Thermodynamic Activity Interaction Coefficients in Fe–C–V Melts*

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The solubility of carbon in Fe–C–V ternary melt was determined in hexa-compartment graphite crucibles at temperatures ranging from 1623 K to 1773 K. The solubility data can be expressed as

\[ X_C = 0.083 + 6.57 \times 10^{-5}T - (0.492 - 5.60 \times 10^{-4}T)X_V. \]

The activity interaction coefficients of vanadium on carbon were estimated with the solubility data as follows:

\[ \eta_{vc} = 2.39 \times 10^4/T - 22.9. \]
\[ \eta_{vc} = 1.86 \times 10^3/T - 1.28. \]
\[ \eta_{vc} = 3.84 \times 10^3/T - 2.98. \]

The second order interaction coefficients, \( \rho_{cv} \) and \( \rho_{vv'c} \), estimated by integrating the Gibbs-Duhem equation, are expressed as

\[ \rho_{cv} = 8.81 \times 10^3/T - 16.1. \]
\[ \rho_{vv'c} = -1.32 \times 10^4/T - 18.0. \]

The lattice ratio as a concentration variable, proposed by J. Chipman, was used to correlate the experimental results of the present work and of those on other eleven carbon saturated iron base ternary systems in the literature. It is shown that there exists a linear relation between the logarithm of the activity coefficient of carbon and the concentration of the third component over a considerably wide concentration range for all these systems except Fe–C–Mn, which needs a quadratic expression.

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I. Introduction

The understanding of the thermodynamic property of Fe–C–V melt is essential for studying both the reduction of vanadium oxide in slag melt into hot metal phase and the oxidation of vanadium in hot metal into the vanadium oxide slag. Though several studies\(^{(1)-(11)}\) for Fe–C–V system have been published, the values of the first order interaction coefficient, \( \eta_C \), are quite divergent by different authors as shown in Table 1. The second order interaction coefficients, which are necessary in dealing with the mentioned reduction or oxidation process, have not been reported yet anywhere. Furthermore, the published works were carried out at rather high temperatures, since the temperature for oxidizing process of vanadium in hot metal with the purpose of obtaining ferro-vanadium oxide slag as raw material of manufacturing vanadium was usually controlled lower than 1673 K\(^{(12)}\). Finally, no thermodynamically consistent interaction coefficients for both carbon and vanadium were

| \( \eta_C \) | Temp./K | Reference |
|-------------|---------|-----------|
| – 8.0       | 1833    | (1)       |
| – 4.49      | 1803    | (7)       |
| – 6.2       | 1823    | (8)       |
| – 11        | 1823    | (9)       |
| – 16.1      | 1833    | (10)      |
| – 6.8       | 1873    | (11)      |
| – 16.1      | 1873    | (13)      |

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reported simultaneously. The present paper is to study experimentally the Fe–C–V melts at a temperature range of 1623–1773 K and to evaluate the activity interaction coefficients, $\varepsilon_C$, $\rho_C^V$ and $\rho_C^V$ for carbon and $\rho_V^C$ and $\rho_V^C$ for vanadium.

In 1960's Chipman(14) proposed a measure of concentration, the lattice ratio as a concentration variable, for the purpose of simplifying the calculation of activities in complex metallic solutions containing interstitial or nonmetallic solutes. Chipman(14)-(16) and Ban-ya and Chipman(17)-(19) applied this concentration measure to many dilute binary and ternary solutions containing interstitial components when correlating their experimental data and others'. They found the variable quite suitable for retaining the simple linear relation between the activity coefficient and concentration variable over a broad concentration range as had been achieved by applying so called $e$-formalism to dilute solutions. It is a promising way for combining data of ternary and quaternary systems to predict the activities of the components in more complex systems. Another purpose of the present work is to use the lattice ratio concentration variable to correlate the experimental results of some carbon saturated iron base ternary melts, with the aim of extending the applicability of the variable to systems of such kind.

II. Experiment

The experiment was carried out with Fe–C and Fe–C–V alloy samples in a hexa-compartment graphite crucible as shown in Fig. 1. The experimental set-up was the same as in a previous study(20). Materials used for the preparation of the alloy samples were

Fe: 0.013% C, 0.002% Si, 0.026% Mn, 0.022% S, 0.003% P;

V: 99.99% V;

Graphite: spectral purity.

