

Estimation of Activity Coefficient of Solute in Infinite Dilute Liquid Iron Based on Surface Tension of Binary Liquid Fe Alloys

Masashi NAKAMOTO^{1)*} and Toshihiro TANAKA²⁾

1) Low Temperature Center, Osaka University, 2-1 Yamadaoka, Suita, Osaka, 565-0871 Japan.

2) Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka, 565-0871 Japan.

(Received on December 12, 2019; accepted on March 3, 2020; originally published in *Tetsu-to-Hagané*, Vol. 105, 2019, No. 3, pp. 395–399)

Expansion of the system for thermodynamic parameters in liquid iron is expected for the improvement in iron & steelmaking processes. The development of their calculation method is one of the issues for its realization. In the present work, we proposed a calculation method for an activity coefficient of solute in infinite dilute liquid iron to element i , γ_i^0 , based on the surface tension of binary liquid Fe alloys. It was found that the estimated values by our proposed method agree with recommended literature data.

KEY WORDS: thermodynamic; activity coefficient; surface tension; Fe; alloy.

1. Introduction

Thermodynamic data such as the activity coefficient, interaction coefficient and excess free energy are regarded as important guidelines for determining the direction of actual operations in various kinds of high-temperature metal production processes. This is because thermodynamic data elucidate the reactions of liquid state substances and the phenomena occurring between them. Therefore, the thermodynamic data in the liquid Fe system related to the removal of impurities and inclusions have been actively obtained in the steelmaking process for steel production.^{1,2)} Many types of models exist for calculating the physicochemical properties, which are the control factors in high-temperature processes. Models for liquid alloy surface tension and viscosity based on thermodynamic data have been developed as the thermodynamic database is improved, and the construction of a calculation system based on this thermodynamic database has progressed.^{3–8)} In particular, a calculation method based on Butler's equation for the surface tension of a liquid alloy via activity has been proposed by Speiser *et al.*,¹⁰⁾ and is considered a good model that correlates well with the measured value. Thus, it is no exaggeration to state that this model sufficiently associates the thermodynamic data to the surface tension for a liquid alloy. From this viewpoint, Gasior *et al.*¹¹⁾ reported a method for calculating the excess free energy from the surface tension of a liquid alloy using the previous method (*i.e.*, calculating the liquid alloy surface tension based on the thermodynamic data) in the opposite

direction. Gasior *et al.* proposed that a polynomial equation can fit the data on the composition dependence of surface tension for liquid alloy in Fe–Ni and Fe–Co systems, and they evaluated the excess free energy in an entire composition range by fitting the surface tension calculated with the model into the polynomial equation. This method of Gasior *et al.* is suitable to calculate the phase equilibrium such as phase diagram because the calculated excess free energy is available in an entire composition range. However, a small amount of many different solute components are often dissolved in the large quantity of solvent refined in a metal refining reaction; *e.g.*, in liquid steel in the steel refining process. In this case, the activity coefficient of the solute constituent based on Wagner's expression¹²⁾ is generally used to calculate an equilibrium partition under the assumption of an infinite dilute liquid as a matter of convenience. Therefore, measurements of the activity coefficients and the interaction coefficient between solutes in an infinite dilute liquid Fe have been carried out even in recent years owing to their indispensability.^{13–17)} In the present work, we were challenged to calculate the activity coefficient of a solute element in an infinite dilute liquid Fe based on the surface tension for a binary liquid Fe-based alloy. Further, the surface tension for liquid metals and alloys was reviewed based on published compilations and the latest data to improve the accuracy of the calculation. This is because great variability among the measured data on surface tension has been reported owing to the considerable variation of surface tension that occurs with a slight amount of impurity element.

* Corresponding author: E-mail: nakamoto@mat.eng.osaka-u.ac.jp



2. Calculation of Activity Coefficient in Infinite Dilute Liquid Based on Surface Tension for a Binary Liquid Alloy

The equation for calculating the surface tension of a liquid A-B alloy⁽³⁻⁸⁾ is given as

