Title	Thermodynamic Relationship between Enthalpy of Mixing and Excess Entropy in Solid Solutions of Binary Alloys
Author(s)	Tanaka, Toshihiro; Gokcen, Nev A.; Kumar, C. Kumar et al.
Citation	Zeitschrift für Metallkunde. 1996, 87(10), p. 779-783
Version Type	VoR
URL	https://hdl.handle.net/11094/26518
rights	©Carl Hanser Verlag, München
Note	

Toshihiro Tanaka, Nev A. Gokcen*, K. C. Hari Kumar**, Shigeta Hara and Zen-ichiro Morita

*(Department of Materials Science and Processing, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan; *East Thornton Lake, Albany, OR, USA; **Departement Metaalkunde en Toegepaste Materiaalkunde, Katholieke Universiteit Leuven, Leuven, Belgium)*

Thermodynamic Relationship between Enthalpy of Mixing and Excess Entropy in Solid Solutions of Binary Alloys

Thermodynamic relationships between enthalpy of mixing and excess entropy, and partial enthalpy of solution and partial excess entropy in solid solutions of binary alloys have been derived based on the free volume theory. Using the above relations, excess entropy and excess Gibbs energy of solid solutions in Ag–Au, Ag–Pd and Au–Pd binary alloys have been calculated from enthalpy of mixing, and compared with the literature values.

Zusammenhang zwischen Mischungsenthalpie und Überschußentropie bei binären Legierungen

Der thermodynamische Zusammenhang zwischen Mischungsenthalpie und Überschußentropie, sowie der partiellen Mischungsenthalpie und der partiellen Exzessentropie in binären Legierungen ist mit der Theorie des freien Volumens abgeleitet worden. Anhand dieses Modells wird die Überschußentropie und die überschüssige freie Enthalpie für die binären Legierungen Ag–Au, Ag–Pd und Au–Pd aus der Mischungsenthalpie berechnet. Die berechneten Überschußentropien und die überschüssigen Enthalpien stimmen gut mit experimentellen Werten überein.

1 Introduction

Some empirical relationships have been reported [1 to 9] for partial enthalpy of solution and partial excess entropy in dilute solid solutions as well as dilute liquid solutions of binary alloys. In previous work [10 to 17], we derived thermodynamic relationships between enthalpy of mixing and excess entropy in liquid binary alloys, partial enthalpy of solution and partial excess entropy in liquid dilute binary alloys, and enthalpy interaction parameter and entropy interaction parameter in liquid dilute ternary alloys on the basis of the free volume solution model. Based on those relationships, we found that the partial excess entropy of solute elements in liquid dilute binary alloys stems from the free volume of the elements, i.e., displacement of the elements from their equilibrium positions. The purpose of this work is to extend the above free volume solution model to solid solutions of binary alloys and to derive thermodynamic relationships between enthalpy of mixing and excess entropy in solid solutions of binary alloys, and partial enthalpy of solution and partial excess entropy of solute element in dilute solid solutions of binary alloys.

2 Thermodynamic Equations

Based on the free volume solution model [16] and the first approximation of regular solutions considering atom configuration in solutions [18], the excess Gibbs energy G^{E}, the enthalpy of mixing ΔH_{MIX} and the excess entropy S^{E} in an A–B binary alloy can be expressed as follows:

$$G^{\mathrm{E}} = \Delta H_{\mathrm{MIX}} - T \cdot S^{\mathrm{E}} \tag{1}$$

$$\Delta H_{\mathrm{MIX}} = \Omega_{\mathrm{AB}} X_{\mathrm{A}} X_{\mathrm{B}} \left(1 - X_{\mathrm{A}} X_{\mathrm{B}} \cdot \frac{\Omega_{\mathrm{AB}}}{RT}\right) \tag{2}$$

$$S^{\mathrm{E}} = S^{\mathrm{E}}_{\mathrm{CONF}} + S^{\mathrm{E}}_{\mathrm{VIB}} \tag{3}$$

$$S^{\mathrm{E}}_{\mathrm{CONF}} = -X_{\mathrm{A}}^2 X_{\mathrm{B}}^2 \frac{\Omega^2_{\mathrm{AB}}}{2RT^2} \tag{4}$$

