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Evaluation of Interaction Parameters in Dilute Liquid Ternary Alloys by a Solution Model Based on the Free Volume Theory

A solution model based on the free volume theory has been applied to derive a Gibbs energy interaction parameter $\varepsilon_{\rm B}^{\rm C}$. The relation between an enthalpy interaction parameter $\eta_{\rm B}^{\rm C}$ and an entropy interaction parameter $\sigma_{\rm B}^{\rm C}$ has been obtained. These parameters were evaluated from some physical properties coupled with Miedema's semi-empirical method.

1 Introduction

In previous publications [1 to 5], a new solution model for liquid binary alloys based on the free volume theory has been presented. This model allows a successful description of the relation between partial enthalpy and partial excess entropy of mixing in infinitely dilute solutions of liquid binary alloys. In addition, it predicts the values of partial excess Gibbs energy of solutions, which are in reasonable agreement with experimental values.

In the present work, this solution model has been applied to ternary alloys to evaluate Gibbs energy interaction parameters in infinite dilution. Moreover, the relation between enthalpy and entropy interaction parameters is discussed.

2 Derivation of Thermodynamic Equations

The solution model is based on the free volume theory advanced by Shimoji and Niwa [6]. Assuming that an atom vibrates harmonically in its cell surrounded by the nearest-neighbor atoms, the partition functions for pure liquid A, B and \tilde{C} is given by the following equation:

$$Q_{XX} = V_{F, X}^{N_X} \cdot \exp(-E_X/kT) = \{-\pi L_{XX}^2 kT/U_{XX}\}^{3N_X/2} \cdot \exp(-N_X U_{XX}/2kT) (XX = AA, BB or CC; X = A, B or C)$$
(1)

where

$$U_{XX} = z \cdot u_{XX} \tag{2}$$

 $V_{\mathrm{F},X}$ is the free volume of X atom in pure liquid (X = A, B or C);

 U_{XX} is the depth of potential energy of an atom X (X = A, B or C) in its cell in pure liquid X, as shown in Fig. 1;

 $u_{\rm XX}$ is the energy of A-A, B-B or C-C pairs;

is the coordination number; \boldsymbol{z}

- L_{XX} is the distance which interatomic potential extends in a cell of pure liquid A, B or C, as shown in Fig. 1;
- N_X is the number of X atom (X = A, B or C);
- is the Boltzmann constant and k
- Tis the temperature in K.

The partition function for an A-B-C ternary alloy is

$$Q = g \cdot \{-\pi L_{\rm A}^2 k T / U_{\rm A}\}^{3N_{\rm A}/2} \cdot \{-\pi L_{\rm B}^2 k T / U_{\rm B}\}^{3N_{\rm B}/2} \cdot \{-\pi L_{\rm C}^2 k T / U_{\rm C}\}^{3N_{\rm C}/2} \cdot \exp\{-(N_{\rm A} U_{\rm A} + N_{\rm B} U_{\rm B} + N_{\rm C} U_{\rm C})/2kT\}$$
(3)

Nearest-neighbor atoms



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

where

g

is a degeneracy factor;

 $U_X(X = A, B \text{ or } C)$ the depth of potential energy of an atom X (X = A, B or C) in its cell in liquid A-B-C ternary alloy and

$$L_X(X = A, B \text{ or } C)$$
 the distance which interatomic potential
extends in a cell of an atom $X(X = A, B \text{ or } C)$ in liquid A-B-C ternary alloy.

The energy $E = (N_A U_A + N_B U_B + N_C U_C)/2$ of an A-B-C ternary alloy in Eq. (3) is assumed to be expressed in terms of the pair interaction energies A-A, B-B, C-C, A-B, A-C and B-C, namely u_{AA} , u_{BB} , u_{CC} , u_{AB} , u_{AC} and u_{BC} as follows:

$$E = N_{\rm A}U_{\rm AA}/2 + N_{\rm B}U_{\rm BB}/2 + N_{\rm C}U_{\rm CC}/2 + N_{\rm AB}\Omega_{\rm AB}/z + N_{\rm BC}\Omega_{\rm BC}/z + N_{\rm AC}\Omega_{\rm AC}/z$$
(4)

where $U_{\mathrm{AA}} = z \cdot u_{\mathrm{AA}}, U_{\mathrm{BB}} = z \cdot u_{\mathrm{BB}}$ and $U_{\mathrm{CC}} = z \cdot u_{\mathrm{CC}}$