Each alloy sample weighed 5–6 g. Each run of the experiment lasted in an argon current for 28.8–36 ks (8–10 h) to ensure the saturation of the alloy samples with graphite at a constant temperature. The duration of 28.8–36 ks was confirmed in the preliminary experiments. At the end of each run the crucible was drawn out of the furnace promptly and quenched in water, and then the alloy samples were taken for analysis for carbon and vanadium.

III. Results

1. Solubility of carbon in iron

The results of the solubility of graphite in pure iron are shown in Table 2 and Fig. 2. The comparison of the present results with those published in the literatures(21)-(23) shows the reliability of the experimental method used by the present authors. The solubility data of carbon in iron can be expressed as

$$\%C = 1.23 + 2.60 \times 10^{-3} t \ (\degree C)$$  \hspace{1cm} (1)

or

$$X_C = 0.083 + 6.57 \times 10^{-5} T.$$  \hspace{1cm} (2)

2. Solubility of carbon in Fe–V melt

The results of the solubility of carbon in Fe–V

| Authors          | 1623 K | 1673 K | 1773 K |
|------------------|-------|-------|-------|
| Chipman et al.    | 4.77  | 4.90  | 5.02  |
| Kitchner et al.   | 4.73  | 4.86  | 4.99  |
| Matoba and Ban-ya | 4.86  | 5.00  | 5.13  |
| The present authors | 4.74 | 4.87  | 5.00  |

Table 2 Solubility of graphite in iron, mass%.
V melt are shown in Table 3 and Figs. 3 and 4 for 1623, 1673 and 1773 K. The solubility of carbon in Fe-V melt varies linearly with the concentration of vanadium,

\[ X_c = X^{\text{c}} + K X_v, \]

where \( X^{\text{c}} \)—the solubility of carbon in pure iron, \( K \)—the slope of the straight lines in Fig. 4. The equations of the lines in Fig. 4 are expressed as follows:

\[ X_c = 0.189 + 0.423 X_v \] (1623 K).

\[ X_c = 0.193 + 0.453 X_v \] (1673 K).

\[ X_c = 0.199 + 0.508 X_v \] (1773 K).

### IV. Discussion

#### 1. Evaluation of activity interaction coefficients in Fe-C-j System

The following relation is true between the Fe-C\textsubscript{sat} binary and Fe-C\textsubscript{sat}-j ternary systems, both of which possess the same \( \alpha_c \):

\[
\ln \gamma^c_v + \gamma^c_v X_v^c + \rho^c_v X_v^j + \ln X_v^c = \ln \gamma^c_v + \varepsilon^c_v X_v^c + \rho^c_v X_v^j + \varepsilon^c_v X_j
\]

### Table 3 Solubility of graphite in Fe-V melt.

| No. | [%C] | [%V] | No. | [%C] | [%V] | No. | [%C] | [%V] |
|-----|------|------|-----|------|------|-----|------|------|
| 191 | 4.74 | 0    | 111 | 4.90 | 0.71 | 181 | 5.06 | 0.61 |
| 192 | 5.37 | 5.20 | 112 | 5.40 | 3.77 | 182 | 5.92 | 5.91 |
| 193 | 4.83 | 0.46 | 113 | 5.10 | 1.69 | 183 | 5.15 | 0.69 |
| 194 | 5.13 | 3.00 | 115 | 5.25 | 2.98 | 184 | 5.64 | 3.97 |
| 195 | 5.08 | 2.46 | 116 | 4.87 | 0    | 185 | 5.31 | 1.77 |
| 201 | 4.73 | 0    | 131 | 4.87 | 0    | 186 | 5.82 | 4.88 |
| 202 | 5.53 | 5.94 | 132 | 5.51 | 4.88 |     |      |      |
| 203 | 4.88 | 0.67 | 134 | 4.89 | 0    |     |      |      |
| 205 | 4.97 | 1.47 | 135 | 5.27 | 3.19 |     |      |      |
| 206 | 5.38 | 4.73 | 136 | 5.20 | 2.34 |     |      |      |
With the substitution for $X_C$ with the linear relation between $X_C$ and $X_j$, $X_C = X_C^b + KX_j$, as shown in the case of Fe–Csat–V system, eq. (7) can be written as

$$-KeC X_j - \rho C(2KX_C^b X_j + K^2 X_j^2) - \ln \left(1 + KX_j/X_C^b\right) = (\epsilon C + \rho C^j X_C^b) X_j + (\rho C + K\rho C^j) X_j. \quad (9)$$

