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

By Qi Guojun**, Ji Chunlin** and Che Yinchang**

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:

$$\varepsilon_C^V = 2.39 \times 10^4 / T - 22.9.$$

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

$$\rho_C^{V,C} = 3.84 \times 10^3 / T - 2.98.$$

The second order interaction coefficients, ρ_V^C and $\rho_V^{V,C}$, estimated by integrating the Gibbs-Duhem equation, are expressed as

$$\rho_V^C = 8.81 \times 10^3 / T - 16.1.$$

$$\rho_V^{V,C} = -1.32 \times 10^4 / T - 18.0.$$

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.

(Received January 8, 1987)

Keywords: thermodynamics, solubility measurement, activity interaction coefficient, iron-carbon-vanadium system, lattice ratio variable

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, ε_C^V , 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

Table 1 ε_C^V by different authors.

ε_C^V	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)

* Project supported by Science Fund of Chinese Academy of Sciences.

** Department of Non-Ferrous Metallurgy, Northeast University of Technology, People's Republic of China.

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, ε_C^V , ρ_C^V and $\rho_C^{C,V}$ for carbon and ρ_V^C and $\rho_V^{C,V}$ 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 ε -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

Fig. 1 Hexa-compartment graphite crucible.

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

$$[\%C] = 1.23 + 2.60 \times 10^{-3}t \text{ (}^\circ\text{C)} \quad (1)$$

or

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

2. Solubility of carbon in Fe-V melt

The results of the solubility of carbon in Fe-

Table 2 Solubility of graphite in iron, mass%.

Authors	Solubility/mass%		
	1623 K	1673 K	1773 K
Chipman <i>et al.</i> ⁽²¹⁾	4.77	4.90	5.02
Kitchner <i>et al.</i> ⁽²²⁾	4.73	4.86	4.99
Matoba and Ban-ya ⁽²³⁾	4.86	5.00	5.13
The present authors	4.74	4.87	5.00

Fig. 2 Solubility of carbon in pure iron.

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,

$$X_C = X_C^b + KX_V, \quad (3)$$

where X_C^b —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:

$$X_C = 0.189 + 0.423X_V \quad (1623 \text{ K}). \quad (4)$$

$$X_C = 0.193 + 0.453X_V \quad (1673 \text{ K}). \quad (5)$$

$$X_C = 0.199 + 0.508X_V \quad (1773 \text{ K}). \quad (6)$$

Fig. 3 Solubility of carbon in Fe-C-V melts.

IV. Discussion

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

The following relation is true between the Fe-C_{sat} binary and Fe-C_{sat}-j ternary systems, both of which possess the same a_C :

$$\begin{aligned} \ln \gamma_C^0 + \varepsilon_C^C X_C^b + \rho_C^C X_C^{b^2} + \ln X_C^b \\ = \ln \gamma_C^0 + \varepsilon_C^C X_C + \rho_C^C X_C^2 + \varepsilon_C^j X_j \end{aligned}$$

Table 3 Solubility of graphite in Fe-V melt.

1623 K			1673 K			1773 K		
No.	[%C]	[%V]	No.	[%C]	[%V]	No.	[%C]	[%V]
191	4.74	0	111	4.90	0.71	181	5.06	0.061
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

Fig. 4 Solubility of carbon in Fe-C-V melts.

Fig. 5 Comparison of ϵ_C^{*V} values of different authors.

- Sanbongi & Ohtani⁽⁶⁾
- ⊗ Fuwa & Chipman⁽¹⁾
- Piwowarsky⁽²⁾
- Neumann & Schenck⁽⁴⁾
- Neumann & Schenck⁽⁵⁾
- Mori *et al.*⁽³⁾
- Shenck & Golz⁽⁷⁾
- This study

$$+ \rho_C^i X_j^2 + \rho_C^{C,j} X_C X_j + \ln X_C \quad (7)$$

or

$$\begin{aligned} \epsilon_C^C (X_C^b - X_C) + \rho_C^C (X_C^{b^2} - X_C^2) - \ln (X_C / X_C^b) \\ = \epsilon_C^i X_j + \rho_C^i X_j^2 + \rho_C^{C,j} X_C X_j. \end{aligned} \quad (8) \quad \text{and}$$