 $N_{\rm AB}, N_{\rm AC}$ and $N_{\rm BC}$ in Eq. (4) are the numbers of A-B, A-C and B-C pairs, respectively. $\Omega_{\rm AB}, \Omega_{\rm BC}$ and $\Omega_{\rm AB}$ are defined as follows:

$$\Omega_{AB} = z \cdot \{ u_{AB} - 1/2 (u_{AA} + u_{BB}) \}$$

$$\Omega_{BC} = z \cdot \{ u_{BC} - 1/2 (u_{BB} + u_{CC}) \}$$

$$\Omega_{AC} = z \cdot \{ u_{AC} - 1/2 (u_{AA} + u_{CC}) \}$$
(5)

For condensed systems and at ordinary pressure levels, the Gibbs energy G may be equivalent to the Helmholtz energy F because their difference, the term PV, is usually negligible. Thus, for all practical purpose

$$G_{XX} \sim F_{XX} = -kT \ln Q_{XX}$$
 (XX = AA, BB or CC) (6)

$$G \sim F = -kT \ln Q \tag{7}$$

From the above equations, the change in Gibbs energy of mixing, $\Delta G_{\rm MIX}$ is

$$\Delta G_{\rm MIX} = G - (G_{\rm AA} + G_{\rm BB} + G_{\rm CC})$$

$$= (N_{\rm AB}\Omega_{\rm AB} + N_{\rm BC}\Omega_{\rm BC} + N_{\rm AC}\Omega_{\rm AC})/z - kT \cdot \ln g$$

$$- kT \cdot 3/2 [N_{\rm A} \cdot \ln (-\pi L_{\rm A}^2 kT/U_{\rm A}) + N_{\rm B} \cdot \ln (-\pi L_{\rm B}^2 kT/U_{\rm B}) + N_{\rm C} \cdot \ln (-\pi L_{\rm C}^2 kT/U_{\rm C})$$

$$- \{N_{\rm A} \cdot \ln (-\pi L_{\rm AA}^2 kT/U_{\rm AA}) + N_{\rm B} \cdot \ln (-\pi L_{\rm BB}^2 kT/U_{\rm BB}) + N_{\rm C} \cdot \ln (-\pi L_{\rm C}^2 kT/U_{\rm C})\}]$$

$$(8)$$

In the following, the enthalpy and entropy terms in the A-B-C ternary alloy will be derived separately.

2.1 The Enthalpy Term

From Eq. (8),

$$\Delta H'_{\rm MIX} = (N_{\rm AB} \Omega_{\rm AB} + N_{\rm BC} \Omega_{\rm BC} + N_{\rm AC} \Omega_{\rm AC})/z \tag{9}$$

With regard to the configuration of atoms in alloys, short range order is taken into account on the basis of the first approximation to the regular solution model proposed by one of the authors [7]. According to this model, N_{AB} , N_{BC} and N_{AC} are given by the following equations for dilute solutions:

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$$N_{\rm AB} = z \cdot N_0 \cdot x_{\rm A} x_{\rm B} \left(1 - x_{\rm A} x_{\rm B} \Omega_{\rm AB} / kT \right) \tag{10}$$

$$N_{\rm BC} = z \cdot N_0 \cdot x_{\rm B} x_{\rm C} \left(1 - x_{\rm B} x_{\rm C} \Omega_{\rm BC} / kT \right) \tag{11}$$

$$N_{\rm AC} = z \cdot N_0 \cdot x_{\rm A} x_{\rm C} \left(1 - x_{\rm A} x_{\rm C} \Omega_{\rm AC} / kT \right) \tag{12}$$

where

$$N_0$$
 is Avogadro's number,

 $x_{\rm A}, x_{\rm B}$ and $x_{\rm C}$ are the mole fractions of A, B and C, respectively.

