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Application of Thermodynamic Databases to Evaluation of Interfacial Tension between Liquid Steels and Molten Slags

The thermodynamic model has been proposed to evaluate the interfacial tension between liquid iron alloys and molten slags based on the Girifalco-Good equation, which is a function of the surface tensions of liquid Fe alloys and molten slags. The surface tensions of liquid iron alloys has been evaluated on the basis of Butler's equation by regarding Fe-O system as Fe-"FeO" system. The thermodynamic model of the surface tension of molten ionic mixtures has been applied to evaluate the surface tension of molten slags.

1 Introduction

Interfacial tension between liquid steels and molten slags is one of the important physico-chemical properties to understand various interfacial phenomena in steel making processes. Information on the interfacial tension, however, has not been accumulated enough so far. Accompanying the accumulation of experimental data on interfacial tensions in the near future, it is attractive to evaluate the interfacial tension from some thermodynamic models, in order to compensate some lack of experimental data, and furthermore to understand interfacial phenomena more deeply.

The authors have been studying the application of thermodynamic databases, which have been constructed to calculate phase diagrams, for the evaluation of the surface tension of liquid alloys, molten salt mixtures and molten oxide mixtures [94Tan, 96Tan, 98Tan1, 98Tan2, 98Tan3, 99Ued]. In previous articles the authors have proposed thermodynamic models for the surface tension of molten salt mixtures in common ion alkali-halide systems, and extended those models to other ionic systems [98Tan3, 99Ued]. In those works, we found that a general relationship between the composition dependence of the excess Gibbs energy in the bulk and that of the surface tension σ in liquid alloys exists (that is to say, negative excess Gibbs energy \Leftrightarrow positive deviation of σ from that of ideal solution, and vice versa), but this relationship does not apply to molten salt mixtures [96Tan, 98Tan1, 98Tan2, 98Tan3]. Furthermore, molten salt mixtures have the tendency to show a strong downward curvature of the composition dependence of the surface tension [80Goo, 96Tan, 98Tan1, 98Tan2, 98Tan3]. Molten oxide mixtures show a similar behavior to the above ionic mixtures, in other words, they show a negative deviation of the composition dependence of the surface tension from that of the ideal mixture even when they have negative excess Gibbs energy.

In the present work, we have extended the above thermodynamic model for the surface tension of molten salt mixtures to molten oxide systems. Furthermore, the thermodynamic model for the surface tension of liquid alloys is applied to liquid iron-oxygen systems. Then, combining those two models, we have proposed a thermodynamic calculation procedure to evaluate the interfacial tension between liquid steels and molten slags.

2 Concept for the Evaluation of Interfacial Tension between Liquid Steels and Molten Slags

Figure 1 shows the concept for the evaluation of the interfacial tension between liquid steels and molten slags. By applying the software ChemSage [90Eri] and using thermodynamic databases, the equilibrium compositions of all components in liquid steel and molten slag are determined. Then, the surface tension of liquid steel and that of molten slag are calculated by using the information on the excess Gibbs energies of each liquid phase on the basis

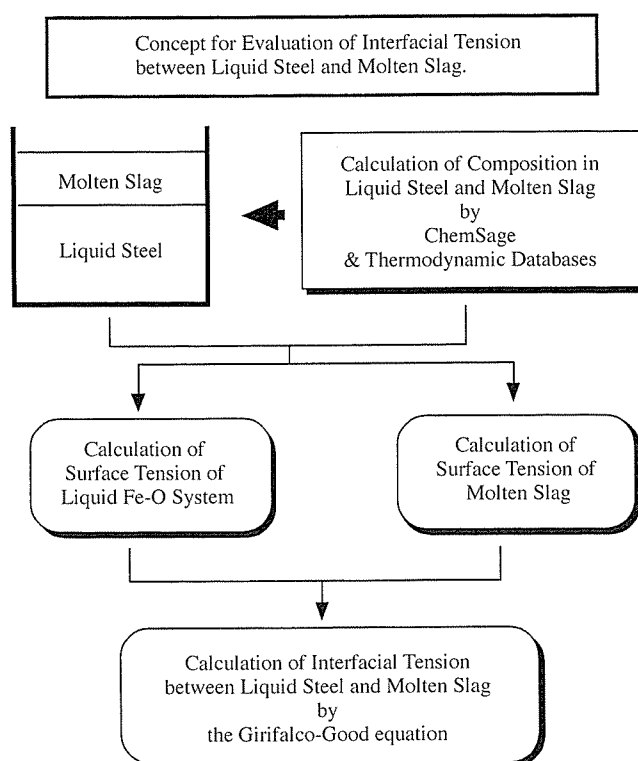


Fig. 1. General concept of calculation system for interfacial tension between liquid steel and molten slags.

Table 1. Data for calculation of the surface tension of the liquid Fe–FeO system.

| Surface Tension of Pure Component [mNm ⁻¹] | | Refs. |
|--|---|---------|
| Fe | $\sigma = 1872.0 - 0.49 (T - 1809)$ | [88Id] |
| FeO | $\sigma = 645.0 - 0.15 (T - 1773)$ | [87Mil] |
| Molar Volume of Pure Component [m ³ mol ⁻¹] | | Refs. |
| Fe | $V = 7.94 \{1 + 1.3 \cdot 10^{-4} (T - 1809)\} \cdot 10^{-6}$ | [88Id] |
| FeO | $V = 15.8 \{1 + 1 \cdot 10^{-4} (T - 1773)\} \cdot 10^{-6}$ | [87Mil] |

of the thermodynamic models for the surface tension. Finally, the interfacial tension is obtained from the Girifalco-Good equation [57Gir].

