



Title	Thermodynamic Relationship between the Enthalpy Interaction Parameter and Entropy Interaction Parameter in Liquid Iron-Nitrogen Based Ternary Alloys
Author(s)	Tanaka, Toshihiro; Gokcen, Nev .A.; Iida, Takamichi et al.
Citation	Zeitschrift für Metallkunde. 1994, 85(10), p. 696-700
Version Type	VoR
URL	https://hdl.handle.net/11094/26513
rights	©Carl Hanser Verlag, München
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

Toshihiro Tanaka, Nev A. Gokcen*, Takamichi Iida and Zen-ichiro Morita

(Department of Materials Science and Processing, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan; * Albany Research Center, U.S. Bureau of Mines, 1450 Queen Avenue SW, Albany, Oregon, 97321-2198, U.S.A.)

Thermodynamic Relationship between the Enthalpy Interaction Parameter and the Entropy Interaction Parameter in Liquid Iron–Nitrogen Based Ternary Alloys

A statistical thermodynamic solution model based on the free volume theory is applied to liquid iron–nitrogen based ternary alloys to derive the relationship between the enthalpy interaction parameter and the entropy interaction parameter. A linear relationship between those parameters is obtained. Then, Wagner's interaction parameters of nitrogen with some metallic elements in liquid iron alloys are evaluated. These results show that the free volume of the solute elements is an important factor to determine the excess entropy terms in those alloys.

1 Introduction

In previous works [1 to 7], the authors explained the thermodynamic relationship between the enthalpy of mixing, ΔH_{MIX} , and the excess entropy, ΔS^{Ex} , between the partial enthalpy of solution, \bar{H}_X , and the partial excess entropy \bar{S}_X^{Ex} , in liquid binary alloys, and between the enthalpy interaction parameter η_X^Y and the entropy interaction parameter σ_X^Y in liquid ternary dilute alloys (X, Y : solute elements) by a statistical thermodynamic solution model based on the free volume theory. Using this model, we evaluated the excess entropy and the excess Gibbs energy of solutions when enthalpy terms were given. Richardson [8] described that there exists a linear relationship between η_X^Y and Wagner's interaction parameter ε_X^Y in liquid iron–nitrogen based ternary alloys, which means that η_X^Y is proportional to σ_X^Y . The ratio of η_X^Y/ε_X^Y has been reported to be 7 kcal at 1873 K in those alloys by Chipman and Corrigan [9]. Although we previously derived the relationship between η_X^Y and σ_X^Y in liquid ternary dilute alloys which consisted of three metallic elements, we could not deal with liquid alloys including gaseous elements such as nitrogen in that derived model. Then, the purpose of the present study is to extend the above free volume solution model to liquid iron–nitrogen based ternary alloys, in which nitrogen dissolves interstitially in the alloys, and to derive the relationship between η_X^Y and σ_X^Y .

2 Derivation of Thermodynamic Equations

The following derivation of ε_X^Y is based on a theoretical work by Tsu and Saito [10], but we introduce the concept

of the free volume into their work. Let us consider an Fe–X–N ternary solution, in which Fe atoms and atoms of the metallic element X occupy substitutional sites and N atoms dissolve in interstitial sites. The structure of liquid iron alloys is assumed to be similar to the face-centered cubic structure as Tsu and Saito [10], and Foo and Lupis [11] assumed. Then, the number of substitutional lattice points is equal to that of interstitial points. The number of arrangements of N_{Fe} atoms of Fe and N_X atoms of X on $(N_{\text{Fe}} + N_X)$ substitutional sites is given by

$$\frac{(N_{\text{Fe}} + N_X)!}{N_{\text{Fe}}!N_X!} \quad (1)$$

Similarly, the number of arrangements of N_N atoms of N on $(N_{\text{Fe}} + N_X)$ interstitial sites is given by

$$\frac{(N_{\text{Fe}} + N_X)!}{N_N!(N_{\text{Fe}} + N_X - N_N)!} \quad (2)$$

Here, we assume that the atoms of Fe, X and N are distributed randomly on their sites. The energy for the above arrangement of atoms is represented by