Consequently, the enthalpy of mixing per atom $\Delta H_{\text{MIX}} = \Delta H'_{\text{MIX}}/N_0$ can be given by the following equation:

$$\Delta H_{MIX} = \Omega_{AB} \cdot x_A \cdot x_B (1 - x_A x_B \Omega_{AB} / kT) + \Omega_{BC} \cdot x_B \cdot x_C (1 - x_B x_C \Omega_{BC} / kT) + \Omega_{AC} \cdot x_A \cdot x_C (1 - x_A x_C \Omega_{AC} / kT)$$
(13)

2.2 Entropy Term

The entropy arising from the atomic configuration in the alloys, $\Delta S_{\text{CONF}} = k \cdot \ln g$, consists of the following two terms:

$$\Delta S_{\rm CONF} = k \cdot \ln g = \Delta S_{\rm CONF}^{\rm Ideal} + \Delta S_{\rm CONF}^{\rm Ex}$$
(14)

For the excess configurational entropy in the alloys, the following equation based on the first approximation to the regular solution model [7] was also adopted.

$$\Delta S_{\text{CONF}}^{\text{Ex}} = -x_{\text{A}}^2 x_{\text{B}}^2 \Omega_{\text{AB}}^2 / 2kT^2 - x_{\text{B}}^2 x_{\text{C}}^2 \Omega_{\text{BC}}^2 / 2kT^2 - x_{\text{A}}^2 x_{\text{C}}^2 \Omega_{\text{AC}}^2 / 2kT^2$$
(15)

The excess entropy arising from nonconfigurational contributions, for example, from the vibration of atoms in their cell, $\Delta S_{\text{VIB}}^{\text{Ex}}$ can be derived from Eq. (8) as follows:

$$\Delta S_{\text{VIB}}^{\text{Ex}} = 3/2 \cdot k N_0 \{ 2x_{\text{A}} \cdot \ln (L_{\text{A}}/L_{\text{AA}}) + 2x_{\text{B}} \cdot \ln (L_{\text{B}}/L_{\text{BB}}) + 2x_{\text{C}} \cdot \ln (L_{\text{C}}/L_{\text{CC}}) + x_{\text{A}} \cdot \ln (U_{\text{AA}}/U_{\text{A}}) + x_{\text{B}} \cdot \ln (U_{\text{BB}}/U_{\text{B}}) + x_{\text{C}} \cdot \ln (U_{\text{CC}}/U_{\text{C}}) \}$$
(16)

In Eq. (16), it is necessary to have information on L_A, L_B, L_C, U_A, U_B and U_C in the A-B-C ternary alloy. In this work, the simplest relations were adopted from Shimoji and Niwa [6], i.e.,

where

$$U_{AB} = z \cdot u_{AB}$$
 $U_{BC} = z \cdot u_{BC}$ $U_{AC} = z \cdot u_{AC}$ (18)

$$L_{A} = 1/2 \{ L_{AA} + (x_{A}L_{AA} + x_{B}L_{BB} + x_{C}L_{CC}) \}$$

$$L_{B} = 1/2 \{ L_{BB} + (x_{A}L_{AA} + x_{B}L_{BB} + x_{C}L_{CC}) \}$$

$$L_{C} = 1/2 \{ L_{CC} + (x_{A}L_{AA} + x_{B}L_{BB} + x_{C}L_{CC}) \}$$

$$\left. \right\} (19)$$

Finally, the excess entropy for vibrational contributions of atoms in their cell per atom, $\Delta S_{\text{VIB}}^{\text{Ex}} = \Delta S_{\text{VIB}}^{\text{Ex}'}/N_0$ is given by

$$\Delta S_{\text{VIB}}^{\text{Ex}} = 3/2 \ k \ x_A x_B \ [(L_{AA} - L_{BB})^2 / (L_{AA} \cdot L_{BB}) \\ + \{4U_{AA}U_{BB} - 2\Omega_{AB}(U_{AA} + U_{BB}) \\ - (U_{AA} + U_{BB})^2\} / (2U_{AA}U_{BB})] \\ + 3/2 \ k \ x_B x_C \ [(L_{BB} - L_{CC})^2 / (L_{BB} \cdot L_{CC}) \\ + \{4U_{BB}U_{CC} - 2\Omega_{BC}(U_{BB} + U_{CC}) \\ - (U_{BB} + U_{CC})^2\} / (2U_{BB}U_{CC})] \\ + 3/2 \ k \ x_A x_C \ [(L_{AA} - L_{CC})^2 / (L_{AA} \cdot L_{CC}) \\ + \{4U_{AA}U_{CC} - 2\Omega_{AC}(U_{AA} + U_{CC}) \\ - (U_{AA} + U_{CC})^2\} / (2U_{AA}U_{CC})]$$
(20)

where the following relations were used:

