Title	Thermodynamic Relationship between Enthalpy of Mixing and Excess Entropy in Liquid Binary Alloys
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Citation	Zeitschrift für Metallkunde. 1993, 84(3), p. 192-200
Version Type	VoR
URL	https://hdl.handle.net/11094/26511
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Thermodynamic Relationship between Enthalpy of Mixing and Excess Entropy in Liquid Binary Alloys

A solution model for liquid binary alloys has been derived, based on the free volume theory considering excess volumes of the alloys. Excess entropy and excess Gibbs energy can be evaluated from the present model using values of enthalpy of mixing and excess volume. In addition, the relationship between enthalpy of mixing and excess entropy in liquid binary alloys has been interpreted based on the present model.

Thermodynamischer Zusammenhang zwischen Mischungsenthalpie und Überschußentropie in flüssigen binären Legierungen

Auf der Basis der Theorie des freien Volumens ist unter Berücksichtigung des Überschußvolumens der Legierungen ein Lösungsmodell für binäre flüssige Legierungen entwickelt worden. Anhand dieses Modells wird die Überschußentropie und die überschüssige freie Enthalpie aus Werten der Mischungsenthalpie und des Überschußvolumens erschlossen. Ferner wird mit Hilfe dieses Modells der Zusammenhang zwischen Mischungsenthalpie und Überschußentropie flüssiger binärer Legierungen interpretiert.

1 Introduction

Several empirical attempts have been made to correlate the enthalpy of mixing ΔH_{MIX} and the excess entropy ΔS^{Ex} in liquid binary alloys [1 to 9]. The present authors have derived the relationship between ΔH_{MIX} and ΔS^{Ex} from a solution model based on the free volume theory [10 to 15]. It was found from this model that the relationship between ΔH_{MIX} and ΔS^{Ex} depended on the temperature of the alloys and that the temperature dependence of the relationship was approximately related to the melting points of the pure components. In the previous work [10], the approximations proposed by Shimoji and Niwa [16] were used to express the potential energy of an atom in its "cell" formed by its nearest-neighbor atoms. Since those approximations were proposed on the basis of the assumption that absolute values of ΔH_{mix} in the alloy are small so that the configuration of atoms is nearly random. Those approximations are, therefore, valid for infinite dilution of liquid binary alloys [11 to 14] but are insufficient in applying to concentrated alloys [10] where the short-range order in the configuration of atoms must be considered. In addition, the relationship between excess volume and excess entropy was not adequately considered in the previous treatments for the above solution model.

The purpose of this work is, therefore, to derive a new solution model based on the free volume theory by considering excess volume and more strict configuration of atoms and then to obtain the relationship between ΔH_{MIX} and ΔS^{Ex} in alloys.

2 Free Volume [4, 17]

Each atom in a liquid metal moves within a restricted region in a cell made by its nearest-neighbor atoms, as shown in Fig. 1. This restricted region is called a "free volume". It is assumed that the potential energy Φ of the liquid metal can be expressed as follows:

$$\Phi = E_{\mathrm{o}} + \sum_{i=1}^{N} \{\psi_i(r) - \psi_i(0)\} \tag{1}$$

where E_{o} is the potential energy of atoms in a liquid metal where all atoms are at their equilibrium positions, and $\psi_i\ (r)$ is the potential energy of an atom i which is located at a distance of r from the center ($r = 0$) of the cell.

Regarding $w\ (T)$ as the partition function of each atom for internal degrees of freedom, the total partition function of the liquid metal Z_N is given by:

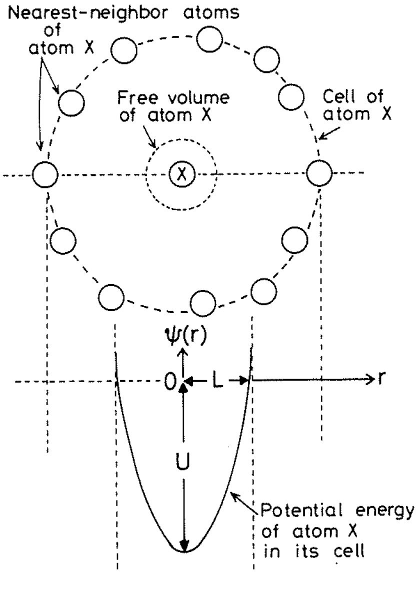

Fig. 1. Schematic diagram of potential energy in a cell of atom X.

$$Z_N = \left(\frac{2\,\pi\, m\, k\, T}{h^2}\right)^{3N/2} \cdot \{w\ (T)\}^N \cdot \exp\left(-\frac{E_o}{k\,T}\right) \cdot \left[\int_{\text{cell}} \exp\left\{-\frac{\psi(r)-\psi(0)}{k\,T}\right\} \mathrm{d}\ v\right]^N \qquad (2)$$

where m is the atomic mass, k is the Boltzmann constant, T the temperature in K, h the Planck constant, N the number of atoms and v the cell volume.

The integration term on the right-hand side in Eq. (2) contains the free volume v_f according to the following equation:

$$v_f = \int_{\text{cell}} \exp\left\{-\frac{\psi(r)-\psi(0)}{k\,T}\right\} \mathrm{d}\ v \qquad (3)$$

From Eq. (2), the partition function Q is related to the potential energy Φ is given as follows:

$$Q = \exp\left(-\frac{E_o}{k\,T}\right) \cdot \left[\int_{\text{cell}} \exp\left\{-\frac{\psi(r)-\psi(0)}{k\,T}\right\} \mathrm{d}\ v\right]^N$$

$$= v_f^N \cdot \exp\left(-\frac{E_o}{k\,T}\right) \qquad (4)$$

When an atom in its cell vibrates harmonically, $\psi\ (r)$ can be expressed as a parabola, i.e. $\psi\ (r) = U\ \{1-(r/L)^2\}$, as in Fig. 1. Then, v_f is given by Eq. (5), as shown in Appendix A.

$$v_f = \left(-\frac{\pi L^2 k\,T}{U}\right)^{3/2} \qquad (5)$$

where L is the distance which interatomic potential extends in a cell of an atom as shown in Fig. 1, and U is the depth of potential energy in a cell of an atom as shown in Fig. 1.

3 Derivation of Excess Gibbs Energy of Liquid Binary Alloys

According to the free volume theory, the partition functions of pure liquid A and B, Q_{AA} and Q_{BB}, are given by the following equations:

$$Q_{AA} = v_{f,\,AA}{}^{N_A} \cdot \exp\left(-\frac{E_{AA}}{k\,T}\right)$$

$$= \left(-\frac{\pi\ L_{AA}{}^2 k\,T}{U_{AA}}\right)^{3\,N_A/2} \cdot \exp\left(-\frac{N_A \cdot U_{AA}}{2\,k\,T}\right) \qquad (6)$$

$$Q_{BB} = v_{f,\,BB}{}^{N_B} \cdot \exp\left(-\frac{E_{BB}}{k\,T}\right)$$

$$= \left(-\frac{\pi\ L_{BB}{}^2 k\,T}{U_{BB}}\right)^{3\,N_B/2} \cdot \exp\left(-\frac{N_B \cdot U_{BB}}{2\,k\,T}\right) \qquad (7)$$

where $v_{f,\,XX}$ is the free volume of atom X in pure liquid X, L_{XX} the distance which interatomic potential extends in a cell of atom X in pure liquid X, U_{XX} the depth of potential energy in a cell of atom X in pure liquid X, and N_X the number of atoms in pure liquid X.

The partition function of liquid A – B alloy is given by:

$$Q = g \cdot v_{f,\,A}{}^{N_A} \cdot v_{f,\,B}{}^{N_B} \cdot \exp\left(-\frac{E}{k\,T}\right)$$

$$= g \cdot \left(-\frac{\pi L_A{}^2\ k\,T}{U_A}\right)^{3\,N_A/2} \cdot \left(-\frac{\pi L_B{}^2\ k\,T}{U_B}\right)^{3\,N_B/2} \cdot \exp\left(-\frac{E}{k\,T}\right) \qquad (8)$$

where $v_{f,\,x}$ is the free volume of atom X in liquid A – B alloy, L_x the distance which interatomic potential extends in a cell of atom X in liquid A – B alloy, U_x the depth of potential energy in a cell of atom X in liquid A – B alloy, and g the degeneracy factor.

