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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  $\Delta H_{\text{MIX}}$  and the excess entropy  $\Delta S^{\text{Ex}}$  in liquid binary alloys [1 to 9]. The present authors have derived the relationship between  $\Delta H_{\text{MIX}}$  and  $\Delta S^{\text{Ex}}$  from a solution model based on the free volume theory [10 to 15]. It was found from this model that the relationship between  $\Delta H_{\text{MIX}}$  and  $\Delta S^{\text{Ex}}$  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  $\Delta H_{\text{mix}}$  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  $\Delta H_{\text{MIX}}$  and  $\Delta S^{\text{Ex}}$  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  $\Phi$  of the liquid metal can be expressed as follows:

$$\Phi = E_0 + \sum_{i=1}^N \{\psi_i(r) - \psi_i(0)\} \quad (1)$$

where  $E_0$  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:

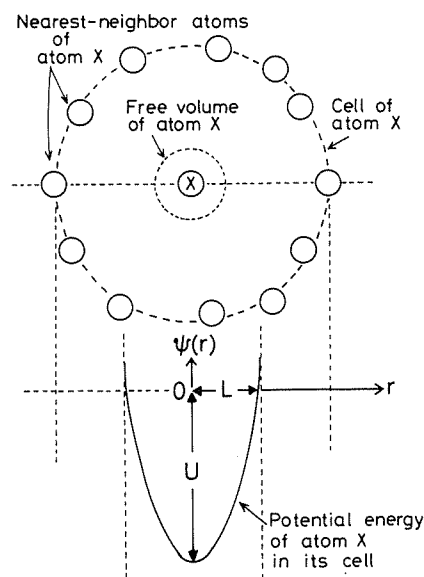


Fig. 1. Schematic diagram of potential energy in a cell of atom X.

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

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:

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

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

$$Q = \exp\left(-\frac{E_o}{k T}\right) \cdot \left[ \int_{\text{cell}} \exp\left\{-\frac{\psi(r) - \psi(0)}{k T}\right\} d v \right]^N = v_f^N \cdot \exp\left(-\frac{E_o}{k T}\right) \quad (4)$$

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.

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

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:

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

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

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:

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

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

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:

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

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

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

$$\Omega_{AB} = z \left( u_{AB} - \frac{u_{AA} + u_{BB}}{2} \right) = U_{AB} - \frac{U_{AA} + U_{BB}}{2} \quad (11)$$

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

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

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

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

The Gibbs energy of mixing is then

$$\begin{aligned} \Delta G_{\text{MIX}} &= G - (G_{AA} + G_{BB}) \\ &= \frac{N_{AB} \Omega_{AB}}{z} - k T \ln g \\ &\quad - k T \cdot \frac{3}{2} \cdot \left[ N_A \ln \left( -\frac{\pi L_A^2 k T}{U_A} \right) \right. \\ &\quad \left. + N_B \ln \left( -\frac{\pi L_B^2 k T}{U_B} \right) \right. \\ &\quad \left. - \{ N_A \ln \left( -\frac{\pi L_{AA}^2 k T}{U_{AA}} \right) \right. \right. \\ &\quad \left. \left. + N_B \ln \left( -\frac{\pi L_{BB}^2 k T}{U_{BB}} \right) \right] \end{aligned} \quad (15)$$

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  $\Delta H_{\text{MIX}}'$  can be obtained by the Gibbs-Helmholtz relation as follows:

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

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]

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

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

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  $\Delta H_{\text{MIX}}$  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

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

### 3.2 Entropy Terms

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

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

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

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

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  $\Delta H_{\text{MIX}}$  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:

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

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

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

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

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

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

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.

$$U_{AB} = \Omega_{AB} + \frac{U_{AA} + U_{BB}}{2} \quad (26)$$

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  $\Omega_{AB}$  is known.