Dividing both sides by $X_j$ gives

$$A = (\epsilon C + \rho C^j X_C^b) + (\rho C + K\rho C^j) X_j,$$

where

$$A = -KeC - \rho C(2KX_C^b X_j + K^2 X_j^2) - \ln \left(1 + KX_j/X_C^b\right)/X_j. \quad (10)$$

Plotting $A$ versus $X_j$ should give a straight line, the intercept of which with the ordinate is

$$d = \epsilon C + \rho C^j X_C^b \quad (12)$$

and the slope of which is

$$m = \rho C + K\rho C^j. \quad (13)$$

On the other hand, Lupis(24) has shown

$$\rho C^j = \rho C \left(\frac{e C + 2\epsilon C}{e C + 2\epsilon C} X_C^b \right), \quad (14)$$

where

$$D = 1 + e C X_C^b + 2\rho C X_C^b, \quad (15)$$

$$e C^j = \left(\frac{\partial \ln \gamma C/\partial X_C}{X_C} \right)_{X_C = 1} = -\left(\frac{\partial \ln \gamma C/\partial X_C}{X_C} \right)_{X_C = 1} \quad (16)$$

and

$$\rho C^j = 1/2 \left(\frac{\partial^2 \ln \gamma C}{\partial X_C^2} \right)_{X_C = 1} X_C = 0 \quad (17)$$

Solving the simultaneous eqs. (12), (13) and (14) with known $e C^j$, $\rho C^j$, $e C$ and $\rho C$ yields $\epsilon C$, $\rho C$ and $\rho C^j$.

### 2. Evaluation of $e C$, $\rho C$ and $\rho C^j$ in Fe–C–V ternary system

According to Sigworth and Elliott(13), $e C$ and $\rho C$ can be expressed as

$$e C = 7.82 \times 10^3 / T + 3.66 \quad (18)$$

and
\[ \rho V = 1.56 \times 10^4 / T + 5.33. \]  
(19)

From the experimental results of the present study, the following are obtained.

\[ D = 3.20 + 2.30 \times 10^{-4} T. \]  
(20)

\[ \varepsilon_{cv} = 5.93 \times 10^3 / T - 5.84. \]  
(21)

\[ \rho_{cv} = -1.41 \times 10^3 / T + 11.1. \]  
(22)

The comparison of \( \varepsilon_{cv} \) values of different authors is shown in Fig. 5.

With all those terms from eqs. (3), (4), (5), (6), (18) and (19) inserted in eq. (10), the following expressions for \( A \) are obtained.

\[ A = -8.22 - 0.38 X_V \quad (1623 \text{ K}). \]  
(23)

\[ A = -8.69 - 0.48 X_V \quad (1673 \text{ K}). \]  
(24)

\[ A = -9.51 - 0.64 X_V \quad (1773 \text{ K}). \]  
(25)

By solving simultaneous eqs. (12), (13) and (14) with all necessary terms through (18) to (25) \( \varepsilon_{cv} \), \( \rho_{cv} \) and \( \rho_{cv}^V \) are estimated:

\[ \varepsilon_{cv} = 2.39 \times 10^4 / T - 22.9. \]  
(26)

\[ \rho_{cv} = 1.86 \times 10^3 / T - 1.28. \]  
(27)

\[ \rho_{cv}^V = 3.84 \times 10^3 / T - 2.98. \]  
(28)

The comparison of the result for \( \varepsilon_{cv} \) of the present study with those of various authors is shown in Fig. 6.

3. In \( \gamma_V \) by Gibbs-Duhem equation

The logarithm of activity coefficients for components in a 1–2–3 ternary system are interrelated by Gibbs-Duhem equation. The activity coefficients of components 2 and 3 can be estimated by integrating the Gibbs-Duhem equation with the experimentally determined activity data of component 1, expressed as a function of component concentration \( (25)-(30) \). This kind of calculation is quite useful, not only because it saves much hard experimental work at high temperatures, but also because it assures the thermodynamic consistency of the activity data. For certain systems there might be a component of which the activity cannot be determined experimentally. In this case the integration of the Gibbs-Duhem equation appears to be the only approach to the problem.