3 Thermodynamic Model for Surface Tension of the Liquid Iron–oxygen System

The authors have applied Butler's equation to evaluate the surface tension of liquid alloys [94Tan, 96Tan]. In the present work, Butler's equation is also applied to the evaluation of the surface tension of the liquid Fe–O system on the basis of the assumption that the liquid Fe–O system is regarded as Fe–“FeO” system. This assumption has been already proposed by Monma and Sudo [61Mon2] and Utigard [94Uti] to calculate the surface tension of liquid Cu–O and Fe–O systems. Hajra et al. [91Haj] have also calculated the surface tension of liquid Fe–S alloys by regarding it as Fe–FeS mixtures. Butler's equation for A–B binary solution is given as follows

$$\begin{aligned} \sigma &= \sigma_A + \frac{RT}{A_A} \ln \frac{(1 - N_B^S)}{(1 - N_B^B)} + \frac{1}{A_A} \bar{G}_A^{E,S}(T, N_B^S) \\ &\quad - \frac{1}{A_A} \bar{G}_A^{E,B}(T, N_B^B) \\ &= \sigma_B + \frac{RT}{A_B} \ln \frac{N_B^S}{N_B^B} + \frac{1}{A_B} \bar{G}_B^{E,S}(T, N_B^S) - \frac{1}{A_B} \bar{G}_B^{E,B}(T, N_B^B) \end{aligned} \quad (1)$$

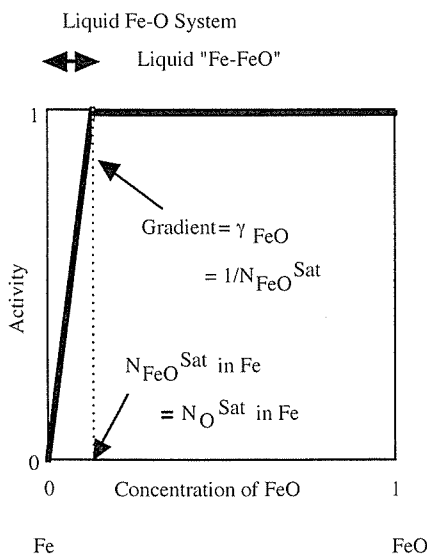


Fig. 2. Activity of FeO in Fe.

where R is the gas constant, T temperature, σ_X surface tension of pure liquid X , A_X surface area in a monolayer of pure liquid X ($X = A$ or B). A_X can be obtained from the following equation

$$A_X = LN_0^{1/3} V_X^{2/3} \quad (2)$$

N_0 is the Avogadro number, V_X the molar volume of the pure liquid X . L in Eq. (2) is usually set to be 1.091 for liquid metals assuming closed packed structures. L is set to be 1 for molten ionic melts. Butler derived Eq. (1) by assuming an equilibrium between a bulk and a surface [32But]. In Eq. (1), superscripts S and B show the surface and the bulk, respectively. N_X^S and N_X^B in Eq. (1) are mole fractions of a component X in the surface and the bulk; $\bar{G}_X^{E,S}(T, N_B^S)$ partial excess Gibbs energy of X in the surface as a function of T and N_B^S ; $\bar{G}_X^{E,B}(T, N_B^B)$ partial excess Gibbs energy of X in the bulk as a function of T and N_B^B ($X = A$ or B).

Since the excess Gibbs energy in the bulk $\bar{G}_X^{E,B}(T, N_B^B)$ in Eq. (1) can be obtained directly from thermodynamic databases, we now need the information on the excess Gibbs energy in the surface phase $\bar{G}_X^{E,S}(T, N_B^S)$. Speiser et al. [87Spe, 89Yeu], Hoar & Melford [57Hoa] and Monma and Sudo [61Mon1, 61Mon2] have proposed their own models for $\bar{G}_X^{E,S}(T, N_B^S)$, and their models can be summarized as follows:

$$\bar{G}_X^{E,S}(T, N_B^S) = \beta \cdot \bar{G}_X^{E,B}(T, N_B^S) \quad (3)$$

This equation means that the partial excess Gibbs energy in the surface phase has the same formula as that in the bulk phase, but the mole fraction N_B^B in the bulk phase is replaced by the mole fraction N_B^S in the surface phase. In addition, a coefficient β is multiplied to the right-hand side. This β is a parameter corresponding to the ratio of the coordination number in the surface to that in the bulk phase Z^S/Z^B . For example, Speiser et al. assumed that the excess Gibbs energy is proportional to the coordination number, and that the coordination number in the surface is reduced by the ratio Z^S/Z^B . Then, they gave $\beta = Z^S/Z^B = 9/12$ by assuming the closed packed structure. The value of β is, however, supposed to be affected by the surface relaxation and so on. In addition, there have not been any exact information on Z^S/Z^B for liquid state, especially molten ionic melts. Thus, the authors have derived the relation between the surface tension and the heat of evaporation divided by the molar surface area for pure liquids to determine the following value [96Tan, 98Tan1]

$$\beta = (Z^S)' / Z^B = 0.83 \quad \text{for liquid alloys} \quad (4)$$

where $(Z^S)'$ is the apparent ratio of the coordination number in the surface to that in the bulk considering the relaxation of the surface.