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

where subscript *i* indicates either the A or B metal; σ_i is the surface tension of the pure liquid metal *i*; *R* is the gas constant; *T* is the absolute temperature; and *A_i* is the surface area of a monolayer of pure liquid metal *i*, expressed as $A_i = LN_0^{1/3}V_i^{2/3}$ where *L* is typically 1.091 for liquid metals, *N₀* is the Avogadro’s number, and *V_i* is the molar volume of pure liquid metal *i*. Further, X_i^P (where P = S (surface) or B (bulk)) is the mole fraction of pure liquid metal *i* in the surface or the bulk, $\bar{G}_i^{E,P}(T, X_B^P)$ (P=S or B) is the partial excess Gibbs energy of metal *i* in the surface or bulk as a function of *T* and X_B^B or X_B^S . In terms of $\bar{G}_i^{E,S}(T, X_B^S)$, the equation⁽³⁻⁸⁾ proposed by Yeum *et al.*⁽¹⁸⁾ was used herein, given as

$$\bar{G}_i^{E,S}(T, X_B^S) = \beta \cdot \bar{G}_i^{E,B}(T, X_B^B). \quad (2)$$

Equation (2) signifies that the partial excess Gibbs energy in the surface phase, $\bar{G}_i^{E,S}(T, X_B^S)$, has the same formula as that in the bulk phase. It is noted that the mole fraction in the bulk phase (X_B^B) was replaced by the mole fraction in the surface, X_B^S , and the coefficient β was multiplied with $\bar{G}_i^{E,B}(T, X_B^B)$. The parameter β , which corresponds to the ratio of the coordination number in the surface to that in the bulk, is generally given as 0.75 by assuming a close-packed structure. However, Tanaka *et al.*⁽³⁻⁸⁾ have derived a relation between the surface tension and the heat of evaporation divided by the molar surface area for pure liquid metals, and determined the value $\beta=0.83$ for liquid alloys. The surface tension for a liquid alloy, σ , based on thermodynamic data $\bar{G}_i^{E,P}(T, X_B^P)$ can be calculated by solving the system of equations with the two unknown parameters of the surface tension for liquid alloy, σ , and the mole fraction of B in the surface, X_B^S . This is possible when the surface tensions of the pure liquid metals A, σ_A , and B, σ_B , the surface area in a monolayer of the pure liquid metals A, A_A , and B, A_B , and the mole fraction of B in the bulk, X_B^B , are known. Equation (1) can then be rewritten using the relation of Eq. (3) to Eq. (4), such that

$$\bar{G}_i^{E,P} = RT \ln \gamma_i^P \quad (P = S \text{ or } B) \quad (3)$$

where γ_i^P is the activity coefficient of metal *i* in the surface (superscript S) or the bulk (superscript B). Further,

$$\begin{aligned} \sigma &= \sigma_A + \frac{RT}{A_A} \ln \frac{1 - X_B^S}{1 - X_B^B} + \frac{1}{A_A} \beta RT \ln \gamma_A^S - \frac{1}{A_A} RT \ln \gamma_A^B \\ &= \sigma_B + \frac{RT}{A_B} \ln \frac{X_B^S}{X_B^B} + \frac{1}{A_B} \beta RT \ln \gamma_B^S - \frac{1}{A_B} RT \ln \gamma_B^B. \end{aligned} \quad (4)$$

Here, the calculation of the activity coefficient from the surface tension of the liquid A-B alloy, which is the proposed method in the present work, is considered based on Eq. (4). When the known parameters are σ , σ_A , σ_B , A_A , A_B and X_B^B , there are five unknown parameters in the two expressions in Eq. (4); namely, X_B^S , γ_A^S , γ_A^B , γ_B^S and γ_B^B . Thus it is impossible to determine the activity coefficient based on Eq. (4). Therefore, this study focused on an infinite dilute solution. In an infinite dilute liquid, the activity coefficient for the solute is a constant based on Henry’s law, and the activity coefficient for the solvent is a constant based on Raoult’s law. For example, the relationships $\gamma_A^B = \gamma_A^S = 1$ and $\gamma_B^B = \gamma_B^S = \gamma_B^0 = \text{const.}$ are satisfied in the system where solute B exists in an infinite solute liquid A. Therefore, we can obtain

$$\begin{aligned} \sigma &= \sigma_A + \frac{RT}{A_A} \ln \frac{1 - X_B^S}{1 - X_B^B} \\ &= \sigma_B + \frac{RT}{A_B} \ln \frac{X_B^S}{X_B^B} + \frac{(\beta - 1)}{A_B} RT \ln \gamma_B^0. \end{aligned} \quad (5)$$

Here, it is assumed that the surface and bulk layers are both regarded as an infinite dilute liquid, where a solute B is infinitely diluted in a liquid A in the surface layer. Because only two parameters are unknown in Eq. (5) (namely, the activity coefficient for solute B in an infinite dilute liquid A (γ_B^0) and the mole fraction of B in the surface (X_B^S)), γ_B^0 can be calculated by simultaneously solving the two expressions of Eq. (5). In the present work, the activity coefficients for the solute elements Al, Ce, Co, Cr, Cu, La, Mn, Ni, Si, Sn, Ti in an infinite dilute liquid Fe at 1 873 K were calculated based on Eq. (5).