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

$$L_A = (\text{fraction of A atoms in the nearest-neighbors of atom A}) \cdot L_{AA} + (\text{fraction of B atoms in the nearest-neighbors of atom A}) \cdot L_{AB} \\ = \left( 1 - \frac{2 x_B}{P + 1} \right) \cdot L_{AA} + \left( \frac{2 x_B}{P + 1} \right) \cdot L_{AB} \quad (27)$$

$$L_B = (\text{fraction of B atoms in the nearest-neighbors of atom B}) \cdot L_{BB} + (\text{fraction of A atoms in the nearest-neighbors of atom B}) \cdot L_{AB} \\ = \left( 1 - \frac{2 x_A}{P + 1} \right) \cdot L_{BB} + \left( \frac{2 x_A}{P + 1} \right) \cdot L_{AB} \quad (28)$$

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]:

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

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

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.

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

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

Then, the excess volume of an A – B alloy,  $\Delta V^{\text{Ex}}$ , can be expressed by:

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

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

#### 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):

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

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

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

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

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

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  $\beta_X$  are not available,  $\beta_X$  can be set approximately to 0.5 [19].

When the unit of  $\Omega_{AB}$  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:

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

Since the unit of  $U_{XX}$  calculated from Eqs. (34) and (35) is  $\text{erg} \cdot \text{atom}^{-1}$ , the unit of  $U_{XX}$  is transformed from  $\text{erg} \cdot \text{atom}^{-1}$  to  $\text{J} \cdot \text{mol}^{-1}$  in the derivation of the above equation. Equation (37) shows that  $U_{XX}$  can be calculated from  $\beta_X$  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],  $\beta_X$  from Ref. [19]).

Elements	$T_{m, X}/K$	$\beta_X$	$V_X^{\text{Pure}}/\text{cm}^3 \cdot \text{mol}^{-1}$ ( $T/K$ ) [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 $\Delta S^{\text{Ex}}$ and $\Delta G^{\text{Ex}}$

As described in the preceding sections,  $\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  can be calculated from  $\Delta H_{\text{MIX}}$ ,  $\Delta V^{\text{Ex}}$  and certain physical properties. The procedure for the calculation is described below:

- 1)  $\Omega_{AB}$  is calculated from Eqs. (18) and (19) using the values of  $\Delta H_{\text{MIX}}$  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  $\Delta V^{\text{Ex}}$  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  $\Omega_{AB}$ ,  $T_{m, X}$  and  $\beta_X$  ( $X = A \text{ or } B$ ).
- 5) Then,  $\Delta S_{\text{VIB}}^{\text{Ex}}$  is obtained from Eq. (23).
- 6) The excess entropy  $\Delta S^{\text{Ex}}$  and the excess Gibbs energy  $\Delta G^{\text{Ex}}$  are obtained from:

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

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

#### 6 Calculation of $\Delta S^{\text{Ex}}$ and $\Delta G^{\text{Ex}}$ Considering $\Delta V^{\text{Ex}}$

$\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  in liquid Fe – Si, Fe – Cu, Hg – Na and Cd – Pb binary alloys, for which  $\Delta V^{\text{Ex}}$  [20 to 23] and  $\Delta H_{\text{MIX}}$  [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  $\Delta S_{\text{CONF}}^{\text{Ex}}$ ,  $\Delta S_{\text{VIB}}^{\text{Ex}}$ ,  $\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  for the above binary alloys are shown in Tables 2 to 5 with the values of  $\Delta V^{\text{Ex}}$  [20 to 23]; see Appendix B) and  $\Delta H_{\text{MIX}}$  [24]. Figures 2 shows the comparison of the calculated results for  $\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  from the present model with the experimental values [24]. As shown in these tables and figures, the calculated results for  $\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  are in reasonable agreement with the experimental results. Thus, the present model shows that  $\Delta V^{\text{Ex}}$ ,  $\Delta H_{\text{MIX}}$  and  $\Delta S^{\text{Ex}}$  in liquid binary alloys are related to each other through the preceding equations.

#### 7 Approximate Relationship Between $\Delta H_{\text{MIX}}$ and $\Delta S^{\text{Ex}}$ in Liquid Binary Alloys

As described in the previous work [10, 11],  $N_{AB}$  in Eq. (17),  $\Delta H_{\text{MIX}}$  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  $\Omega_{AB}$  are small and the config-

Table 2. Calculated results for  $\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  with the values of  $\Delta H_{\text{MIX}}$  and  $\Delta V^{\text{Ex}}$  at 773 K in liquid Cd – Pb alloys.