The method proposed by Chou \( ^{29} \) is used in the present paper with minor alteration. The direct application of Chou’s method to obtain \( \ln \gamma_V \) for Fe–C–V melt needs the data of C–V binary system which in fact cannot be determined. Instead the data of Fe–V binary system was used instead of C–V binary in the integration of the Gibbs-Duhem equation here. The method can be summarized as follows.

Following Chou \( ^{29} \), for ternary system 1–2–3, a function \( R' \) and a variable \( y \) are defined as

\[ R' = G^E / (1 - X_1) \]  
(29)

and

\[ y = X_3 / (X_2 + X_3), \]  
(30)

where \( G^E \) is the molar excess free energy of the solution and \( X_1, X_2 \) and \( X_3 \) are the mole fractions of components 1, 2 and 3, respectively. Chou \( ^{29} \) gives

\[ \tilde{G}^E = [\partial (R'/y)/\partial (1/y)]_{X_1} - X_1\tilde{G}^E / (1 - X_1), \]  
(31)
where $\tilde{G}^E_i$ and $\tilde{G}^F_i$ are the partial molar excess free energies of components 1 and 2, respectively. The function $R'$ is determined with the following equation,

$$R' = R^* + \int_{X_1 = X_1^*}^{X_1 = X_1^*} \frac{\tilde{G}^F_i}{(1 - X_1)^2} \, dX_1 \quad (y=\text{constant}).$$  \hfill (32)

Dividing the two sides of eq. (31) and (32) with $RT$, where $R$ is the gas constant and $T$ the absolute temperature, one gets

$$\ln \gamma_1 = -y^2 \left[ \frac{\partial (R' / RT)}{RT} \right]_{X_1} - X_1 \ln \gamma_1/(1 - X_1)$$  \hfill (33)

and

$$\frac{R' / RT}{R^* / RT} = R^* / RT + \int_{X_1 = X_1^*}^{X_1 = X_1^*} \ln \gamma_1/(1 - X_1)^2 \, dX_1 \quad (y=\text{constant}).$$  \hfill (34)

For Fe–C–V system, let C, V and Fe stand for components 1, 2 and 3, respectively, and $\ln \gamma_v$ in eqs. (33) and (34) be expressed as

$$\ln \gamma_v = \ln \gamma_v^C + e_v^C X_v + \rho_v^C X_1^C + e_v^C X_C + \rho_v^C X_2^C + \rho_v^C X_v X_C.$$  \hfill (35)

Substituting eqs. (18), (19), (26), (27) and (28) into eq. (35), $\ln \gamma_v$ can be calculated.

Before the $R'$ value corresponding to a certain $y$ can be calculated with eq. (34), the integration constant $R^*$ must be determined. The $G^E$ of the Fe–V binary system (i.e., $X_1 = X_1^* = 0$, point $a$ in Fig. 7) is chosen as the $R^*$ constant. At 1873 K the activity coefficient of vanadium in Fe–V binary system is

$$\ln \gamma_v^C = 2010 / T - 1.71$$  \hfill (31)

into eq. (35), $\ln \gamma_v$ can be calculated.

The activity coefficient of vanadium is converted to other temperatures by the regular solution model assumption of Fe–V binary system,

$$\ln \gamma_v = 1873 / T(-1.80 + 4.70 X_v - 2.35 X_v^2)$$  \hfill (37)

and

$$R^* = (G^E)_{Fe-V} = RT(X_1^C \ln \gamma_v^C + X_2^C \ln \gamma_v^C + X_v^C \ln \gamma_v^C).$$  \hfill (38)

Fig. 7 Path of the Gibbs-Duhem equation integration for eq. (34).

where $\ln \gamma_v^C$ is determined by the integration of Gibbs Duhem equation of Fe–V binary system.

$\ln \gamma_v$ is calculated through the following procedure:

(a) Integrate eq. (34) for different $y$’s to the intersects of lines of constant $y$ and $X_1$, for example, point $P$ in Fig. 7;

(b) Determine the value of $[\partial (R'/RT)/\partial y]_{X_1}$;

(c) Substitute $[\partial (R'/RT)/\partial y]_{X_1}$ and $\ln \gamma_v$ into eq. (33), which results in $\ln \gamma_v$ at $X_C$ and $X_v = (1 - y)(1 - X_C)$.