3. Properties for Calculation of Activity Coefficient

3.1. Molar Volume and Surface Tension for Pure Liquid Metal

Table 1 shows the molar volume and surface tension for a pure liquid metal used in the activity coefficient of solute element in an infinite dilute liquid Fe. The molar

Table 1. Molar volume at melting point,⁽¹⁹⁾ thermal expansion coefficient⁽¹⁹⁾ and surface tension for element.^(21,22,25,26)

<i>i</i>	<i>V_{mp,i}</i> (10 ⁻⁶ m ³ /mol)	α_i (10 ⁻⁴ /K)	σ_i (mN/m)
Al	11.3	1.5	979 – 0.271 (<i>T</i> – 933) ⁽²²⁾
Ce	20.9	0.34	751 – 0.07 (<i>T</i> – 1 071) ⁽²⁶⁾
Co	7.60	1.4	1 900 – 0.35 (<i>T</i> – 1 768) ⁽²¹⁾
Cr	8.27	1.1	1 710 – 0.54 (<i>T</i> – 2 176) ⁽²¹⁾
Cu	7.94	1.0	1 320 – 0.28 (<i>T</i> – 1 358) ⁽²¹⁾
Fe	7.94	1.3	1 880 – 0.41 (<i>T</i> – 1 811) ⁽²¹⁾
La	23.3	0.40	752 – 0.056 (<i>T</i> – 1 193) ^(25,26)
Mn	9.54	1.6	1 152 – 0.35 (<i>T</i> – 1 518) ⁽²¹⁾
Ni	7.43	1.51	1 880 – 0.41 (<i>T</i> – 1 811) ⁽²¹⁾
Si	11.1	1.4	850 – 0.25 (<i>T</i> – 1 683) ⁽²¹⁾
Sn	17.0	0.87	550 – 0.07 (<i>T</i> – 505) ⁽²¹⁾
Ti	11.6	0.56	1 670 – 0.16 (<i>T</i> – 1 943) ⁽²¹⁾

volume at 1 873 K for each solute i was calculated using the molar volume at the melting point, $V_{mp,i}$ and the thermal expansion coefficient, α_i , given in Ref. [19]. Several data compilations giving the surface tension for a pure liquid metal have been reported, such as in the book by Iida and Guthrie,¹⁹⁾ and the reviews by Keene²⁰⁾ and Mills *et al.*²¹⁾ It is well known that surface tension is affected by impurities such as surface active elements. In some cases, a significant decrease in the surface tension can result from only a small amount of the impurity element, which leads to the large scatter of measured surface tension values. It is considered that the impurity sources are the sample, the atmosphere and the contact material used in the experiments. To obtain reliable experimental measurement data, therefore, a great deal of attention has been given to improving the purity of the sample and the atmosphere and preventing reactions between the sample and contact material. The review papers by Keene and by Mills *et al.* evaluated the surface tension data for liquid metals from this viewpoint, primarily focusing on the surface tension reduction induced by the presence of impurities. Recently, the levitated oscillating drop method has been used to measure the surface tension of liquid metals, where contact between the liquid metal sample and the contact material is avoided by levitating the liquid metal sample. This method has provided reliable surface tension data even for high-reactivity metals by eliminating the effect of impurities originating from the contact materials. While the review by Mills *et al.* partially included data obtained by the levitated oscillating drop method, the reliability of the surface tension data for liquid metals has increased by the additional measurements acquired by this method since the review of Mills *et al.* From the above viewpoints, the surface tension for pure liquid metals was reassessed in the present work.

