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INTERACTION COEFFICIENTS IN MULTICOMPONENT METALLIC SOLUTIONS
AT CONSTANT ACTIVITY AND CONSTANT CONCENTRATION

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Synopsis: Determination of interaction coefficients of solutes in metal melt with the solubility measurements by two ways of evaluation, namely, the logarithm formulation and the solubility equation, was studied. The interaction coefficients of Ca in the Mn-Ca-Cr system were calculated as an example. It has been found that with the same experimental data the two ways of evaluation give quite different results, although the values are of the same order of magnitude. Determination of interaction coefficients in metallic melt by four kinds of equilibrium methods, namely, the gas-metal equilibrium, the electrochemical equilibrium, the gas-liquid dissolution equilibrium and the distribution equilibrium, was discussed. It has been ascertained that through change in condition of treatment of experimental data, interaction coefficients either at constant concentration or at constant activity can be evaluated, a general relationship between the two ways of evaluation being derived. Correct use of Wagner's formalism as regards the conversion of interaction coefficient at constant activity to that at constant concentration was emphasized.

Key words: interaction coefficient, multicomponent metallic solution

I. Introduction

Interaction coefficients of elements in multicomponent metallic solutions are widely used in making thermodynamic analysis of the relevant metallurgical reactions. Various experimental methods of determination of the interaction coefficients have been derived. But discrepancy and scatter of results for the same system from different sources have often been met in the literature. Different ways of approach in the elaboration of the same experimental data for the same system, arisen either from different ways of calculation or from conceptual confusion or misunderstanding might be a main cause for this inconsistency. It is the purpose of this paper to make a study on this aspect, the two ways of evaluation by the solubility method at constant activity, as well as the evaluation by the equilibrium methods at constant concentration and at constant activity being investigated.

II. The solubility method at constant activity

The solubility method has been used for determination of interaction coefficients in the systems Fe-C-j [1-5], Mn-C-j [6], Ni-C-j [6], Co-C-j [6], Fe-H-j [7-8], Fe-N-j [9-10], Fe-Ca-j [11] and Mn-Ca-j [12]. From the effect of the 3rd element j upon the change in the solubility of the solute i in the metal melt Me, two ways of evaluation of the interaction coefficients at constant activity, namely, the logarithm formulation and the solubility equation, are prevalent in the literature.

2-1 The logarithm formulation

In the system Me-i-j, the solubility of i in the metal melt Me is measured in and without the presence of the 3rd element j. In these saturated solutions, $a_i = \text{constant}$.

$$a_i = \gamma_i^{\text{I}} \dot{N}_i^{\text{I}} = \gamma_i^{\text{II}} N_i$$

in which γ_i^{I} , γ_i^{II} represent the activity coefficient of i in the binary and ternary system respectively, with pure substance as the standard. And \dot{N}_i^{I} , N_i represent the solubility of i expressed in mol fraction for the binary and ternary system respectively.

The effect brought by the presence of j upon i is designated as

$$\gamma_i^{\text{I}} = \frac{\gamma_i^{\text{II}}}{\gamma_i^{\text{I}}} = \frac{\dot{N}_i^{\text{I}}}{N_i}$$

By plotting $\ln \gamma_i^j$ or $\ln N_i^j/N_i$ against N_j , the slope at $N_j \rightarrow 0$ is the interaction coefficient ξ_i^j , the asterisk being used to designate the value at constant activity.

$$\xi_i^j = \left. \left\{ \frac{\partial \ln \gamma_i^j}{\partial N_j} \right\}_{a_i; N_j \rightarrow 0} = \left. \left(\frac{N_i^j}{N_i} \frac{\partial \ln \frac{N_i^j}{N_i}}{\partial N_j} \right)_{a_i; N_j \rightarrow 0} \right.$$