4. Calculation of $\rho_v^C$ and $\rho_v^C C$

The activity coefficient of vanadium in ternary Fe–C–V melt is written as

$$\ln \gamma_v = \ln \gamma_v^C + \epsilon_v^C X_v + \rho_v^C X_v^C + \epsilon_v^C X_C + \rho_v^C X_1^C + \rho_v^C X_v X_C.$$  \hfill (39)

Rearranging eq. (39) gives

$$Y = \rho_v^C + \rho_v^C X_v / X_C,$$  \hfill (40)

where

$$Y = (\ln \gamma_v - \ln \gamma_v^C - \epsilon_v^C X_v - \rho_v^C X_v^C + \epsilon_v^C X_C) / X_v^2.$$  \hfill (41)

Comparing the following expression for Fe–V binary system

$$\ln \gamma_v = \ln \gamma_v^C + \gamma_v^C X_v + \rho_v^C X_v^2$$

with eq. (37) leads to
(42) \[ \rho^C \varphi = -3.36 \times 10^3 / T, \]
(43) \[ \rho^V \varphi = 8.8 \times 10^3 / T \]
(44) \[ \rho^\psi \varphi = -4.4 \times 10^3 / T. \]

From eq. (26) one can get \[ \rho^C \varphi = \rho^V \varphi = 2.39 \times 10^4 / T - 22.9. \]

With all of these results the value of \( Y \) for different \( X_c \)’s and \( X_v \)’s can be calculated, and hence the regression linear relation shown in eq. (40), the intercept of which is \( \rho^C \psi \) and the slope \( \rho^V \psi \), can be obtained. The calculated results are shown in Table 4, by which the following expressions for the second order interaction coefficients are obtained as

(45) \[ \rho^C \psi = 8.8 \times 10^3 / T - 16.1 \]
(46) \[ \rho^V \psi = 1.32 \times 10^4 / T - 18.0. \]

5. Self-consistency check among the results of above calculation

Application of the reciprocal relation deduced by Lupis and Elliott\(^{33}\),

\[ x = 2 \rho^V + e \] (47)
to Fe–C–V system results in

(48) \[ \rho^C \psi + e = 2 \rho^V + e^C \]
(49) \[ \rho^V \psi + e = 2 \rho^C + e^V. \]

Substituting eqs. (18), (26) and (28) into (48) one can get at 1773 K

(50) \[ \rho^V = -9.12, \]

which agrees quite well with that listed in Table 3. Similarly, combining eqs. (26), (27), (43) and (49) leads to \( \rho^V \psi = 13.8 \) at 1773 K, the agreement of which with that calculated by the Gibbs-Duhem equation integration, \( \rho^V \psi = 10.6 \), can be accepted, as the second order interaction coefficient has not been reported so far.

V. Application of the Lattice Ratio as a Concentration Variable to Carbon Saturated Iron Base Ternary Melts

1. Activity interaction coefficients based on lattice ratio concentration in carbon saturated solutions

According to Chipman\(^{14}\), the lattice ratio variable is defined as follows: For a multicomponent solution containing substitutional (metallic) and interstitial (nonmetallic) solutes, with component 1 as solvent, the lattice ratio concentration of an interstitial component \( i \), \( \bar{Z}_i \), is proportional to the ratio of the interstitial sites filled by component \( i \) to the remaining unfilled interstitial sites. Thus for a lattice in which there are \( b \) interstitial sites per lattice atom the ratio of the sites filled by \( i \) to the remaining unfilled is \( \bar{Z}_i / b \). Here

(50) \[ \bar{Z}_i = n_i / (n_1 + v_1 n_1), \]

in which \( n \) represents the mole number and \( v_1 = +1 \) for substitutional and \( -1/b \) for interstitial solutes. The activity coefficient \( \bar{\psi}_i \) and activity interaction coefficient \( \bar{\psi}_{ij} \) based on this concentration measure are defined like those based on any other concentration measures,

(51) \[ \bar{\psi}_i = a_i / \bar{Z}_i, \]
(52) \[ \bar{\psi}_{ij} = (\partial \ln \bar{\psi}_i / \partial \bar{Z}_j)_{Z_i=0}. \]

For carbon saturated Fe–C–j system, \( a_c = 1 \), i.e., \( \bar{\psi}_c Z_c = 1 \), therefore,

(53) \[ \ln \bar{\psi}_c = -\ln Z_c. \]

It has been a known fact that the addition of a third component to the Fe–C binary system will increase or decrease the solubility of carbon in iron. With the adoption of the lattice ratio as a concentration variable, it is expected that this effect may be represented by a linear relation,