With the substitution for X_C with the linear relation between X_C and X_j , $X_C = X_C^b + K X_j$, as shown in the case of Fe-C_{sat}-V system, eq. (7) can be written as

$$\begin{aligned} -K \epsilon_C^C X_j - \rho_C^C (2K X_C^b X_j + K^2 X_j^2) \\ - \ln (1 + K X_j / X_C^b) \\ = (\epsilon_C^i + \rho_C^{C,j} X_C^b) X_j + (\rho_C^i + K \rho_C^{C,j}) X_j. \end{aligned} \quad (9)$$

Dividing both sides by X_j gives

$$A = (\epsilon_C^i + \rho_C^{C,j} X_C^b) + (\rho_C^i + K \rho_C^{C,j}) X_j,$$

where

$$A = -K \epsilon_C^C - \rho_C^C (2K X_C^b + K^2 X_j) \quad (10)$$

$$- (\ln (1 + K X_j / X_C^b)) / X_j. \quad (11)$$

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

$$d = \epsilon_C^i + \rho_C^{C,j} X_C^b \quad (12)$$

and the slope of which is

$$m = \rho_C^i + K \rho_C^{C,j}. \quad (13)$$

On the other hand, Lupis⁽²⁴⁾ has shown

$$\begin{aligned} \rho_C^{*j} = [\rho_C^i + \epsilon_C^C (\epsilon_C^{*j})^2 X_C^b / 2 + 2 \rho_C^C (\epsilon_C^{*j})^2 X_C^{b^2} \\ - \rho_C^{C,j} \epsilon_C^{*j} X_C^{b^2}] / D, \end{aligned} \quad (14)$$

where

$$D = 1 + \epsilon_C^C X_C^b + 2 \rho_C^C X_C^{b^2}, \quad (15)$$

$$\epsilon_C^{*j} = (\partial \ln \gamma_C / \partial X_j)_{a_C=1} = - (\partial \ln X_C / \partial X_j)_{a_C=1} \quad (16)$$

and

$$\begin{aligned} \rho_C^{*j} &= 1/2 (\partial^2 \ln \gamma_C / \partial X_C^2)_{a_C=1} \\ &= -1/2 (\partial^2 \ln X_C / \partial X_j^2)_{a_C=1}. \end{aligned} \quad (17)$$

Solving the simultaneous eqs. (12), (13) and (14) with known ϵ_C^{*j} , ρ_C^{*j} , ϵ_C^C and ρ_C^C yields ϵ_C^i , ρ_C^i and $\rho_C^{C,j}$.

2. Evaluation of ϵ_C^V , ρ_C^V and $\rho_C^{C,V}$ in Fe-C-V ternary system

According to Sigworth and Elliott⁽¹³⁾, ϵ_C^C and ρ_C^C can be expressed as

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

$$\rho_C^C = 1.56 \times 10^4 / T + 5.33. \quad (19)$$

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

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

$$\varepsilon_C^{*V} = 5.93 \times 10^3 / T - 5.84. \quad (21)$$

$$\rho_C^{*V} = -1.41 \times 10^3 / T + 11.1. \quad (22)$$

The comparison of ε_C^{*V} 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.

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

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

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

By solving simultaneous eqs. (12), (13) and (14) with all necessary terms through (18) to (25) ε_C^V , ρ_C^V and ρ_C^{*V} are estimated:

$$\varepsilon_C^V = 2.39 \times 10^4 / T - 22.9. \quad (26)$$

$$\rho_C^V = 1.86 \times 10^3 / T - 1.28. \quad (27)$$

$$\rho_C^{*V} = 3.84 \times 10^3 / T - 2.98. \quad (28)$$

The comparison of the result for ε_C^V of the present study with those of various authors is shown in Fig. 6.