$$E = N_{\text{Fe}X}u_{\text{Fe}X} + N_{\text{FeFe}}u_{\text{FeFe}} + N_{XX}u_{XX} + N_{\text{FeN}}u_{\text{FeN}} + N_{XN}u_{XN} + N_{NN}u_{NN} \quad (3)$$

where u_{ij} is the pair interaction energy of the i – j pair. N_{ij} ($i, j = \text{Fe}, X$ or N) in Eq. (3), which is the number of i – j pairs, is given as follows

$$\left. \begin{aligned} N_{\text{Fe}X} &= \frac{ZN_{\text{Fe}}N_X}{N_{\text{Fe}} + N_X} & N_{\text{FeN}} &= \frac{Z'N_{\text{Fe}}N_N}{N_{\text{Fe}} + N_X} \\ N_{\text{FeFe}} &= \frac{ZN_{\text{Fe}}^2}{2(N_{\text{Fe}} + N_X)} & N_{XN} &= \frac{Z'N_XN_N}{N_{\text{Fe}} + N_X} \\ N_{XX} &= \frac{ZN_X^2}{2(N_{\text{Fe}} + N_X)} & N_{NN} &= \frac{Z'N_N^2}{2(N_{\text{Fe}} + N_X)} \end{aligned} \right\} \quad (4)$$

The random configuration of atoms on their sites is assumed in Eq. (4). In the above equations, Z is the number of substitutional nearest-neighbors to a substitutional site or the number of interstitial nearest-neighbors to an interstitial site. Z' is the number of substitutional nearest-neighbors to an interstitial site or the number of interstitial nearest-neighbors to a substitutional site. When the free volumes of Fe, X and N atoms in the solution are expressed

as $V_{f,Fe}$, $V_{f,X}$ and $V_{f,N}$, respectively, the partition function of the system is given by

$$Q = \frac{(N_{Fe} + N_X)!}{N_{Fe}!N_X!} \frac{(N_{Fe} + N_X)!}{N_N!(N_{Fe} + N_X - N_N)!} V_{f,Fe}^{N_{Fe}} V_{f,X}^{N_X} V_{f,N}^{N_N} \exp\left(-\frac{E}{kT}\right) \quad (5)$$

where k is the Boltzmann constant and T is the temperature in K.

The Gibbs energy can be obtained by the following equation

$$G \approx -kT \ln Q$$

$$= -kT \{ 2(N_{Fe} + N_X) \ln (N_{Fe} + N_X) - N_{Fe} \ln N_{Fe} - N_X \ln N_X - N_N \ln N_N - (N_{Fe} + N_X - N_N) \ln (N_{Fe} + N_X - N_N) \}$$

$$- kT \{ N_{Fe} \ln V_{f,Fe} + N_X \ln V_{f,X} + N_N \ln V_{f,N} \}$$

$$+ Z u_{FeX} \frac{N_{Fe} N_X}{N_{Fe} + N_X} + Z u_{FeFe} \frac{N_{Fe}^2}{2(N_{Fe} + N_X)}$$

$$+ Z u_{XX} \frac{N_X^2}{2(N_{Fe} + N_X)} + Z' u_{FeN} \frac{N_{Fe} N_N}{N_{Fe} + N_X}$$

$$+ Z' u_{XN} \frac{N_X N_N}{N_{Fe} + N_X} + Z u_{NN} \frac{N_N^2}{2(N_{Fe} + N_X)} \quad (6)$$

where Stirling's relation $\ln x! = x \ln x - x$ is used.

From Eq. (6), the chemical potential of the solute element N in liquid iron alloy can be obtained as follows

$$\mu_N^L = \frac{\partial G}{\partial N_N}$$

$$= kT \ln \left\{ \frac{N_N}{(N_{Fe} + N_X) - N_N} \right\} - kT \ln V_{f,N}$$

$$+ Z' u_{FeN} \frac{N_{Fe}}{N_{Fe} + N_X} + Z' u_{XN} \frac{N_X}{N_{Fe} + N_X}$$