$$S^{\mathrm{E}}_{\mathrm{VIB}} = \frac{3}{2} R X_{\mathrm{A}} X_{\mathrm{B}} \left[\frac{(L_{\mathrm{AA}} - L_{\mathrm{BB}})^2}{L_{\mathrm{AA}} L_{\mathrm{BB}}} + \frac{4U_{\mathrm{AA}}U_{\mathrm{BB}} - 2\Omega_{\mathrm{AB}}(U_{\mathrm{AA}} + U_{\mathrm{BB}}) - (U_{\mathrm{AA}} + U_{\mathrm{BB}})^2}{2U_{\mathrm{AA}}U_{\mathrm{BB}}} \right] \tag{5}$$

where X_{A} and X_{B} are mole fractions of components A and B; R is the gas constant, T is the temperature in K and Ω_{AB} is the interaction parameter.

L_{XX} (XX = AA or BB) is the distance which the interatomic potential energy $\Psi(r)$ extends in a cell of atom X in pure metal X as shown in Fig. 1. U_{XX} (XX = AA or BB) is the depth of the potential energy in a cell of atom X in pure metal X as shown in Fig. 1. In addition, the above model gives us the following equations [16] for the partial enthalpy of solution $\bar{H}_{\mathrm{B}}$ and the partial excess entropy $\bar{S}^{\mathrm{E}}_{\mathrm{B}}$ of solute element B in an infinitely dilute solution of A–B binary alloy

$$\bar{H}_{\mathrm{B}} = \Omega_{\mathrm{AB}} \tag{6}$$

$$\bar{S}^{\mathrm{E}}_{\mathrm{B}} = \bar{S}^{\mathrm{E}}_{\mathrm{B,CONF}} + \bar{S}^{\mathrm{E}}_{\mathrm{B,VIB}} \tag{7}$$

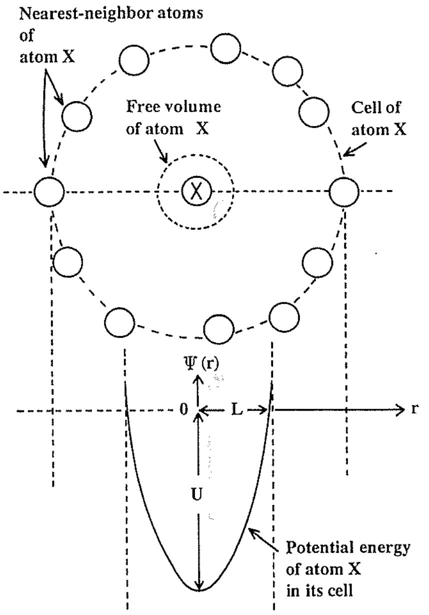


Fig. 1. Schematic diagram of potential energy in a cell of atom X.

$$\bar{S}^{E}_{B,CONF} = 0 \tag{8}$$

$$\bar{S}^{E}_{B,VIB} = \frac{3}{2}R\left[\frac{(L_{AA}-L_{BB})^2}{L_{AA}L_{BB}} + \frac{4U_{AA}U_{BB} - 2\Omega_{AB}(U_{AA}+U_{BB}) - (U_{AA}+U_{BB})^2}{2U_{AA}U_{BB}}\right] \tag{9}$$

The above equations are held for not only liquid solutions but also solid solutions. U_{AA} and U_{BB} for liquid metals have been described in details in the previous work [16]. In the present work, we have derived some equations of U_{AA} and U_{BB} for solid metals as described below. The binding energies in liquid and solid, E^{L}_{X} and E^{S}_{X} (X = A or B), are expressed by $U^{L}_{XX}/\mathrm{J \cdot mol^{-1}}$ and $U^{S}_{XX}/\mathrm{J \cdot mol^{-1}}$ (XX = AA or BB) as follows [10, 15, 16]

$$E^{L}_{X} = \frac{1}{2}U^{L}_{XX} \tag{10}$$

$$E^{S}_{X} = \frac{1}{2}U^{S}_{XX} \tag{11}$$

where superscripts L and S show liquid state and solid state, respectively.

Richard's rule [19] gives the following relationship between U^{L}_{XX} and U^{S}_{XX}

$$E^{L}_{X} - E^{S}_{X} = \frac{1}{2}U^{L}_{XX} - \frac{1}{2}U^{S}_{XX} = \Delta H_{m,X} = 8.8\ T_{m,X}/\mathrm{J \cdot mol^{-1}} \tag{12}$$

where $\Delta H_{m,X}$ and $T_{m,X}$ are the enthalpy of fusion and the melting point of element X.