$x_{\text{Pb}}$	$\Delta H_{\text{MIX}}$ kJ·mol <sup>-1</sup>	$\Omega_{\text{CdPb}}$ kJ·mol <sup>-1</sup>	$P$	$U_{\text{Cd}}$ kJ·mol <sup>-1</sup>	$U_{\text{Pb}}$ kJ·mol <sup>-1</sup>	$\Delta V^{\text{Ex}}$ cm <sup>3</sup> ·mol <sup>-1</sup>	$L_{\text{CdPb}}$ 10 <sup>-8</sup> 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

$x_{\text{Pb}}$	$L_{\text{Cd}}$ 10 <sup>-8</sup> cm	$L_{\text{Pb}}$ 10 <sup>-8</sup> cm	$\Delta S_{\text{VIB}}^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta S_{\text{CONF}}^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta S^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta G^{\text{Ex}}$ kJ·mol <sup>-1</sup>
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

$$U_{\text{XX}}^{\text{Pure}} \quad L_{\text{XX}}^{\text{Pure}}$$

$$\text{kJ} \cdot \text{mol}^{-1} \quad 10^{-8} \text{cm}$$

Cd	-127.6	1.62
Pb	-124.5	1.80

Table 3. Calculated results for  $\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  with the values of  $\Delta H_{\text{MIX}}$  and  $\Delta V^{\text{Ex}}$  at 673 K in liquid Hg – Na alloys.

$x_{\text{Na}}$	$\Delta H_{\text{MIX}}$ kJ·mol <sup>-1</sup>	$\Omega_{\text{HgNa}}$ kJ·mol <sup>-1</sup>	$P$	$U_{\text{Hg}}$ kJ·mol <sup>-1</sup>	$U_{\text{Na}}$ kJ·mol <sup>-1</sup>	$\Delta V^{\text{Ex}}$ cm <sup>3</sup> ·mol <sup>-1</sup>	$L_{\text{HgNa}}$ 10 <sup>-8</sup> 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

$x_{\text{Na}}$	$L_{\text{Hg}}$ 10 <sup>-8</sup> cm	$L_{\text{Na}}$ 10 <sup>-8</sup> cm	$\Delta S_{\text{VIB}}^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta S_{\text{CONF}}^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta S^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta G^{\text{Ex}}$ kJ·mol <sup>-1</sup>
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

$$U_{\text{XX}}^{\text{Pure}} \quad L_{\text{XX}}^{\text{Pure}}$$

$$\text{kJ} \cdot \text{mol}^{-1} \quad 10^{-8} \text{cm}$$

Hg	-113.1	1.67
Na	-61.0	1.99

Table 4. Calculated results for  $\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  with the values of  $\Delta H_{\text{MIX}}$  and  $\Delta V^{\text{Ex}}$  at 1873 K in liquid Fe – Si alloys.

$x_{\text{Si}}$	$\Delta H_{\text{MIX}}$ kJ·mol <sup>-1</sup>	$\Omega_{\text{FeSi}}$ kJ·mol <sup>-1</sup>	$P$	$U_{\text{Fe}}$ kJ·mol <sup>-1</sup>	$U_{\text{Si}}$ kJ·mol <sup>-1</sup>	$\Delta V^{\text{Ex}}$ cm <sup>3</sup> ·mol <sup>-1</sup>	$L_{\text{FeSi}}$ 10 <sup>-8</sup> 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

$x_{\text{Si}}$	$L_{\text{Fe}}$ 10 <sup>-8</sup> cm	$L_{\text{Si}}$ 10 <sup>-8</sup> cm	$\Delta S_{\text{VIB}}^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta S_{\text{CONF}}^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta S^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta G^{\text{Ex}}$ kJ·mol <sup>-1</sup>
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

$$U_{\text{XX}}^{\text{Pure}} \quad L_{\text{XX}}^{\text{Pure}}$$

$$\text{kJ} \cdot \text{mol}^{-1} \quad 10^{-8} \text{cm}$$

Fe	-285.3	1.33
Si	-166.9	1.50

Table 5. Calculated results for  $\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  with the values of  $\Delta H_{\text{MIX}}$  and  $\Delta V^{\text{Ex}}$  at 1823 K in liquid Fe – Cu alloys.