3. In γ_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

Fig. 6 Comparison of ε_C^V values of different authors.

- Suzuki and Ban-ya⁽¹⁰⁾
- Sigworth & Elliott⁽¹³⁾
- Mori, *et al.*⁽⁹⁾
- ⊗ Fuwa & Chipman⁽¹⁾
- ⊙ Stermmitz *et al.*⁽¹¹⁾
- ⊗ Foo & Lupis⁽⁸⁾
- Shenck & Golz⁽⁷⁾
- This study

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 can not 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

$$R' = G^E / (1 - X_1) \quad (29)$$

and

$$y = X_3 / (X_2 + X_3), \quad (30)$$

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

$$\bar{G}_2^E = [\partial(R'/y) / \partial(1/y)]_{X_1} - X_1 \bar{G}_1^E / (1 - X_1), \quad (31)$$

where $\bar{G}_1^E$ and $\bar{G}_2^E$ are the partial molar excess free energies of components 1 and 2, respectively. The function R' is determined with the following equation,

$$R' = R^* + \int_{X_1=X_1^*}^{X_1=X_1} \bar{G}_1^E / (1-X_1)^2 dX_1 \quad (y=\text{constant}). \quad (32)$$

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

$$\ln \gamma_2 = -y^2 [\partial(R'/RTy) / \partial y]_{X_1} - X_1 \ln \gamma_1 / (1-X_1) \quad (33)$$

and

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

For Fe-C-V system, let C, V and Fe stand for components 1, 2 and 3, respectively, and $\ln \gamma_1$ in eqs. (33) and (34) be expressed as

$$\ln \gamma_1 = \ln \gamma_C = \ln \gamma_C^0 + \varepsilon_C^C X_C + \rho_C^C X_C^2 + \varepsilon_C^V X_C + \rho_C^V X_V^2 + \rho_C^{V,C} X_C X_V. \quad (35)$$

Substituting eqs. (18), (19), (26), (27) and (28) and

$$\ln \gamma_C^0 = 2010/T - 1.71^{(31)} \quad (36)$$

into eq. (35), $\ln \gamma_C$ 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⁽²⁵⁾ is

$$\ln \gamma_V^b = -1.02X_{Fe}^2 + 0.24 \quad (X_V \leq 0.20).$$

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

$$\ln \gamma_V^b = 1873/T (-1.80 + 4.70X_V - 2.35X_V^2) \quad (37)$$

and

$$R^* = (G^E)_{Fe-V} = RT(X_V^b \ln \gamma_V^b + X_{Fe}^b \ln \gamma_{Fe}^b), \quad (38)$$

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

where $\ln \gamma_{Fe}^b$ 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 $[\partial(R'/RT) / \partial y]_{X_C}$;

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

4. Calculation of ρ_V^C and $\rho_V^{V,C}$

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

$$\ln \gamma_V = \ln \gamma_V^0 + \varepsilon_V^V X_V + \rho_V^V X_V^2 + \varepsilon_V^C X_C + \rho_V^C X_C^2 + \rho_V^{V,C} X_V X_C. \quad (39)$$

Rearranging eq. (39) gives

$$Y = \rho_V^C + \rho_V^{V,C} X_V / X_C, \quad (40)$$

where

$$Y = (\ln \gamma_V - \ln \gamma_V^0 - \varepsilon_V^V X_V - \rho_V^V X_V^2 - \varepsilon_V^C X_C) / X_C^2. \quad (41)$$

Comparing the following expression for Fe-V binary system

$$\ln \gamma_V^b = \ln \gamma_V^0 + \gamma_V^V X_V + \rho_V^V X_V^2$$

with eq. (37) leads to

Table 4 ρ_V^C and $\rho_V^{C,V}$ calculated in section IV.4.