Usually, regression analysis is carried out with abandonment of those points deviating much from the linear relationship. The regression equation takes the form of

$$\ln \gamma_i^j = \ln \frac{N_i^j}{N_i} = \xi_i^j N_j \quad (1)$$

Eq. 1 might be called as the logarithm formulation for the evaluation of ξ_i^j . The corresponding equation for the wt. % concentration is:

$$\lg f_i^j = \lg \left[\frac{\%j}{\%i} \right] = \xi_i^j [\%j] \quad (2)$$

2-2 The solubility equation

It has been well known [13-14] that the change in solubility due to the presence of the 3rd element j is directly proportional to the amount of j :

$$\Delta N_i = N_i - N_i^j = m N_j \quad (3)$$

in which m is the proportional constant. ξ_i^j is related with m by:

$$\xi_i^j = - \frac{m}{N_i} \quad (4)$$

Eq. 3 might be named as the solubility equation and has been used by Schenck and his associates [3-6] for calculating the interaction coefficients of the Me-C-j systems. The corresponding equations for the wt. concentration and the 1 wt. % solution standard are:

$$[\%i] - [\%i]^0 = m [\%j] \quad (5)$$

$$\xi_i^j = - \frac{m'}{2.30[\%i]^0} \quad (6)$$

2-3 The 2nd order interaction coefficients

According to Lupis [15] the logarithm formulation is written as:

$$\ln \gamma_i^j = \xi_i^j N_j + \rho_i^j N_j^2 \quad (7)$$

The coefficients ξ_i^j and ρ_i^j can be found by the regression analysis.

The solubility equation could be written as:

$$N_i - N_i^j = m N_j + \rho_i^j N_j^2 \quad (8)$$

$$\xi_i^j = - \frac{m}{N_i} \quad (9)$$

$$\rho_i^j = - \frac{I}{N_i} + \frac{1}{2} \left[\frac{m}{N_i} \right]^2 \quad (10)$$

Similarly, for the 1 wt. % solution standard, the logarithm formulation is:

$$\lg \bar{c}_i^j = \bar{c}_i^j [\%j] + \bar{r}_i^j [\%j]^2 \quad (11)$$

For the solubility equation,

$$[\%i] - [\%i]^* = m [\%j] + l' [\%j]^2 \quad (12)$$

$$\bar{c}_i^j = -\frac{m'}{2.30[\%i]^*} \quad (13)$$

$$\bar{r}_i^j = -\frac{l'}{2.30[\%i]^*} + \frac{1}{4.60} \left(\frac{m'}{[\%i]^*} \right)^2 \quad (14)$$

Derivation of Equ. 9, 10, 13 and 14 have been given elsewhere [16].

2-4 Conversion formulae

The conversion between \bar{c}_i^j and \bar{c}_i^j is exactly the same as ϵ_i^j and ϵ_i^j (at constant concentration) with the following formulae:

$$\bar{c}_i^j = 2.30 \frac{M_1}{M_i} \bar{c}_i^j + \frac{M_1 - M_i}{M_1} \quad (15)$$

The conversion formula between \bar{b}_i^j and \bar{r}_i^j is given by Lupis [15]:

$$\bar{b}_i^j = \frac{23000M_1^2 \bar{r}_i^j + M_1(M_1 - M_i)\bar{c}_i^j - \frac{1}{2}M_1(M_1 - M_i)(\bar{c}_i^j)^2 N_i' - \frac{1}{2}(M_1 - M_i)^2}{[M_1 - N_i'(M_1 - M_i)]M_1} \quad (16)$$

In the above formulae, M_1 , M_i and M_j represent the molecular weight of the solvent, solute and the 3rd element respectively.