$x_{\text{Cu}}$	$\Delta H_{\text{MIX}}$ kJ·mol <sup>-1</sup>	$\Omega_{\text{FeCu}}$ kJ·mol <sup>-1</sup>	$P$	$U_{\text{Fe}}$ kJ·mol <sup>-1</sup>	$U_{\text{Cu}}$ kJ·mol <sup>-1</sup>	$\Delta V^{\text{Ex}}$ cm <sup>3</sup> ·mol <sup>-1</sup>	$L_{\text{FeCu}}$ 10 <sup>-8</sup> 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

$x_{\text{Cu}}$	$L_{\text{Fe}}$ 10 <sup>-8</sup> cm	$L_{\text{Cu}}$ 10 <sup>-8</sup> cm	$\Delta S_{\text{VIB}}^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta S_{\text{CONF}}^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta S^{\text{Ex}}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta G^{\text{Ex}}$ kJ·mol <sup>-1</sup>
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

$$U_{\text{XX}}^{\text{Pure}} \quad L_{\text{XX}}^{\text{Pure}}$$

$$\text{kJ} \cdot \text{mol}^{-1} \quad 10^{-8} \text{cm}$$

Fe	-285.3	1.33
Cu	-196.5	1.35

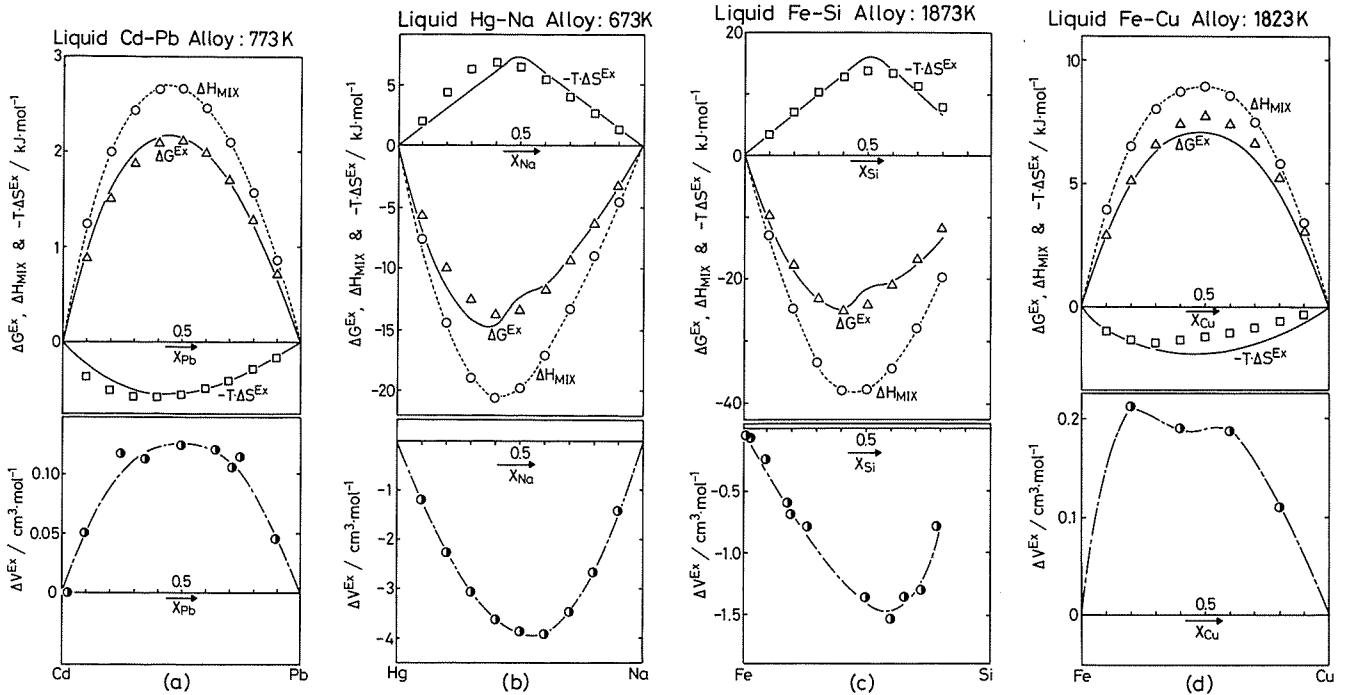


Fig. 2a to d. Calculated results for  $\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  with the experimental values for  $\Delta H_{\text{MIX}}$ ,  $\Delta S^{\text{Ex}}$ ,  $\Delta G^{\text{Ex}}$  and  $\Delta V^{\text{Ex}}$  in liquid binary alloys at temperature indicated (— calculated;  $\cdots \circ \cdots$ ,  $\Delta$ ,  $\square$ ,  $\bullet$  experimental; ---- for  $\Delta V^{\text{Ex}}$ : 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]:

$$N_{AB} = N_0 z x_A x_B \left( 1 - \frac{x_A x_B \Omega_{AB}}{k T} \right) \quad (40)$$

$$\Delta H_{\text{MIX}} = \Omega_{AB} x_A x_B \left( 1 - \frac{x_A x_B \Omega_{AB}}{k T} \right) \quad (41)$$

$$\Delta S_{\text{CONF}}^{\text{Ex}} = - \frac{x_A^2 x_B^2 \Omega_{AB}^2}{2 k T^2} \quad (42)$$

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:

$$U_A = x_A U_{AA} + x_B U_{AB}, \quad U_B = x_B U_{BB} + x_A U_{AB} \quad (43)$$

$$L_A = 1/2 \{ L_{AA} + (x_A L_{AA} + x_B L_{BB}) \} \quad (44)$$

$$L_B = 1/2 \{ L_{BB} + (x_A L_{AA} + x_B L_{BB}) \} \quad (45)$$