When a liquid A – B alloy with N (= $N_A + N_B$) atoms is formed from N_A atoms of pure liquid metal A and N_B atoms of pure liquid metal B, the energy E of liquid A – B alloy in Eq. (8) is assumed to be the sum of the energies of A – A, B – B and A – B pairs, i.e. u_{AA}, u_{BB} and u_{AB} as follows:

$$E = \frac{N_A U_{AA}}{2} + \frac{N_B U_{BB}}{2} + \frac{N_{AB} \Omega_{AB}}{z} \qquad (9)$$

$$\text{where } U_{AA} = z \cdot u_{AA},\ \ U_{BB} = z \cdot u_{BB} \qquad (10)$$

(z: is the coordination number), N_{AB} is the number of A – B pairs and Ω_{AB} the exchange energy defined as:

$$\Omega_{AB} = z\left(u_{AB} - \frac{u_{AA}+u_{BB}}{2}\right)$$

$$= U_{AB} - \frac{U_{AA}+U_{BB}}{2} \qquad (11)$$

$$U_{AB} = z \cdot u_{AB} \qquad (12)$$

The Gibbs energies of liquid A, B, and alloy A – B are given by

$$G_{AA} = -k\ T\ \ln\ Q_{AA},\ \ G_{BB} = -k\ T\ \ln\ Q_{BB} \qquad (13)$$

$$G\ \ = -k\ T\ \ln\ Q \qquad (14)$$

The Gibbs energy of mixing is then

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

$$= \frac{N_{AB}\Omega_{AB}}{z} - k\ T\ \ln\ g$$

$$- k\ T \cdot \frac{3}{2} \cdot [N_A \ln\left(-\frac{\pi\ L_A{}^2\ k\ T}{U_A}\right)$$

$$+ N_B\ \ln\left(-\frac{\pi\ L_B{}^2\ k\ T}{U_B}\right)$$

$$- \{N_A \ln\left(-\frac{\pi\ L_{AA}{}^2\ k\ T}{U_{AA}}\right)$$

$$+ N_B\ \ln\left(-\frac{\pi\ L_{BB}{}^2\ k\ T}{U_{BB}}\right)\}] \qquad (15)$$

Later, the enthalpy and entropy terms in the A – B binary alloy will be derived separately.

3.1 Enthalpy Term

From Eq. (15), the enthalpy of mixing $\Delta H_{MIX}'$ can be obtained by the Gibbs-Helmholtz relation as follows:

$$\Delta H_{MIX}' = \frac{N_{AB} \cdot \Omega_{AB}}{z} \qquad (16)$$

According to the first approximation of the regular solution model, in which the short-range order in the configuration of atoms has been considered, the number of A – B pairs N_{AB} is given by [18]

$$N_{AB} = \frac{2\ N\ z\ x_A\ x_B}{P+1} \tag{17}$$

$$P = [1 - 4\ x_A\ x_B\ \{1 - \exp\left(\frac{\Omega_{AB}}{k\ T}\right)\}]^{1/2} \tag{18}$$

where x_A and x_B are the mole fractions of A and B, respectively. As shown in the above equation, N_{AB} in the proposed model [18] is $2/(P+1)$ times larger than the number of A – B pairs in random alloys, for which $N_{AB}{}^{\text{Random}} = N\ z\ x_A\ x_B$. When ΔH_{MIX} shows positive values, P in Eq. (18) can be set approximately unity because the configuration of atoms in such an alloy is considered to be nearly random. From Eqs. (16) to (18), the enthalpy of mixing per atom $\Delta H_{\text{MIX}} = \Delta H_{\text{MIX}}{}'/N$ is

$$\Delta H_{\text{MIX}} = \frac{2\ x_A\ x_B \cdot \Omega_{AB}}{P+1} \tag{19}$$

3.2 Entropy Terms

The entropy arising from configuration of atoms in alloys, ΔS_{CONF}, consists of the two terms, as shown in Eqs. (20) to (22):

$$\Delta S_{\text{CONF}} = k\ \ln\ g = \Delta S_{\text{CONF}}{}^{\text{Ideal}} + \Delta S_{\text{CONF}}{}^{\text{Ex}} \tag{20}$$

$$\Delta S_{\text{CONF}}{}^{\text{Ideal}} = -k\ (x_A\ \ln\ x_A + x_B\ \ln\ x_B) \tag{21}$$

$$\Delta S_{\text{CONF}}{}^{\text{Ex}} = \frac{2\ x_A\ x_B \cdot \Omega_{AB}}{(P+1)\cdot T} - k\ x_A\ \ln\left(\frac{P + x_A - x_B}{x_A(P+1)}\right) - k\ x_B\ \ln\left(\frac{P + x_B - x_A}{x_B(P+1)}\right) \tag{22}$$

In these equations, the excess entropy arising from configuration of atoms in alloys $\Delta S_{\text{CONF}}{}^{\text{Ex}}$ is also obtained from the first approximation of the regular solution model [18]. As described in the preceding section, when ΔH_{MIX} shows positive values, $\Delta S_{\text{CONF}}{}^{\text{EX}}$ is set to be approximately zero because the configuration of atoms in such an alloy is considered to be nearly random.

The excess entropy per atom arising from harmonic vibration of an atom in its cell $\Delta S_{\text{VIB}}{}^{\text{Ex}}$ is derived from Eq. (15) as follows:

$$\Delta S_{\text{VIB}}{}^{\text{Ex}} = \frac{3}{2}\cdot k\ \{2\ x_A\ \ln\left(\frac{L_A}{L_{AA}}\right) + 2\ x_B\ \ln\left(\frac{L_B}{L_{BB}}\right) + x_A\ \ln\left(\frac{U_{AA}}{U_A}\right) + x_B\ \ln\left(\frac{U_{BB}}{U_B}\right)\} \tag{23}$$

In the present work, U_A and U_B in A – B alloy are assumed to be given by the following relations.

U_A = (fraction of A atoms in the nearest-neighbors of atom A) $\cdot\ z \cdot u_{AA}$
+ (fraction of B atoms in the nearest-neighbors of atom A) $\cdot\ z \cdot u_{AB}$

$$= \left(1 - \frac{2\ x_B}{P+1}\right)\cdot U_{AA} + \left(\frac{2\ x_B}{P+1}\right)\cdot U_{AB}$$

$$= \left(1 - \frac{2\ x_B}{P+1}\right)\cdot U_{AA} + \left(\frac{2\ x_B}{P+1}\right)\cdot\left(\Omega_{AB} + \frac{U_{AA} + U_{BB}}{2}\right) \tag{24}$$

U_B = (fraction of B atoms in the nearest-neighbors of atom B) $\cdot\ z \cdot u_{BB}$
+ (fraction of A atoms in the nearest-neighbors of atom B) $\cdot\ z \cdot u_{AB}$

$$= \left(1 - \frac{2\ x_A}{P+1}\right)\cdot U_{BB} + \left(\frac{2\ x_A}{P+1}\right)\cdot U_{AB}$$

$$= \left(1 - \frac{2\ x_A}{P+1}\right)\cdot U_{BB} + \left(\frac{2\ x_A}{P+1}\right)\cdot\left(\Omega_{AB} + \frac{U_{AA} + U_{BB}}{2}\right) \tag{25}$$

It is quite difficult to evaluate U_{AB} in Eqs. (24) and (25) from physical properties of A – B alloy. It is, therefore, proposed that U_{AB} from Eq. (11) be used for this purpose, i.e.

$$U_{AB} = \Omega_{AB} + \frac{U_{AA} + U_{BB}}{2} \tag{26}$$

From Eqs. (18) and (24) to (26), U_A and U_B can be obtained from U_{AA} and U_{BB} for pure components A and B if the value of Ω_{AB} is known.

