Thermodynamic Assessment of Liquid Mn–Fe–C System by Unified Interaction Parameter Model

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The present study assesses the available experimental data and proposes a model based on the Unified Interaction Parameter Formalism to describe the solution properties of the Mn–Fe–C system. The experimental information developed from the recent works by Katsnelson et al., Fenstad, and Kim et al. defines the solution properties as the ratio of the activity of C to Mn in the Mn–Fe–C system. These data were used to determine the activity coefficient of carbon at infinite dilute solution of Mn in the Mn–C system at various temperatures.

\[
\ln \gamma_C([\text{Mn}]) = 0.32 - 2.679/T \quad (1628 - 1773 \text{ K})
\]

A determination of the individual activity of C and Mn from experimental data requires additional information. As it meets the necessary condition for the task by virtue of satisfying the Gibbs–Duhem relationship, the Unified Interaction Parameter (UIP) model was correlated with the experimental data of the Mn–Fe–C system. The interaction parameters of the UIP model were determined by multiple regression analysis of the correlated equations. The activity coefficients of carbon and manganese in reference to graphite and liquid Mn as respective standard states in the Mn–Fe–C system are determined as follows:

\[
\ln \gamma_C = \ln \gamma_C^{[\text{Mn}]} + \varepsilon_{\text{CO}} x_C + \varepsilon_{\text{CFe}} x_C x_F - \varepsilon_{\text{CCFe}} x_C^2 x_F x_{\text{Fe}} + \varepsilon_{\text{CFeFe}} x_C x_F x_{\text{Fe}}^2
\]

where \(\varepsilon_{\text{CC}} = 9.24 - 16.060/T, \varepsilon_{\text{CCC}} = -51.8 + 157.800/T, \varepsilon_{\text{CFe}} = 7.52 - 7.250/T, \varepsilon_{\text{CCFe}} = -8.39 + 16.190/T, \varepsilon_{\text{CCFeFe}} = -9.93 + 12.790/T, \varepsilon_{\text{FeFeFe}} = 0, \varepsilon_{\text{FeFeFeFe}} = 0.

KEY WORDS: thermodynamics; activity; carbon; manganese; unified interaction parameter model.

1. Introduction

The development of processes for high-manganese-containing steels and ferromanganese alloys has been hampered by a dearth of experimental data. Often, this deficiency has been supplemented by using solution models to describe thermodynamic properties. However, models developed in analytical formulas from insufficient experimental data may not adequately represent the solution properties. An appropriate experimental information is essential to define parameters for effective and representative models.

For example, Katsnelson et al.\(^1\) determined the compositions of Mn–C melt in equilibrium with Ar–CO gas under a condition of MnO saturation at 1628 K, but the range of their investigated composition was limited from \(x_C = 0.114\) to 0.269. They assessed the experimental results according to the following reaction:

\[
\begin{align*}
\text{[C]}_{\text{Mn}} + \text{MnO} & = \text{[Mn]} + \text{CO} \\
\Delta G^o & = 286,800 - 170.2 T \quad (\text{J/mol})^2 \\
\end{align*}
\]

Adopting the interaction parameter formalism, they proposed the following models to represent the activity coefficients of Mn and C in the liquid Mn–C system at 1628 K.

\[
\ln \gamma^{\text{Mn}} = 5.47 x_C^2 - 46.8 x_C^3 \quad \text{......(2)}
\]

\[
\ln \gamma^{\text{C}} = -0.291 - 10.9 x_C + 75.6 x_C^2 - 46.8 x_C^3 \quad \text{......(4)}
\]

where the standard states for Mn and C are liquid Mn and graphite, respectively. However, the activity coefficient of C at infinite dilute solution of Mn, \(\gamma_C^o\), determined by the Eq. (4) is higher than that suggested by their experimental data. Their experimental data, when combined with the recent works by Fenstad\(^5\) and Kim et al.,\(^4,5\) do indicate that the value for \(\gamma_C^o\) is lower than that given by Eq. (4). Such discrepancy is often encountered in terminal composition ranges when the solution model is developed in polynomial series from insufficient data. Similarly, the value for \(\gamma_C^o\) by the solution model proposed by Li et al.\(^6\) is found to be higher than that expected from the experiments. This is due to the fact that they developed the model without benefit of
the recent experimental data.3–5)