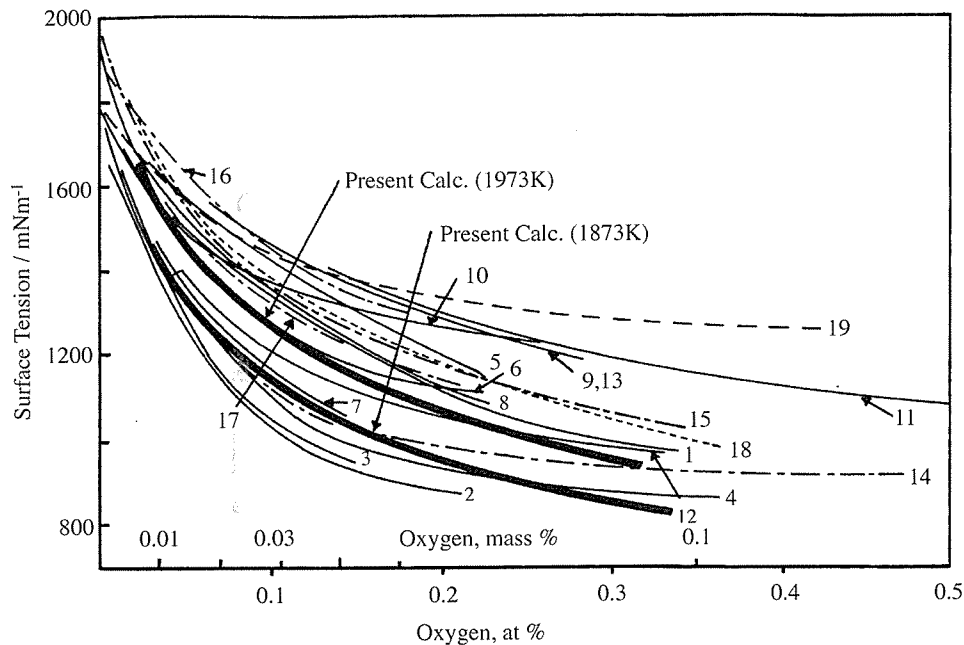


Fig. 3. Comparison of calculated results of surface tension of liquid Fe-O alloy with literature values 1: [73Muk], 2: [73Ogi], 3: [75Pop], 4: [56Vor], 5: [55Hal], 6: [61Koz], 7: [83Ogi], 8: [75Ers], 9: [83Kas], 10: [60Tsa], 11: [71Pov], 12: [74Fil], 13: [92Jim], 14: [84Ogi], 15: [91Tak1], 16: [91Tak2], 17: [91Nak], 18: [92Muk], 19: [92Tai].

In the present work, we regard the liquid Fe-O system as liquid Fe-“FeO” system. As shown in Fig. 2, at the saturated composition of oxygen in liquid iron, the hypothetical “FeO” deposits and its activity becomes unity at the composition in the Fe-FeO system. We assume here the regular solution model to express the excess Gibbs energy in Fe-FeO system as follows

$$G^{\text{Ex,B}} = W_{\text{Fe-FeO}} (1 - N_{\text{FeO}}^{\text{B}}) N_{\text{FeO}}^{\text{B}} \quad (5)$$

$$\bar{G}_{\text{FeO}}^{\text{Ex,B}} = RT \ln \gamma_{\text{FeO}}^{\text{B}} = W_{\text{Fe-FeO}} (1 - N_{\text{FeO}}^{\text{B}})^2 \quad (6)$$

$$\bar{G}_{\text{Fe}}^{\text{Ex,B}} = RT \ln \gamma_{\text{Fe}}^{\text{B}} = W_{\text{Fe-FeO}} (N_{\text{FeO}}^{\text{B}})^2 \quad (7)$$

where $W_{\text{Fe-FeO}}$ is the interaction parameter between Fe and FeO. $\gamma_{\text{FeO}}^{\text{B}}$ and $\gamma_{\text{Fe}}^{\text{B}}$ are activity coefficients of FeO and Fe.

Since we treat here only very dilute composition of oxygen or FeO in liquid iron, the value of $W_{\text{Fe-FeO}}$ can be determined as follows

$$\begin{aligned} \{\bar{G}_{\text{FeO}}^{\text{Ex,B}}\}_{N_{\text{FeO}} \rightarrow 0} &= \{W_{\text{Fe-FeO}} (1 - N_{\text{FeO}}^{\text{B}})^2\}_{N_{\text{FeO}} \rightarrow 0} = W_{\text{Fe-FeO}} \\ &= RT \ln \gamma_{\text{FeO}}^{\text{B},0} = RT \ln \left(\frac{1}{N_{\text{FeO,Sat}}} \right) = RT \ln \left(\frac{1 - N_{\text{O,Sat}}}{N_{\text{O,Sat}}} \right) \end{aligned} \quad (8)$$

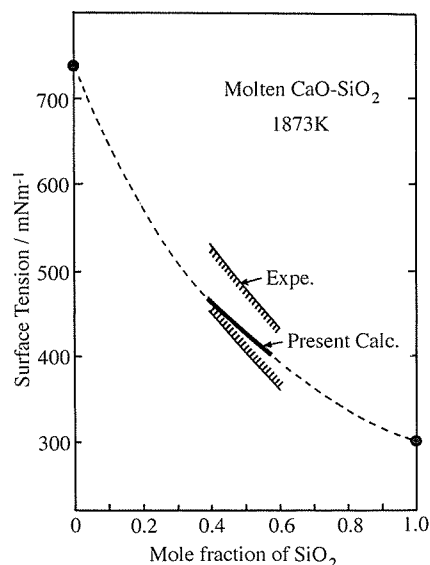


Fig. 4. Comparison of calculated Results of surface tension of molten CaO-SiO₂ system with literature values [51Kin, 69Ono, 71Sha, 774Gun, 81Muk].