$$U_{AB} = \Omega_{AB} + (U_{AA} + U_{BB})/2$$

$$U_{BC} = \Omega_{BC} + (U_{BB} + U_{CC})/2$$

$$U_{AC} = \Omega_{AC} + (U_{AA} + U_{CC})/2$$

$$\left.\right\}$$

$$(21)$$

The first order Gibbs energy interaction parameter $\varepsilon_{\rm B}^{\rm C}$, proposed by Wagner [8], may be written as

$$\varepsilon_{\rm B}^{\rm C} = \{ (\partial^2 \Delta G^{\rm Ex} / \partial x_{\rm C} \ \partial x_{\rm B})_{x_{\rm B} \to 0, x_{\rm C} \to 0} \} / k T
= (\eta_{\rm B}^{\rm C} - T \ \sigma_{\rm B}^{\rm C}) / k T$$
(22)

where η_B^C and σ_B^C are the enthalpy and entropy interaction parameters, respectively, and according to Lupis and Elliott [9] are defined as follows:

$$\eta_{\rm B}^{\rm C} = \left(\partial^2 \Delta H_{\rm MIX} / \partial x_{\rm C} \partial x_{\rm B}\right)_{x_{\rm B} \to 0, \ x_{\rm C} \to 0} \tag{23}$$

$$\sigma_{\rm B}^{\rm C} = (\partial^2 \Delta S^{\rm Ex} / \partial x_{\rm C} \partial x_{\rm B})_{x_{\rm B} \to 0, x_{\rm C} \to 0} = \{\partial^2 (\Delta S^{\rm Ex}_{\rm CONF} + \Delta S^{\rm Ex}_{\rm VIB}) / \partial x_{\rm C} \partial x_{\rm B}\}_{x_{\rm B} \to 0, x_{\rm C} \to 0}$$
(24)

From Eqs. (13), (15), (20), (23) and (24), η_B^C and σ_B^C can be written as

$$\eta_{\rm B}^{\rm C} = \Omega_{\rm BC} - \Omega_{\rm AB} - \Omega_{\rm AC} \tag{25}$$

$$\sigma_{\rm B}^{\rm C} = 3/2k \left[(L_{\rm BB} - L_{\rm CC})^2 / (L_{\rm BB} L_{\rm CC}) + \{4U_{\rm BB} U_{\rm CC} - 2\Omega_{\rm BC} (U_{\rm BB} + U_{\rm CC}) - (U_{\rm BB} + U_{\rm CC})^2 \} / (2U_{\rm BB} U_{\rm CC}) - (L_{\rm AA} - L_{\rm BB})^2 / (L_{\rm AA} L_{\rm BB}) - \{4U_{\rm AA} U_{\rm BB} - 2\Omega_{\rm AB} (U_{\rm AA} + U_{\rm BB}) - (U_{\rm AA} + U_{\rm BB})^2 \} / (2U_{\rm AA} U_{\rm BB}) - (L_{\rm AA} - L_{\rm CC})^2 / (L_{\rm AA} L_{\rm CC}) - \{4U_{\rm AA} U_{\rm CC} - 2\Omega_{\rm AC} (U_{\rm AA} + U_{\rm CC}) - (U_{\rm AA} + U_{\rm CC})^2 \} / (2U_{\rm AA} U_{\rm CC}) \right]$$

$$(26)$$

From Eqs. (22), (25) and (26), the following relation can be obtained.

$$\varepsilon_{\rm B}^{\rm C} = \varepsilon_{\rm C}^{\rm B}$$
 (27)

Further, $\varepsilon_{\rm B}^{\rm B}$ can be expressed as follows:

$$\varepsilon_{\rm B}^{\rm B} = (\eta_{\rm B}^{\rm B} - T\sigma_{\rm B}^{\rm B})/kT \tag{28}$$

$$\eta_{\rm B}^{\rm B} = -2\Omega_{\rm AB} \tag{29}$$

$$\sigma_{\rm B}^{\rm B} = -3k[(L_{\rm AA} - L_{\rm BB})^2 / L_{\rm AA} L_{\rm BB} + \{4U_{\rm AA} U_{\rm BB} - 2\Omega_{\rm AB} (U_{\rm AA} + U_{\rm BB}) - (U_{\rm AA} + U_{\rm BB})^2\} / (2U_{\rm AA} U_{\rm BB})]$$
(30)

According to the solution model, as applied to binary alloys in our previous work [2 to 5], the relation between $\varepsilon_{\rm B}^{\rm B}$ and the activity coefficient at infinite dilution $\gamma_{\rm B}^{\rm 0}$ can be expressed by

$$r_{\rm B}^{\rm B} = -2\ln\gamma_{\rm B}^0\tag{31}$$

 L_{XX} (XX = AA, BB or CC) in Eq. (26) is assumed to be half of the nearest- neighbor distance and is obtained from the following equation [1 to 5]:

$$L_{XX} = 1/2 \cdot \left(2^{1/2} V_X / N_0\right)^{1/3} \tag{32}$$

where V_X is a molar volume of pure X (X = A, B or C).