(54) \[ \ln \bar{\psi}_c = \ln \bar{\psi}_c^0 + \theta_{c1} Z_i, \]

where \( \ln \bar{\psi}_c = -\ln Z_c^0 \) is for the solubility of carbon in pure iron and

(55) \[ \theta_{c1} = (\partial \ln \bar{\psi}_c / \partial Z_i)_{Z_i=0} \]
may be taken as the activity interaction coefficient of $j$ on $C$ under the condition of carbon saturation. Equation (53) is similar to those for carbon saturated systems treated with other concentration variables, e.g., weight percent, mole fraction, etc.

1. Correlation of the experimental results of Fe–C$_{sat}$–$j$ systems

Shown in Fig. 8 through Fig. 19 and Table 5 are the experimental results of the present study and published works$^{(34)-(42)}$ correlated with the lattice ratio as a concentration variable. It can be seen that for all these systems except Fe–C–Mn a linear relation between the logarithm of the activity coefficient of carbon and the concentration of the third
component is valid over a considerable range of concentration, which, if treated with other concentration variables, may hold true within a rather limited range as in some of the original papers. For Fe–C–Mn system, a quadratic equation is needed to express the relation, and hence the second order interaction parameter, $\pi_{ij}^{2}$, has been employed as shown in Table 5. Another point to be noticed is that there exists some discrepancies among the values of the
solubility of carbon in pure iron derived from different ternary systems, as may be seen from the intercepts of the figures or the A’s in Table 5. This discrepancy arises from the disagreement among the original results of different authors.

In view of the lack of information on the structure of liquid metallic solution, Chipman\(^{(14)}\) chose values of \(v_j\) for Fe–i–j system in such a way that the values would lead to the linear relation between \(\ln \psi_i\) and \(Z_j\). For metallic solutes \(v_j=1\) and for nonmetallic \(v_j=-1\), which implied \(b=1\), were used in their studies\(^{(14)}\)–\(^{(19)}\). Though this value of \(b\) has led to the desired linear relation for many dilute solutions, it is not the case for all of the carbon saturated systems. It is found that for Fe–C\(_{sat}\)–j ternary melts with j being non-metallic, parameter \(b\) must be chosen greater than one, as is shown in Table 5, to obtain a better linear relation.

Figure 20 shows the regular change in \(\theta_j^{\psi_c}\), where \(j\) is a metallic solute, with the atomic number of \(j\) at 1873 K. For nonmetallic solutes, there is no such relation because of the different values of \(b\) for different elements. The regularity shown in Fig. 20 is similar to what has been achieved by means of other concentration variables.

**VI. Conclusion**

The solubility of carbon in Fe–C–V melt was experimentally determined at a temperature range of 1623–1773 K. The solubility data can be expressed as

\[
X_C = 0.083 + 6.57 \times 10^{-5}T - (0.492 - 5.60 \times 10^{-4}T)X_V.
\]
The activity interaction coefficients of vanadium on carbon were calculated with the solubility data as follows:

\[ \ln \psi_C = A + \theta_C^{\text{li}} Z_i + \pi_C^{\text{li}} Z_i^2 \]

| Third component | Temp./K | \[ \ln \psi_C = A + \theta_C^{\text{li}} | \theta_C^{\text{li}} \] | Correl. coeff. \( \gamma \) | \( b \) | Applicable concen. of \( j \), mass% | Ref. |
|-----------------|---------|------------------|-----------------|----------------|-----------------------------------|-----|
| B               | 1673    | 1.45             | 2.68            | 0.98           | 0-3.7*                           | (34) |
|                 | 1723    | 1.38             | 2.80            | 0.98           | 8                                |     |
|                 | 1773    | 1.35             | 2.17            | 0.98           |                                   |     |
| Al              | 1873    | 1.17             | 3.03            | 0.997          | 2                                | 0-24* (35) |
| Si              | 1573    | 1.22             | 2.17            | 0.999          |                                   |     |
|                 | 1673    | 1.16             | 1.89            | 0.998          |                                   |     |
|                 | 1773    | 1.10             | 1.70            | 0.998          | 1                                | 0-20* (36) |
|                 | 1873    | 1.04             | 1.48            | 0.996          |                                   |     |
|                 | 1973    | 0.98             | 1.35            | 0.996          |                                   |     |