This work assessed the surface tension of pure liquid Al, Ce and La because the high reactivity of these elements are considered to greatly affect the surface tension. Although Cr and Ti are also high-reactivity metals, the data for these elements using the levitated oscillating drop method in the compilation by Mills *et al.* are regarded as appropriate measurement values. In addition, the surface tension values of pure liquid Co, Cu, Fe, Mn, Ni, Si, and Sn evaluated in the compilation of Mills *et al.* are also appropriate because these elements are less reactive than Cr, Ti, Al, Ce and La. Further, the assessment of some metals were conducted by including the data from the levitated oscillating drop method. Kobatake *et al.*,²²⁾ Brillo *et al.*²³⁾ and Leitner *et al.*²⁴⁾ have measured the surface tension for pure liquid Al with the levitated oscillating drop method. In the calculations herein, the value measured by Kobatake *et al.* was selected as the most appropriate value of the three based on the report that the concentration of oxygen in the sample of Kobatake *et al.* is lowest. Recently, the surface tension values of pure liquid rare earth elements including Ce and La have been measured systematically by Ishikawa *et al.* with the electrostatic levitated oscillating drop method.^{25,26)} The temperature range in their measurement of Ce is narrow (1 079–1 185 K), while that of La is broad (1 150–1 525 K). Although some may argue the justifiability of extrapolating the surface tension data for Ce at 1 873 K from the temperature dependence of surface tension for Ce given

by Ishikawa *et al.*, the surface tension data for La^{25,26)} and Ce²⁶⁾ was used in the present work owing to the fact that this represents the sole measurement by the levitated oscillating drop method for Ce.

3.2. Surface Tension for Binary Liquid Fe Alloy

In this calculation, the surface tension for an infinite dilute liquid Fe-solute element i must be considered as the surface tension of a binary liquid Fe alloy to calculate the activity coefficient for the solute element i in an infinite dilute liquid Fe, γ_i° . Here, to consider the surface tension for an infinite dilute liquid Fe-solute element i , we applied the concept regarding the effect of additive elements on the surface tension for a Fe-based binary liquid alloy reported by Keene.²⁷⁾ Keene reported the value of $d\sigma/(d[at\%])$ (mN/m[at%]) in the composition range adjacent to a pure liquid Fe based on the tendency that, when adding a solute element to liquid Fe, the surface tension decreases linearly in a certain solute concentration range. The surface tension for an infinite dilute liquid Fe-solute element i , σ , was calculated by decreasing the concentration of the solute element to the utmost limits in accordance with this linear relationship, *i.e.* lowering the concentration of the solute element in the region of an infinite dilute liquid Fe was used for the calculation of the activity coefficient for solute element i in an infinite dilute liquid Fe (γ_i°). **Table 2** shows the value of $d\sigma/d[at\%]$ (mN/m[at%]) in the composition range adjacent to the pure liquid Fe for the calculation of the surface tension for liquid Fe alloy, *viz.* an infinite dilute liquid Fe-solute element i , σ . The $d\sigma/d[at\%]$ (mN/m[at%]) values in Table 2 were assessed in this study based on the value given in the compilation by Keene and by additionally considering newly-obtained data via the levitated oscillating drop method and the other methods.

As discussed above, it is preferable to use the surface tension data for liquid Fe–Al alloy measured by the levitated oscillating method for the present calculation owing to the high reactivity of Al. However, the measurement of surface tension for the liquid Fe–Al alloy with a low Al concentration range has not been carried out since the Keene compilation. Therefore, the value $d\sigma/d[at\%] = -18$ in that compilation was selected herein. Two values of $d\sigma/d[at\%]$

Table 2. Surface activity of solute relative to iron.^{27,30,33,36)}

i	$d\sigma/d[at\%]$ (mN/m[at%])	Range (in at%)
Al	-18 ²⁷⁾	0–10
Ce	-1 750 ²⁷⁾	0–0.04
Co	0 ³⁶⁾	0–10
Cr	0 ³⁰⁾	0–10
Cu	-30 ²⁷⁾	0–10
La	-1 500 ²⁷⁾	0–0.4
Mn	-50 ²⁷⁾	0–5
Ni	-0.4 ³³⁾	0–20
Si	-13 ²⁷⁾	0–5
Sn	-1 630 ²⁷⁾	0–0.15
Ti	0 ²⁷⁾	0–1