 $\Omega_{\rm BC}$, $\Omega_{\rm AB}$ and $\Omega_{\rm AC}$ can be assumed to be equal to the partial enthalpy of mixing in infinite dilution $\Delta \bar{H}_{\rm C(B)}$ of solute C in solvent B, $\Delta \bar{H}_{\rm B}$ (A) of solute B and $\Delta \bar{H}_{\rm C}$ (A) of solute C in solvent A, respectively [2 to 5].

 $U_{\rm AA}, U_{\rm BB}$ and $U_{\rm CC}$ in Eq. (26) are calculated from the following equation [4 to 5] when the units of $\Omega_{\rm BC}$, $\Omega_{\rm AB}$ and $\Omega_{\rm AC}$ are taken as $J \cdot {\rm mol}^{-1}$, and k in Eqs. (1) to (30) is taken as gas constant $R/J \cdot {\rm K}^{-1} \cdot {\rm mol}^{-1}$.

$$U_{XX} = -685.3 \cdot (\beta_X)^2 \cdot T_{\mathrm{m,X}} \qquad /\mathrm{J} \cdot \mathrm{mol}^{-1}$$
(33)

where $T_{m,X}$ is the melting point of element X and β_X the coefficient to transfer the solid state frequency to that in the liquid at the melting point [10 to 12].

The values of β_X for various elements were obtained from the experimental data on surface tension of pure liquid metals [10]. When the values of β_X are not available, it can be set approximately [10, 12] to 0.5.

The derivation of the above Eq. (33) and the physical meaning of β_X were described in detail in our previous work [1 to 5, 10 to 12].

Consequently, $\eta_{\rm B}^{\rm C}$ and $\sigma_{\rm B}^{\rm C}$ can be obtained from Eqs. (25) to (33), together with the partial enthalpy of mixing in infinite dilution and some fundamental physical properties, i.e., $T_{{\rm m},X}$, V_X and β_X of the components in the pure state.

3 Calculation of the Gibbs Energy Interaction Parameter, the Enthalpy Interaction Parameter and the Entropy Interaction Parameter

As shown in Eqs. (4), (13) and (25), ΔH_{MIX} in ternary alloys according to the present model consists of the summation of the interaction energies between each pair of elements. Extra terms describing the interactions between the three elements in ternary systems, however, are not considered. If each binary in the ternary system shows large interaction energies, i. e. large absolute values of ΔH_{MIX} , it seems inappropriate to apply the present model for the calculation of $\varepsilon_{\text{B}}^{\text{C}}$ values. The calculation of $\varepsilon_{\text{B}}^{\text{C}}$, $\eta_{\text{B}}^{\text{C}}$ and $\sigma_{\text{B}}^{\text{C}}$, therefore, was carried out for non-ferrous ternary alloys formed from Bi, Cd, In, Pb, Sb, Sn and Zn and also in Fe-Mn base and Fe-Cr base alloys. The components in these systems have similar physical properties and the interaction energies of each pair do not seem to be too great.

The values of $T_{m,X}$, V_X and β_X for various elements are shown in Table 1 [10, 13]. To evaluate Ω_{BC} , Ω_{AB} and Ω_{AC} in Eqs. (25) and (26), the values of partial enthalpy of mixing $\Delta \tilde{H}_{C(B)}$ in solvent B, and $\Delta \tilde{H}_{B(A)}$ and $\Delta \tilde{H}_{C(A)}$ in solvent A were calculated using Miedema's semi-empirical method [13], as shown in Table 2.