The conversion from the interaction coefficient at constant activity to that at constant concentration has been studied by Fuwa and Chipman [1], Mori et al [17], Schenck et al [4] and Lupis [15], who gave the following formulae:

$$\bar{c}_i^j = \frac{\epsilon_i^j + \rho_i^j N_i'}{1 + \epsilon_i^j N_i' + 2\rho_i^j (N_i')^2} \quad (17)$$

$$\rho_i^j = \frac{\rho_i^j - \bar{c}_i^j \rho_i^j N_i' + \frac{1}{2}(\bar{c}_i^j)^2 4\rho_i^j (N_i')^2 + \epsilon_i^j N_i'}{1 + \epsilon_i^j N_i' + 2\rho_i^j (N_i')^2} \quad (18)$$

With neglect of terms of higher orders, Equ. 17 becomes:

$$\bar{c}_i^j = \bar{c}_i^j (1 + \epsilon_i^j N_i') \quad (19)$$

which is the same formula already derived by Mori [17], Schenck [4] and their associates. The corresponding formula on the wt. % basis is accordingly:

$$e_i^j = e_i^{j'} (1 + 2.30 e_i^j [\%i]) \quad (20)$$

Obviously, in case that the self interaction coefficient e_i^i or $e_i^i = 0$, or the concentration for the binary system is extremely small, then $e_i^j = e_i^{j'}$ or $e_i^j = e_i^{j'}$.

2-5 Numerical calculation

The experimental data for the system Mn-Ca-Cr (Table 1 [12]) has been used as an example for calculation. The first order interaction coefficients e_{Ca}^{Cr} , e_{Cr}^{Ca} are given in Tab. 2 [16]), and the 2nd order interaction coefficients e_{Ca}^{Cr} in Tab. 3 [16]).

Table 1. Effect of Cr upon the solubility of Ca in Mn at 1350°C

% Ca	N_{Ca}	% Cr	N_{Cr}
0.15	0.002055	0	0
0.15	0.002054	0.88	0.009288
0.14	0.001915	2.59	0.027310
0.12	0.001640	4.28	0.045091
0.12	0.001635	9.48	0.099582
0.098	0.001334	11.02	0.115668
0.084	0.001143	13.40	0.140468

Table 2. 1st order interaction coefficients of Cr upon Ca in Mn at constant activity at 1350°C

a) Mole fraction basis	
Logarithm formulation	Solubility equation
$\ln \gamma_i^j = b N_j$	$N_i \cdot N_i^j = m N_j$
$\ln \gamma_{Ca}^{Cr} = 3.6447 N_{Cr} \quad (r = 0.95)$	$N_{Ca} \cdot N_{Ca}^{Cr} = -0.006011 N_{Cr} \quad (r = 0.96)$
$e_{Ca}^{Cr} = 3.6$	$e_{Ca}^{Cr} = -\frac{m}{N_{Ca}} = 2.9$
b) wt. % basis	
Logarithm formulation	Solubility equation
$\lg f_i^j = b' [\%j]$	$[\%i] \cdot [\%i]^j = m' [\%j]$
$\lg f_{Ca}^{Cr} = 0.01638 [\%Cr] \quad (r = 0.95)$	$[\%Ca] \cdot [\%Ca]^{Cr} = -0.004551 [\%Cr] \quad (r = 0.96)$
$e_{Ca}^{Cr} = 0.016$	$e_{Ca}^{Cr} = -\frac{m'}{2.30 [\%Ca]} = 0.013$
By conversion with Equ. (15),	By conversion with Equ. (15),
$e_{Ca}^{Cr} = 3.6$	$e_{Ca}^{Cr} = 2.9$

Table 3. 2nd order interaction coefficients of Cr upon Ca in Mn at constant activity at 1350°C