L_A and L_B in Eq. (23) is assumed to be given by the following equations:

L_A = (fraction of A atoms in the nearest-neighbors of atom A) $\cdot\ L_{AA}$
+ (fraction of B atoms in the nearest-neighbors of atom A) $\cdot\ L_{AB}$

$$= \left(1 - \frac{2\ x_B}{P+1}\right)\cdot L_{AA} + \left(\frac{2\ x_B}{P+1}\right)\cdot L_{AB} \tag{27}$$

L_B = (fraction of B atoms in the nearest-neighbors of atom B) $\cdot\ L_{BB}$
+ (fraction of A atoms in the nearest-neighbors of atom B) $\cdot\ L_{AB}$

$$= \left(1 - \frac{2\ x_A}{P+1}\right)\cdot L_{BB} + \left(\frac{2\ x_A}{P+1}\right)\cdot L_{AB} \tag{28}$$

Here, L_{AA} and L_{BB} for pure components A and B are assumed to be half of the nearest-neighbor distance and then they can be calculated from their molar volume $V_A{}^{\text{Pure}}$ and $V_B{}^{\text{Pure}}$ as follows [10, 11, 13]:

$$L_{AA} = \frac{1}{2}\left(\frac{2^{1/2} V_A{}^{\text{Pure}}}{N_0}\right)^{1/3} \tag{29}$$

$$L_{BB} = \frac{1}{2}\left(\frac{2^{1/2} V_B{}^{\text{Pure}}}{N_0}\right)^{1/3} \tag{30}$$

where N_0 is Avogadro's number. In addition, L_A and L_B in an A – B alloy are assumed to be given in the same form as L_{AA} and L_{BB} in Eqs. (29) and (30), i.e.

$$L_A = \frac{1}{2}\left(\frac{2^{1/2} V_A{}^{\text{Alloy}}}{N_0}\right)^{1/3} \qquad (31)$$

$$L_B = \frac{1}{2}\left(\frac{2^{1/2} V_B{}^{\text{Alloy}}}{N_0}\right)^{1/3} \qquad (32)$$

Then, the excess volume of an A – B alloy, ΔV^{Ex}, can be expressed by:

$$\Delta V^{\text{Ex}} = (x_A \cdot V_A{}^{\text{Alloy}} + x_B \cdot V_B{}^{\text{Alloy}}) \\ -(x_A \cdot V_A{}^{\text{Pure}} + x_B \cdot V_B{}^{\text{Pure}}) \qquad (33)$$

Consequently, by substituting Eqs. (18) and (27) to (32) into Eq. (33), L_{AB} can be calculated from ΔV^{Ex} of an A – B alloy, $V_A{}^{\text{Pure}}$ and $V_B{}^{\text{Pure}}$ for pure components, and Ω_{AB}.

4 Calculation of U_{AA} and U_{BB}

The depth of the potential energy of an atom in its cell for pure components U_{AA} and U_{BB} can be evaluated by assuming that an atom vibrates harmonically in its cell, and U_{AA} and U_{BB} can be expressed as follows [10, 11, 13]; see Appendix A):

$$U_{XX} = -\frac{2\,\pi^2\, L_{XX}^2\, M_X\, \nu_X{}^2}{N_0} \qquad (X = A \text{ or } B) \qquad (34)$$

where $M_X(\text{g} \cdot \text{mol}^{-1})$ is the atomic weight, L_{XX} is obtained from Eqs. (29) and (30), ν_X is the frequency for harmonic vibration of atom X given by the following revised Lindemann's equation [10, 11, 13, 19]:

$$\nu_X = 2.8 \cdot 10^{12} \beta_X \left\{\frac{T_{m,X}}{M_X \cdot (V_X{}^{\text{Pure}})^{2/3}}\right\}^{1/2} \qquad (X = A \text{ or } B) \qquad (35)$$

where $T_{m,X}$ is the melting point of pure X, $V_X{}^{\text{Pure}}$ the molar volume of pure X ($\text{cm}^3 \cdot \text{mol}^{-1}$) and β_x the coefficient of pure X to transform the solid state frequency into that of the liquid state at the melting point. [19]

Since Lindemann's equation gives the frequency ν_{SOL} of an atom in the solid state at its melting point, the above coefficient β_X is necessary to obtain the frequency ν_X in the liquid state, i.e., $\nu_X = \beta_X \cdot \nu_{\text{SOL}}$. The values of β_X were obtained from the experimental data for the surface tension of pure liquid X as follows [19]:

$$\beta_X = \frac{1.1 \cdot 10^3\, V_{X,m}{}^{1/3}}{1.97\eta_{X,m}{}^{1/3} - 1}\left(\frac{\sigma_{X,m}}{R\, T_{m,X}}\right)^{1/2} \qquad (36)$$

In this equation, $V_{X,m}$ ($\text{m}^3 \cdot \text{g} - \text{atom}^{-1}$), $\sigma_{X,m}$ ($\text{mN} \cdot \text{m}^{-1}$) and $\eta_{X,m}$ are the molar volume, the surface tension and the packing fraction of pure liquid X at its melting point, respectively. When the values of β_X are not available, β_X can be set approximately to 0.5 [19].

When the unit of Ω_{AB} is $\text{J} \cdot \text{mol}^{-1}$ and k in the preceding equations is replaced by the gas constant $R/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, then U_{XX} in $\text{J} \cdot \text{mol}^{-1}$ is obtained from Eqs. (34) and (35) as follows:

$$U_{XX} = -685 \cdot \beta_X{}^2\, T_{m,X} \qquad (X = A \text{ or } B) \qquad (37)$$

Since the unit of U_{XX} calculated from Eqs. (34) and (35) is erg · atom^{-1}, the unit of U_{XX} is transformed from erg · atom^{-1} to J · mol^{-1} in the derivation of the above equation. Equation (37) shows that U_{XX} can be calculated from β_X and $T_{m,X}$ for pure component X.

Table 1. Physical properties of some elements used in the calculation of U_{XX} and L_{XX} ($T_{m,X}$ from Ref. [19], β_X from Ref. [19]).

Elements	$T_{m,X}/K$	β_X	$V_X{}^{\text{Pure}}/\text{cm}^3 \cdot \text{mol}^{-1}$ (T/K) [Ref.]
Fe	1808	0.48	7.94 (1823) [22]
			8.00 (1873) [23]
Cu	1356	0.46	8.41 (1823) [22]
Si	1687	0.38	11.43 (1873) [23]
Hg	234	0.84	15.79 (673) [19]
Na	371	0.49	26.70 (673) [19]
Cd	594	0.56	14.453 (773) [26]
Pb	601	0.55	19.830 (773) [27]

5 Procedure of the Calculation for ΔS^{Ex} and ΔG^{Ex}

As described in the preceding sections, ΔS^{Ex} and ΔG^{Ex} can be calculated from ΔH_{MIX}, ΔV^{Ex} and certain physical properties. The procedure for the calculation is described below:

1) Ω_{AB} is calculated from Eqs. (18) and (19) using the values of ΔH_{MIX} given in the literature. For $\Delta H_{\text{MIX}} > 0$, P in Eq. (18) is set to unity.
2) $\Delta S_{\text{CONF}}{}^{\text{Ex}}$ is calculated from Eqs. (18) and (22). For $\Delta H_{\text{MIX}} > 0$, $\Delta S_{\text{CONF}}{}^{\text{Ex}}$ is set to zero.
3) L_{AA}, L_{BB}, L_A and L_B are calculated from Eqs. (18) and (27) to (33) using the values of ΔV^{Ex} in A – B alloys and molar volumes for pure components given in the literature.
4) U_{AA}, U_{BB}, U_A and U_B are calculated from Eqs. (18), (24) to (26) and (37) using Ω_{AB}, $T_{m,X}$ and β_X ($X = A$ or B).
5) Then, $\Delta S_{\text{VIB}}{}^{\text{Ex}}$ is obtained from Eq. (23).
6) The excess entropy ΔS^{Ex} and the excess Gibbs energy ΔG^{Ex} are obtained from:

$$\Delta S^{\text{Ex}} = \Delta S_{\text{CONF}}{}^{\text{Ex}} + \Delta S_{\text{VIB}}{}^{\text{Ex}} \qquad (38)$$

$$\Delta G^{\text{Ex}} = \Delta H_{\text{MIX}} - T\Delta S^{\text{Ex}} \qquad (39)$$