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  $L_{AB} = 1/2 (L_{AA} + L_{BB})$  in Eqs. (27) and (28). Then,  $\Delta S_{\text{VIB}}^{\text{Ex}}$  in Eq. (23) is rewritten as follows [10]:

$$\Delta S_{\text{VIB}}^{\text{Ex}} = \frac{3}{2} \cdot k x_A x_B \left[ \frac{(L_{AA} - L_{BB})^2}{L_{AA} L_{BB}} + \left\{ \frac{4 U_{AA} U_{BB} - 2 \Omega_{AB} (U_{AA} + U_{BB}) - (U_{AA} + U_{BB})^2}{2 U_{AA} U_{BB}} \right\} \right] \quad (46)$$

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

$$\Omega_{AB} = \frac{k T}{2 x_A x_B} \left\{ 1 - \left( 1 - \frac{4 \Delta H_{\text{MIX}}}{k T} \right)^{1/2} \right\} \quad (47)$$

Next, it is first assumed that

$$T_{m,A} \approx T_{m,B}, \quad V_A^{\text{Pure}} \approx V_B^{\text{Pure}}, \quad \beta_A = \beta_B = 0.5 \quad (48)$$

The approximate relationship between  $\Delta H_{\text{MIX}}$  and  $\Delta S^{\text{Ex}}$  in Eq. (49) can now be obtained from Eqs. (41), (42) and (46); thus,

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

The calculated results from Eqs. (40) to (47) for  $\Delta S^{\text{Ex}}$  and  $\Delta G^{\text{Ex}}$  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  $\Delta \bar{H}_B$  and the partial excess entropy  $\Delta \bar{S}_B^{\text{Ex}}$  of solute element B can be derived as follows [11 to 14]:

$$\Delta \bar{H}_B = \Omega_{AB} \quad (50)$$

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

wt.%Si	$x_{Si}$	$\rho = A - B \cdot (T - T_L) / g \cdot cm^{-3}$ ( $T_L$ : liquidus temperature)			$V(1873\text{ K})$ $cm^3 \cdot mol^{-1}$	$\Delta V^{Ex}(1873\text{ K})$ $cm^3 \cdot mol^{-1}$	
		A	B $\times 10^3$	$T_L/K$			$\rho$ (1873 K)
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
		$\rho = A - B \cdot T(K) / g \cdot cm^{-3}$			$V_X^{Pure}(1873\text{ K})$ $cm^3 \cdot mol^{-1}$		
		A	B $\times 10^3$	$\rho(1873\text{ K})$			
		Ref. [23]					
Pure Fe		8.586	0.857	6.98	8.00		
Pure Si		3.117	0.352	2.46	11.43		