a) Mole fraction basis	
Logarithm formulation	Solubility equation
$\ln \gamma_j^i = bN_j + cN_j^2$	$N_i - N_j = mN_j + jN_j^2$
$\ln \gamma_{Ca}^{Cr} = 2.1998N_{Cr} + 12.2333N_{Cr}^2$ ($r = 0.96$)	$N_{Ca} - N_{Ca}^i = -0.005349N_{Cr} - 0.005607N_{Cr}^2$ ($r = 0.96$)
$\epsilon_{Ca}^{Cr} = 2.2$	$\epsilon_{Ca}^{Cr} = -\frac{m}{N_{Ca}} = 2.6$
$\rho_{Ca}^{Cr} = 12.2$	$\rho_{Ca}^{Cr} = -\frac{j}{N_{Ca}} + \frac{1}{2} \left[\frac{m}{N_{Ca}} \right]^2 = 6.1$
b) wt. % basis	
Logarithm formulation	Solubility equation
$\lg f_j^i = b[\%j] + c[\%j]^2$	$[\%i] - [\%i] = m[\%j] + r[\%j]^2$
$\lg f_{Ca}^{Cr} = 0.009814[\%Cr] + 0.000582[\%Cr]^2$ ($r = 0.96$)	$[\%Ca] - [\%Ca] = -0.004016[\%Cr] - 0.000047[\%Cr]^2$ ($r=0.99$)
$\epsilon_{Ca}^{Cr} = 0.0098$	$\epsilon_{Ca}^{Cr} = -\frac{m'}{2.30[\%Ca]} = 0.012$
$\gamma_{Ca}^{Cr} = 0.00058$	$\gamma_{Ca}^{Cr} = -\frac{r}{2.30[\%Ca]} + \frac{1}{4.60} \left[\frac{m'}{[\%Ca]} \right]^2 = 0.00029$
By conversion with Equ. (15) and (16),	By conversion with Equ. (15) and (16),
$\epsilon_{Ca}^{Cr} = 2.2$	$\epsilon_{Ca}^{Cr} = 2.6$
$\rho_{Ca}^{Cr} = 12.1$	$\rho_{Ca}^{Cr} = 6.1$

It has been shown that from the same experimental data of the solubility measurements, the two ways of evaluation, namely, the logarithm formulation and the solubility equation for calculating the interaction coefficients give quite different results, although the values are of the same order of magnitude. To avoid the discrepancy arising from different ways of evaluation, it would be preferable to choose a standard way of evaluation. It might be recommended to choose the logarithm formulation as the standard way of evaluation because of its direct relationship with the definition of the interaction coefficient.

III. The equilibrium methods

3-1 The gas-metal chemical equilibrium

The Fe-S-j system is taken as an example. A mixture of H₂S and H₂ gas was equilibrated with [S] in liquid iron [18-20].



$$K = \left(\frac{P_{H_2S}}{P_{H_2}} \right) \cdot \frac{1}{f_S [\%S]} = \left(\frac{P_{H_2S}}{P_{H_2}} \right) \frac{1}{f_S^i [\%S]} \quad (21)$$

The prime refers to the binary system.

$$\text{Let } K_{bin} = \left(\frac{P_{H_2S}}{P_{H_2}} \right) \frac{1}{f_S^i [\%S]} \text{ and } K_{tern} = \left(\frac{P_{H_2S}}{P_{H_2}} \right) \frac{1}{f_S [\%S]} \quad (22)$$

K is found by extrapolating the curve of K_{bin} vs. [%S] to zero concentration.

$$f_S^i = \frac{f_S}{f_S^i} = \frac{K_{tern}}{K_{bin}} \quad (23)$$

For a certain value of [%S], K_{tem} is calculated from the experimental data, while K_{bin} for the same value of S can be read from the curve of K_{bin} plotted against [%S]. The value f_S^j thus found is at constant concentration of S. By plotting $\lg f_S^j$ against [%j], the slope at [%j] = 0 equals the interaction coefficient e_S^j . Usually regression analysis through those points pertaining to the linear relationship is made:

$$\lg f_S^j = b[\%j]$$

and $e_S^j = b$. The regression line passes naturally through the origin. Recommended values of e_i^j (e_i^j) as given in the literature [21-24] are supposed to be the conventional interaction coefficients at constant concentration.

Should the evaluation of f_S^j (an asterisk being added for distinction) is required, then $a_S^j = a_S$

$$f_S^{*j} = \frac{f_S^j}{f_S} = \frac{[\%S]^j}{[\%S]} \quad (24)$$

Since f_S^j and f_S can be calculated from the experimental data, curves of a_S^j against [%S] for both the binary and ternary systems can be drawn. For a certain value of ternary [%S], the corresponding value of binary [%S]^{*} at constant activity can be read from the activity curves. Thus different values of f_S^j are calculated, and e_S^j will be evaluated as usually.

