood's formula.

6. References

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