$$+ Z u_{NN} \frac{N_N}{N_{Fe} + N_X}$$

$$= kT \ln \left(\frac{x_N}{1 - x_N} \right) - kT \ln V_{f,N}$$

$$+ Z' u_{FeN} x_{Fe} + Z' u_{XN} x_X + Z u_{NN} x_N \quad (7)$$

where x_{Fe} , x_X and x_N are the mole fractions of Fe, X and N, i.e., $x_{Fe} = N_{Fe}/(N_{Fe} + N_X + N_N) \approx N_{Fe}/(N_{Fe} + N_X)$, $x_X = N_X/(N_{Fe} + N_X + N_N) \approx N_X/(N_{Fe} + N_X)$, and $x_N = N_N/(N_{Fe} + N_X + N_N) \approx N_N/(N_{Fe} + N_X)$. Here, the approximation of $(N_{Fe} + N_X + N_N) \approx (N_{Fe} + N_X)$ is used because $N_N \ll (N_{Fe} + N_X)$.

The chemical potential of N (N_2 gas) in the gas phase is

$$\mu_N^G = \mu_N^G + kT \ln p_{N_2}^{1/2} \quad (8)$$

where μ_N^G is the standard chemical potential of monoatomic N.

From the equilibrium condition $\mu_N^L = \mu_N^G$

$$\mu_N^G + kT \ln p_{N_2}^{1/2} = kT \ln \left(\frac{x_N}{1 - x_N} \right) - kT \ln V_{f,N}$$

$$+ (Z' u_{FeN} x_{Fe} + Z' u_{XN} x_X + Z u_{NN} x_N) \quad (9)$$

Since $x_N \ll 1$, we obtained the following approximations

$$\left. \begin{aligned} \frac{x_N}{1 - x_N} &\approx x_N \\ (Z' u_{FeN} x_{Fe} + Z' u_{XN} x_X) &\gg Z u_{NN} x_N \\ x_{Fe} &\approx (1 - x_X) \end{aligned} \right\} \quad (10)$$

From Eqs. (9) and (10)

$$\ln x_N = \frac{N_0 \mu_N^G}{N_0 kT} + \ln p_{N_2}^{1/2} + \ln V_{f,N}$$

$$- \frac{Z' u_{FeN} N_0 - (Z' u_{FeN} - Z' u_{XN}) N_0 x_X}{N_0 kT}$$

$$= \frac{N_0 \mu_N^G}{RT} + \ln p_{N_2}^{1/2} + \ln V_{f,N} - \frac{U_{FeN} - (U_{FeN} - U_{XN}) x_X}{RT} \quad (11)$$

where $U_{FeN} = Z' u_{FeN} N_0$ and $U_{XN} = Z' u_{XN} N_0$ and N_0 is the Avogadro number. $R = N_0 k$ is the gas constant.

When the infinitely dilute solution is taken as the reference state of the activity of the solute elements, the activity coefficient $f_N = f_N^N$ of nitrogen in liquid iron-nitrogen binary alloys becomes unity from Sievert's law. Then, the interaction coefficient f_N^X (the effect of the solute element X on the activity coefficient of nitrogen f_N) in liquid iron alloys equilibrated with gas phase of 1 atm partial pressure of nitrogen is given as follows [10]

$$\ln f_N^X = \ln x_N(\text{Fe-N binary}) - \ln x_N(\text{Fe-X-N ternary}) \quad (12)$$

The first term on the right-hand side of Eq. (12) is obtained from Eq. (11) when $x_X = 0$. Then

$$\ln f_N^X = \left\{ \ln V_{f,N}(\text{Fe-N binary}) - \frac{U_{FeN}}{RT} \right\}$$

$$- \left\{ \ln V_{f,N}(\text{Fe-X-N ternary}) - \frac{U_{FeN} - (U_{FeN} - U_{XN}) x_X}{RT} \right\}$$

$$= \ln \left\{ \frac{V_{f,N}(\text{Fe-N binary})}{V_{f,N}(\text{Fe-X-N ternary})} \right\} + \frac{(U_{XN} - U_{FeN}) x_X}{RT} \quad (13)$$

where $V_{f,N}(\text{Fe-N binary})$ and $V_{f,N}(\text{Fe-X-N ternary})$ are the free volumes of the solute element N in Fe-N binary and Fe-X-N ternary alloys. These are given by the following equations [1 to 7]