Elements	$T_{\mathrm{m, X}}/\mathrm{K}$	$V_X/\mathrm{cm}^3\mathrm{mol}^{-1}$	β_X	
Bi	544	19.32	0.54	
Cd	594	13.00	0.56	
Ce	1068	21.62	0.50	
Co	1765	6.69	0.48	
Cr	2178	7.23	0.50	
Cu	1356	7.12	0.46	
Fe	1808	7.09	0.48	
In	430	15.74	0.68	
La	1193	22.54	0.50	
Mn	1517	7.35	0.50	
Mo	2895	9.39	0.50	
Nb	2740	10.81	0.50	
Ni	1728	6.60	0.47	
Pb	601	18.28	0.55	
Sb	904	16.96	0.40	
Si	1687	8.61	0.38	
Sn	505	16.30	0.64	
Ta	3123	10.81	0.50	
Ti	1998	10.58	0.50	
v	1973	8.36	0.50	
W	3655	9.55	0.50	
Zn	693	9.17	0.54	

Table 1. Physical properties of some elements used in the calculation of $\sigma_{\rm B}^{\rm C}$. $T_{\rm m, X}$: Ref. [10], V_X : Ref. [13] and β_X : Ref. [10].

Table 3. Calculated results for $\eta_{B,C}^C \sigma_B^C$ and ε_B^C in liquid ternary alloys with the experimental values of ε_B^C .

Table 2. Partia	al enthalpy	of mixing	$\Delta \bar{H}_{X(Y)}/kJ$	$\cdot \text{mol}^{-1}$	calculated
from Miedema	's semi-emp	irical metho	od [13].		

Solvent	Solute	$\Delta \tilde{H}_{X(Y)}$	Solvent	Solute	$\Delta \hat{H}_{X(Y)}$	Solvent	Solute	$\Delta \ddot{H}_{X(Y)}$
(Y)	(X)		(Y)	(X)		(Y)	(X)	
Bi	Cd	4	Bi	In	-5	Bi	Pb	0
Bi	Sb	3	Bi	Sn	5	Bi	Zn	14
Cd	Bi	5	Cd	Pb	7	Cd	Sb	-11
Cd	Sn	-1	Cd	Zn	3	In	Pb	-3
In	Sn	-1	In	Zn	10	Pb	Bi	0
Pb	Cd	5	Pb	In	-3	Pb	Sb	2
Pb	Sn	6	Pb	Zn	16	Sb	Cd	8
Sb	Pb	2	Sn	Cd	-1	Sn	In	-1
Sn	Pb	7	Sn	Zn	3	Zn	Bi	23
Zn	Cd	4	Zn	In	14	Zn	Pb	25
Zn	Sb	-5	Zn	Sn	5	Fe	Co	-2
Fe	Cr	-6	Fe	Cu	50	Fe	La	25
Fe	Mn	1	Fe	Mo	9	Fe	Nb	-70
Fe	Ni	6	Fe	Pb	160	Fe	Si	75
Fe	Sn	56	Fe	Ta	67	Fe	Ti	74
Fe	V	-29	Fe	W	0	Cr	Co	-18
Cr	Cu	49	Cr	Mn	8	Cr	Mo	2
Cr	Ni	-27	Cr	Pb	153	Cr	Si	-87
Cr	Sn	53	Cr	V	-8	Mn	Co	-21
Mn	Cr	9	Mn	La	14	Mn	Mo	22
Mn	Nb	-17	Mn	Ni	-33	Mn	Pb	38
Mn	Si	-120	Mn	Ta	-17	Mn	Ti	-36
Mn	V	-3	Mn	W	28			