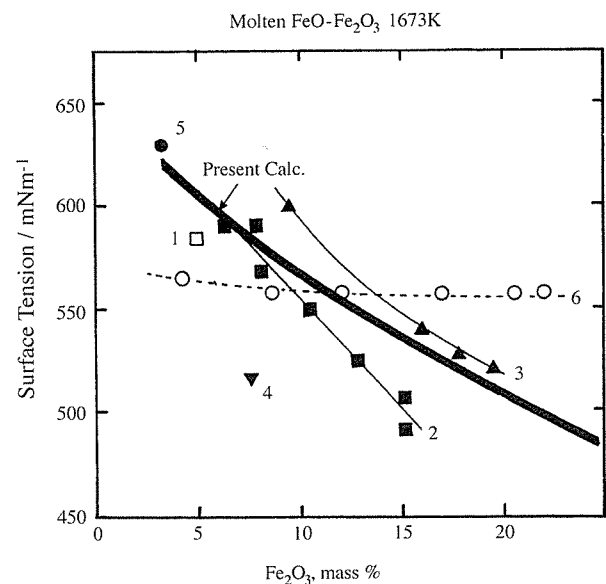


Fig. 5. Comparison of calculated results of surface tension of molten FeO-Fe₂O₃ system with literature values 1: [49Koz1], 2: [56Pop], 3: [63Din], 4: [76Kaw], 5: [69Pop], 6: [96Bha].

where $\gamma_{\text{FeO}}^{\text{B},0}$ is the activity coefficient of FeO at infinitely dilute solution. $N_{\text{FeO,Sat}}$ is the mole fraction of FeO saturated in liquid Fe as shown in Fig. 2. In Eq. (8), all of oxygen atoms in liquid Fe are assumed to be combined with Fe atoms to obtain the final equation.

In Eq. (8), the saturated composition of oxygen $N_{\text{O,Sat}}$ in liquid iron is obtained by the following Eqs. (9) and (10) [88Jap]

$$\log [\text{mass}\% \text{O}]_{\text{Sat}} = -\frac{6320.0}{T} + 2.734 \quad (9)$$

$$N_{\text{O,Sat}} = \frac{\frac{[\text{mass}\% \text{O}]_{\text{Sat}}}{16.0}}{\frac{(100.0 - [\text{mass}\% \text{O}]_{\text{Sat}})}{55.85} + \frac{[\text{mass}\% \text{O}]_{\text{Sat}}}{16.0}} \quad (10)$$

The activity coefficient of Fe is set to be unity because the composition of “FeO” is very dilute. Then,

$$\bar{G}_{\text{Fe}}^{\text{Ex},\text{B}} = RT \ln \gamma_{\text{Fe}}^{\text{B}} = 0 \quad (11)$$

Even under these conditions of the dilute solution of “FeO” in liquid Fe, “FeO” is approximated to be almost saturated in the surface. Then, its activity coefficient is assumed to be unity.

$$\bar{G}_{\text{FeO}}^{\text{Ex},\text{S}} = RT \ln \gamma_{\text{FeO}}^{\text{S}} = 0 \quad (12)$$

In addition, based on Eq. (3), the partial excess Gibbs energy of Fe in the surface is given by the following equation

$$\bar{G}_{\text{Fe}}^{\text{Ex},\text{S}} = RT \ln \gamma_{\text{Fe}}^{\text{S}} = \beta \cdot W_{\text{Fe-FeO}} (N_{\text{FeO}}^{\text{S}})^2 \quad (13)$$

The surface tension σ of liquid alloys in Eq. (1) can be calculated as follows:

- 1) Setting values for the temperature T and the composition N_{B}^{B} of an alloy.
- 2) Inserting the values for surface tension σ_{X} and molar volume V_{X} of pure liquid substances at the above temperature in Eqs. (1) and (2).

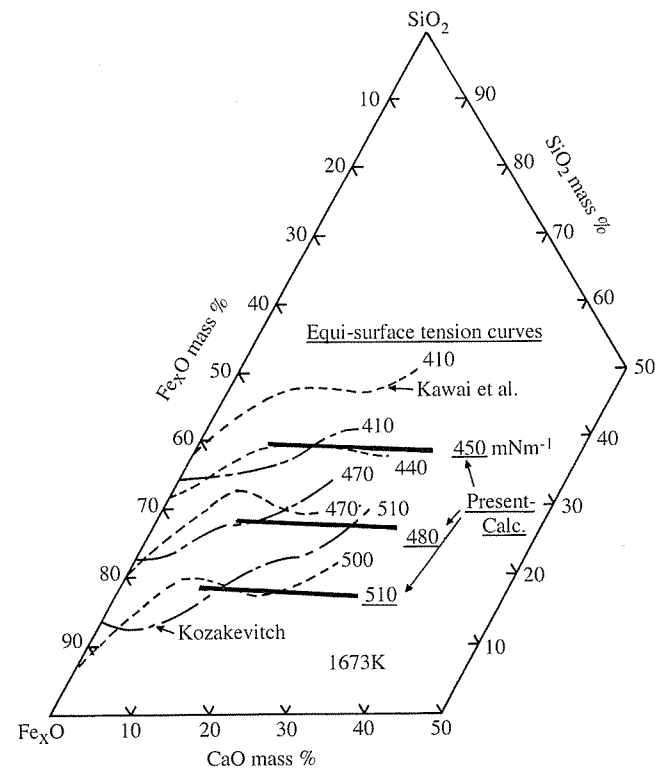


Fig. 6. Comparison of calculated results of surface tension of molten CaO-SiO₂-FeO system with literature Values [49Koz2, 76Kaw].

- 3) Determining excess Gibbs energies in the bulk at the above temperature and composition, and substituting them in Eq. (1).
- 4) Then, one pair between the two equations on the right-hand side of Eq. (1) becomes the equation with unknown N_{B}^{S} . This equation is solved for N_{B}^{S} , and the value of N_{B}^{S} is substituted again into e. g. the first equation of the right-hand side of Eq. (1) to calculate the surface tension σ of the liquid alloy on the left-hand side of Eq. (1).