Then,

$$U^{L}_{XX} - U^{S}_{XX} = 2\Delta H_{m,X} = 17.6\ T_{m,X}/\mathrm{J \cdot mol^{-1}} \tag{13}$$

In general, the free volume theory [16] gives the following equation for $U_{XX}/\mathrm{J \cdot mol^{-1}}$ for solid or liquid pure metals when each atom vibrates harmonically in its cell, which is made by its nearest-neighbor atoms

$$U_{XX} = \left(\frac{-2\pi^2 L^2_{XX} M_X \nu^2_X}{N_0}\right) \cdot N_0 \cdot 10^{-7} \tag{14}$$

where M_X ($\mathrm{g \cdot mol^{-1}}$) is the atomic weight of element X. N_0 is the Avogadro number. Since the unit of the quantity $-2\pi^2 L^2_{XX} M_X \nu^2_X / N_0$ in the parentheses in Eq. (14) is $\mathrm{erg \cdot atom^{-1}}$, $U_{XX}/\mathrm{J \cdot mol^{-1}}$ is obtained [16] by multiplying $N_0 \cdot 10^{-7}$ to $(-2\pi^2 L^2_{XX} M_X \nu^2_X / N_0)$. L_{XX} is expressed as follows [16, 19]

$$L_{XX} = \alpha_X \left(\frac{2^{1/2} V_X}{N_0}\right)^{1/3} \tag{15}$$

where V_X ($\mathrm{cm^3 \cdot mol^{-1}}$) is the molar volume of element X.

α_X in Eq. (15) is a parameter [19] determining the distance which the interatomic potential energy extends in a cell of atom X in pure metal X against the average interactomic distance $(2^{1/2} V_X / N_0)^{1/3}$. The value of α_X is approximately equal to $0.51 \fallingdotseq 1/2$ for liquid metals [19].

ν_X in Eq. (14) can be expressed in Eq. (16) when the harmonic oscillation is assumed [19] for an atom in its cell

$$\nu_X = 2.8 \cdot 10^{12} \beta_X \left\{\frac{T_{m,X}}{M_X (V_X)^{2/3}}\right\}^{1/2} \tag{16}$$

where β_X is a coefficient converting the solid state frequency to that in the liquid at the melting point [16, 19]. The values of β_X for various elements were obtained from the experimental data on surface tension of pure liquid metals. When the values of β_X are not available, it can be set approximately to 0.5 of the pure liquid metals [16, 19].

Substituting Eqs. (15) and (16) into Eq. (14), we obtain

$$\begin{aligned} U_{XX} &= -2\pi^2 \left\{\alpha_X \left(\frac{2^{1/2} V_X}{N_0}\right)^{1/3}\right\}^2 M_X \\ &\quad \left[2.8 \cdot 10^{12} \beta_X \left\{\frac{T_{m,X}}{M_X (V_X)^{2/3}}\right\}^{1/2}\right]^2 \frac{1}{N_0} \cdot N_0 \cdot 10^{-7} \\ &= -2\pi^2 \left(\frac{2^{1/2}}{N_0}\right)^{2/3} (2.8 \cdot 10^{12})^2 \cdot 10^{-7} (\alpha_X)^2 (\beta_X)^2 T_{m,X} \\ &= K (\alpha_X)^2 (\beta_X)^2 T_{m,X} \end{aligned} \tag{17}$$

$$\text{where } K = -2\pi^2 \left(\frac{2^{1/2}}{N_0}\right)^{2/3} (2.8 \cdot 10^{12})^2 \cdot 10^{-7} = -2740 \tag{18}$$

For liquid metals $\alpha_X = 1/2$, then

$$U^{L}_{XX} = -685 (\beta_X)^2 T_{m,X}/\mathrm{J \cdot mol^{-1}} \tag{19}$$

For solid metals, $\beta_X = 1$ but the values of α_X for solid metals are not available. Therefore,