This report re-examines the available experimental data and proposes a representative model for the thermodynamic properties of the liquid Mn–Fe–C system. In addition to Katsnelson et al.,11 Fenstad,8 Kim et al.,4,5) and Saxena et al.5) examined the thermodynamic properties of the Mn–C and Mn–Fe–C systems using the same experimental technique used by Katsnelson et al. When combined together, their works provide sufficient information to develop a solution model that adequately represents the thermodynamic properties of the Mn–Fe–C system. The experimental method that they adopted defines the solution properties only as the ratio of γC to γMn, by virtue of Eq. (2). A determination of the values for individual γi and γMn requires additional information.

The Unified Interaction Parameter (UIP) model proposed by Bale and Pelton8,9) is thermodynamically valid at all compositions and satisfies the Gibbs–Duhem relationship. This study correlates the UIP model with the experimental data to determine the individual solution properties. In addition to those data, the present assessment is complemented by experimentally determined carbon solubility in the Mn–Fe–C system as well as the solution properties of Fe–C system.

2. Unified Interaction Parameter (UIP) Model

As mentioned above, the experimental technique employed by Katsnelson et al.,11 Fenstad,8 Kim et al.,4,5) and Saxena et al.5) presents the solution properties only as the solution properties of Fe–C system. The experimental technique employed by Katsnelson et al.7) presents the solution properties only as the solution properties of Mn–C alloys in equilibrium with MnO(s) and CO.

Table 1. Carbon content of Mn–C alloys in equilibrium with MnO(s) and CO.

| temp. K | pO2 (atm) | wt% C | xC | references |
|---------|-----------|------|----|------------|
| 1628    | 0.025     | 2.73 | 0.114 | Katsnelson et al.11 |
| 1628    | 0.025     | 2.39 | 0.101 | |
| 1628    | 0.075     | 4.28 | 0.170 | |
| 1628    | 0.1       | 4.51 | 0.178 | |
| 1628    | 0.1       | 4.59 | 0.180 | |
| 1628    | 0.15      | 5.12 | 0.198 | |
| 1628    | 0.175     | 5.56 | 0.212 | |
| 1628    | 0.25      | 6.12 | 0.230 | |
| 1628    | 0.75      | 6.79 | 0.250 | |
| 1628    | 0.8       | 7.24 | 0.263 | |
| 1628    | 0.9       | 7.32 | 0.265 | |
| 1628    | 1.0       | 7.45 | 0.269 | |
| 1628    | 1.0       | 7.48 | 0.269 | |
| 1633    | 0.0113    | 1.3  | 0.0569 | Fenstad8 |
| 1633    | 0.0113    | 1.36 | 0.0594 | |
| 1667    | 0.02      | 1.25 | 0.0548 | Kim et al.4,5) |
| 1673    | 0.03      | 1.65 | 0.0713 | |
| 1673    | 0.05      | 2.35 | 0.0992 | |
| 1673    | 0.07      | 3.1  | 0.128  | |
| 1673    | 0.1       | 3.88 | 0.156  | |
| 1673    | 0.2       | 4.69 | 0.184  | |
| 1673    | 0.4       | 5.5  | 0.210  | |
| 1673    | 0.6       | 6.04 | 0.227  | |
| 1673    | 1         | 6.57 | 0.244  | |
| 1673    | 0.02      | 0.84 | 0.0373 | Kim et al.4,5) |
| 1673    | 0.03      | 1.13 | 0.0497 | |
| 1673    | 0.05      | 1.7  | 0.0734 | |
| 1673    | 0.07      | 2.29 | 0.0969 | |
| 1673    | 0.1       | 2.96 | 0.123  | |
| 1673    | 0.15      | 3.38 | 0.138  | |
| 1673    | 0.2       | 3.7  | 0.150  | |
| 1673    | 0.2       | 4.64 | 0.182  | |
| 1673    | 0.4       | 5.31 | 0.204  | |
| 1673    | 0.6       | 5.75 | 0.218  | |
| 1673    | 0.8       | 5.75 | 0.225  | |
| 1673    | 0.02      | 0.5  | 0.0225 | |
| 1673    | 0.03      | 0.73 | 0.0326 | |
| 1673    | 0.05      | 1.05 | 0.0463 | |
| 1673    | 0.1       | 1.84 | 0.0790 | |
| 1673    | 0.15      | 2.54 | 0.107  | |
| 1673    | 0.2       | 2.85 | 0.118  | |
| 1673    | 0.3       | 3.74 | 0.151  | |
| 1673    | 0.4       | 4.25 | 0.172  | |
| 1673    | 0.6       | 4.82 | 0.188  | |
| 1673    | 1         | 5.32 | 0.205  | |