$$V_{f,N}(\text{Fe-N binary}) = \left\{ -\frac{\pi(L_{FeN})^2 N_0 kT}{U_{FeN}} \right\}^{3/2} \quad (14)$$

$$V_{f,N}(\text{Fe-X-N ternary}) = \left\{ -\frac{\pi(L_{FeXN})^2 N_0 kT}{U_{FeXN}} \right\}^{3/2} \quad (15)$$

where $U_{FeN}/N_0 (= Z' u_{FeN})$ and U_{FeXN}/N_0 are the depth of potential energy of the solute element N in its cell in Fe-N binary and Fe-X-N ternary alloys in Fig. 1. L_{FeN} and L_{FeXN} are the distances which the potential energy of the solute element N extends in its cell in Fe-N binary and Fe-X-N ternary alloys in Fig. 1. Then

$$\ln \left\{ \frac{V_{f,N}(\text{Fe-N binary})}{V_{f,N}(\text{Fe-X-N ternary})} \right\} = 3 \ln \left(\frac{L_{FeN}}{L_{FeXN}} \right) + \frac{3}{2} \ln \left(\frac{U_{FeXN}}{U_{FeN}} \right) \quad (16)$$

The second term on the right-hand side of Eq. (16) can be approximated as follows

$$\ln \left(\frac{U_{FeXN}}{U_{FeN}} \right) = \ln \left(\frac{x_{Fe} U_{FeN} + x_X U_{XN}}{U_{FeN}} \right)$$

$$= \ln \left\{ \frac{(1 - x_X) U_{FeN} + x_X U_{XN}}{U_{FeN}} \right\}$$

$$= \ln \left\{ \frac{U_{FeN} + (U_{XN} - U_{FeN}) x_X}{U_{FeN}} \right\}$$

$$= \ln \left(1 + \frac{U_{XN} - U_{FeN}}{U_{FeN}} x_X \right)$$

$$\approx \frac{U_{XN} - U_{FeN}}{U_{FeN}} x_X \quad (17)$$

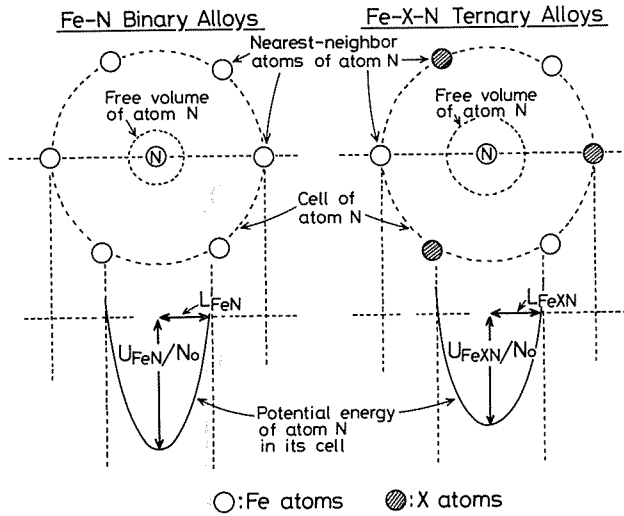


Fig. 1. Schematic diagram of potential energy in a cell of a nitrogen atom in Fe-N binary and Fe-N-X ternary alloys.

Similarly, the first term in the right-hand side of Eq. (16) can be expressed as follows

$$\begin{aligned} \ln \left(\frac{L_{\text{FeN}}}{L_{\text{FeXN}}} \right) &= -\ln \left(\frac{x_{\text{Fe}} L_{\text{FeN}} + x_{\text{X}} L_{\text{XN}}}{L_{\text{FeN}}} \right) \\ &= -\ln \left\{ \frac{(1 - x_{\text{X}}) L_{\text{FeN}} + x_{\text{X}} L_{\text{XN}}}{L_{\text{FeN}}} \right\} \\ &= -\ln \left(1 + \frac{L_{\text{XN}} - L_{\text{FeN}}}{L_{\text{FeN}}} x_{\text{X}} \right) \\ &\approx -\frac{L_{\text{XN}} - L_{\text{FeN}}}{L_{\text{FeN}}} x_{\text{X}} \end{aligned} \quad (18)$$