$$U^{S}_{XX} = -2740 (\alpha_X)^2 T_{m,X}/\mathrm{J \cdot mol^{-1}} \tag{20}$$

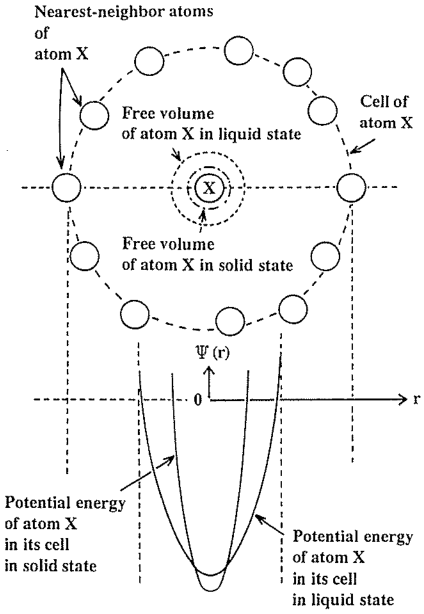


Fig. 2. Schematic diagram of potential energy in a cell in liquid pure element and solid pure element with $T_{m,X} = 1000$ K, $\beta_X = 0.5$ and $\alpha = 0.262$.

However, from Eq. (13),

$$U^L_{XX} - U^S_{XX} = -685(\beta_X)^2 T_{m,X} + 2740(\alpha_X)^2 T_{m,X} = 17.6\, T_{m,X}/\mathrm{J \cdot mol^{-1}} \qquad (21)$$

Thus, the following equation for U^S_{XX} is obtained from Eqs. (19) to (21)

$$U^S_{XX} = -\{685(\beta_X)^2 + 17.6\} T_{m,X}/\mathrm{J \cdot mol^{-1}} \qquad (22)$$

The value of α_X for solid metal X is determined from Eqs. (20) and (22) as follows

$$\alpha_X = \left(\frac{685(\beta_X)^2 + 17.6}{2740} \right)^{1/2} \qquad (23)$$

When we set $\beta_X = 0.5$, we obtain $\alpha_X = 0.263$. Schematic diagram for U^L_{XX} and U^S_{XX} with $T_{m,X} = 1000$ K, $\beta_X = 0.5$ and $\alpha_X = 0.263$ is shown in Fig. 2. From this figure, U^S_{XX} has a deeper and narrower potential well than U^L_{XX}. This means that atoms in solid state can move freely in smaller region around their equilibrium position than those in liquid state. In other words, atoms in solid state have smaller free volume than those in liquid state.

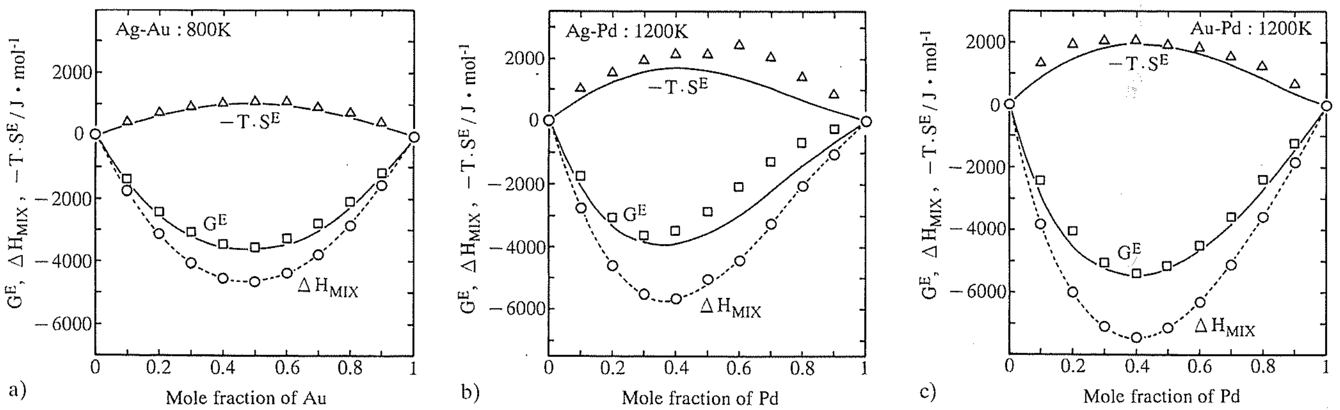
3 Calculation of Excess Entropy and Excess Gibbs Energy from Enthalpy of Mixing in Solid Solutions of Binary Alloys based on the Free Volume Solution Model