Temp./K	1623	1673	1723	1773
ρ_V^C	-10.6	-10.8	-10.9	-11.1
$\rho_V^{C,V}$	9.93	10.2	10.4	10.6

$$\ln \gamma_V^0 = -3.36 \times 10^3 / T, \quad (42)$$

$$\varepsilon_V^V = 8.8 \times 10^3 / T \quad (43)$$

and

$$\rho_V^V = -4.4 \times 10^3 / T. \quad (44)$$

From eq. (26) one can get $\varepsilon_V^C = \varepsilon_C^V = 2.39 \times 10^4 / T - 22.9$.

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 ρ_V^C and the slope $\rho_V^{C,V}$, 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

$$\rho_V^C = 8.80 \times 10^3 / T - 16.1 \quad (45)$$

and

$$\rho_V^{C,V} = 1.32 \times 10^4 / T - 18.0. \quad (46)$$

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

Application of the reciprocal relation deduced by Lupis and Elliott⁽³³⁾,

$$\rho_i^{j,j} + \varepsilon_i^j = 2\rho_j^j + \varepsilon_i^j, \quad (47)$$

to Fe-C-V system results in

$$\rho_C^{C,V} + \varepsilon_C^V = 2\rho_V^C + \varepsilon_C^C \quad (48)$$

and

$$\rho_V^{V,C} + \varepsilon_V^C = 2\rho_C^V + \varepsilon_V^V. \quad (49)$$

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

$$\rho_V^C = -9.12,$$

which agrees quite well with that listed in Table 3. Similarly, combining eqs. (26), (27), (43) and (49) leads to $\rho_V^{V,C} = 13.8$ at 1773 K, the agreement of which with that calculated by the Gibbs-Duhem equation integration, $\rho_V^{V,C} = 10.6$, can be accepted, as the second order in-

teraction 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 , 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 Z_i/b . Here

$$Z_i = n_i / (n_i + v_i n_j), \quad (50)$$

in which n represents the mole number and $v_j = +1$ for substitutional and $-1/b$ for interstitial solutes. The activity coefficient ψ_i and activity interaction coefficient θ_i^j based on this concentration measure are defined like those based on any other concentration measures,

$$\psi_i = a_i / z_i, \quad \theta_i^j = (\partial \ln \psi_i / \partial Z_j)_{Z_j \rightarrow 0}. \quad (51)$$

For carbon saturated Fe-C_{sat}-j system, $a_C = 1$, i.e., $\psi_C Z_C = 1$, therefore,

$$\ln \psi_C = -\ln Z_C. \quad (52)$$

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,

$$\ln \psi_C = \ln \psi_C^b + \theta_C^{*j} Z_j, \quad (53)$$

where $\ln \psi_C^b = -\ln Z_C^b$ is for the solubility of carbon in pure iron and

$$\theta_C^{*j} = (\partial \ln \psi_C / \partial Z_j)_{a_C=1, Z_i \rightarrow 0}$$

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

Fig. 8 $\ln \psi_C$ versus Z_B .
(Data from Ref. (34)).

Fig. 9 $\ln \psi_C$ versus Z_{Al} .
(Data from Ref. (35)).

Fig. 10 $\ln \psi_C$ versus Z_{Si} .
(Data from Ref. (36)).

Fig. 11 $\ln \psi_C$ versus Z_P .
(Data from Ref. (37)).

Fig. 12 $\ln \psi_C$ versus Z_S .
(Data from Ref. (38)).

Fig. 13 $\ln \psi_C$ versus Z_{Ti} .
(Data from Ref. (39)).

Fig. 15 $\ln \psi_C$ versus Z_{Cr} .
(Data from Ref. (40)).

Fig. 14 $\ln \psi_C$ versus Z_V .
(Present study).

Fig. 16 $\ln \psi_C$ versus Z_{Co} .
(Data from Ref. (41)).

Fig. 17 $\ln \psi_C$ versus Z_{Ni} .
(Data from Ref. (41)).

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, π_C^{*j} , has been employed as shown in Table 5. Another point to be noticed is that there exists some discrepancies among the values of the

Fig. 18 $\ln \psi_C$ versus Z_{Cu} .
(Data from Ref. (42)).