are given for each of the Fe–Ce, Fe–La and Fe–Ti systems in the compilation of Keene: namely, 0 or -1750 for the Fe–Ce system, 0 or -1500 for the Fe–La system, and 0 or -230 for Fe–Ti system. Thus, these values should be assessed. Although Ce, La and Ti have a high reactivity like Al, no surface tension data have been obtained by the levitated oscillating method for a Fe-based liquid alloy containing Ce, La and Ti. Therefore, the $d\sigma/d[at\%]$ was reviewed based on previous reports^{28,29} that are not included in Keene’s compilation. Ryabov *et al.*²⁸) reported that Ce and La act as a surface active component against liquid steel, which means that Ce and La are considered to be surface active components for liquid iron. On the basis of this knowledge, we adopted the $d\sigma/d[at\%]$ values of -1750 for the Fe–Ce system and -1500 for the Fe–La system, which decrease the surface tension for liquid Fe alloy. In terms of the Fe–Ti system, $d\sigma/d[at\%] = 0$ was selected in this calculation because Lee *et al.*²⁹) indicate the result that the surface tension for liquid Fe–Ti alloy rarely changes in the low Ti concentration range. It has been confirmed that the surface tension for liquid Fe–Cr alloy has no composition dependence based on a measurement result via the levitated oscillating drop method by Nogi *et al.*,^{30,31}) although the data on the surface tension for liquid Fe–Cr alloy has exhibited a large scatter in the past because of the high reactivity of Cr. Therefore, it is considered that the surface tension for liquid Fe–Cr alloy does not vary with the composition; *i.e.*, $d\sigma/d[at\%] = 0$. Nogi *et al.*³⁰) also have measured the surface tension for the liquid Fe–Cu system and Fe–Sn system by the levitated oscillating drop method. Their results are in good agreement with past literature values, which indicates that the $d\sigma/d[at\%]$ value of -30 for the liquid Fe–Cu system and -1630 for the liquid Fe–Sn system, provided in Keene’s compilation, are reliable. Since Keene’s compilation was published, the surface tension for the liquid Fe–Si system has been measured by the levitated oscillating drop method by Brooks *et al.*³²) Although their measurement was carried out for varying Si composition, increasing in steps

of 25 at%, their data are not suitable for the calculation for $d\sigma/d[at\%]$ because the range of Si concentration where a linear relationship can be valid is less than 5 at%. Thus, the value found in Keene’s compilation of $d\sigma/d[at\%] = 13$ was used herein. The surface tension of the liquid Fe–Ni system has been newly measured by Seyhan *et al.*,³³) and the value $d\sigma/d[at\%] = -0.4$ given in their study was selected herein. To our knowledge, no data exists on the surface tension for the liquid Fe–Mn system measured by the levitated oscillating drop method. The new $d\sigma/d[at\%]$ value by Lee *et al.*³⁴) obtained by the sessile drop method is in accordance with the value of $d\sigma/d[at\%] = -50$ assessed by Keene, and this value was used in this calculation. The $d\sigma/d[at\%]$ value obtained by Eichel *et al.*³⁵) via the levitated oscillating drop method shows a larger negative concentration dependence of surface tension for the liquid Fe–Co system than before when adding Co to liquid Fe. Gasior *et al.*¹¹) have reported that the data of Eichel *et al.* is unreliable based on their evaluation of the comparison of the excess Gibbs free energy calculated from the surface tension for liquid Fe–Co alloy with that in the literature. Gasior *et al.* further suggest that the surface tension value measured by the sessile drop method by Ogino *et al.*³⁶) possesses higher reliability. Based on the data of Ogino, $d\sigma/d[at\%] = 0$ for liquid Fe–Co alloy was selected in this study. The composition ranges where the surface tension for liquid Fe-based alloy had a linear relationship on its concentration dependence in the compilation of Keene are show in Table 2. The temperatures of the $d\sigma/d[at\%]$ values in Table 2 are 1823 K for the data in Keene’s compilation²⁷) and the measured temperatures for the others; which are different from the temperature of calculation in the present work of 1873 K. However, the $d\sigma/d[at\%]$ values shown in Table 2 were used as the values at 1873 K in this calculation because the temperature dependence of $d\sigma/d[at\%]$ is regarded as negligible similar to that of surface tension.