6 Calculation of ΔS^{Ex} and ΔG^{Ex} Considering ΔV^{Ex}

ΔS^{Ex} and ΔG^{Ex} in liquid Fe – Si, Fe – Cu, Hg – Na and Cd – Pb binary alloys, for which ΔV^{Ex} [20 to 23] and ΔH_{MIX} [24] have been published, were calculated to discuss the validity of the present model. The physical properties necessary for the calculation in each alloy are listed in Table 1 [19, 22, 23, 26, 27]. The calculated results of $\Delta S_{\text{CONF}}{}^{\text{Ex}}$, $\Delta S_{\text{VIB}}{}^{\text{Ex}}$, ΔS^{Ex} and ΔG^{Ex} for the above binary alloys are shown in Tables 2 to 5 with the values of ΔV^{Ex} [20 to 23]; see Appendix B) and ΔH_{MIX} [24]. Figures 2 shows the comparison of the calculated results for ΔS^{Ex} and ΔG^{Ex} from the present model with the experimental values [24]. As shown in these tables and figures, the calculated results for ΔS^{Ex} and ΔG^{Ex} are in reasonable agreement with the experimental results. Thus, the present model shows that ΔV^{Ex}, ΔH_{MIX} and ΔS^{Ex} in liquid binary alloys are related to each other through the preceding equations.

7 Approximate Relationship Between ΔH_{MIX} and ΔS^{Ex} in Liquid Binary Alloys

As described in the previous work [10, 11], N_{AB} in Eq. (17), ΔH_{MIX} in Eq. (19) and $\Delta S_{\text{CONF}}{}^{\text{Ex}}$ in Eq. (22) can be approximately represented by the following equations on the conditions that the absolute values of Ω_{AB} are small and the config-

Table 2. Calculated results for ΔS^{Ex} and ΔG^{Ex} with the values of ΔH_{MIX} and ΔV^{Ex} at 773 K in liquid Cd – Pb alloys.

x_{Pb}	ΔH_{MIX} kJ·mol^{-1}	Ω_{CdPb} kJ·mol^{-1}	P	U_{Cd} kJ·mol^{-1}	U_{Pb} kJ·mol^{-1}	ΔV^{Ex} cm^3·mol^{-1}	L_{CdPb} 10^{-8}cm
0.1	1.2	13.8	1.000	−126.1	−113.5	0.050	1.73
0.2	2.0	12.5	1.000	−124.8	−115.8	0.088	1.73
0.3	2.4	11.7	1.000	−123.6	−117.4	0.113	1.73
0.4	2.7	11.1	1.000	−122.6	−118.8	0.122	1.73
0.5	2.7	10.6	1.000	−121.5	−120.0	0.125	1.73
0.6	2.5	10.3	1.000	−120.5	−121.0	0.122	1.73
0.7	2.1	10.0	1.000	−119.5	−122.0	0.110	1.73
0.8	1.6	9.8	1.000	−118.6	−122.9	0.085	1.73
0.9	0.9	9.5	1.000	−117.6	−123.7	0.045	1.73

x_{Pb}	L_{Cd} 10^{-8}cm	L_{Pb} 10^{-8}cm	$\Delta S_{VIB}{}^{Ex}$ J·K^{-1}·mol^{-1}	$\Delta S_{CONF}{}^{Ex}$ J·K^{-1}·mol^{-1}	ΔS^{Ex} J·K^{-1}·mol^{-1}	ΔG^{Ex} kJ·mol^{-1}
0.1	1.63	1.74	0.31	0.00	0.31	1.0
0.2	1.64	1.74	0.50	0.00	0.50	1.6
0.3	1.65	1.75	0.62	0.00	0.62	2.0
0.4	1.66	1.76	0.67	0.00	0.67	2.1
0.5	1.67	1.76	0.67	0.00	0.67	2.1
0.6	1.68	1.77	0.63	0.00	0.63	2.0
0.7	1.70	1.78	0.54	0.00	0.54	1.7
0.8	1.71	1.79	0.40	0.00	0.40	1.2
0.9	1.72	1.79	0.22	0.00	0.22	0.7

	$U_{XX}{}^{Pure}$ kJ·mol^{-1}	$L_{XX}{}^{Pure}$ 10^{-8}cm
Cd	−127.6	1.62
Pb	−124.5	1.80

Table 3. Calculated results for ΔS^{Ex} and ΔG^{Ex} with the values of ΔH_{MIX} and ΔV^{Ex} at 673 K in liquid Hg – Na alloys.

x_{Na}	ΔH_{MIX} kJ·mol^{-1}	Ω_{HgNa} kJ·mol^{-1}	P	U_{Hg} kJ·mol^{-1}	U_{Na} kJ·mol^{-1}	ΔV^{Ex} cm^3·mol^{-1}	L_{HgNa} 10^{-8}cm
0.1	−7.6	−76.1	0.800	−118.7	−163.2	−1.18	1.65
0.2	−14.4	−71.9	0.600	−124.6	−159.0	−2.26	1.66
0.3	−18.9	−62.9	0.400	−128.9	−150.0	−3.08	1.68
0.4	−20.6	−51.4	0.200	−130.0	−138.5	−3.64	1.70
0.5	−19.8	−40.7	0.026	−127.4	−126.1	−3.87	1.72
0.6	−17.1	−42.9	0.201	−129.9	−106.9	−3.94	1.70
0.7	−13.3	−44.3	0.400	−131.3	−91.1	−3.49	1.68
0.8	−9.0	−45.0	0.600	−132.1	−78.8	−2.69	1.65
0.9	−4.6	−46.4	0.800	−133.5	−69.1	−1.43	1.64

x_{Na}	L_{Hg} 10^{-8}cm	L_{Na} 10^{-8}cm	$\Delta S_{VIB}{}^{Ex}$ J·K^{-1}·mol^{-1}	$\Delta S_{CONF}{}^{Ex}$ J·K^{-1}·mol^{-1}	ΔS^{Ex} J·K^{-1}·mol^{-1}	ΔG^{Ex} kJ·mol^{-1}
0.1	1.67	1.65	−2.25	−0.31	−2.56	−5.9
0.2	1.67	1.66	−4.27	−0.32	−4.58	−11.3
0.3	1.67	1.68	−5.72	−1.10	−6.82	−14.3
0.4	1.69	1.70	−6.51	−2.41	−8.92	−14.6
0.5	1.72	1.73	−6.66	−4.77	−11.43	−12.1
0.6	1.70	1.79	−6.27	−2.39	−8.66	−11.3
0.7	1.68	1.86	−5.26	−1.10	−6.36	−9.0
0.8	1.65	1.91	−3.85	−0.42	−4.27	−6.1
0.9	1.64	1.95	−2.07	−0.09	−2.16	−3.2

	$U_{XX}{}^{Pure}$ kJ·mol^{-1}	$L_{XX}{}^{Pure}$ 10^{-8}cm
Hg	−113.1	1.67
Na	−61.0	1.99

Table 4. Calculated results for ΔS^{Ex} and ΔG^{Ex} with the values of ΔH_{MIX} and ΔV^{Ex} at 1873 K in liquid Fe – Si alloys.