From Equ. 21, it can be shown that for constant activity,

$$\left(\frac{P_{H_2S}}{P_{H_2}} \right)' = \left(\frac{P_{H_2S}}{P_{H_2}} \right)$$

So the evaluation of interaction coefficient at constant activity is really based on the performance of the equilibrium experiment at constant gas pressure ratio. Furthermore, from Equ. 21,

$$\left(\frac{P_{H_2S}}{P_{H_2}} \right)' / \left(\frac{P_{H_2S}}{P_{H_2}} \right) = \frac{a_S^j}{a_S}$$

By comparison with Equ. 23,

$$f_S^j = \frac{a_S^j}{a_S} \cdot \frac{[\%S]^j}{[\%S]} \quad (25)$$

Equ. 25 is the general equation for calculating f_S^j .

At constant concentration,

$$f_S^j = \frac{K_{\text{tem}}}{K_{\text{bin}}} = \frac{a_S^j}{a_S} \quad (23)$$

At constant activity,

$$f_S^j = \frac{[\%S]^j}{[\%S]} \quad (24)$$

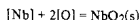
Therefore with the experimental data from both the binary and the ternary systems, by change in condition of treatment of data, either the interaction coefficient at constant concentration or at constant activity can be evaluated.

3-2 The electrochemical equilibrium

For the determination of the interaction coefficient of Nb in the Fe-Nb-Mn system with the solid electrolyte cell technique, the following cell assembly is used:

Mol/Mo, MoO₂/ZrO₂(MgO)/(Nb), NbO₂/Mo, Mo-cermet

The overall reaction is:



$$K = \frac{1}{a_{\text{Nb}} \cdot a_{\text{O}}^2} = \frac{1}{a_{\text{Nb}} \cdot a_{\text{O}}^2}$$

K is found by extrapolation at zero concentration of Nb. Due to the small content of [O] in the melt, the effect of f_{Nb}^{O} is neglected.

$$f_{\text{Nb}}^{\text{Mn}} = \frac{a_{\text{O}}^2 [\% \text{Nb}]'}{a_{\text{O}}^2 [\% \text{Nb}]} = \frac{a_{\text{Nb}}}{a_{\text{Nb}}} \cdot \frac{[\% \text{Nb}]'}{[\% \text{Nb}]} \quad (26)$$

Equ. 26 is similar to Equ. 25, and evaluation of $\epsilon_{\text{Nb}}^{\text{Mn}}$ and $\epsilon_{\text{Nb}}^{\text{Mn}}$ [25, 26] as well as $\epsilon_{\text{Nb}}^{\text{Si}}$ and $\epsilon_{\text{Nb}}^{\text{Si}}$ [27] have been reported elsewhere.

3-3 The gas-liquid dissolution equilibrium

For dissolution of a monoatomic gas, Henry's law holds true.

$$M(\text{g}) \rightarrow [M]$$

$$K = \frac{f_{\text{M}}' [\% M]'}{p_{\text{M}}} = \frac{f_{\text{M}} [\% M]}{p_{\text{M}}}$$

K is really the Henry's constant and can be found by extrapolation as usually. In the same way as the chemical equilibrium,

$$f_{\text{M}}^j = \frac{p_{\text{M}} [\% M]'}{p_{\text{M}}' [\% M]'} = \frac{a_{\text{M}} [\% M]'}{a_{\text{M}}' [\% M]'} \quad (27)$$

For dissolution of a diatomic gas, Sievert's law holds true, and derivation leads to the same Equ. 27. The latter is similar to Equ. 25 for calculation of ϵ_{M}^j and ϵ_{M}^j . The isopiestic methods [28, 29] belongs to this category.