For the Mn–Fe–C system, Mn is taken as solvent and C as solute, and the activity coefficients are represented as follows:

\[ \ln \gamma_{\text{Mn}} = \sum_{j,k} \epsilon_{\text{Mn,C}} x_j x_k \]

\[ \ln \gamma_{\text{Fe}} = \sum_{j,k} \epsilon_{\text{Fe,C}} x_j x_k \]

\[ \ln \gamma_{\text{C}} = \ln \gamma_{\text{C,Fe}} + \sum_{j,k} \epsilon_{\text{C,C}} x_j x_k + \sum_{j,k} \epsilon_{\text{C,Fe}} x_j x_k \]

where the standard states for Mn and C are liquid Mn and graphite, respectively. An adequate representation of the UIP model requires evaluation of the interaction parameters. The first- and second-order interaction parameters were defined with the available experimental data.

3. Evaluation of the Interaction Parameters for the Mn–C Binary System

The evaluation for the interaction parameters begins with the Mn–C binary system. The activity coefficient of C takes a finite value in infinite dilute solution of Mn and needs to be determined first. This value defines and serves as a boundary in developing the analytical representation for the solution properties.

The available experimental data are presented as the ratio of the solution properties. The present study determines the activity coefficient of C at infinite dilute solution of Mn, \( \ln \gamma_{\text{C}} \), by examining the behavior of the experimentally determined ratio of activity coefficient of C to that of Mn in a Mn–C melt. The data for the Mn–C binary system were taken from the works of Katsnelson et al.11 at 1 628 K.
Fenstad\textsuperscript{13} at 1 633 K, and Kim \textit{et al.} \textsuperscript{3,5} at 1 673, 1 723, and 1 773 K. Table 1 lists their experimentally determined carbon content in Mn–C melts in equilibrium with MnO(s) and CO.

In the present evaluation, the data by Fenstad were combined with those by Katsnelson \textit{et al.} without correcting for small temperature difference as the values at 1 628 K. A transformation of Eq. (2) allows the ratio of the activity coefficient of C to that of Mn, $\ln \gamma_C / \gamma_{Mn} = \ln \gamma_C - \ln \gamma_{Mn}$, to be represented in terms of the experimental parameters, which are composition, partial pressure of CO, and the equilibrium constant as shown in the following Eq. (9).