x_{Si}	ΔH_{MIX} kJ·mol^{-1}	Ω_{FeSi} kJ·mol^{-1}	P	U_{Fe} kJ·mol^{-1}	U_{Si} kJ·mol^{-1}	ΔV^{Ex} cm^3·mol^{-1}	L_{FeSi} 10^{-8}cm
0.1	−12.9	−128.8	0.800	−293.1	−354.9	−0.37	1.32
0.2	−24.6	−122.9	0.600	−301.2	−348.9	−0.70	1.33
0.3	−33.4	−111.5	0.401	−307.7	−337.5	−0.98	1.34
0.4	−37.9	−95.2	0.205	−309.2	−320.6	−1.22	1.34
0.5	−37.9	−81.3	0.074	−305.9	−297.8	−1.41	1.34
0.6	−34.2	−86.2	0.209	−312.1	−263.1	−1.47	1.33
0.7	−27.9	−93.1	0.403	−319.1	−232.0	−1.30	1.31
0.8	−19.7	−98.3	0.601	−324.4	−206.2	−0.80	1.32

x_{Si}	L_{Fe} 10^{-8}cm	L_{Si} 10^{-8}cm	$\Delta S_{VIB}{}^{Ex}$ J·K^{-1}·mol^{-1}	$\Delta S_{CONF}{}^{Ex}$ J·K^{-1}·mol^{-1}	ΔS^{Ex} J·K^{-1}·mol^{-1}	ΔG^{Ex} kJ·mol^{-1}
0.1	1.33	1.32	−1.57	−0.09	−1.66	−9.8
0.2	1.33	1.33	−2.99	−0.42	−3.41	−18.2
0.3	1.33	1.34	−4.13	−1.09	−5.23	−23.6
0.4	1.34	1.34	−4.89	−2.32	−7.21	−24.4
0.5	1.34	1.35	−5.22	−3.69	−8.90	−21.2
0.6	1.33	1.39	−5.06	−2.25	−7.32	−20.5
0.7	1.31	1.42	−4.35	−1.07	−5.42	−17.7
0.8	1.32	1.46	−3.05	−0.41	−3.46	−13.2

	$U_{XX}{}^{Pure}$ kJ·mol^{-1}	$L_{XX}{}^{Pure}$ 10^{-8}cm
Fe	−285.3	1.33
Si	−166.9	1.50

Table 5. Calculated results for ΔS^{Ex} and ΔG^{Ex} with the values of ΔH_{MIX} and ΔV^{Ex} at 1823 K in liquid Fe – Cu alloys.

x_{Cu}	ΔH_{MIX} kJ·mol^{-1}	Ω_{FeCu} kJ·mol^{-1}	P	U_{Fe} kJ·mol^{-1}	U_{Cu} kJ·mol^{-1}	ΔV^{Ex} cm^3·mol^{-1}	L_{FeCu} 10^{-8}cm
0.1	4.0	44.2	1.000	−276.5	−196.8	0.15	1.39
0.2	6.5	40.8	1.000	−268.3	−199.4	0.21	1.38
0.3	8.0	38.2	1.000	−260.6	−200.9	0.20	1.37
0.4	8.8	36.5	1.000	−253.0	−201.3	0.19	1.36
0.5	8.9	35.7	1.000	−245.3	−200.9	0.19	1.36
0.6	8.5	35.4	1.000	−237.4	−200.1	0.19	1.36
0.7	7.5	35.6	1.000	−229.3	−199.2	0.16	1.36
0.8	5.8	36.3	1.000	−220.8	−198.2	0.11	1.36
0.9	3.4	37.4	1.000	−211.7	−197.2	0.06	1.36

x_{Cu}	L_{Fe} 10^{-8}cm	L_{Cu} 10^{-8}cm	$\Delta S_{VIB}{}^{Ex}$ J·K^{-1}·mol^{-1}	$\Delta S_{CONF}{}^{Ex}$ J·K^{-1}·mol^{-1}	ΔS^{Ex} J·K^{-1}·mol^{-1}	ΔG^{Ex} kJ·mol^{-1}
0.1	1.33	1.38	0.50	0.00	0.50	3.1
0.2	1.34	1.37	0.79	0.00	0.79	5.1
0.3	1.34	1.36	0.92	0.00	0.92	6.4
0.4	1.34	1.36	0.98	0.00	0.98	7.0
0.5	1.34	1.36	1.00	0.00	1.00	7.1
0.6	1.35	1.36	0.97	0.00	0.97	6.7
0.7	1.35	1.36	0.86	0.00	0.86	5.9
0.8	1.35	1.35	0.67	0.00	0.67	4.6
0.9	1.36	1.35	0.39	0.00	0.39	2.6

	$U_{XX}{}^{Pure}$ kJ·mol^{-1}	$L_{XX}{}^{Pure}$ 10^{-8}cm
Fe	−285.3	1.33
Cu	−196.5	1.35

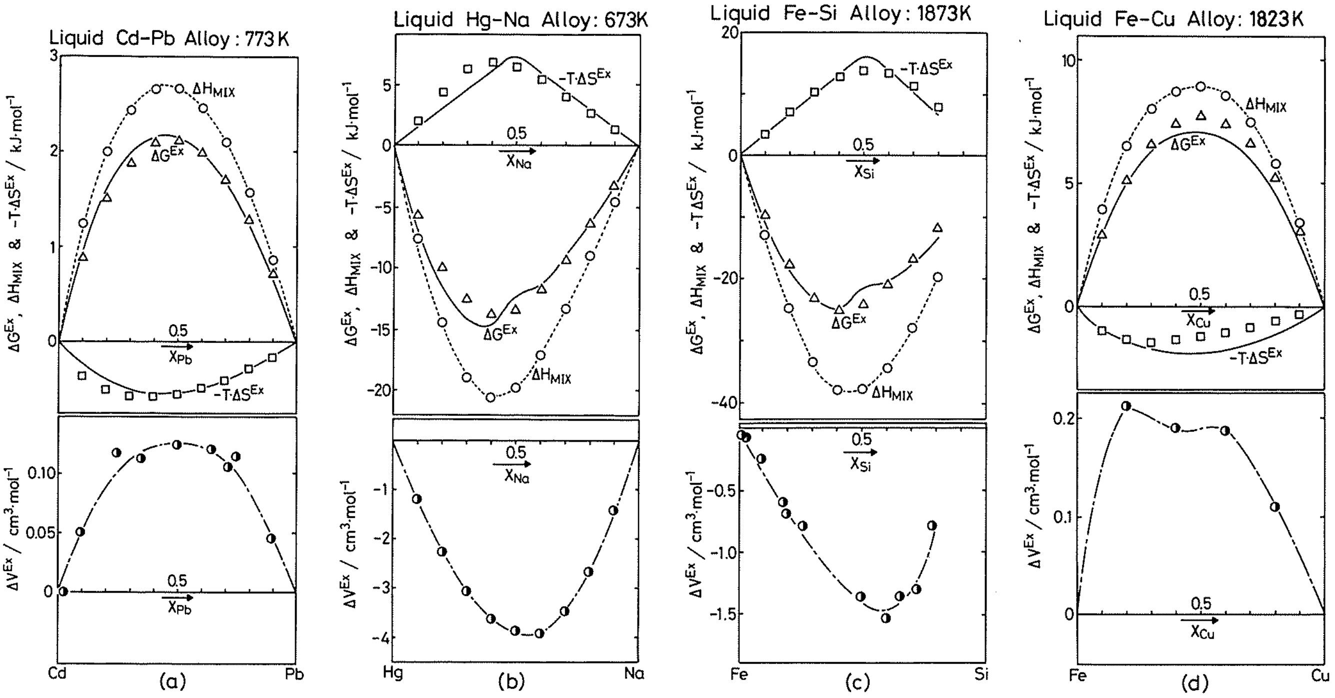

Fig. 2a to d. Calculated results for ΔS^{Ex} and ΔG^{Ex} with the experimental values for ΔH_{MIX}, ΔS^{Ex}, ΔG^{Ex} and ΔV^{Ex} in liquid binary alloys at temperature indicated (— calculated; ···○···, △, □, ◑ experimental; - - - for ΔV^{Ex}: used in the calculation for L_{A} and L_{B}).