Fig. 20 Variation of θ_C^{*j} with the atomic number of j .

Fig. 19 $\ln \psi_C$ versus Z_{Mn} .
(Data from Ref. (36)).

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 nonmetallic, 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 θ_C^{*j} , 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

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

Table 5 Experimental results of Fe-C_{sat}-j systems recorrelated with lattice ratio concentration variable.

Third component j	Temp./K	$\ln \psi_c = A + \theta_c^{*j} Z_j$		Correl. coeff. γ	b	Applicable concn. of j, mass%	Ref.
		A	θ_c^{*j}				
B	1673	1.45	2.68	0.98	8	0-3.7*	(34)
	1723	1.38	2.80	0.98			
	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	1	0-20*	(36)
	1673	1.16	1.89	0.998			
	1773	1.10	1.70	0.998			
	1873	1.04	1.48	0.996			
	1973	0.98	1.35	0.996			
$\theta_c^{*Si} = -1.91 + 6393/T, (\gamma = 0.998)$							
P	1563	1.36	4.99	0.979	4	0-4.2*	(37)
	1763	1.26	4.54	0.979			
	1848	1.19	4.63	0.976			
S	1473	1.50	1.70	0.87	4	0-1.18*	(38)
	1623	1.40	2.18	0.90			
	1773	1.31	2.84	0.84			
$\theta_c^{*S} = 8.34 - 6970/T, (\gamma = 0.99)$							
Ti	1698**	1.15	-3.87	0.979	1	up to where TiC participates	(39)
	1782	1.09	-4.30	0.996			
	1863	1.03	-4.13	0.999			
$\theta_c^{*Ti} = -0.39 - 6970/T$							
V	1623	1.19	-2.12	0.994	1	0-6*	present study
	1673	1.16	-2.25	0.993			
	1773	1.11	-2.36	0.998			
$\theta_c^{*V} = -4.87 + 4440/T, (\gamma = 0.976)$							
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	1	0-80	(41)
	1823	1.00	1.08	0.997			
Cu	1823	1.05	1.58		1	0-7	(42)
$\ln \psi_c = A + \theta_c^{*j} Z_j + \pi_c^{*j} Z_j^2$							
		A	θ_c^{*j}	π_c^{*j}			
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			
	1873	1.00	-0.43	0.072			
	1973	0.95	-0.395	0.550			
$\theta_c^{*Mn} = 0.35 - 1450/T, (\gamma = 0.999)$							
$\pi_c^{*Mn} = -0.39 + 872/T, (\gamma = 0.998)$							

* 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:

$$\epsilon_C^V = 2.39 \times 10^4 / T - 22.9.$$

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

$$\rho_C^{C,V} = 3.84 \times 10^3 / T - 2.98.$$

The integration of ternary Gibbs-Duhem equation resulted in the second order interaction coefficients of carbon on vanadium,

$$\rho_V^C = 8.81 \times 10^3 / T - 16.1$$

and

$$\rho_V^{V,C} = -1.32 \times 10^4 / T - 18.0,$$

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_{sat}-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, θ_C^{*j} , where j is a metallic solute, changes regularly with the atomic number of j.