Table 2. Data for calculation of surface tension of molten oxide mixtures.

| Surface Tension of Pure Component [mNm ⁻¹] | | Refs. |
|--|---|---------|
| SiO ₂ | $\sigma = 243.2 + 0.031 T$ | [87NIS] |
| Al ₂ O ₃ | $\sigma = 721.2 - 0.078 (T - 2313)$ | [94Nak] |
| Fe ₂ O ₃ | $\sigma = 300.0 - 0.15 (T - 1773)$ | [87Mil] |
| CaO | $\sigma = 645.2 - 0.097 (T - 2873)$ | [94Nak] |
| FeO | $\sigma = 645.0 - 0.15 (T - 1773)$ | [87Mil] |
| Molar Volume of Pure Component [m ³ mol ⁻¹] | | Refs. |
| SiO ₂ | $V = 27.516 \{1 + 1 \cdot 10^{-4} (T - 1773)\} \cdot 10^{-6}$ | [87Mil] |
| Al ₂ O ₃ | $V = 28.3 \{1 + 1 \cdot 10^{-4} (T - 1773)\} \cdot 10^{-6}$ | [87Mil] |
| Fe ₂ O ₃ | $V = 38.4 \{1 + 1 \cdot 10^{-4} (T - 1773)\} \cdot 10^{-6}$ | [87Mil] |
| CaO | $V = 20.7 \{1 + 1 \cdot 10^{-4} (T - 1773)\} \cdot 10^{-6}$ | [87Mil] |
| FeO | $V = 15.8 \{1 + 1 \cdot 10^{-4} (T - 1773)\} \cdot 10^{-6}$ | [87Mil] |
| Ionic Radius [Å] | Ionic Distance | Refs. |
| $r_{\text{Si}^{4+}} = 0.40$ | $d_{\text{SiO}_2} = r_{\text{Si}^{4+}} + r_{\text{O}^{2-}} = 1.80$ | [69Sha] |
| $r_{\text{Ca}^{2+}} = 1.00$ | $d_{\text{CaO}} = r_{\text{Ca}^{2+}} + r_{\text{O}^{2-}} = 2.40$ | [69Sha] |
| $r_{\text{Fe}^{3+}} = 0.65$ | $d_{\text{Fe}_2\text{O}_3} = r_{\text{Fe}^{3+}} + r_{\text{O}^{2-}} = 2.05$ | [69Sha] |
| $r_{\text{Fe}^{2+}} = 0.77$ | $d_{\text{FeO}} = r_{\text{Fe}^{2+}} + r_{\text{O}^{2-}} = 2.17$ | [69Sha] |
| $r_{\text{Al}^{3+}} = 0.53$ | $d_{\text{Al}_2\text{O}_3} = r_{\text{Al}^{3+}} + r_{\text{O}^{2-}} = 1.93$ | [69Sha] |
| $r_{\text{O}^{2-}} = 1.40$ | | [69Sha] |

Figure 3 shows the calculated results of the surface tension of the liquid iron–oxygen system at 1873 K and 1973 K with several literature values [73Muk, 73Ogi, 75Pop, 56Vor, 55Hal, 61Koz, 83Ogi, 75Ers, 83Kas, 60Tsa, 71Pov, 74Fil, 92Jim, 84Ogi, 91Tak1, 91Tak2, 91Nak, 92Muk, 92Tai]. Data on σ_X and V_X of pure liquid Fe and FeO are listed in Table 1 [87Mil, 88Iid].

4 Thermodynamic Model of Surface Tension of Molten Slags

As described in a previous paper [96Tan], molten oxide mixtures can be treated in the same way as the molten salt mixtures from the view point of the relationship between surface tension and heat of evaporation divided by the molar surface area for pure liquids. In the present work, our recent model based on Butler's equation for the surface tension of molten ionic mixtures [98Tan1, 98Tan2, 98Tan3, 99Ued] is extended to molten oxide mixtures in multi-component system. This model can be expressed in the following equation

$$\begin{aligned}\sigma &= \sigma_A + \frac{RT}{A_A} \ln \frac{D_A^S}{D_A^B} + \frac{1}{A_A} \bar{G}_A^{E,S}(T, N_B^S, N_C^S, \dots) \\ &\quad - \frac{1}{A_A} \bar{G}_A^{E,B}(T, N_B^B, N_C^B, \dots) \\ &= \sigma_B + \frac{RT}{A_B} \ln \frac{D_B^S}{D_B^B} + \frac{1}{A_B} \bar{G}_B^{E,S}(T, N_B^S, N_C^S, \dots) \\ &\quad - \frac{1}{A_B} \bar{G}_B^{E,B}(T, N_B^B, N_C^B, \dots) \\ &= \sigma_C + \frac{RT}{A_C} \ln \frac{D_C^S}{D_C^B} + \frac{1}{A_C} \bar{G}_C^{E,S}(T, N_B^S, N_C^S, \dots) \\ &\quad - \frac{1}{A_C} \bar{G}_C^{E,B}(T, N_B^B, N_C^B, \dots) \\ &= \dots\end{aligned}\quad (14)$$

$$\text{where } D_X^S = \frac{N_X^S d_X}{\sum_{i=A,B,C,\dots} N_i^S d_i} \text{ and } D_X^B = \frac{N_X^B d_X}{\sum_{i=A,B,C,\dots} N_i^B d_i} \\ (X = A, B, C, \dots).$$

In the above equations, d_X ($X = A, B, C, \dots$) is the ionic distance of the substance X , and it is assumed here to be the sum of the radii of the cation and that of the anion for pure salt X [98Tan1, 98Tan2, 98Tan3]. The excess Gibbs energy in the surface is given by Eq. (15) [98Tan1, 98Tan2, 98Tan3, 99Ued].

$$\frac{\bar{G}_X^{E,S}(T, N_B^S, N_C^S, \dots)}{\bar{G}_X^{E,B}(T, N_B^B, N_C^B, \dots)} = \left\{ \frac{(Z^S)'}{Z^B} \right\} \frac{1}{\xi^4} = 1.1 \\ (X = A, B, C, \dots) \quad (15)$$

where $(Z^S)'/Z^B$ is the apparent ratio of the coordination number considering the relaxation of the surface, and it was evaluated to be 0.94 for molten alkali-halides. ξ is the ratio of the ionic distance in the surface phase, which is caused by the relaxation in the surface, to that in the bulk phase [98Tan1, 98Tan2, 98Tan3, 99Ued]. ξ has been evaluated to be 0.97 by Sawada and Nakamura [79Saw] from their theoretical work on the displacement of ions at the surface for molten alkali-halides.