$$\ln \gamma_C - \ln \gamma_{Mn} = \ln(1-x_C)/x_C + \ln P_{CO} - \ln K$$

As the composition approaches that of pure Mn, the value for $\gamma_{Mn}$ becomes one and that for $\gamma_C$ a finite value at the infinite dilute solution of Mn. Therefore, the activity coefficient of C at the infinite dilution, $\gamma_C^\infty$, can be obtained by extrapolating the experimentally determined ratio of the activity coefficient of C to that of Mn to $x_C = 0$. The extrapolation can be made with confidence if the ratio behaves linearly with the composition in the terminal composition range. This is the case when the solution properties in the composition range near the solvent is represented by the quadratic formalism.\textsuperscript{10}

The experimental data by Katsnelson \textit{et al.}, Fenstad, and Kim \textit{et al.} for the Mn–C system are reproduced in Figs. 1, 2, 3, and 4, at 1 628, 1 673, 1 723, and 1 773 K, respectively. They show the experimentally determined ratio of $\ln \gamma_C / \gamma_{Mn}$ as a function of $x_C$. The ratio, $\ln \gamma_C / \gamma_{Mn}$, does decrease almost linearly with the composition of carbon in the composition range less than about $x_C = 0.15$.

The activity coefficients of C at infinite dilute solution of Mn, $\ln \gamma_C^\infty$, at 1 628, 1 673, 1 723, and 1 773 K, were determined by linear extrapolation in the composition range less than about $x_C = 0.15$, and the effect of temperature was assessed by linear regression analysis. The results are shown in Fig. 5, and the following Eq. (10) is proposed to reproduce the value for $\ln \gamma_C^\infty$ at various temperatures.

$$\ln \gamma_C^\infty(Mn) = 0.32 - 2.679/T(K) \quad (1 628 - 1 773 K)$$

Fig. 1. The ratio of activity coefficient of C to Mn in the Mn–C system at 1 628 K.

Fig. 2. The ratio of activity coefficient of C to Mn in the Mn–C system at 1 673 K.

Fig. 3. The ratio of activity coefficient of C to Mn in the Mn–C system at 1 723 K.

Fig. 4. The ratio of activity coefficient of C to Mn in the Mn–C system at 1 773 K.
tiate it from a similar property in infinite dilute solution of iron, ln $\gamma^0_C(Fe)$, which will be discussed later. Kim et al. proposed it differently as shown in Fig. 5. Their assessment suggests the value for ln $\gamma^0_C(Mn)$ to decrease with the increase of temperature while this study indicates the opposite. This discrepancy is due to the fact that this assessment included the data of Katsnelson et al. as well as those of Kim et al., while Kim et al. relied on their own data. This discrepancy needs to be resolved in the future. In the meantime, the Eq. (10) is used for the present study.

Once the boundary condition is defined, the interaction parameters in the UIP model need to be determined for the Mn–C system. From Eqs. (7) and (8), the activity coefficients of Mn and C for the binary Mn–C system in the UIP model are reduced to the following equations:

$$\ln \gamma_{Mn} = e_{CC}[-1/2 x_C^2] + e_{CCC}[-2/3 x_C^3]$$

$$(7a)$$

$$\ln \gamma_C = \ln \gamma^0_C + \ln \gamma_{Mn} + e_{CC}x_C + e_{CCC}x_C^2$$

$$(8a)$$

These analytical equations are used to describe the two sets of experimental data, the ratio of the activity coefficient of C to Mn, $\ln \gamma_C/\gamma_{Mn}$ and the activity coefficient of C at carbon saturation in a Mn melt, $\ln \gamma_C(\text{sat})$, in terms of the interaction parameters as shown by the following Eqs. (11) and (12).

$$[\ln(1-x_C)/x_C + P_{CO} - \ln K] - \ln \gamma^0_C(Mn) = [\ln \gamma_C - \ln \gamma_{Mn}] - \ln \gamma^0_C(Mn) = e_{CC}x_C + e_{CCC}x_C^2.$$  

$$(11)$$

$$\ln \gamma_C(\text{sat}) - \ln \gamma^0_C(Mn) = e_{CC}x_C - 1/2 x_C^2 + e_{CCC}(2/3 x_C^3)$$

$$(12)$$

where $e_{CC} = a + b/T$ and $e_{CCC} = c + d/T$, and a, b, c, and d are constants.