REFERENCES

- (1) T. Fuwa and J. Chipman: Trans. Met. Soc. AIME, **215** (1958), 708.
- (2) E. Piwowarsky: Gusseisen., (1951), 767.
- (3) T. Mori, K. Fujimaru and H. Kanoshima: Mem. Fac. Engng. Kyoto Univ., **25** (1963), 83.
- (4) F. Neumann and H. Shenck: Gieberei., **49** (1962), 21.
- (5) F. Neumann and H. Shenck: Arch. Eisenhüttenw., **430** (1959), 477.
- (6) K. Sanbongi, M. Ohtani and K. Yoita: Sci. Res. Inst., Tohoku Univ. Ser., **A9** (1957), 147.
- (7) H. Shenck and M. Golz: Arch. Eisenhüttenw., **41** (1970), 1.
- (8) E. H. Foo and C. H. P. Lupis: Metall. Trans., **3** (1972), 790.
- (9) T. Mori, K. Fujimaru and I. Noda: Tetsu-to-Hagané, **52** (1966), 1443.
- (10) Y. Suzuki, S. Ban-ya and T. Fuwa: Tetsu-to-Hagané, **56** (1970), 1809.
- (11) E. Stermmittz, S. Bochum, R. Franzen and H. Shenck: Arch. Eisenhüttenw., **44** (1973), 743.
- (12) Wei Shoukun: *Thermodynamics in Metallurgy*, Shanghai, (1980), p. 85.
- (13) G. K. Sigworth and J. F. Elliott: Metal Sci., **8** (1974), 298.
- (14) J. Chipman: Trans. Met. Soc. AIME, **239** (1967), 1332.
- (15) J. Chipman: Metall. Trans., **1** (1970), 1313.
- (16) J. Chipman: *ibid.*, **1** (1970), 2163.
- (17) S. Ban-ya and J. Chipman: Trans. Met. Soc. AIME, **242** (1968), 940.
- (18) S. Ban-ya and J. Chipman: *ibid.*, **245** (1969), 133.
- (19) S. Ban-ya and J. Chipman: *ibid.*, **245** (1969), 391.
- (20) Ji Chunlin and Qi Guojun: Trans. JIM, **26** (1985), 832.
- (21) J. Chipman, E. F. Brush, Trans. Met. Soc. AIME, **242** (1968), 35.
- (22) J. A. Kitchner, J. Bockris and D. A. Spratt: Trans. Faraday Soc., **48** (1952), 608.
- (23) S. Matoba and S. Ban-ya: Tetsu-to-Hagané, **43** (1957), 790.
- (24) C. H. P. Lupis: Acta Met., **16** (1968), 1365.
- (25) L. S. Darken: J. Amer. Chem. Soc., **72** (1950), 2909.
- (26) C. Wagner: *Thermodynamics of Alloys*, Addison Wesley, (1952), p. 19.
- (27) S. Schuhmann: Acta Met., **3** (1955), 219.
- (28) N. A. Gokcen: J. Phys. Chem., **64** (1960), 401.
- (29) Chou Guozhi: Scientia Sinica, **5** (1977), 456.
- (30) Wang Zhichang and Chou Guozhi: *ibid.*, **A** (1984), 959.
- (31) T. Furukawa and E. Kato: Tetsu-to-Hagané, **61** (1975), 3050.
- (32) S. Ban-ya and S. Matoba: *ibid.*, **48** (1962), 925.
- (33) C. H. P. Lupis and J. F. Elliott: Acta Met., **14** (1966), 529.
- (34) Yu Rongxiang and Ji Chunlin: to be published.
- (35) J. Chipman and T. P. Flokids: Acta Met., **3** (1955), 456.
- (36) J. Chipman, R. W. Alfred, L. W. Gott, R. B. Small, D. W. Wilson, C. N. Thomson, D. L. Guersey and J. C. Fulton: Trans. ASM, **44** (1952), 1215.
- (37) E. T. Turkdogan and L. E. Leak: J. Iron Steel Inst., **179** (1955), 39.
- (38) E. T. Turkdogan and R. A. Hancock: J. Iron Steel Inst., **179** (1955), 155.
- (39) Peng Ruiwu and Zou Yuanxi: *Proceedings of the First Conference on the Physical Chemistry of Process Metallurgy*, China, (1964), p. 409.
- (40) H. G. Hadrys, M. G. Froberg and J. F. Elliott: Metall. Trans., **1** (1970), 1867.
- (41) E. T. Turkdogan, R. A. Hancock, S. I. Herlitz and J. Dentan: J. Iron Steel Inst., **183** (1956), 69.
- (42) Peng Ruiwu, Wang Guangyu and Zhang Junyue: Acta Metallurgica Sinica, **19** (1983), A237.