Equation (15) can be applied to various ionic mixtures other than molten alkali-halide systems [98Tan4, 99Ued]. Equation (15) is, therefore, assumed to be extended to molten oxide mixtures in the present work. The calculation procedure for σ is the same as that for Eq. (1) described in the previous section although the unknown mole fractions of the components in the surface increase as accompanying the increase of the equations in the right-hand side of Eq. (14).

Figures 4, 5 and 6 show the calculated results of molten oxide mixtures in CaO–SiO₂, FeO–Fe₂O₃ and CaO–SiO₂–Fe_xO (= FeO+Fe₂O₃) systems with several literature values [51Kin, 69Ono, 71Sha, 74Gun, 81Muk, 49Koz1, 56Pop, 63Din, 76Kaw, 69Pop, 96Bha, 49Koz2, 76Kaw]. In CaO–SiO₂–Fe_xO systems, the mole fractions of FeO and Fe₂O₃ equilibrated with Fe were calculated by ChemSage [90Eri]

Table 3. Calculated results of surface tensions and the interfacial tension between of liquid Fe and molten slags at 1853K.

| No. | Compositions of Molten Slag (mole fraction) | | | | | Surface Tension of Molten Slag |
|-----|---|--------------------------------|--------------------------------|-------|-------|--------------------------------|
| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | FeO | [mNm ⁻¹] |
| 1 | 0.279 | 0.141 | 0.001035 | 0.299 | 0.281 | 498 |
| 2 | 0.316 | 0.160 | 0.000502 | 0.338 | 0.186 | 479 |
| 3 | 0.345 | 0.174 | 0.000214 | 0.370 | 0.111 | 481 |
| 4 | 0.366 | 0.185 | 0.000072 | 0.393 | 0.056 | 494 |
| 5 | 0.376 | 0.190 | 0.000027 | 0.404 | 0.030 | 495 |

| No. | Composition of liquid Fe (mole fraction) | | | Surface Tension of Liquid Fe | Interfacial Tension |
|-----|--|----------|------------|------------------------------|----------------------|
| | [O] | [Si] | [Al] | [mNm ⁻¹] | [mNm ⁻¹] |
| 1 | 0.00187 | 0.000013 | 0.00000014 | 999 | 673 |
| 2 | 0.00133 | 0.000031 | 0.00000021 | 1088 | 764 |
| 3 | 0.00085 | 0.000089 | 0.00000035 | 1205 | 874 |
| 4 | 0.00045 | 0.00035 | 0.00000081 | 1371 | 1015 |
| 5 | 0.00025 | 0.0012 | 0.0000018 | 1527 | 1137 |

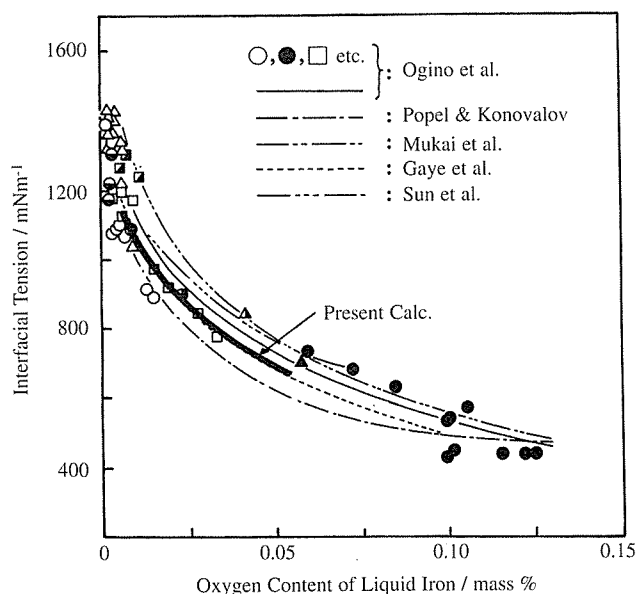


Fig. 7. Comparison of calculated results of interfacial Tension between liquid steel and molten slag with literature values [59Pop, 73Muk, 81Gay, 84Ogi, 94Sun].

with thermodynamic databases. Data used for these calculations are listed in Table 2 [69Sha, 84Gay, 87NIS, 87Mil, 94Nak]. Since the calculated results of σ of molten slags are dependent upon the values of the surface tension σ_X of pure components, it is very important to select those values. In the present work, for Fe_2O_3 and FeO , the values given by Mills and Keene [87Mil] in their compilation of physical properties of BOS (the Basic Oxygen Steelmaking) slags have been used with their temperature dependence ($d\sigma_X/dT = -0.15 \text{ mNm}^{-1}\text{T}^{-1}$). Nakajima [94Nak] reported the temperature dependence of σ_X of Al_2O_3 and CaO , which have very high melting points. σ_X of SiO_2 are compiled in the NIST molten salt database [87NIS].

The ionic radii have been compiled as the effective ionic radii for oxide by Shannon and Prewitt [69Sha]. In addition, Gaye's model [84Gay] has been used to obtain the excess Gibbs energies of molten oxide mixtures, which are stored in the thermodynamic database of ChemSage.