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

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

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

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]).

$x_{Pb}$	$\rho = A + B T (^{\circ}C) / g \cdot cm^{-3}$				$V(500^{\circ}C)$ $cm^3 \cdot mol^{-1}$	$\Delta V^{Ex}(500^{\circ}C)$ $cm^3 \cdot mol^{-1}$
	A	B $\times 10^3$	$\rho(500^{\circ}C)$	Ref.		
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

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

### 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  $\Delta H_{MIX}$  and  $\Delta S^{Ex}$  is necessary. This problem, however, also requires carefully obtained experimental data since such alloys are near the origin of  $\Delta H_{MIX} - \Delta S^{Ex}$  maps. The absolute values of  $\Delta H_{MIX}$  and  $\Delta S^{Ex}$  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  $\Delta H_{MIX}$  and  $\Delta S^{Ex}$  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  $\nu$  and mass  $m$  ( $= M/N_0$ ), as shown in Fig. 1:

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

$$C = 4 \pi^2 m \nu^2 \quad (A2)$$

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:

$$U = - \frac{2 \pi^2 L^2 M \nu^2}{N_0} \quad (A3)$$

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]:

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



**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  $\Delta V^{\text{Ex}}$  for each composition are obtained by the following equations (A5) and (A6):

$$V = \frac{x_A \cdot M_A + x_B \cdot M_B}{\rho} \quad (\text{A5})$$

$$\Delta V^{\text{Ex}} = V - (x_A \cdot V_A^{\text{Pure}} + x_B \cdot V_B^{\text{Pure}}) \quad (\text{A6})$$

where  $\rho$  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  $V_A^{\text{Pure}}, V_B^{\text{Pure}}$  the molar volumes of components A and B.

The values of  $\Delta V^{\text{Ex}}$  obtained for each alloy are shown in Tables A1–A3 and also in Figs. 2a, c and d. The values of  $\Delta V^{\text{Ex}}$  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],  $\Delta V^{\text{Ex}}$  at 673 K is obtained from the following equation (A7) assuming that the ratio  $\Delta V^{\text{Ex}} / (x_A \cdot V_A^{\text{Pure}} + x_B \cdot V_B^{\text{Pure}})$  at 573 K holds also at 673 K (A = Hg, B = Na):

$$\Delta V^{\text{Ex}}_{673 \text{ K}} = \Delta V^{\text{Ex}}_{573 \text{ K}} \cdot \frac{(x_A \cdot V_A^{\text{Pure}} + x_B \cdot V_B^{\text{Pure}})_{673 \text{ K}}}{(x_A \cdot V_A^{\text{Pure}} + x_B \cdot V_B^{\text{Pure}})_{573 \text{ K}}} \quad (\text{A7})$$

The values of  $\Delta V^{\text{Ex}}$  at 673 K are shown in Table A4 and Figure 2b.

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

$x_{\text{Fe}}$	$\rho = A - B T (\text{K}) / \text{g} \cdot \text{cm}^{-3}$		$V (1823 \text{ K})$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\Delta V^{\text{Ex}} (1823 \text{ K})$ $\text{cm}^3 \cdot \text{mol}^{-1}$	
	$A \cdot B \times 10^3$ Ref. [22]	$\rho (1823 \text{ K})$			
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.