uration of atoms in A − B alloys is nearly random in A − B alloys [10]:

$$N_{\mathrm{AB}} = N_0\ z\ x_{\mathrm{A}}\ x_{\mathrm{B}} \left(1 - \frac{x_{\mathrm{A}}\ x_{\mathrm{B}}\ \Omega_{\mathrm{AB}}}{k\ T}\right) \qquad (40)$$

$$\Delta H_{\mathrm{MIX}} = \Omega_{\mathrm{AB}}\ x_{\mathrm{A}}\ x_{\mathrm{B}} \left(1 - \frac{x_{\mathrm{A}}\ x_{\mathrm{B}}\ \Omega_{\mathrm{AB}}}{k\ T}\right) \qquad (41)$$

$$\Delta S_{\mathrm{CONF}}{}^{\mathrm{Ex}} = -\frac{x_{\mathrm{A}}{}^2\ x_{\mathrm{B}}{}^2\ \Omega_{\mathrm{AB}}{}^2}{2\ k\ T^2} \qquad (42)$$

According to Shimoji and Niwa [16], U_{A}, U_{B}, L_{A} and L_{B} in A − B alloy can be approximately expressed in Eqs. (43) to (45) by assuming the random configuration of atoms:

$$U_{\mathrm{A}} = x_{\mathrm{A}} U_{\mathrm{AA}} + x_{\mathrm{B}}\ U_{\mathrm{AB}}, \quad U_{\mathrm{B}} = x_{\mathrm{B}}\ U_{\mathrm{BB}} + x_{\mathrm{A}}\ U_{\mathrm{AB}} \qquad (43)$$

$$L_{\mathrm{A}} = 1/2\ \{L_{\mathrm{AA}} + (x_{\mathrm{A}}\ L_{\mathrm{AA}} + x_{\mathrm{B}}\ L_{\mathrm{BB}})\} \qquad (44)$$

$$L_{\mathrm{B}} = 1/2\ \{L_{\mathrm{BB}} + (x_{\mathrm{A}}\ L_{\mathrm{AA}} + x_{\mathrm{B}}\ L_{\mathrm{BB}})\} \qquad (45)$$

One can derive Eq. (43) by setting $P = 1$ in Eqs. (24) and (25), and also obtain Eqs. (44) and (45) by setting $P = 1$ and $L_{\mathrm{AB}} = 1/2\ (L_{\mathrm{AA}} + L_{\mathrm{BB}})$ in Eqs. (27) and (28). Then, $\Delta S_{\mathrm{VIB}}{}^{\mathrm{Ex}}$ in Eq. (23) is rewritten as follows [10]:

$$\Delta S_{\mathrm{VIB}}{}^{\mathrm{Ex}} = \frac{3}{2} \cdot k\ x_{\mathrm{A}}\ x_{\mathrm{B}} \left[\frac{(L_{\mathrm{AA}} - L_{\mathrm{BB}})^2}{L_{\mathrm{AA}}\ L_{\mathrm{BB}}} + \left\{\frac{4\ U_{\mathrm{AA}}\ U_{\mathrm{BB}} - 2\ \Omega_{\mathrm{AB}}\ (U_{\mathrm{AA}} + U_{\mathrm{BB}}) - (U_{\mathrm{AA}} + U_{\mathrm{BB}})^2}{2\ U_{\mathrm{AA}}\ U_{\mathrm{BB}}}\right\}\right] \qquad (46)$$

As can be seen in Eq. (46), $\Delta S_{\mathrm{VIB}}{}^{\mathrm{Ex}}$ is calculated from the molar volume, melting points and β_{X} for pure components through Eqs. (29), (30) and (37) if the value of Ω_{AB} is given. The value of Ω_{AB} can be obtained from ΔH_{MIX} in the following equation derived from Eq. (41), as shown in the previous work [10], i.e.

$$\Omega_{\mathrm{AB}} = \frac{k\ T}{2\ x_{\mathrm{A}}\ x_{\mathrm{B}}} \left\{1 - \left(1 - \frac{4 \Delta H_{\mathrm{MIX}}}{k\ T}\right)^{1/2}\right\} \qquad (47)$$

Next, it is first assumed that

$$T_{\mathrm{m,\,A}} \approx T_{\mathrm{m,\,B}}, \quad V_{\mathrm{A}}{}^{\mathrm{Pure}} \approx V_{\mathrm{B}}{}^{\mathrm{Pure}}, \quad \beta_{\mathrm{A}} = \beta_{\mathrm{B}} = 0.5 \qquad (48)$$

The approximate relationship between ΔH_{MIX} and ΔS^{Ex} in Eq. (49) can now be obtained from Eqs. (41), (42) and (46); thus,

$$\Delta H_{\mathrm{MIX}} \approx \left(\frac{14}{1/T_{\mathrm{m,\,A}} + 1/T_{\mathrm{m,\,B}}}\right) \cdot \Delta S^{\mathrm{Ex}} \qquad (49)$$

The calculated results from Eqs. (40) to (47) for ΔS^{Ex} and ΔG^{Ex} in liquid binary alloys were described in details in the previous work [10].

8 Relationship Between Partial Enthalpy of Mixing and Partial Excess Entropy in Infinitely Dilute Liquid Binary Alloys

The approximations in Eqs. (40) to (46) are valid for infinite dilutions of liquid binary alloys. From these equations, the partial enthalpy of mixing $\Delta \bar{H}_{\mathrm{B}}$ and the partial excess entropy $\Delta\ \bar{S}_{\mathrm{B}}{}^{\mathrm{Ex}}$ of solute element B can be derived as follows [11 to 14]:

$$\Delta \bar{H}_{\mathrm{B}} = \Omega_{\mathrm{AB}} \qquad (50)$$

Table A1. Excess volume in liquid Fe – Si alloys (M_{Fe} = 55.84 and M_{Si} = 28.085 from Ref. [19]).

wt.% Si	x_{Si}	$\rho = A - B \cdot (T - T_L)$/ g·cm^{-3} ($T_L$: liquidus temperature) A	B ×10^3 Ref. [23]	T_L/K Ref. [29]	ρ (1873 K)	V (1873 K) cm^3·mol^{-1}	ΔV^{Ex} (1873 K) cm^3·mol^{-1}
0.8	0.02	6.98	0.803	1798	6.92	8.01	−0.05
2.0	0.04	6.86	0.796	1783	6.79	8.07	−0.07
5.0	0.10	6.69	0.749	1733	6.59	8.08	−0.24
10.0	0.18	6.52	0.750	1633	6.34	8.02	−0.60
11.0	0.20	6.49	0.701	1613	6.31	7.99	−0.69
15.0	0.26	6.25	0.700	1523	6.01	8.10	−0.79
32.7	0.49	5.19	0.602	1682	5.08	8.32	−1.37
42.0	0.59	4.81	0.601	1608	4.65	8.49	−1.54
49.1	0.66	4.45	0.601	1508	4.23	8.89	−1.36
56.5	0.72	4.10	0.500	1488	3.91	9.17	−1.30
64.3	0.78	3.59	0.434	1553	3.45	9.89	−0.78

	$\rho = A - B \cdot T$(K) / g·cm^{-3} A Ref. [23]	B × 10^3	ρ(1873 K)	V_X^{Pure} (1873 K) cm^3·mol^{-1}
Pure Fe	8.586	0.857	6.98	8.00
Pure Si	3.117	0.352	2.46	11.43

$$\Delta \bar{S}_{B,\,CONF}{}^{Ex} = 0 \tag{51}$$

$$\Delta \bar{S}_{B,\,VIB}{}^{Ex} = \frac{3}{2} \cdot k \left[\frac{(L_{AA} - L_{BB})^2}{L_{AA}\, L_{BB}} + \left\{ \frac{4\, U_{AA}\, U_{BB} - 2\Omega_{AB}\,(U_{AA} + U_{BB}) - (U_{AA} + U_{BB})^2}{2\, U_{AA}\, U_{BB}} \right\} \right] \tag{52}$$

$$\Delta \bar{S}_B{}^{Ex} = \Delta \bar{S}_{B,\,CONF}{}^{Ex} + \Delta \bar{S}_{B,\,VIB}{}^{Ex} = \Delta \bar{S}_{B,\,VIB}{}^{Ex} \tag{53}$$

Assuming the approximation in Eq. (48) for Eqs. (50) to (53), the following relationship between $\Delta \bar{H}_B$ and $\Delta \bar{S}_B{}^{Ex}$ can be obtained [11 to 14].