The interaction parameters are determined by correlating the above equations to the respective experimental data. The experimental data for the ratio of $\gamma_C$ to $\gamma_{Mn}$ in the Mn–C system were taken from the works of Katsnelson et al.\(^1\) Fenstad,\(^1\) and Kim et al.\(^4,5\) The data for the saturation of carbon in Mn melt were taken from the works of Katsnelson et al.\(^1\) Fenstad,\(^3\) Kim et al.\(^4,5\) Turkdogan et al.,\(^11,12\) Schenck et al.,\(^13\) and Ni et al.\(^14\) Table 2 shows their experimentally determined solubility of carbon in Mn melt. The correlation to determine the interaction parameters, $e_{CC}$ and $e_{CCC}$, requires a combination of the activity coefficient of carbon at saturation with that in infinite dilute solution of Mn. However, the range of the effective temperatures for $\ln \gamma^0_C(Mn)$ by Eq. (10) is limited in comparison to that for experimentally determined solubility of carbon in Mn melt. A wider range of temperatures for the carbon solubility was accommodated by extrapolation of Eq. (10) beyond its effective temperature range. The interaction parameters, $e_{CC}$ and $e_{CCC}$, were determined by multiple regression analysis of experimentally determined parameters organized by Eqs. (11) and (12). The results are as follows:

$$e_{CC} = 9.24 - 16 060/T \quad (1628 - 1919 K)$$

$$(13)$$

$$e_{CCC} = -51.8 + 157 800/T \quad (1628 - 1919 K)$$

$$(14)$$

These parameters reproduce the experimental data with a high correlation, $r^2 = 0.983$.

### 4. Evaluation of the Interaction Parameters for the Mn–Fe–C System

The remaining interaction parameters of Eqs. (7) and (8) are determined from the experimental data of the Mn–Fe–C system. The following three sets of equations were developed by correlating the model equations with experimentally determined properties: (1) the ratio of the activity coefficients of C to Mn in the Mn–Fe–C system, (2) the activity coefficient of C at carbon saturation in the Mn–Fe system and the activity coefficient of C at infinite dilution of Fe in...
melt, and (3) the activity coefficient of Mn in the Mn–Fe–C system.

\[
\ln \gamma_{\text{Mn}} - \ln \gamma_{\text{Fe}} - \ln \gamma_{\text{C(sat)}} = e^{C_{\text{Fe}}-Fe + C_{\text{CC}}(2C_{\text{Fe}})+e^{C_{\text{CC}}(2C_{\text{Fe}})}}
\]

The data for the ratio of the activity coefficients of C to Mn in the Mn–Fe–C system were taken from the works of Kim et al.4,5) and Saxena et al.7) Table 3 shows their experimentally determined carbon contents in Mn–Fe–C alloys in equilibrium with MnO(s) and CO. The activity coefficients of carbon at carbon saturation, \(\ln \gamma_{\text{C(sat)}}\), in the Mn–Fe–C were obtained from the studies by Fenstad, 3) Kim et al.,4,5) Turkdogan et al.,12,16) Ni et al.,14) and Chipman et al.15) Table 4 lists the solubility of carbon in Mn–Fe melts determined by them. These data were further supplemented by the solubility equation of carbon in iron, Eq. (15), \(\log x_{\text{C}} = -12.728/T + 0.727 \log T - 3.049\), in Steelmaking Data Sourcebook (SDSB).17) This equation was used to develop the solubility of carbon in Fe melt at regular temperature intervals from the eutectic temperature through 2 173 K. The results are also listed in Table 4. The activity coefficient of carbon at infinite dilute solution of Fe, In \(\gamma_{\text{C(Fe)}}\), was included because it defines the property in the Fe-rich terminal composition, and the necessary information was developed from the assessment of Chipman18) and Sigworth and Elliott.19) In \(\gamma_{\text{C(Fe)}}\) = −0.200 + 2 718/T. Again, the values for \(\ln \gamma_{\text{C(Fe)}}\) at temperatures below the melting point of iron were obtained by extrapolation in order to accommodate

\[
\ln \gamma_{\text{C(Fe)}} = -2.000 + 2 718/T.
\]