No.	El	eme	nts	Temp./	$\eta_{\rm B}^{\rm C}/$	$\sigma_{\rm B}^{\rm C}$ /	$\varepsilon_{\rm B}^{\rm C}/$	$\varepsilon_{\rm B}^{\rm C}$ /	Ref.
	Α	В	С	K k.	$J \cdot mol^{-1}$	$J \cdot K^{-1} mol^{-1}$	(calc.)	(exp.)	
	D:	<u> </u>	DL	772	 ?	0.7	0.4	1.60	1.4
	BI D:	Ca Zn	PD	773	3 14	0.7	1.0	1.02	14
2	DI D:	Zn	Cu Tn	723	-14	-3.5	-1.9	-0.5	15
3	DI D:	Zn	III DL	723	5 11	1.0	0.7	2.2	15
	DI D:	Zn	PD	723	11	2.2	1.0	1.4	15
5	Bl D:	Zn	SD	723	-22	-3.2	-3.0	-5.4	15
0	BI	Zn D:	20	723	-14	-2.5	-2.0	-0.5	15
	Ca	BI	PD	773	-12	-2.8	-1.5	-3.2	14
8	Ca	Pb	Sb	773	6	1.4	0.8	0.0	14
9	Cd	Pb	Sn	773	0	-0.3	0.0	2.86	14
10	Cd	Sn	Pb	113	1	0.1	0.2	2.86	14
	Cd	Zn	Pb	805	15	3.1	1.9	0.95	16
12	Cd	Zn	Sn	805	3	0.8	0.3	-1.10	16
13	In	Zn	Pb	805	18	3.7	2.2	1.00	16
14	In	Zn	Sn	805	- 4	-0.7	-0.5	-0.63	16
15	Pb	Bi	Cd	773	- 1	-0.1	-0.1	-0.86	14
16	Pb	Cd	Sn	773	-12	-2.4	-1.6	1.35	14
17	Pb	Sb	Cd	773	-15	-3.4	-1.9	-1.60	14
18	Pb	Zn	Bi	805	7	1.6	0.9	-0.70	16
19	Pb	Zn	Cd	805	-17	-3.9	-2.1	-2.05	16
20	Pb	Zn	In	805	1	-0.1	0.2	-1.90	16
21	Pb	Zn	Sn	805	-17	-3.3	-2.1	-4.20	16
22	Sb	Cd	Pb	773	13	3.5	1.6	2.8	14
23	Sn	Cd	Pb	773	1	0.5	0.1	0.0	14
24	Sn	Cd	Zn	973	1	-0.1	0.1	-1.65	14
25	Sn	Zn	In	805	12	2.2	1.5	0.41	16
26	Sn	Zn	Pb	805	15	3.1	1.9	1.22	16
27	Fe	Mn	Co	1843	-20	-1.8	-1.1	-0.9	17
28	Fe	Mn	Cr	1843	14	0.8	0.8	0.9	17
29	Fe	Mn	La	1873	-12	-0.9	-0.7	61.6	17
30	Fe	Mn	Mo	1843	30	1.4	1.8	1.1	17
31	Fe	Mn	Nb	1843	52	2.9	3.0	2.1	17
32	Fe	Mn	Ni	1843	28	-2.6	-1.5	-1.8	17
33	Fe	Mn	Pb	1823	-123	-16.5	-6.1	-5.2	17
34	Fe	Mn	Si	1873	-46	-5.3	-2.3	-3.3	17
35	Fe	Mn	Та	1843	49	2.3	2.9	0.4	17
36	Fe	Mn	Ti	1873	37	2.5	2.1	-9.7*	17
37	Fe	Mn	V	1843	25	1.8	1.4	1.3	17
38	Fe	Mn	W	1843	27	0.7	1.7	3.1	17
39	Fe	Cr	Co	1903	-10	-0.8	-0.5	-4.7	17
40	Fe	Cr	Cu	1873	5	-1.5	0.5	4.1	17
41	Fe	Cr	Mn	1843	13	0.7	0.8	0.9	17
42	Fe	Cr	Mo	1873	17	3.1	0.7	0.0	17
43	Fe	Cr	Ni	1873	-15	-1.5	-0.8	0.0	17
44	Fe	Cr	Pb	1873	-1	-5.5	0.6	4.4	17
45	Fe	Cr	Si	1903	-6	-2.0	-0.1	0.0	17
46	Fe	Cr	Sn	1823	3	-3.2	0.6	3.3	17
47	Fe	Cr	V	1873	27	2.8	1.4	2.6	17

* As Ueno et al. [18] pointed out, $\varepsilon_{Mn}^{Ti}(exp.) = 3.9[21]$.

The calculated results of $\varepsilon_{\rm B}^{\rm C}$, $\eta_{\rm B}^{\rm C}$ and $\sigma_{\rm B}^{\rm C}$ in the above systems are shown in Table 3 together with the experimental values of $\varepsilon_{\rm B}^{\rm C}$ [14 to 17]. Figure 2 presents a comparison of the calculated $\varepsilon_{\rm B}^{\rm C}$ with their experimental values. As shown in Table 3 and Fig. 2, most of the calculated $\varepsilon_{\rm B}^{\rm C}$ values have the same sign as those for the experimental values. Since the simple assumptions were

used to extend the model to ternary systems in this work, it is difficult to make a reliable comparison of the calculated and experimental $\varepsilon_{\rm B}^{\rm C}$ results. In addition, the accuracy of the calculated results for $\varepsilon_{\rm B}^{\rm C}$ in this model depends on that of $\Delta \bar{H}_{X(Y)}$ (X = A, B or C; Y = A or B) calculated from Miedema's semi-empirical method.