$U_{\text{XN}}/N_0 (= Z'u_{\text{XN}})$ in Eq. (17) and L_{XN} in Eq. (18) are the depth of the potential energy of N in its cell and the distance which the potential energy extends in its cell in X-N binary alloys. Equations (14) to (18) are based on the assumption that a nitrogen atom in its cell is surrounded by the nearest-neighbor atoms, which consist of only Fe atoms in Fe-N binary alloys, or of Fe and X atoms in Fe-X-N ternary alloys as shown in Fig. 1. From Eqs. (13) to (18)

$$\begin{aligned} \ln f_{\text{N}}^{\text{X}} &= -3 \frac{L_{\text{XN}} - L_{\text{FeN}}}{L_{\text{FeN}}} x_{\text{X}} + \frac{3}{2} \frac{U_{\text{XN}} - U_{\text{FeN}}}{U_{\text{FeN}}} x_{\text{X}} \\ &\quad + \frac{U_{\text{XN}} - U_{\text{FeN}}}{RT} x_{\text{X}} \end{aligned} \quad (19)$$

By differentiating both sides of Eq. (19) with x_{X} , the interaction parameter $\varepsilon_{\text{N}}^{\text{X}}$ can be obtained as follows

$$\begin{aligned} \varepsilon_{\text{N}}^{\text{X}} &= \frac{\partial \ln f_{\text{N}}^{\text{X}}}{\partial x_{\text{X}}} \\ &= -3 \frac{L_{\text{XN}} - L_{\text{FeN}}}{L_{\text{FeN}}} + \frac{3}{2} \frac{U_{\text{XN}} - U_{\text{FeN}}}{U_{\text{FeN}}} + \frac{U_{\text{XN}} - U_{\text{FeN}}}{RT} \\ &\quad - \left(3 \frac{L_{\text{XN}} - L_{\text{FeN}}}{L_{\text{FeN}}} - \frac{3}{2} \frac{U_{\text{XN}} - U_{\text{FeN}}}{U_{\text{FeN}}} \right) \frac{RT}{(U_{\text{XN}} - U_{\text{FeN}})} \\ &= \frac{\eta_{\text{N}}^{\text{X}} - \sigma_{\text{N}}^{\text{X}} T}{RT} \end{aligned} \quad (20)$$

where enthalpy interaction parameter $\eta_{\text{N}}^{\text{X}}$

$$\eta_{\text{N}}^{\text{X}} = U_{\text{XN}} - U_{\text{FeN}} \quad (21)$$

entropy interaction parameter $\sigma_{\text{N}}^{\text{X}}$

$$\sigma_{\text{N}}^{\text{X}} = 3 \frac{L_{\text{XN}} - L_{\text{FeN}}}{L_{\text{FeN}}} R - \frac{3}{2} \frac{U_{\text{XN}} - U_{\text{FeN}}}{U_{\text{FeN}}} R \quad (22)$$

3 Relationship between $\eta_{\text{N}}^{\text{X}}$ and $\varepsilon_{\text{N}}^{\text{X}}$, and between $\eta_{\text{N}}^{\text{X}}$ and $\sigma_{\text{N}}^{\text{X}}$

In Eq. (22), the following approximation may be applied, as shown numerically later, which shows that the first term with L is much smaller than the second term with U in the excess entropy term,

$$3 \frac{L_{\text{XN}} - L_{\text{FeN}}}{L_{\text{FeN}}} R \ll \frac{3}{2} \frac{U_{\text{XN}} - U_{\text{FeN}}}{U_{\text{FeN}}} R \quad (23)$$

Then, Eq. (22) becomes

$$\sigma_{\text{N}}^{\text{X}} \approx -\frac{3}{2} \frac{U_{\text{XN}} - U_{\text{FeN}}}{U_{\text{FeN}}} R \quad (24)$$