Table A2. Excess volume in liquid Cd – Pb alloys (M_{Cd} = 112.41 and M_{Pb} = 207.2 from Ref. [19]).

x_{Pb}	$\rho = A + B\,T$ (°C)/g·cm^{-3} A	−B × 10^3	ρ(500 °C)	Ref.	V (500 °C) cm^3·mol^{-1}	ΔV^{Ex} (500 °C) cm^3·mol^{-1}
0.000 (Pure Cd)	8.388	1.2205	7.778	[26]	14.453	0.000
0.028	8.458	1.1571	7.879	[21]	14.603	0.000
0.100	8.669	1.1308	8.104		15.041	0.051
0.250	9.140	1.1751	8.552		15.914	0.117
0.352	9.457	1.1995	8.857		16.458	0.113
0.500	9.852	1.1921	9.256		17.265	0.124
0.645	10.278	1.3168	9.620		18.041	0.120
0.719	10.438	1.2747	9.801		18.424	0.105
0.750	10.518	1.3035	9.866		18.599	0.114
0.900	10.844	1.2375	10.225		19.337	0.045
1.000 (Pure Pb)	11.060	1.2220	10.449	[27]	19.830	0.000

$$\Delta \bar{H}_B \approx \left(\frac{14}{1/T_{m,\,A} + 1/T_{m,\,B}} \right) \cdot \Delta \bar{S}_B{}^{Ex} \tag{54}$$

9 Some Problems in the Present Model

The present model is successful in the evaluation of some thermodynamic properties of binary alloys. The following improvements, however, should be made in the future:

1) A more satisfactory treatment of alloys which show complicated behaviour of thermodynamic properties versus compositions.
2) A better treatment of alloys exhibiting different signs between ΔH_{MIX} and ΔS^{Ex} is necessary. This problem, however, also requires carefully obtained experimental data since such alloys are near the origin of ΔH_{MIX} –ΔS^{Ex} maps. The absolute values of ΔH_{MIX} and ΔS^{Ex} in such alloys are usually small.

10 Conclusion

A new solution model for liquid binary alloys has been derived on the basis of the free volume theory considering excess volumes and short-range order in the configuration of atoms. From this model, the excess entropy and excess Gibbs energy in liquid binary alloys can be calculated using some physical properties of pure components of the alloy when the values of enthalpy of mixing and excess volume at each composition of the alloy are given. The present model can evaluate the excess entropy term arising from a non-configurational contribution which has been difficult to evaluate so far. The present model shows that the relationship between ΔH_{MIX} and ΔS^{Ex} and also that of $\Delta \bar{H}_B$ and $\Delta \bar{S}_B{}^{Ex}$ in liquid binary alloys can be derived from the free volume theory.

Appendix A

The following equations (A1) and (A2) show the potential energy [28] of a particle with its frequency of harmonic oscillation ν and mass m ($= M/N_0$), as shown in Fig. 1:

$$\psi\,(r) = \frac{1}{2} C\, r^2 + U \tag{A1}$$

$$C = 4\,\pi^2\, m\, \nu^2 \tag{A2}$$

where r is the displacement of the particle from its equilibrium position. When the potential energy has the value of $\psi\,(L) = 0$ for $r = L$, as shown in Fig. 1, the following relation can be obtained:

$$U = -\frac{2\,\pi^2\, L^2\, M\, \nu^2}{N_0} \tag{A3}$$

Under the assumption that $\psi\,(r)$ is parabolic with respect to r, for example $\psi\,(r) = U\,\{1 - (r/L)^2\}$, as shown in Fig. 1, the free volume v_f is proportional to $\{\partial^2\,\psi\,(r)/\partial\, r^2\}^{-3/2}$ and can be calculated from the above $\psi\,(r)$ as follows [4]:

$$v_f = \left[\frac{1}{2\,\pi\, k\, T} \cdot \left\{ \frac{\partial^2\, \psi\,(r)}{\partial\, r^2} \right\} \right]^{-3/2} = \left(-\frac{\pi\, L^2\, k\, T}{U} \right)^{3/2} \tag{A4}$$

Appendix B
Data for Excess Volume in Liquid Binary Alloys

B.1 Liquid Fe – Cu, Cd – Pb and Fe – Si Alloys

Using the values of density given in Refs. [21 to 23], the molar volume V and the excess volume ΔV^{Ex} for each composition are obtained by the following equations (A5) and (A6):

$$V = \frac{x_{\mathrm{A}} \cdot M_{\mathrm{A}} + x_{\mathrm{B}} \cdot M_{\mathrm{B}}}{\rho} \tag{A5}$$

$$\Delta V^{\mathrm{Ex}} = V - (x_{\mathrm{A}} \cdot V_{\mathrm{A}}{}^{\mathrm{Pure}} + x_{\mathrm{B}} \cdot V_{\mathrm{B}}{}^{\mathrm{Pure}}) \tag{A6}$$

where ρ is the density of liquid alloys, x_{A}, x_{B} are the mole fractions of components A and B, M_{A}, M_{B} the atomic weights of components A and B, and $V_{\mathrm{A}}{}^{\mathrm{Pure}}$, $V_{\mathrm{B}}{}^{\mathrm{Pure}}$ the molar volumes of components A and B.

The values of ΔV^{Ex} obtained for each alloy are shown in Tables A1–A3 and also in Figs. 2a, c and d. The values of ΔV^{Ex} used in the calculation for L_{A} and L_{B} in Tables 2, 4 and 5 are read off the dash-dotted lines in Figures 2a, c and d.

B.2 Liquid Hg – Na Alloy

Since only the values of the molar volume at 573 K for this system are given in Ref. [20], ΔV^{Ex} at 673 K is obtained from the following equation (A7) assuming that the ratio $\Delta V^{\mathrm{Ex}}/(x_{\mathrm{A}} \cdot V_{\mathrm{A}}{}^{\mathrm{Pure}} + x_{\mathrm{B}} \cdot V_{\mathrm{B}}{}^{\mathrm{Pure}})$ at 573 K holds also at 673 K (A = Hg, B = Na):

$$\Delta V^{\mathrm{Ex}}{}_{673\,\mathrm{K}} = \Delta V^{\mathrm{Ex}}{}_{573\,\mathrm{K}} \cdot \frac{(x_{\mathrm{A}} \cdot V_{\mathrm{A}}{}^{\mathrm{Pure}} + x_{\mathrm{B}} \cdot V_{\mathrm{B}}{}^{\mathrm{Pure}})_{673\,\mathrm{K}}}{(x_{\mathrm{A}} \cdot V_{\mathrm{A}}{}^{\mathrm{Pure}} + x_{\mathrm{B}} \cdot V_{\mathrm{B}}{}^{\mathrm{Pure}})_{573\,\mathrm{K}}} \tag{A7}$$

The values of ΔV^{Ex} at 673 K are shown in Table A4 and Figure 2b.