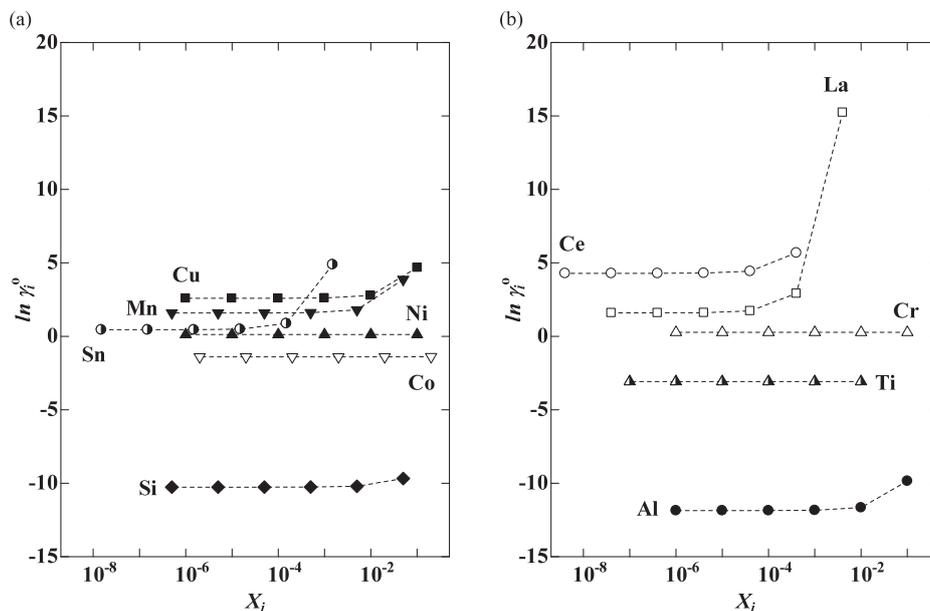


Fig. 1. The relationship between the calculated $\ln \gamma_i^0$ and the content of solute i . (a) Co, Cu, Mn, Ni, Si and Sn, and (b) Al, Ce, Cr, La and Ti.

4. Calculation Results

The activity coefficient for a solute element i in an infinite dilute liquid Fe, γ_i° , was calculated based on the surface tension of liquid Fe- i alloy, and are shown in Fig. 1, where the effect of the solute concentration on the calculated activity coefficient was investigated. Figure 1 plots the activity coefficient calculated by the proposed method for a bulk concentration of the solute element, X_B^B , decreasing every digit in the composition range, which satisfied the linear relationship of the surface tension for a liquid Fe- i alloy suggested by Mills. The activity coefficient of each solute element converged to a certain value with decreasing solute element concentration. In this study, the convergent value obtained at the low concentration was defined as the activity coefficient for the solute element i in an infinite dilute liquid Fe, γ_i° . The activity coefficient for Co, Cr, Ni or Ti was constant with no dependence on the solute element concentration. The surface tension for the liquid Fe-based alloy containing Co, Cr, Ni, or Ti exhibited little or no change with varying solute concentration. This signifies that the ratio of the bulk concentration of solute, X_B^B , to the surface concentration of solute, X_B^S , is maintained at a constant to provide a constant activity coefficient. The activity coefficient for the other solutes decreased from a certain value and reached a constant value as the solute element concentration decreased. In particular, the activity coefficient decrease for the solutes La and Sn was sharp. Liquid La and Sn have a low surface tension compared with that of liquid Fe and a negative $d\sigma/dX$ with a large absolute value. A solute element whose surface tension is lower than the surface tension for liquid alloy tends to be segregated on the surface of the liquid Fe-based alloy. This leads to the situation where the surface concentration of the solute is remarkably higher than the bulk concentration of the solute. In this study, it was assumed that an infinite dilute liquid was satisfied in both the bulk and the surface in the calculation of the activity

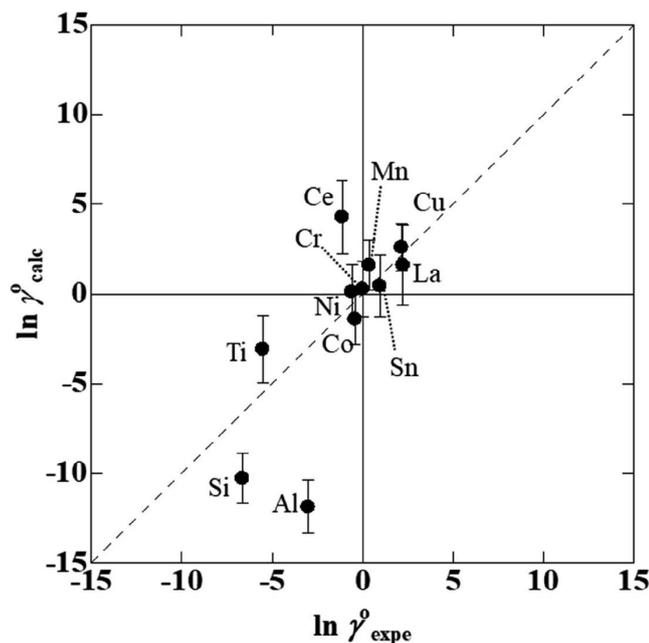


Fig. 2. Comparison between calculated $\ln \gamma_i^\circ$ based on surface tension for alloy and literature $\ln \gamma_i^\circ$.