The results are also listed in Table 4. The activity coefficient of carbon at infinite dilute solution of Fe, In \(\gamma_{\text{C(Fe)}}\), was included because it defines the property in the Fe-rich terminal composition, and the necessary information was developed from the assessment of Chipman18) and Sigworth and Elliott.19) In \(\gamma_{\text{C(Fe)}}\) = −0.200 + 2 718/T. Again, the values for \(\ln \gamma_{\text{C(Fe)}}\) at temperatures below the melting point of iron were obtained by extrapolation in order to accommodate
other data. The data for the activity coefficient of Mn, lnγMn, in the Mn–Fe–C system was obtained from the works of Enokido et al.\textsuperscript{20} and Tanaka.\textsuperscript{21} These properties were correlated with the UIP model equations to develop three sets of data organized by Eqs. (15), (16), and (17), and the interaction parameters were determined by multiple regression analysis.

A preliminary examination indicates that the interaction parameters, $e_{\text{FeFe}}$ and $e_{\text{FeFeFe}}$, are negligibly small and taken to be zero. The remaining interaction parameters were determined as follows:

$$e_{\text{CFe}} = 7.52 - 7250/T \quad (1563 - 2173 \text{ K}) \quad (18)$$

$$e_{\text{CCFe}} = -8.39 + 16190/T \quad (1563 - 2173 \text{ K}) \quad (19)$$

$$e_{\text{CFeFe}} = -9.93 + 12790/T \quad (1563 - 2173 \text{ K}) \quad (20)$$

The assessed parameters of the present UIP model are summarized in Table 5.

### Table 5. Summary of parameters of the UIP model for the Mn–Fe–C system.

| temperature, K | parameters | \( \ln \gamma_{\text{C}}(\text{Mn}) \) | $e_{\text{FeFe}}$ | $e_{\text{FeFeFe}}$ | $e_{\text{CFe}}$ | $e_{\text{CCFe}}$ | $e_{\text{CFeFe}}$ |
|----------------|------------|---------------------------------|-----------------|-----------------|---------------|-------------|----------------|
| 1628 - 1773    | $e_{\text{CFe}}$ | 0.32 - 2.679/T                  | 1628 - 1773     |
| 1628 - 1919    | $e_{\text{CCFe}}$ | 5.46 - 16.607/T                 | 1628 - 1919     |
| 1563 - 2173    | $e_{\text{CFeFe}}$ | 7.52 - 7250/T                   | 1563 - 2173     |
| 1563 - 2173    | $e_{\text{CFeFe}}$ | -8.39 + 16190/T                 | 1563 - 2173     |
| 1563 - 2173    | $e_{\text{CFeFe}}$ | -9.93 + 12790/T                 | 1563 - 2173     |
| 1563 - 2173    | $e_{\text{CFeFe}}$ | 0.32 - 2.679/T                  | 1628 - 1773     |
| 1628 - 1919    | $e_{\text{CFeFe}}$ | 5.46 - 16.607/T                 | 1628 - 1919     |
| 1563 - 2173    | $e_{\text{CFeFe}}$ | 7.52 - 7250/T                   | 1563 - 2173     |
| 1563 - 2173    | $e_{\text{CFeFe}}$ | -8.39 + 16190/T                 | 1563 - 2173     |
| 1563 - 2173    | $e_{\text{CFeFe}}$ | -9.93 + 12790/T                 | 1563 - 2173     |

5. Discussion

The validity of this assessment is demonstrated by comparing the present UIP model with the relevant experimental data in the Mn–Fe–C system.