As some examples of the application of Eqs. (1) to (5), (15) and (22), we calculated the excess entropy and the excess Gibbs energy from enthalpy of mixing for solid solutions of Au–Ag, Ag–Pd and Au–Pd binary alloys. These alloys, which have solid solutions over whole concentration ranges, have been selected to compare the calculated results with the selected values by Hultgren et al.[20] for Ag–Pd and Ag–Au alloys and the experimental values more recently presented by Hohn and Herzig [21] for Au–Pd alloys. The procedure for the above calculation has been described in detail in Ref. [16]. The data [19, 22] necessary for the calculation of U^S_{XX} and L_{XX} are listed in Table 1. Table 2 shows the calculated results for each term in Eqs. (1) to (5) for solid solutions in the above three binary alloys. Since we have paid attention to the relationship between ΔH_{MIX} and S^E at each composition of an alloy including the relationship between $\bar{H}_B$ and $\bar{S}^E_B$ at an infinitely dilute solution, Ω_{AB} has been obtained from ΔH_{MIX} at each composition to obtain S^E and G^E in Table 2. In other words, although the calculated results in Table 2 show the composition dependence of Ω_{AB}, we have confirmed here that the relationship between ΔH_{MIX} and S^E in Eqs. (1) to (5) hold at each composition of the above alloys when Ω_{AB} has the same composition dependence in the equation of ΔH_{MIX} as that of S^E. Figures 3a to c show the

Table 1. Parameters of pure elements used in the calculation for excess entropy term.

	$V_X/\mathrm{cm^3 \cdot mol^{-1}}$	β_X	$T_{m,X}/\mathrm{K}$
Ag	10.25	0.47	1234
Au	10.19	0.49	1336
Pd	8.89	0.5	1828

V_X: Ref. [22]; β_X: Ref. [19]; $T_{m,X}$: Ref. [19]



Figs. 3a to c. Comparison of calculated results for excess Gibbs energy and excess entropy in solid solutions of (a) Ag–Au, (b) Ag–Pd, (c) Au–Pd binary alloys. △, □, ○: Experimental, — : Calculation.

Table 2. Calculated results for excess entropy and excess Gibbs energy with literature values.

Ag–Au at 800 K		$U_{\mathrm{AgAg}} = -208443$ J · mol^{-1}		$U_{\mathrm{AuAu}} = -243244$ J · mol^{-1}		$\alpha_{\mathrm{Ag}} = 0.248$ $\alpha_{\mathrm{Au}} = 0.258$		
X_{Au}	ΔH_{MIX} /J · mol^{-1}	Ω_{AgAu} /J · mol^{-1}	$T \cdot S^{\mathrm{E}}_{\mathrm{VIB}}$ /J · mol^{-1}	$T \cdot S^{\mathrm{E}}_{\mathrm{CONF}}$ /J · mol^{-1}	$T \cdot S^{\mathrm{E}}$ /J · mol^{-1} (Calc.)	$T \cdot S^{\mathrm{E}}$ /J · mol^{-1} (Expe.)	G^{E} /J · mol^{-1} (Calc.)	G^{E} /J · mol^{-1} (Expe.)
0.10	−1795	−16334	−140	−162	−302	−408	−1492	−1385
0.20	−3138	−14532	−224	−406	−630	−730	−2508	−2410
0.30	−4046	−13507	−274	−605	−879	−961	−3167	−3088
0.40	−4544	−12915	−301	−722	−1023	−1098	−3521	−3443
0.50	−4648	−12614	−307	−748	−1055	−1148	−3594	−3502
0.60	−4381	−12560	−293	−683	−976	−1105	−3404	−3276
0.70	−3761	−12766	−261	−540	−801	−967	−2960	−2795
0.80	−2812	−13311	−206	−341	−547	−740	−2264	−2075
0.90	−1552	−14430	−125	−127	−252	−418	−1300	−1134