coefficient for solute i in an infinite dilute liquid Fe. This assumption may be satisfied in the bulk but is not satisfied in the surface when the surface concentration of the solute is remarkably higher than the bulk concentration of the solute. Consequently, it is considered that the calculated activity coefficient changes with the solute concentration. However, the infinite dilute liquid assumption can be applicable even in the surface when decreasing the concentration of solute in bulk without limit, which converges the activity coefficient to a certain value.

Figure 2 compares the activity coefficient of solute i in an infinite dilute liquid Fe calculated based on the surface tension for the liquid Fe- i alloy with the value in the literature. The literature value in Fig. 2 is the recommended activity coefficient reported in the compilation of thermodynamic data for steelmaking.¹⁾ It is generally reported that an impurity significantly affects the surface tension of the liquid metal, as described above, and several percentage of scatter arising from the measurement method itself is included in the measured value.^{37,38)} The scatter of the activity coefficient calculated by considering the surface tension for a pure liquid metal with $\pm 3\%$ of error was shown as an error bar in Fig. 2. The plots including the scatter showed data that existed in the first and third quadrants, and it was found that the sign of the calculated activity coefficient roughly agreed with the literature. The reproducibility of the absolute value of the activity coefficient was also confirmed to some extent because (excepting Al and Ce) the plots were located along the line of the ratio of the calculated value to the literature value, whose slope equals 1. Consequently, it is concluded that the activity coefficient of a solute in an infinite dilute liquid Fe can be calculated based on the surface tension for binary liquid Fe alloy by the method proposed in the present work. Ono *et al.*³⁹⁾ regard the difficulty of measurement as one of the reasons why the sufficiency rate for interaction coefficients is low, and urge the necessity of establishing a non-conventional measurement method. The measurements of the surface tension for liquid metals and alloys via the levitated oscillating drop method, which minimizes the effect of impurities on the surface tension in a non-contact manner as described above, have largely been conducted in recent year. This method has actualized the measurement of the surface tension for reactive metals^{22–26)} and alloys.^{30,40,41)} It is therefore expected that the method proposed in this study will lead to the acquisition of thermodynamic data in alloy systems that are not obtainable by conventional methods because the proposed method is available for all alloy systems whose surface tension can be measured. In addition, we expect that the activity coefficient for Al and Ce calculated based on our proposed method, which accords poorly with the recommended value (Fig. 2), will agree with the recommended value when the surface tension for liquid Fe–Al and Fe–Ce alloys is measured by the levitated oscillating drop method.

5. Conclusions

The activity coefficient of the solute element in an infinite dilute liquid Fe was calculated using the surface tension for a binary liquid Fe-based alloy obtained via the method for calculating the surface tension for liquid alloy based on

the thermodynamic data in reverse. The new equation was derived by modifying Butler's equation under an assumption of an infinite dilute liquid. The resulting value calculated from the surface tension for binary liquid Fe-based alloy by the derived equation generally agrees with the recommended value in the literature.