\[ \theta_C^{\text{Si}} = -1.91 + 6393/T, \ (\gamma=0.998) \]

| P               | 1563    | 1.36             | 4.99            | 0.979          | 0-4.2*                           | (37) |
|                 | 1763    | 1.26             | 4.54            | 0.979          | 4                                |     |
|                 | 1848    | 1.19             | 4.63            | 0.976          |                                   |     |
| S               | 1473    | 1.50             | 1.70            | 0.87           |                                   |     |
|                 | 1623    | 1.40             | 2.18            | 0.90           | 4                                | 0-1.18* (38) |
|                 | 1773    | 1.31             | 2.84            | 0.84           |                                   |     |

\[ \theta_C^{\text{Si}} = 8.34 - 6970/T, \ (\gamma=0.999) \]

| Ti              | 1698**  | 1.15             | -3.87           | 0.979          | up to                           |     |
|                 | 1782    | 1.09             | -4.30           | 0.996          | 4                                |     |
|                 | 1863    | 1.03             | -4.13           | 0.999          |                                   |     |

\[ \theta_C^{\text{Ti}} = -0.39 - 6970/T \]

| V               | 1623    | 1.19             | -2.12           | 0.994          |                                   |     |
|                 | 1673    | 1.16             | -2.25           | 0.993          | 1                                | 0-6* (39) |
|                 | 1773    | 1.11             | -2.36           | 0.998          |                                   |     |

\[ \theta_C^{\text{V}} = -4.87 + 4440/T, \ (\gamma=0.976) \]

| Cr              | 1873    | 0.99             | -0.92           | 0.988          | 1                                | 0-17 (40) |
| Co              | 1623    | 1.18             | 0.62            | 1.0            | 1                                | 0-80 (41) |
|                 | 1823    | 1.00             | 0.49            | 0.998          |                                   |     |
| Ni              | 1623    | 1.02             | 1.70            | 0.987          |                                   |     |
|                 | 1823    | 1.00             | 1.08            | 0.997          | 1                                | 0-75 (41) |
| Cu              | 1823    | 1.05             | 1.58            | 0.998          |                                   |     |

| Mn              | 1573    | 1.18             | -0.58           | 0.166          | 1                                | 0-70 (36) |
|                 | 1673    | 1.12             | -0.52           | 0.129          |                                   |     |
|                 | 1773    | 1.06             | -0.47           | 0.098          | 1                                | 0-70 (36) |
|                 | 1873    | 1.00             | -0.43           | 0.072          |                                   |     |
|                 | 1973    | 0.95             | -0.395          | 0.550          |                                   |     |

\[ \theta_C^{\text{Mn}} = 0.35 - 1450/T, \ (\gamma=0.999) \]

\[ \pi_C^{\text{Mn}} = -0.39 + 872/T, \ (\gamma=0.999) \]

* The maximum of the concentration in the experimental work.
** Relatively unreliable according to the original authors.

The activity interaction coefficients of vanadium on carbon were calculated with the solubility data as follows:

\[ \rho_C^V = 2.39 \times 10^4 / T - 22.9. \]

\[ \rho_C^V = 1.86 \times 10^3 / T - 1.28. \]

\[ \rho_C^V = 3.84 \times 10^3 / T - 2.98. \]
The integration of ternary Gibbs-Duhem equation resulted in the second order interaction coefficients of carbon on vanadium,

\[ \rho_{C \text{v}} = 8.81 \times 10^3 / T - 16.1 \]

and

\[ \rho_{\text{v}, C} = -1.32 \times 10^4 / T - 18.0, \]

which confirmed quite well the reciprocal relation deduced by Lupis and Elliott\(^{(33)}\).

The lattice ratio as a concentration variable has been used to correlate experimental results on Fe–C–j (j = B, Al, Si, S, V, Ti, Cr, Co, Ni and Cu) systems and has led to a linear relation between \( \ln \psi_C \) and \( Z_j \) over quite wide ranges of j concentration. For Fe–C–Mn system, a quadratic expression is needed to represent the experimental results. The parameter \( b \) in the lattice ratio variable is unity for metallic solutes, and greater values must be employed for achieving the linear relation for systems with the third component j being nonmetallic. The first order activity interaction coefficient, \( \theta_{C j} \), where j is a metallic solute, changes regularly with the atomic number of j.

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