Fig. 2. Comparison of the calculated ε_B^C with the experimental values (numbers in the figure correspond to those in Table 3).

Ueno et al. have also calculated $\varepsilon_{\rm B}^{\rm C}$ using Miedema's semiempirical method on the basis of the pseudopotential formalism coupled with the Gibbs energy of the hard sphere system [18, 19]. They did not, however, refer to the relationship between $\eta_{\rm B}^{\rm C}$ and $\sigma_{\rm B}^{\rm C}$.



Fig. 3. Relationship between η_B^C and σ_B^C (calculated) for liquid non-ferrous ternary alloys (numbers in the figure correspond to those in Table 3).

4 Relation Between Enthalpy and Entropy Interaction Parameters in Liquid Ternary Alloys

Lupis and Elliott [9] and Richardson [20] have shown that certain correlations exist between η_B^C and σ_B^C in some liquid ternary systems on the basis of the available experimental values. Figures 3 and 4 show the relation between η_B^C and σ_B^C calculated from the present model in non-ferrous alloys and ferrous alloys, respectively. From these figures, there seem to be linear correlations between η_B^C and σ_B^C . From Eqs. (25), (26), (32) and (33), if the components in the ternary alloys have similar physical properties, i.e.

$$\begin{cases} \beta_{\rm A} = \beta_{\rm B} = \beta_{\rm C} \ (= 0.50) \\ V_{\rm A} \approx V_{\rm B} \approx V_{\rm C} \\ T_{\rm m,A} \approx T_{\rm m,B} \approx T_{\rm m,C} (= T_{\rm m,Ave}) \end{cases}$$

$$\end{cases}$$

$$(34)$$

the following approximate equation applies:

ŋ

$$\eta_{\rm B}^{\rm C} \approx 7.0 \cdot T_{\rm m, Ave} \cdot \sigma_{\rm B}^{\rm C} \tag{35}$$



Fig. 4. Relationship between η_B^C and σ_B^C (calculated) for liquid ferrous ternary alloys (numbers in the figure correspond to those in Table 3).

where $T_{\rm m, Ave}$ is the arithmetic average of $T_{\rm m, A}$, $T_{\rm m, B}$ and $T_{\rm m, C}$.

The above equation implies that the alloy, for which the components have the higher melting points, will show a larger value of the ratio η_B^C/σ_B^C . The relation in Eq. (35) with the average value of the melting points of Bi, Cd, In, Pb, Sb, Sn and Zn $(T_{m, Ave} = 610 \text{ K})$ is shown in Fig. 3, where the approximation in Eq. (35) satisfies the relation between η_B^C and σ_B^C for the alloys formed by the above metals. The dotted line in Fig. 4 indicates the relation in Eq. (35) with the average value of the melting point of Fe, Mn and Cr ($T_{m,Ave} = 1834 \text{ K}$). As shown in this figure, when the melting point of the third element C is much different from those of Fe, Mn and Cr, their points (e.g., No. 33 for Fe – Mn – Pb, No. 44 for Fe – Cr – Pb and so on) are located away from the line. Hence, if the second or third element in $\varepsilon_{\rm B}^{\rm C}$ is a gaseous element such as oxygen or nitrogen, another relationship between $\eta_{\rm B}^{\rm C}$ and $\sigma_{\rm B}^{\rm C}$ instead of Eq. (35) should be derived because U_{XX} can not be expressed in terms of the melting points of those elements as in Eq. (33).

5 Concluding Remarks

In the present work, a previously described solution model based on the free volume theory was applied to ternary alloys to calculate the interaction parameter $\varepsilon_{\rm B}^{\rm C}$, as well as the enthalpy and entropy interaction parameters, $\eta_{\rm B}^{\rm C}$ and $\sigma_{\rm B}^{\rm C}$, in some non-ferrous and ferrous alloys. The values of $\varepsilon_{\rm B}^{\rm C}$, $\eta_{\rm B}^{\rm C}$ and $\sigma_{\rm B}^{\rm C}$ can be evaluated from the partial enthalpy of mixing $\Delta \tilde{H}_{X(Y)}$ obtained by Miedema's semi-empirical method and some physical properties of pure components. The relationship between $\eta_{\rm B}^{\rm C}$ and $\sigma_{\rm B}^{\rm C}$ can be expressed approximately as a linear relation dependent upon the melting points of the components.

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