REFERENCES

- 1) The 19th Committee on Steelmaking, The Japan Society for the Promotion of Science: Steelmaking Data Sourcebook, Gordon and Breach Science Publishers, New York, (1988).
- 2) M. Hino and K. Ito, eds.: Thermodynamic Data for Steelmaking, Tohoku University Press, Sendai, (2010).
- 3) T. Tanaka and T. Iida: *Steel Res.*, **65** (1994), 21.
- 4) T. Tanaka, K. Hack, T. Iida and S. Hara: *Z. Metallkd.*, **87** (1996), 380.
- 5) T. Tanaka and S. Hara: *Materia Jpn.*, **36** (1997), 47.
- 6) T. Tanaka, S. Hara, M. Ogawa and T. Ueda: *Z. Metallkd.*, **89** (1998), 368.
- 7) T. Tanaka, K. Hack and S. Hara: *MRS Bull.*, **24** (1999), 45.
- 8) T. Tanaka, K. Hack and S. Hara: *Calphad*, **24** (2001), 463.
- 9) J. A. V. Butler: *Proc. R. Soc. A*, **135** (1932), 348.
- 10) R. Speiser, D. R. Poirier and K. Yeum: *Scr. Metall.*, **21** (1987), 687.
- 11) W. Gąsior, P. Fima and Z. Moser: *Arch. Metall. Mater.*, **56** (2011), 13.
- 12) C. Wagner: Thermodynamics of Alloys, Addison-Wesley Press, Cambridge, MA, (1952), 47.
- 13) T. Miki and H. Ono-Nakazato: *Bull. Iron Steel Inst. Jpn.*, **11** (2006), 74 (in Japanese).
- 14) H. Ono-Nakazato, K. Taguchi, R. Maruo and T. Usui: *ISIJ Int.*, **47** (2007), 365.
- 15) W.-Y. Cha, T. Miki, Y. Sasaki and M. Hino: *ISIJ Int.*, **48** (2008), 729.
- 16) Y. Kang and K. Morita: *ISIJ Int.*, **51** (2011), 2002.
- 17) K. Sugiyama, S. Ueda, X. Gao, S. Kim and S. Kitamura: *ISIJ Int.*, **57** (2017), 625.
- 18) K. S. Yeum, R. Speiser and D. R. Poirier: *Metall. Trans. B*, **20** (1989), 693.
- 19) T. Iida and R. I. L. Guthrie: The Physical Properties of Liquid Metals, Clarendon Press, Oxford, UK, (1988), 71.
- 20) B. J. Keene: *Int. Mater. Rev.*, **38** (1993), 157.
- 21) K. C. Mills and Y. C. Su: *Int. Mater. Rev.*, **51** (2006), 329.
- 22) H. Kobatake, J. Brillo, J. Schmitz and P.-Y. Pichon: *J. Mater. Sci.*, **50** (2015), 3351.
- 23) J. Brillo and G. Kolland: *J. Mater. Sci.*, **51** (2016), 4888.
- 24) M. Leitner, T. Leitner, A. Schmon, K. Aziz and G. Pottlacher: *Metall. Mater. Trans. A*, **48** (2017), 3036.
- 25) P.-F. Paradis, T. Ishikawa, N. Koike and Y. Watanabe: *Int. J. Microgravity Sci. Appl.*, **25** (2008), 407.
- 26) T. Ishikawa, J. T. Okada, J. Li, P.-F. Paradis and Y. Watanabe: JAXA Research and Development Report, JAXA-RR-08-003E, Japan Aerospace Exploration Agency (JAXA), Tokyo, (2009), 1.
- 27) B. J. Keene: *Int. Mater. Rev.*, **33** (1988), 1.
- 28) V. R. Ryabov and G. F. Deev: Surface Phenomena in Welding and Surfacing, Harwood Academic Publishers, Amsterdam, (1998), 166.
- 29) J. Lee, A. Kiyose, M. Tanaka and T. Tanaka: *ISIJ Int.*, **46** (2006), 467.
- 30) K. Nogi, W. B. Chung, A. McLean and W. A. Miller: *Mater. Trans., JIM*, **32** (1991), 164.
- 31) J. Lee, K. Yamamoto and K. Morita: *Metall. Mater. Trans. B*, **36** (2005), 241.
- 32) R. Brooks and A. Cameron: *ISIJ Int.*, **40** (2000), S157.
- 33) I. Seyhan and I. Egry: *Int. J. Thermophys.*, **20** (1999), 1017.
- 34) J. Lee, L. T. Hoai and M. Shin: *Metall. Mater. Trans. B*, **42** (2011), 546.
- 35) R.-A. Eichel and I. Egry: *Z. Metallkd.*, **90** (1999), 371.
- 36) K. Ogino, H. Taimatsu and F. Nakatani: *J. Jpn. Inst. Met.*, **46** (1982), 1049 (in Japanese).
- 37) T. Tanaka, M. Nakamoto, R. Oguni, J. Lee and S. Hara: *Z. Metallkd.*, **95** (2004), 818.
- 38) J. Lee, A. Kiyose, S. Nakatsuka, M. Nakamoto and T. Tanaka: *ISIJ Int.*, **44** (2004), 1793.
- 39) H. Ono and M. Nakamoto: *Bull. Iron Steel Inst. Jpn.*, **23** (2018), 253 (in Japanese).
- 40) S. Ozawa, K. Morohoshi and T. Hibiya: *ISIJ Int.*, **54** (2014), 2097.
- 41) J. Choe, H. G. Kim, Y. Jeon, H. J. Park, Y. Kang, S. Ozawa and J. Lee: *ISIJ Int.*, **54** (2014), 2104.