Ag–Pd at 1200 K		$U_{\mathrm{AgAg}} = -208443$ J · mol^{-1}		$U_{\mathrm{PdPd}} = -345218$ J · mol^{-1}		$\alpha_{\mathrm{Ag}} = 0.248$ $\alpha_{\mathrm{Pd}} = 0.263$		
X_{Pd} /J · mol^{-1}	ΔH_{MIX} /J · mol^{-1}	Ω_{AgPd} /J · mol^{-1}	$T \cdot S^{\mathrm{E}}_{\mathrm{VIB}}$ /J · mol^{-1}	$T \cdot S^{\mathrm{E}}_{\mathrm{CONF}}$ /J · mol^{-1}	$T \cdot S^{\mathrm{E}}$ /J · mol^{-1} (Calc.)	$T \cdot S^{\mathrm{E}}$ /J · mol^{-1} (Expe.)	G^{E} /J · mol^{-1} (Calc.)	G^{E} /J · mol^{-1} (Expe.)
0.10	−2778	−25159	−436	−257	−693	−1019	−2086	−1757
0.20	−4602	−21412	−706	−588	−1294	−1531	−3309	−3071
0.30	−5510	−18800	−863	−781	−1644	−1908	−3866	−3602
0.40	−5648	−16770	−930	−812	−1742	−2199	−3907	−3448
0.50	−5021	−14682	−909	−675	−1584	−2199	−3437	−2820
0.60	−4477	−13963	−852	−563	−1415	−2455	−3062	−2021
0.70	−3264	−12337	−707	−336	−1043	−2033	−2221	−1230
0.80	−2008	−10712	−508	−147	−655	−1401	−1353	−607
0.90	−1046	−10607	−285	−46	−331	−838	−715	−209

Au–Pd at 1200 K		$U_{\mathrm{AuAu}} = -243244$ J · mol^{-1}		$U_{\mathrm{PdPd}} = -345218$ J · mol^{-1}		$\alpha_{\mathrm{Au}} = 0.258$ $\alpha_{\mathrm{Pd}} = 0.263$		
X_{Pd} /J · mol^{-1}	ΔH_{MIX} /J · mol^{-1}	Ω_{AuPd} /J · mol^{-1}	$T \cdot S^{\mathrm{E}}_{\mathrm{VIB}}$ /J · mol^{-1}	$T \cdot S^{\mathrm{E}}_{\mathrm{CONF}}$ /J · mol^{-1}	$T \cdot S^{\mathrm{E}}$ /J · mol^{-1} (Calc.)	$T \cdot S^{\mathrm{E}}$ /J · mol^{-1} (Expe.)*	G^{E} /J · mol^{-1} (Calc.)	G^{E} /J · mol^{-1} (Expe.)
0.10	−3820	−32762	−392	−436	−828	−1360	−2993	−2460
0.20	−6000	−26358	−589	−891	−1480	−1990	−4520	−4010
0.30	−7100	−22834	−695	−1152	−1847	−2090	−5252	−5010
0.40	−7420	−20654	−740	−1231	−1971	−2050	−5449	−5370
0.50	−7110	−19201	−732	−1155	−1887	−1970	−5223	−5140
0.60	−6300	−18244	−679	−961	−1640	−1820	−4660	−4480
0.70	−5100	−17695	−582	−692	−1274	−1580	−3826	−3520
0.80	−3590	−17517	−440	−394	−834	−1220	−2756	−2370
0.90	−1860	−17806	−250	−129	−379	−660	−1481	−1200

* $T \cdot S^{\mathrm{Ex}}$ (Exp.) = $\Delta H_{\mathrm{M}} - G^{\mathrm{Ex}}$ (Exp.) in Ref. [21].

comparison of the calculated results of S^{E} and G^{E} with the literature values [20, 21]. As shown in these figures, the calculated results agree well with the literature values [20, 21].

4 Relationship between Partial Enthalpy of Solution and Partial Excess Entropy of Solute Elements in Infinitely Dilute Solid Solutions of Binary Alloys

From Eqs. (6) to (9), (15) and (22), we have derived the approximate relationship between partial enthalpy of solution $\bar{H}_{\mathrm{B}}$ and partial excess entropy $\bar{S}^{\mathrm{E}}_{\mathrm{B}}$ of solute element B in an infinitely dilute solid solution of a A–B binary alloy on the basis of the assumption in Eq. (24)

$$T_{\mathrm{m,A}} \approx T_{\mathrm{m,B}}, V_{\mathrm{A}} \approx V_{\mathrm{B}}, \beta_{\mathrm{A}} = \beta_{\mathrm{B}} = 0.5 \tag{24}$$

Then,

$$L_{\mathrm{AA}} \approx L_{\mathrm{BB}}, U^{\mathrm{S}}_{\mathrm{AA}} = -189\ T_{\mathrm{m,A}}, U^{\mathrm{S}}_{\mathrm{BB}} = -189\ T_{\mathrm{m,B}} \tag{25}$$

Finally,

$$\bar{H}_{\mathrm{B}} \approx \frac{15.1}{1/T_{\mathrm{m,A}} + 1/T_{\mathrm{m,B}}} \bar{S}^{\mathrm{E}}_{\mathrm{B}} \tag{26}$$

for solid solutions of binary alloys.