Table A3. Excess volume in liquid Fe – Cu alloys $M_{\mathrm{Cu}} = 63.54$ and $M_{\mathrm{Fe}} = 55.84$ from Ref. [19]).

x_{Fe}	$\rho = A - B\,T(\mathrm{K})/\mathrm{g \cdot cm^{-3}}$			V (1823 K) $\mathrm{cm^3 \cdot mol^{-1}}$	ΔV^{Ex} (1823 K) $\mathrm{cm^3 \cdot mol^{-1}}$
	A Ref. [22]	$B \times 10^3$ Ref. [22]	ρ (1823 K)		
0.0 (Pure Cu)	8.75	0.657	7.55	8.41	0.00
0.2	8.90	0.847	7.36	8.43	0.11
0.4	9.20	1.104	7.19	8.41	0.19
0.6	7.88	0.438	7.08	8.32	0.19
0.8	8.81	1.016	6.96	8.25	0.21
1.0 (Pure Fe)	8.78	0.958	7.03	7.94	0.00

Table A4. Excess volume in liquid Hg – Na alloys.

x_{Na}	$V/\mathrm{cm^3 \cdot mol^{-1}}$ (573 K) Ref. [20]	$\Delta V^{\mathrm{Ex}}/\mathrm{cm^3 \cdot mol^{-1}}$ (573 K)	$\Delta V^{\mathrm{Ex}}/V_{\mathrm{Add}}$ × 100	$\Delta V^{\mathrm{Ex}}/\mathrm{cm^3 \cdot mol^{-1}}$ (673 K)
0.1	15.42	–1.16	–7.0	–1.18
0.2	15.42	–2.22	–12.6	–2.26
0.3	15.67	–3.02	–16.2	–3.08
0.4	16.18	–3.57	–18.1	–3.64
0.5	17.01	–3.79	–18.2	–3.87
0.6	18.00	–3.86	–17.6	–3.94
0.7	19.50	–3.41	–14.9	–3.49
0.8	21.34	–2.62	–10.9	–2.68
0.9	23.62	–1.40	–5.6	–1.43

$$V_{\mathrm{X}}{}^{\mathrm{Pure}} = V_{\mathrm{m,\,X}} \cdot \{1 + \alpha_{\mathrm{X}} \cdot (T - T_{\mathrm{m,\,X}})\}/\mathrm{cm^3 \cdot mol^{-1}}$$

	$V_{\mathrm{m,\,X}}/\mathrm{cm^3 \cdot mol^{-1}}$ Ref. [19]	$\alpha_{\mathrm{X}}/\mathrm{K^{-1}}$ Ref. [19]	$T_{\mathrm{m,\,X}}/\mathrm{K}$ Ref. [19]	$V_{\mathrm{X}}{}^{\mathrm{Pure}}/\mathrm{cm^3 \cdot mol^{-1}}$	
				573 K	673 K
Hg	14.65	1.77×10^{-4}	234	15.53	15.79
Na	24.80	2.54×10^{-4}	371	26.07	26.70

$$V_{\mathrm{Add}} = \{(1 - X_{\mathrm{Na}}) \cdot V_{\mathrm{Hg}}{}^{\mathrm{Pure}} + X_{\mathrm{Na}} \cdot V_{\mathrm{Na}}{}^{\mathrm{Pure}}\}_{\ 573\,\mathrm{K}}$$

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(Received May 8, 1992)

Errata in Ref. [10] (T. Tanaka et al.: Z. Metallkd. *81* (1990) 49–54)

1) Eq. (18)
(Wrong) $\Delta S_{\mathrm{CONF}}{}^{\mathrm{Ex}} = -\, x_{\mathrm{A}}{}^2\, x_{\mathrm{B}}{}^2\, \Omega_{\mathrm{AB}}{}^2/2\, k\, T$
(Right) $\Delta S_{\mathrm{CONF}}{}^{\mathrm{Ex}} = -\, x_{\mathrm{A}}{}^2\, x_{\mathrm{B}}{}^2\, \Omega_{\mathrm{AB}}{}^2/2\, k\, T^2$

2) Eq. (20)
(Wrong) $U_{\mathrm{A}} = x_{\mathrm{A}}\, U_{\mathrm{AA}} + x_{\mathrm{A}}\, U_{\mathrm{AB}},\ U_{\mathrm{B}} = x_{\mathrm{B}}\, U_{\mathrm{BB}} + x_{\mathrm{A}}\, U_{\mathrm{AB}}$
(Right) $U_{\mathrm{A}} = x_{\mathrm{A}}\, U_{\mathrm{AA}} + x_{\mathrm{B}}\, U_{\mathrm{AB}},\ U_{\mathrm{B}} = x_{\mathrm{B}}\, U_{\mathrm{BB}} + x_{\mathrm{A}}\, U_{\mathrm{AB}}$

3) Eq. (23)
(Wrong) $\Delta S_{\mathrm{VIB}}{}^{\mathrm{Ex}} = 3/2 \cdot k\, x_{\mathrm{A}}\, x_{\mathrm{B}}\, [(R_{\mathrm{AA}} - R_{\mathrm{BB}})^2 / R_{\mathrm{AA}}\, R_{\mathrm{BB}} + \{2\, U_{\mathrm{AA}}\, U_{\mathrm{BB}} - U_{\mathrm{AB}}\, (U_{\mathrm{AA}} + U_{\mathrm{BB}})\}\, U_{\mathrm{AA}}\, U_{\mathrm{BB}}]$
(Right) $\Delta S_{\mathrm{VIB}}{}^{\mathrm{Ex}} = 3/2 \cdot k\, x_{\mathrm{A}}\, x_{\mathrm{B}}\, [(R_{\mathrm{AA}} - R_{\mathrm{BB}})^2 / R_{\mathrm{AA}}\, R_{\mathrm{BB}} + \{2\, U_{\mathrm{AA}}\, U_{\mathrm{BB}} - U_{\mathrm{AB}}\, (U_{\mathrm{AA}} + U_{\mathrm{BB}})/\, U_{\mathrm{AA}}\, U_{\mathrm{BB}}]^2$

4) Eqs. (28) and (29)
(Wrong) $v_{\mathrm{AA}} = (k\, T/2\, \pi\, M_{\mathrm{AA}}\, \nu_{\mathrm{AA}}{}^2)^{3/2}$ (28)
$v_{\mathrm{BB}} = (k\, T/2\, \pi\, M_{\mathrm{BB}}\, \nu_{\mathrm{BB}}{}^2)^{3/2}$ (29)
(Right) $v_{\mathrm{AA}} = (N_0\, k\, T/2\, \pi\, M_{\mathrm{AA}}\, \nu_{\mathrm{AA}}{}^2)^{3/2}$ (28)
$v_{\mathrm{BB}} = (N_0\, k\, T/2\, \pi\, M_{\mathrm{BB}}\, \nu_{\mathrm{BB}}{}^2)^{3/2}$ (29)

5) Eqs. (30) and (31)
(Wrong) $U_{\mathrm{AA}} = -2\, \pi^2\, R_{\mathrm{AA}}{}^2\, M_{\mathrm{AA}}\, \nu_{\mathrm{AA}}{}^2$ (30)
$U_{\mathrm{BB}} = -2\, \pi^2\, R_{\mathrm{BB}}{}^2\, M_{\mathrm{BB}}\, \nu_{\mathrm{BB}}{}^2$ (31)
(Right) $U_{\mathrm{AA}} = -2\, \pi^2\, R_{\mathrm{AA}}{}^2\, M_{\mathrm{AA}}\, \nu_{\mathrm{AA}}{}^2/N_0$ (30)
$U_{\mathrm{BB}} = -2\, \pi^2\, R_{\mathrm{BB}}{}^2\, M_{\mathrm{BB}}\, \nu_{\mathrm{BB}}{}^2/N_0$ (31)

6) Eqs. (37)
(Wrong) $\Omega_{\mathrm{AB}} = k\, T\, \{1 - (1 + 4\, \Delta H_{\mathrm{MIX}}/k\, T)^{1/2}\} / 2 x_{\mathrm{A}}\, x_{\mathrm{B}}$
(Right) $\Omega_{\mathrm{AB}} = k\, T\, \{1 - (1 - 4\, \Delta H_{\mathrm{MIX}}/k\, T)^{1/2}\} / 2 x_{\mathrm{A}}\, x_{\mathrm{B}}$

7) Table 2
(Wrong) The values of ΔS^{Ex}: $-\ 1.84\ (x_{\mathrm{Zn}} = 0.80)$, $-\ 1.36\ (x_{\mathrm{Zn}} = 0.90)$
(Right) The values of ΔS^{Ex}: $-\ 0.84\ (x_{\mathrm{Zn}} = 0.80)$, $-\ 0.36\ (x_{\mathrm{Zn}} = 0.90)$