3-4 The distribution equilibrium

Since Fe and Ag are insoluble in the molten state, distribution equilibrium of a certain element i which is both soluble in Fe and Ag is often used to study the activity of i. If a third element j which is soluble in Fe but not in Ag, the distribution equilibrium can be used to evaluate the interaction coefficient of j upon i. Usually, this method is used to evaluate the interaction coefficient at constant activity, but that at constant concentration could also be calculated as well.

For the Fe-Si-C [30, 31],

$$[\text{Si}]_{\text{Ag}} = [\text{Si}]_{\text{Fe}}$$

$$K = \frac{f_{\text{Si(Fe)}}' [\% \text{Si}]'_{\text{Fe}}}{f_{\text{Si(Ag)}}' [\% \text{Si}]'_{\text{Ag}}} = \frac{f_{\text{Si(Fe)}} [\% \text{Si}]_{\text{Fe}}}{f_{\text{Si(Ag)}} [\% \text{Si}]_{\text{Ag}}}$$

Since the solubility of Si in Ag is rather small, it might be assumed that $f_{\text{Si(Ag)}}' = f_{\text{Si(Ag)}} = 1$. The true equilibrium constant K is found by plotting $[\% \text{Si}]'_{\text{Fe}} / [\% \text{Si}]'_{\text{Ag}}$ against $[\% \text{Si}]_{\text{Fe}}$ and extrapolating to zero concentration of Si in Fe.

$$f_{\text{Si}}^j = \frac{a_{\text{Si(Ag)}}' [\% \text{Si}]'_{\text{Fe}}}{a_{\text{Si(Ag)}} [\% \text{Si}]_{\text{Fe}}} = \frac{a_{\text{Si(Fe)}} [\% \text{Si}]_{\text{Fe}}}{a_{\text{Si(Fe)}} [\% \text{Si}]_{\text{Fe}}} \quad (28)$$

Equ. 28 is similar to Equ. 25. Hence, it might be concluded that for the different equilibrium methods, be they physical or chemical, both the interaction coefficients at constant concentration and at constant activity could be

evaluated. As the Wagner's formalism [32] is used conventionally at constant concentration, there would be no necessity for calculating the interaction coefficients at constant activity by the equilibrium methods.

IV. Restriction of the constant-activity evaluation

4-1 The gas-metal chemical equilibrium

For the reaction $[C] + CO_2 = 2CO$, should the equilibrium be operated under constant p_{CO}^2 / p_{CO_2} , then the condition for evaluating the interaction coefficient at constant activity is warranted. Table 4 is quoted from Schenck, Steinmetz and Rhee [33] with some additional calculations made by the present author. It is to be noted that:

- (1) The experiments were conducted at constant p_{CO_2} ($p_{CO} + p_{CO_2} = 1 \text{ atm.}$), hence p_{CO}^2 / p_{CO_2} being constant.
- (2) No experiments of the binary system were conducted. For conversion with Equ. 19, $\epsilon_C^C = 11.5$ being taken from the literature.
- (3) In the calculation of ϵ_C^{Cr} , no γ_C^{Cr} was used, only the experimental data of the ternary system being used. A regression line of

$$-\ln N_C = a + bN_{Cr}$$

was calculated. The slope b , which equals $-\partial \ln N_C / \partial N_{Cr}$, is the ϵ_C^{Cr} , and the intercept equals $-\ln N_C'$. This is due to the fact that since $\partial \ln \gamma_C' / \partial N_{Cr} = 0$, therefore $\partial \ln \gamma_C' / \partial N_{Cr} = \partial \ln \gamma_C^{Cr} / \partial N_{Cr}$. Because of constant activity, $\partial \ln \gamma_C = -\partial \ln N_C$.

- (4) For every isoactivity line of $-\ln N_C = a + bN_{Cr}$, there is a definite value of ϵ_C^{Cr} .
- (5) This constant-activity evaluation is subjected to the restriction that a great number of experiments should be performed, each of the different ϵ_C^{Cr} values should be converted into ϵ_C^{Cr} separately, and these ϵ_C^{Cr} values should be finally averaged.