The behavior of the ratio of the activity coefficient of C to Mn in the Mn–C system was calculated by the present UIP model and compared with experimental data in Figs. 1 through 4. The model favorably reproduces the experimental results at 1628, 1673, 1723, and 1773 K. However, Fig. 1 points out a difference between the calculation by the UIP model and that by Katsnelson et al.,\textsuperscript{16} Eqs. (3) and (4). The UIP model describes well the experimentally determined ratio of the activity coefficients of C to Mn in the entire composition range from the Mn-rich terminal region to carbon saturation. In contrast to this, the model by Katsnelson et al. results in a positive deviation from the experimental trend in the terminal composition range, although it reproduces well their experimental data in the composition range higher than about $x_C = 0.15$. Consequently, their model predicts the value for the activity coefficient of carbon at infinite dilute solution of Mn, $\ln \gamma_C(\text{Mn})$, to be higher than that expected from the experiment. The addition of data by Fenstad\textsuperscript{30} to those of Katsnelson et al. follows the trend of the UIP model. As mentioned above, such consequence may arise when model equations in polynomial series are developed without sufficient experimental information in the terminal composition region. Similarly, the model by Li et al.\textsuperscript{6} also predicts higher values than the experimental data as shown in Fig. 1. As mentioned above, Li et al.\textsuperscript{6} did not have the benefit of recent experimental data.\textsuperscript{5–9}

The carbon content at graphite saturation in Mn, Fe, and Mn–Fe melts was calculated by the present UIP model and compared with the experimental data. As shown in Fig. 6, the UIP model reproduces reasonably well the experimentally determined solubility of carbon in both Mn and Fe melts. Figure 7 shows the solubility of carbon in Mn–Fe melts. Again, the UIP model compares favorably with the experimentally determined solubility of carbon in Mn–Fe melts.

The present model adequately describes the solution property of carbon in the Mn–C system as demonstrated above. Also, it does the same for the solubility of carbon in
Fe melts as shown in Fig. 6. If it reproduces the property at infinite dilute solution of Fe, the present model may be considered to be adequate in representing the Fe–C system as well. The activity coefficient of carbon in infinite dilute solution of Fe was calculated by the present UIP model, and the results are compared with the established information by Chipman and Sigworth and Elliott in Fig. 8. The value for \( \ln \gamma_C(\text{Fe}) \) at temperatures below the melting point of Fe represents that in a super-cooled liquid iron. It shows that the activity coefficient of carbon in infinite dilute solution of Fe, \( \ln \gamma_C(\text{Fe}) \), by the UIP model agrees very well with those by Chipman and Sigworth and Elliott. This exercise substantiates that the present UIP model adequately describes the solution property of carbon in the binary Fe–C system as well.

In his assessment of the thermodynamic properties of the liquid Mn–Fe–C system, Lee assumed that the activity coefficient of carbon in the ternary Mn–Fe–C system varies linearly from that of a terminal binary Mn–C system to that of Fe–C in proportion to the ratio of Fe to Mn. This assumption is examined by calculating the activity coefficient of carbon in the ternary Mn–Fe–C system at 1 873 K with the present UIP model. Again, the values for \( \ln \gamma_C(\text{Mn}) \) at 1 873 K were obtained by extrapolation of Eq. (10). In Fig. 9, the calculated activity coefficient of carbon in the Mn–Fe–C system is shown at various carbon contents as the ratio of Fe to Mn, \( x_{\text{Fe}}/(x_{\text{Fe}} + x_{\text{Mn}}) \), varies from the binary Mn–C system to that of Fe–C. The activity coefficient of carbon in infinite dilute solution of a Mn–Fe melt shows a positive deviation from the linear relationship between the two terminal binary systems. However, the degree of deviation decreases gradually as the carbon content increases. At saturation with graphite, the activity coefficient of carbon varies almost linearly with the atomic ratio of Fe to Mn. It is interpreted that carbon associates preferentially with Mn or Fe atoms in the respective terminal regions and such preferential association becomes progressively weaker as the carbon content increases. The previous work by Lee does not adequately describe the aspect of non-random mixing of carbon in a Mn–Fe melt.