From Eqs. (20), (21) and (24)

$$\frac{\eta_{\text{N}}^{\text{X}}}{\varepsilon_{\text{N}}^{\text{X}}} \approx \frac{RT}{1 + \frac{3RT}{2U_{\text{FeN}}}} \quad (25)$$

$$\frac{\eta_{\text{N}}^{\text{X}}}{\sigma_{\text{N}}^{\text{X}}} \approx -\frac{2}{3R} U_{\text{FeN}} \quad (26)$$

As shown in Eqs. (25) and (26), the relationships between $\eta_{\text{N}}^{\text{X}}$ and $\varepsilon_{\text{N}}^{\text{X}}$, and between $\eta_{\text{N}}^{\text{X}}$ and $\sigma_{\text{N}}^{\text{X}}$ depend on the interaction of the solvent with the gaseous element. Here, we assume that the following relations, which have been used for metallic solutions in the previous work [1 to 7], could be applied to the above liquid iron-nitrogen ternary alloys

$$\left. \begin{aligned} U_{\text{FeN}} &= \Omega_{\text{FeN}} + \frac{U_{\text{FeFe}} + U_{\text{NN}}}{2} = \Delta H_{\text{N(Fe)}} + \frac{U_{\text{FeFe}} + U_{\text{NN}}}{2} \\ U_{\text{XN}} &= \Omega_{\text{XN}} + \frac{U_{\text{XX}} + U_{\text{NN}}}{2} = \Delta H_{\text{N(X)}} + \frac{U_{\text{XX}} + U_{\text{NN}}}{2} \end{aligned} \right\} \quad (27)$$

In the above equations, Ω_{FeN} and Ω_{XN} are interaction energies. $\Delta H_{\text{N(Fe)}}$ and $\Delta H_{\text{N(X)}}$ are the partial enthalpy of solution of N in Fe and X, respectively. The values of $\Delta H_{\text{N(Fe)}}$ and $\Delta H_{\text{N(X)}}$ are obtained from Miedema's semi-empirical method [12]. From Eq. (27), the term $(U_{\text{XN}} - U_{\text{FeN}})$ in Eqs. (21) and (22) is written as follows

$$U_{\text{XN}} - U_{\text{FeN}} = (\Delta H_{\text{N(X)}} - \Delta H_{\text{N(Fe)}}) + \left(\frac{U_{\text{XX}} - U_{\text{FeFe}}}{2} \right) \quad (28)$$

In Eq. (28), U_{FeFe} and U_{XX} can be obtained by [1 to 7]

$$\begin{aligned} U_{\text{FeFe}} &= -685 \beta_{\text{Fe}}^2 T_{\text{m,Fe}} / \text{J mol}^{-1} \\ U_{\text{XX}} &= -685 \beta_{\text{X}}^2 T_{\text{m,X}} / \text{J mol}^{-1} \end{aligned} \quad (29)$$

where β_{Fe} and β_{X} are the ratio of the frequency of an atom in liquid state to that in solid state [1 to 7, 13]. $T_{\text{m,Fe}}$ and $T_{\text{m,X}}$ are the melting points of pure elements Fe and X. We assume that L_{FeN} and L_{XN} in Eq. (22) could be calculated from the following equation

$$L_{\text{FeN}} = \frac{(L_{\text{NN}} + L_{\text{FeFe}})}{2} \quad L_{\text{XN}} = \frac{(L_{\text{NN}} + L_{\text{XX}})}{2} \quad (30)$$

Table 1. Physical properties of elements used in the calculation for η_N^X , σ_N^X and ε_N^X .

Element <i>i</i>	$\Delta H_{N(i)}$ kJ mol ⁻¹	$T_{m,i}$ K	β_i ^{a)}	$V_{m,i}$ cm ³ mol
Co	28	1765	0.48	6.69
Cr	-91	2178	0.50	7.23
Mn	-140	1517	0.50	7.35
Mo	-91	2895	0.50	9.39
Ni	50	1728	0.47	6.60
W	-45	3655	0.50	9.55
Fe	-13	1808	0.48	7.09
N	-	-	-	4.10

$\Delta H_{N(i)}$: Ref. [12], $T_{m,i}$ and β_i : Ref. [13], $V_{m,i} = (V^{2/3})^{3/2}$; $V^{2/3}$: Ref. [12].