Table 4. ϵ_C^{Cr} for the Fe-C-Cr system at constant activity

$t, ^\circ C$	p_{CO_2} atm	a%	Regression line $-\ln N_C = a + bN_{Cr}$	ϵ_C^{Cr}	N_C' ($N_{Cr} = 0$)	ϵ_C^{Cr}
1600	4.6×10^{-5}	37.8	Saturated solution	-1.36	0.210	-4.64
1600	0.0022	0.78	$-\ln N_C = 3.6266 - 3.10N_{Cr}$	-3.10	0.0266	-4.05
1600	0.0043	0.40	$-\ln N_C = 4.1792 - 4.26N_{Cr}$	-4.26	0.0153	-5.00
1600	0.0086	0.20	$-\ln N_C = 4.8469 - 7.36N_{Cr}$	-7.36	0.0078	-8.02

4-2 The distribution equilibrium

In the literature the distribution method is often used for evaluation of interaction coefficient at constant activity with only the experimental data of the ternary system. For the Fe-Si-j system,

$$K = \frac{\gamma_{Si(Fe-j)} N_{Si(Fe-j)}}{\gamma_{Si(Ag)} N_{Si(Ag)}}$$

Since the concentration of the Ag bath is kept constant, $a_{Si(Ag)} = a_{Si(Fe-j)} = \text{constant}$. The concentration $N_{Si(Fe-j)}$ can be changed by adding different amount of j in the Fe bath, and regression analysis of the isoactivity line $-\ln N_{Si} = a + bN_j$ was made, its slope being equal to ϵ_{Si}^j , and its intercept equal to $-\ln N_{Si}'$. ϵ_{Si}^j should be converted into ϵ_{Si}^j with

N_{Si}^I for the binary system and e_{Si}^{Si} from the literature. To insure the reliability of the averaged e_{Si}^I , a great number of experiments have to be done. So for the Fe-Si-C system, 13 experiments by Schroeder and Chipman [30] and 19 experiments by Murakami, Ban-ya and Fuwa [31] have been reported.

V. Discussion

Since the interaction coefficients at constant concentration and at constant activity for the same system are quite different in magnitude, it would not be justifiable to list these values from different sources together for comparison, as occurred sometimes in the literature. As Wagner's formalism is originally justified for application at constant concentration, no interaction coefficients at constant activity should be introduced into the Wanger's formalism before being converted into those at constant concentration.

As already mentioned for the distribution equilibrium with the Ag bath, a great number of experiments giving more isoactivity lines, and the conversion from e_i^I into e_i^A , should be accomplished. But in some recent papers using the

distribution equilibrium to evaluate the interaction coefficients at constant activity for the systems Fe-Si-C [34], Fe-Cr-C [35], Fe-Ti-C [36] and Fe-Ti-C-i [37], two important points have escaped the notice of the original authors:

- (1) The distribution equilibrium in the Ag bath was carried out with only 2 or at most 4 experiments. With these few experiments no reliability of the results could be credited.
- (2) The interaction coefficients at constant activity were directly introduced into the Wanger's formalism for further elaboration without conversion. This procedure is theoretically questionable. Because of these, their results are doubtful and might not be accepted.

VI. Concluding remarks

Attention should be paid to avoid conceptual confusion and misunderstanding between interaction coefficients at constant concentration and at constant activity.

Excepting the solubility method for determining the interaction coefficient at constant activity, it would be always preferable to determine the interaction coefficient at constant concentration, in order to save the trouble of conversion.

For the solubility method of saturated solution, it might be suggested to adopt the logarithm formulation for calculating e_i^I to minimizing the discrepancy.

For unsaturated solution, should any method at constant activity, for instance, the distribution equilibrium, be used for determining the interaction coefficient, care should be taken to perform a great number of experiments in order to insure the reliability of the results.

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