Compared with the following similar relation for liquid binary alloys [16], the difference between the relationship $\bar{H}_{\mathrm{B}}$ vs. $\mathrm{S}^{\mathrm{E}}_{\mathrm{B}}$ in solid solutions and that in liquid solutions is not so large, which corresponds to the empirical results reported by Kubaschewski [3] and Lupis [4]

$$\bar{H}_B \approx \frac{13.7}{1/T_{m,A} + 1/T_{m,B}} \bar{S}_B^E \tag{27}$$

for liquid binary alloys.

5 Concluding Remarks

In the present work, we discussed the thermodynamic relationship between enthalpy of mixing and excess entropy in solid solutions of binary alloys based on the free volume theory. The excess entropy and excess Gibbs energy in some solid solutions were calculated from the enthalpy of mixing using the model obtained here, and compared with the literature values. We also obtained the approximate relationship between the partial enthalpy of solution $\bar{H}_X$ and the partial excess entropy $\bar{S}_X^E$ of solute elements in dilute solid solutions of binary alloys.

Literature

1. *Kubaschewski, O.:* in: P. S. Rudman, J. Stringer, R. Jaffee (eds.), Phase Stability in Metals and Alloys, McGraw-Hill (1967) 63.
2. *Kubaschewski,O.; Alcock,C. B.; Spencer, P. J.:* Materials Thermochemistry, 6th ed., Pergamon Press (1993) 55.
3. *Kubaschewski,O.:* High Temp. – High Press *13* (1981) 435–440.
4. *Lupis, C. H. P.; Elliott, J. F.:* Acta Metall. *15* (1967) 265–276.
5. *Slough, W.:* in: O. Kubaschewski (ed.), Metallurgical Chemistry, HMSO, London (1972) 301.
6. *Richardson, F. D.:* Physical Chemistry of Melts in Metallurgy, Vol. 1, Academic Press (1974) 165.
7. *Crombie, R.; Downie, D. B.:* Scripta Metall. *6* (1972) 277–286.
8. *Williams, R. O.:* CALPHAD *8* (1984) 135–148.
9. *Williams, R. O.:* CALPHAD *15* (1991) 1–10.
10. *Tanaka, T.; Gokcen N. A.; Morita, Z.:* Z. Metallkd. *81* (1990) 49–54.
11. *Tanaka, T.; Gokcen, N. A.; Morita, Z.:* Z. Metallkd. *81* (1990) 349–353.
12. *Tanaka, T.; Gokcen, N. A.; Morita, Z.; Spencer P. J.:* Anales de Fisica-Serie B *86* (1991) 104–107.
13. *Tanaka, T.; Gokcen, N. A.; Neuschütz, D.; Spencer, P. J.; Morita, Z.:* Steel Research *62* (1991) 385–389.
14. *Tanaka, T.; Imai, N.; Kiyose, A.; Iida, T.; Morita, Z.:* Z. Metallkd. *82* (1991) 836–840.
15. *Tanaka, T.; Gokcen, N. A.; Spencer, P. J.; Morita, Z.; Iida T.:* Z. Metallkd. *84* (1993) 100–105.
16. *Tanaka, T.; Gokcen, N. A.; Morita, Z.; Iida, T.:* Z. Metallkd. *84* (1993) 192–200.
17. *Tanaka, T.; Gokcen, N. A.; Iida, T.; Morita, Z.:* Z. Metallkd. *85* (1994) 696–700.
18. *Gokcen, N. A.:* Statistical Thermodynamics of Alloys, Plenum Press, NY (1986).
19. *Iida, T.; Guthrie, R. I. L.:* The Physical Properties of Liquid Metals, Clarendon Press, Oxford (1988) 6, 10, 17, 97–100 and 130.
20. *Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelley, K. K.:* Selected Values of the Thermodynamic Properties of Binary Alloys, ASM, Metals Park, OH (1973) 28, 85.
21. *Hohn, R.; Herzig, C.:* Z. Metallkd. *77* (1986) 291–297.
22. *Niessen, A. K.; de Boer, F. R.; Boom, R.; de Chatel, P. F.; Mattens, W. C. M.; Miedema, A. R.:* CALPHAD *7* (1983) 51–70.

(Received October 23, 1995)