5 Thermodynamic Model for Interfacial Tension between Liquid Steel and Molten Slag

Cramb and Jimbo [89Cra] have accumulated the information on the surface tension of liquid steels and molten slags, and their interfacial tensions. Then, they described that the above interfacial tensions can be related to the surface tensions of liquid steels and molten slags on the basis of the Girifalso-Good equation. In the present work, the following Girifalso-Good equation [57Gri] has been also applied to evaluate the interfacial tension between liquid steel and molten slag from the surface tensions of these two liquid phases which have been calculated in the previous sections

$$\sigma_{\text{Fe-Slag}} = \sigma_{\text{Fe}} + \sigma_{\text{Slag}} - 2 \Phi (\sigma_{\text{Fe}} \cdot \sigma_{\text{Slag}})^{1/2} \quad (16)$$

Based on the report by Cramb and Jimbo [89Cra] that Φ in Eq. (16) becomes 0.5 for molten slag without FeO and 0.8 for high content of FeO , the following composition dependence of Φ is assumed:

$$\Phi = 0.5 + 0.3 \cdot N_{\text{FeO}} \quad (17)$$

The calculation of the interfacial tension between liquid iron and molten $35\text{CaO-}35\text{SiO}_2\text{-}30\text{Al}_2\text{O}_3\text{-(}2 \sim 30\text{)FeO}$ slag has been carried out in the present work. The procedure is as follows

- 1) By applying the software ChemSage [90Eri] and thermodynamic databases, the equilibrium compositions of all components have been calculated in liquid iron alloys and molten $35\text{CaO-}35\text{SiO}_2\text{-}30\text{Al}_2\text{O}_3\text{-(}2 \sim 30\text{)FeO}$ slags.
- 2) The surface tensions of liquid iron alloys is calculated from Eqs (1) to (13) by using data on the oxygen content and the saturated oxygen content for a given temperature.
- 3) The surface tensions of molten slag is calculated from Eqs (14) and (15) by using data on the excess Gibbs energy of liquid phase.
- 4) The interfacial tension is obtained from the Girifalso-Good equation (16) [57Gir] with Eq. (17).

The calculated results of the interfacial tension are shown in Table 3. Since the contents of Si and Al are very dilute in liquid Fe as shown in Table 3, the effect of those elements on the surface tension of liquid Fe alloy has been ignored. In other words, although the Fe alloy in Table 3 is 4 components system (Fe, O, Si and Al), Eq. (1) has been applied directly to Fe-O system to evaluate the surface tension of liquid steel. Figure 7 shows the comparison of the calculated results of the interfacial tension with some literature values [59Pop, 73Muk, 81Gay, 84Ogi, 94Sun]. As shown in this figure, the calculated results agree well with those literature values.

6 Concluding Remarks

In the present work, we have proposed a thermodynamic evaluation procedure of the interfacial tension between liquid iron alloys and molten slags by using the Girifalso-Good equation, which is a function of the surface tensions of liquid Fe alloys and molten slags. The surface tension of liquid iron alloys can be evaluated on the basis of Butler's equation by regarding the Fe-O system as a Fe- FeO system. In addition, the thermodynamic model of the surface tension of molten ionic mixtures is extended to molten slags.

Based on the procedures described in the present work, we can develop a multi-functional thermodynamic databank system [98Tan1, 98Tan3, 99Tan], which will be of wide applicability in the evaluation of physico-chemical properties of the liquid state with the simultaneous calculation of the phase diagrams in salt mixtures and oxide mixtures as well as alloys.

Literature

- 32But Butler, J. A. V.: Proc. Roy. Soc. A 135 (1932) 348–375.
 49Koz1 Kozakevitch, P.: Rev. Metall. 46 (1949) 505.
 49Koz2 Kozakevitch, P.: Rev. Metall. 46 (1949) 572.
 51Kin King, T. B.: J. Soc. Glass. Technol. 35 (1951) 241–259.
 55Hal Halden, F. A.; Kingery, W. D.: J. Phys. Chem. 59 (1955) 557–559.
 56Pop Popel, S. I.; Esin, O. A.: Zh. Fiz. Khim. 30 (1956) 1193.
 56Vor Vor dem Esche, W.; Peter, O.: Arch. Eisenhuettenwes. 27 (1956) 355–366.