The ratios of the activity coefficient of C to Mn in the ternary Mn–Fe–C system were calculated by the present UIP model and compared with the experimental works of Kim et al. and Saxena et al. in Fig. 10. The model reproduces the experimental data reasonably well.

The experimentally determined activities of Mn in the Mn–Fe–C system by Enokido et al. and Tanaka were compared with the present UIP model in Fig. 11. The experimental data were taken by reading the values of the activity of Mn from Fig. 2 in the report by Enokido et al. and from Fig. 1 in the article by Tanaka. As shown in Fig. 11, the UIP model reproduces the experimentally determined activities of Mn in the Mn–Fe–C system reasonably well.

An assessment of the refining process of high carbon ferromanganese alloy require information on the activities of carbon and manganese. The decarburization reaction is considered to progress by closely following the composition path along the ratio of Fe to Mn at about \( x_{\text{Fe}}/(x_{\text{Fe}} + x_{\text{Mn}}) = 0.153 \) in ferromanganese alloys. The present UIP model calculated the variation of the activity of carbon and man-
ganese along this composition path at 1873 K. Figure 12 shows the result. Also shown in Fig. 12 is the variation of the activity of carbon calculated by the model of Kim et al.4,5) that describes the solution property as the Henrian activity coefficient of carbon, $f_{C}^{H}$, as follows:

$$\log f_{C}^{H} = \frac{0.0294\text{wt}%C}{H} + 0.0137\text{wt}%C^{2} + 0.00884\text{wt}%Fe$$

$$\ln g_{C}^{\circ}(Mn) = -4.1 + 5.040/T$$

The activity of carbon by Kim et al. is more negative than that by the present UIP model. As Kim et al. did not specify it, their corresponding activity of Mn is not presented in Fig. 12.

The above exercise demonstrates that the present UIP model adequately describes the solution properties of the Mn–Fe–C system at all compositions and reproduces the observed experimental data very well.

6. Conclusion

The experimental data from the equilibrium of Mn and Mn–Fe melts with Ar–CO gas under a condition of MnO saturation may permit the determination of the activity coefficient of carbon in infinite dilute solution of Mn, $\ln g_{C}^{\circ}(Mn)$. However, these data alone are not sufficient enough to resolve the individual activity of carbon and manganese and require additional information that defines their relationship. As it satisfies the Gibbs–Duhem relationship, the UIP model provides the necessary condition to determine the individual activity of carbon and manganese from the above mentioned experimental data.

The UIP model for the Mn–Fe–C system is represented by seven interaction parameters as described in Eqs. (7) and (8). The model is used to define the various experimental information of the Mn–Fe–C system, and the resulting equations are solved by multiple regression analysis to determine the interaction parameters. The following parameters are recommended to describe the solution properties of C and Mn in the Mn–Fe–C system.

$$\ln g_{C}^{\circ}(Mn) = 0.32 - 2.679/T(K) \quad (1628–1773 K)$$

$$\varepsilon_{CC} = 9.24 - 16.060/T \quad (1628–1919 K)$$

$$\varepsilon_{CFe} = -51.8 + 157.800/T \quad (1628–1919 K)$$

$$\varepsilon_{CFeFe} = -8.39 + 16.190/T \quad (1563–2173 K)$$

$$\varepsilon_{FeFeFe} = -9.93 + 12.790/T \quad (1563–2173 K)$$

$$\varepsilon_{FeFe} = 0$$

$$\varepsilon_{FeFeFe} = 0$$

The present UIP model adequately represents the activity of carbon and manganese in the Mn–Fe–C system.

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