^{a)} When values of β_i are not available, it can be set approximately to 0.5 [1 to 7].

In the above equation, L_{NN} , L_{FeFe} and L_{XX} can be obtained by [1 to 7]

$$L_{ii} = \frac{1}{2} \left\{ \frac{2^{1/2} V_{m,i}}{N_0} \right\}^{1/3} \quad (i = \text{Fe, X or N}) \quad (31)$$

where $V_{m,i}$ is the molar volume of pure element *i*.

The values [12, 13] of $\Delta H_{N(i)}$, $T_{m,i}$, β_i and $V_{m,i}$ (*i* = Fe or X) in Eqs. (28), (29) and (31) are listed in Table 1. From Eq. (25), the ratio of η_N^X to ε_N^X can be obtained when the value of U_{FeN} is known. According to Miedema, the energy change ΔE for the reaction $1/2 \text{N}_2 \rightarrow \text{N}(\text{metal})$, which means that the gaseous nitrogen becomes the hypothetical metallic monoatomic element, was reported to be 240 [14, 15] to 310 [12] kJ mol⁻¹. We therefore assume, that U_{NN} , the hypothetical binding energy of nitrogen in pure metallic state in Eq. (27), has the similar value as ΔE , and that

$U_{NN} = 215 \text{ kJ mol}^{-1}$. Then, from Eqs. (25), (27) and (29), we obtain the ratio η_N^X/ε_N^X (at 1873 K) $\approx 29 \text{ kJ}$ ($\approx 7 \text{ kcal}$), which corresponds to the value reported by Chipman and Corrigan [9]. The calculated results for η_N^X , σ_N^X and ε_N^X at 1873 K obtained from Eqs. (20) to (22) and (27) to (31) using $U_{NN} = 215 \text{ kJ mol}^{-1}$ are shown in Table 2, and Figs. 2 and 3. Table 2 shows that the assumption in Eq. (23) is reasonable for liquid iron–nitrogen ternary alloys. As shown in Fig. 2, there exists a linear relationship between η_N^X and ε_N^X with a slope of 29 kJ. Figure 3 shows that η_N^X is proportional to σ_N^X , and that η_N^X has the same sign as σ_N^X , as Richardson [8] pointed out. The approximation, e.g. Eqs. (17) and (18), used in the derivation of the equations in the present model can be applied only to alloy systems with small values of $\eta_N^X = (U_{XN} - U_{FeN})$ such as X = Ni, Co, W etc. listed in Table 1. Table 2 shows that the calculated results for ε_N^X agree with the measured values [16]. Ueno et al. [17] have also calculated ε_N^X using Miedema's semi-empirical method on the basis of the pseudopotential formalism coupled with Gibbs energy of the hard sphere system. They did not, however, refer to the relationship between η_N^X and σ_N^X .

4 Concluding Remarks

The consideration of the free volumes of the solute elements leads to the thermodynamic relationship between η_N^X and ε_N^X and between η_N^X and σ_N^X in liquid iron–nitrogen ternary alloys as well as in the metallic systems [6]. The free volume, strictly the displacement of the atoms from their equilibrium positions [7], is considered to be a main factor determining the excess entropy term of the infinitely dilute solutions.

Table 2. Calculated results for η_N^X , σ_N^X and ε_N^X with measured ε_N^X at 1873 K in liquid iron–nitrogen based ternary alloys.

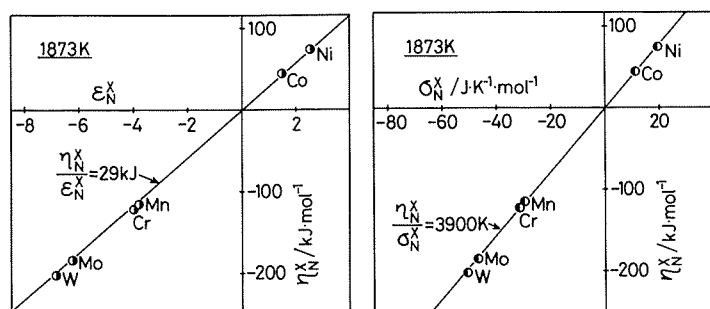
Elements	η_N^X /kJ mol ⁻¹	1st term in σ_N^X		2nd term in σ_N^X		σ_N^X		ε_N^X (1873 K)	
			/J K ⁻¹ mol ⁻¹					calc.	exp. ^{a)}
Co	44	-0.3	11.5	11.2	1.5	2.9			
Cr	-122	0.1	-31.5	-31.4	-4.0	-9.8			
Mn	-114	0.2	-29.6	-29.4	-3.8	-4.5			
Mo	-183	1.3	-47.4	-46.1	-6.2	-5.1			
Ni	75	-0.3	19.4	19.1	2.5	1.6			
W	-202	1.4	-52.4	-51.0	-6.8	-3.8 ^{b)}			