- 57Gir *Girifalco, L. A.; Good, R. J.*: J. Phys. Chem. 61 (1957) 904–909.
- 57Hoa *Hoar, T. P.; Melford, D. A.*: Trans. Faraday Soc. 53 (1957) 315–326.
- 59Pop *Popel, S. I.; Konovalov, G. F.*: Izv. VUZ Chernaya Metall. 8 (1959) 3.
- 60Tsa *Tsarevskii, B. V.; Popel, S. I.*: Izv. VUZ Chernaya Metall. 12 (1960) 12–16.
- 61Koz *Kozakevitch, P.; Urbain, G.*: Mem. Sci. Rev. Metall. 58 (1961) 517–534.
- 61Mon1 *Monma, K.; Sudo, H.*: J. Jpn. Inst. Metals 25 (1961) 65–68.
- 61Mon2 *Monma, K.; Sudo, H.*: J. Jpn. Inst. Metals 25 (1961) 143–147.
- 63Din *Din-Fen, U.; Vishkarev, A. F.; Yavoiskii, V. I.*: Izv. VUZ Chernaya Metall. 6 (1963) 27.
- 69Ono *Ono, K.; Gunji, K.; Araki, T.*: J. Jpn. Inst. Metals 33 (1969) 299–304.
- 69Pop *Popel, S. I.; Sokolov, V. I.; Esin, O. A.*: Russ. J. Phys. Chem. 43 (1969) 1782.
- 69Sha *Shannon, R. D.; Prewitt, C. T.*: Acta. Cryst. B 25 (1969), 925–946.
- 71Pov *Povolotskii, D. Yu.; Stroganov, A. I.; Puzyrez, A. V.*: Izv. Akad. Nauk SSSR Met. 4 (1971) 87–90.
- 71Sha *Sharma, S. K.; Philbrook, W. O.*: Proc. ICSTIS, Suppl. Trans. ISIJ 11 (1971). 569.
- 73Muk *Mukai, K.; Kato, T.; Sakao, H.*: Tetsu-to-Hagane 59 (1973) 55–62.
- 73Ogi *Ogino, K.; Nogi, K.; Koshida, Y.*: Tetsu-to-Hagane 59 (1973) 1380–1387.
- 74Fil *Filippov, S. I.; Goncharenko, O. M.*: Izv. VUZ Chernaya Metall. 9 (1974) 10–16.
- 74Gun *Gunji, K.; Dan, T.*: Trans. ISIJ 14 (1974) 162–169.
- 75Ers *Ershov, G. S.; Bychev, V. M.*: Russ. Metall. 4 (1975) 45–46.
- 75Pop *Popel, S. I.; Tsarevskii, B. V.; Pavlov, V. V.; Furman, E. L.*: Izv. Akad. Nauk SSSR Met. 4 (1975) 54–58.
- 76Kaw *Kawai, Y.; Mori, K.; Shiraishi, Y.; Yamada, N.*: Tetsu-to-Hagane 62 (1976) 53–61.
- 79Saw *Sawada, S.; Nakamura, K.*: J. Phys. C 12 (1979) 1183–1193.
- 80Goo *Goodisman, J.*: J. Colloid & Interface Sci. 73 (1980) 115–123.
- 81Gay *Gaye, H.; Lucas, L. D.; Olette, M.; Riboud, P. V.*: Intern. Symp. on Interface Phenomena in Metallurgical Systems, Canad. Inst. Min. Met., Hamilton, Canada (1981).
- 81Muk *Mukai, K.; Ishikawa, T.*: J. Jpn. Inst. Metals 45 (1981) 147–154.
- 83Kas *Kasama, A.; McLean, A.; Miller, W. A.; Morita, Z.; Ward, M. J.*: Canad. Metall. Quant. 22 (1983) 9–17.
- 83Ogi *Ogino, K.; Nogi, K.; Hosoi, C.*: Tetsu-to-Hagane 69 (1983) 1989–1994.
- 84Gay *Gaye, H.; Welfringer, J.*: Proc. 2nd Int. Symp. Metall. Slags & Fluxes (1984) 357–375.
- 84Ogi *Ogino, K.; Hara, S.; Niwa, T.; Kimoto, S.*: Trans. ISIJ 24 (1984) 522–531.
- 87Mil *Mills, K. C.; Keene, B. J.*: Intern. Mater. Rev. 32 (1987) 1–120.
- 87NIS *NIST Molten Salt Database, National Institute of Standards and Technology, Gaithersburg (1987).*
- 87Spe *Speiser, R.; Poirier, D. R.; Yeum, K. S.*: Script Metall. 21 (1987) 687–692.
- 88Jap *The Japan Society for the Promotion of Science, The 19th Committee on Steelmaking, Steelmaking Data Sourcebook, Gordon and Breach Pub., New York, (1988) 113.*
- 88Iid *Iida, T.; Guthrie, R. I. L.*: The Physical Properties of Liquid Metals, Clarendon Press, Oxford (1988) 71 and 134.
- 89Cra *Cramb, A. W.; Jimbo, I.*: Steel Research 60 (1989) 157–165.
- 89Yeu *Yeum, K. S.; Speiser, R.; Poirier, D. R.*: Metall. Trans. B 20B (1989) 693–703.
- 90Eri *Eriksson, G.; Hack, K.*: Metall. Trans. B 21B (1990) 1013–1023.
- 91Haj *Hajra, J. P.; Froberg, M. G.; Lee, H. K.*: Z. Metallk. 82 (1991) 718–720.
- 91Nak *Nakashima, K.; Takihira, K.; Mori, K.; Shinozaki, S.*: J. Jpn. Inst. Met. 55 (1991), 1199–1206.
- 91Tak1 *Takiuchi, N.; Taniguchi, T.; Shinozaki, N.; Mukai, K.*: J. Jpn. Inst. Met. 55 (1991), 44–49.
- 91Tak2 *Takiuchi, N.; Taniguchi, T.; Tanaka, Y.; Shinozaki, N.; Mukai, K.*: J. Jpn. Inst. Met. 55 (1991), 180–185.
- 92Jim *Jimbo, I.; Cramb, A.*: ISIJ Intern. 32 (1992) 26–35.
- 92Muk *Mukai, K.; Shinozaki, N.*: Mater. Trans. JIM 33 (1992) 45–50.
- 92Tai *Taimatsu, H.; Nogi, K.; Ogino, K.*: J. High Temp. Soc. 18 (1992) 14–19.
- 94Nak *Nakajima, K.*: Tetsu-to-Hagane 80 (1994) 599–604.
- 94Sun *Sun, H.; Nakashima, K.; Mori, K.*: ISIJ Intern. 37 (1994) 323–331.
- 94Tan *Tanaka, T.; Iida, T.*: Steel Research 65 (1994) 21–28.
- 94Uti *Utigard, T.*: ISIJ Intern. 34 (1994) 951–959.
- 96Bha *Bhattacharyya, P. K.; Gaskell, D. R.*: Metall. Mater. Trans. B. 27B (1996) 139–141.
- 96Tan *Tanaka, T.; Hack, K.; Iida, T.; Hara, S.*: Z. Metallkd. 87 (1996) 380–389.
- 98Tan1 *Tanaka, T.; Hara, S.; Ogawa, M.; Ueda, T.*: Z. Metallkd., 89 (1998) 368–374.
- 98Tan2 *Tanaka, T.; Hara, S.; Ogawa, M.; Ueda, T.*: Molten Salt Forum, 5–6 (1998) 213–216.
- 98Tan3 *Tanaka, T.; Hara, S.; Ueda, T.*: Proc. 11th Intern. Symp. on Molten Salts, San Diego, USA, (1998) 645–650.
- 99Tan *Tanaka, T.; Hack, K.; Hara, S.*: Z. Metallkd. (to be submitted).
- 99Ued *Ueda, T.; Tanaka, T.; Hara, S.*: Z. Metallkd. 90 (1999) 342–347.

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