^{a)} The values of ε_N^X are given as $\varepsilon_N^X = (\partial \ln f_N^X / \partial [\text{wt}\% X])$ in Ref. [16]. ε_N^X has been transformed from e_N^X by the following relation [16]

$$\varepsilon_N^X = \frac{M_X}{55.85} \left(\frac{e_N^X}{0.00434} - 1 \right) + 1$$

where $M_X/\text{g mol}^{-1}$ is the atomic weight of element X.

^{b)} (1879 K)

Fig. 2 (left). Relationship between η_N^X and ε_N^X at 1873 K in liquid iron–nitrogen based ternary alloys.Fig. 3 (right). Relationship between η_N^X and σ_N^X at 1873 K in liquid iron–nitrogen based ternary alloys.

Literature

1. Tanaka, T.; Gokcen, N. A.; Morita, Z.: *Z. Metallkd.* 81 (1990) 49–54.
2. Tanaka, T.; Gokcen, N. A.; Morita, Z.: *Z. Metallkd.* 81 (1990) 349–353.
3. Tanaka, T.; Gokcen, N. A.; Morita, Z.; Spencer, P. J.: *Anales de Fisica-Ser. B.* 86 (1990) 104–107.
4. Tanaka, T.; Gokcen, N. A.; Neuschütz, D.; Spencer, P. J.; Morita, Z.: *Steel Research* 62 (1991) 385–389.
5. Tanaka, T.; Imai, N.; Kiyose, A.; Iida, T.; Morita, Z.: *Z. Metallkd.* 82 (1991) 836–840.
6. Tanaka, T.; Gokcen, N. A.; Spencer, P. J.; Morita, Z.; Iida, T.: *Z. Metallkd.* 84 (1993) 100–105.
7. Tanaka, T.; Gokcen, N. A.; Morita, Z.; Iida, T.: *Z. Metallkd.* 84 (1993) 192–200.
8. Richardson, F. D.: *Physical Chemistry of Melts in Metallurgy*, Vol. 1, Academic Press, London (1974) 186–187.
9. Chipman, J.; Corrigan, D. A.: in: G. R. Fitterer (ed.), *Applications of Fundamental Thermodynamics to Metallurgical Processes*, Gordon and Breach, New York (1967) 23.
10. Tsu, Y.; Saito, T.: *Trans. Jpn. Inst. Metals* 14 (1973) 339–346.
11. Foo, E.-H.; Lupis, C. H. P.: *Acta metall.* 21 (1973) 1409–1430.
12. de Boer, F. R.; Boom, R.; Mattens, W. C. M.; Miedema, A. R.; Niessen, A. K.: *Cohesion in Metals*, North-Holland, Amsterdam (1988).
13. Iida, T.; Guthrie, R. I. L.: *The Physical Properties of Liquid Metals*, Clarendon Press, Oxford (1988) 6, 100.
14. Miedema, A. R.; de Chatel, P. F.; de Boer, F. R.: *Physica 100B* (1980) 1–28.
15. Bouten, P. C. P.; Miedema, A. R.: *J. Less-Common Met.* 65 (1979) 217–228.
16. *Steelmaking Data Sourcebook*, The Japan Society for the Promotion of Science, The 19th Committee on Steelmaking, Gordon and Breach, New York (1988) 273.
17. Ueno, S.; Waseda, Y.; Jacob, K. T.; Tamaki, S.: *Steel Research* 59 (1988) 474–483.

(Received December 9, 1993)