$x_{\text{Na}}$	$V / \text{cm}^3 \cdot \text{mol}^{-1}$ (573 K) Ref. [20]	$\Delta V^{\text{Ex}} / \text{cm}^3 \cdot \text{mol}^{-1}$ (573 K)	$\Delta V^{\text{Ex}} / V_{\text{Add}}$ $\times 100$	$\Delta V^{\text{Ex}} / \text{cm}^3 \cdot \text{mol}^{-1}$ (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

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

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

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

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

1) Eq. (18)

$$\begin{aligned} \text{(Wrong)} \quad \Delta S_{\text{CONF}}^{\text{Ex}} &= -x_A^2 x_B^2 \Omega_{\text{AB}}^2 / 2 k T \\ \text{(Right)} \quad \Delta S_{\text{CONF}}^{\text{Ex}} &= -x_A^2 x_B^2 \Omega_{\text{AB}}^2 / 2 k T^2 \end{aligned}$$

$$\begin{aligned} \text{(Right)} \quad v_{\text{AA}} &= (N_0 k T / 2 \pi M_{\text{AA}} \nu_{\text{AA}}^2)^{3/2} & (28) \\ v_{\text{BB}} &= (N_0 k T / 2 \pi M_{\text{BB}} \nu_{\text{BB}}^2)^{3/2} & (29) \end{aligned}$$

2) Eq. (20)

$$\begin{aligned} \text{(Wrong)} \quad U_{\text{A}} &= x_{\text{A}} U_{\text{AA}} + x_{\text{A}} U_{\text{AB}}, \quad U_{\text{B}} = x_{\text{B}} U_{\text{BB}} \\ &\quad + x_{\text{A}} U_{\text{AB}} \\ \text{(Right)} \quad U_{\text{A}} &= x_{\text{A}} U_{\text{AA}} + x_{\text{B}} U_{\text{AB}}, \quad U_{\text{B}} = x_{\text{B}} U_{\text{BB}} \\ &\quad + x_{\text{A}} U_{\text{AB}} \end{aligned}$$

5) Eqs. (30) and (31)

$$\begin{aligned} \text{(Wrong)} \quad U_{\text{AA}} &= -2 \pi^2 R_{\text{AA}}^2 M_{\text{AA}} \nu_{\text{AA}}^2 & (30) \\ U_{\text{BB}} &= -2 \pi^2 R_{\text{BB}}^2 M_{\text{BB}} \nu_{\text{BB}}^2 & (31) \\ \text{(Right)} \quad U_{\text{AA}} &= -2 \pi^2 R_{\text{AA}}^2 M_{\text{AA}} \nu_{\text{AA}}^2 / N_0 & (30) \\ U_{\text{BB}} &= -2 \pi^2 R_{\text{BB}}^2 M_{\text{BB}} \nu_{\text{BB}}^2 / N_0 & (31) \end{aligned}$$

3) Eq. (23)

$$\begin{aligned} \text{(Wrong)} \quad \Delta S_{\text{VIB}}^{\text{Ex}} &= 3/2 \cdot k x_{\text{A}} x_{\text{B}} [(R_{\text{AA}} - R_{\text{BB}})^2 \\ &\quad / R_{\text{AA}} R_{\text{BB}} + \{2 U_{\text{AA}} U_{\text{BB}} - U_{\text{AB}} \\ &\quad (U_{\text{AA}} + U_{\text{BB}})\} U_{\text{AA}} U_{\text{BB}}] \\ \text{(Right)} \quad \Delta S_{\text{VIB}}^{\text{Ex}} &= 3/2 \cdot k x_{\text{A}} x_{\text{B}} [(R_{\text{AA}} - R_{\text{BB}})^2 \\ &\quad / R_{\text{AA}} R_{\text{BB}} + \{2 U_{\text{AA}} U_{\text{BB}} - U_{\text{AB}} \\ &\quad (U_{\text{AA}} + U_{\text{BB}}) / U_{\text{AA}} U_{\text{BB}}] \end{aligned}$$

6) Eqs. (37)

$$\begin{aligned} \text{(Wrong)} \quad \Omega_{\text{AB}} &= k T \{1 - (1 + 4 \Delta H_{\text{MIX}} / k T)^{1/2}\} \\ &\quad / 2 x_{\text{A}} x_{\text{B}} \\ \text{(Right)} \quad \Omega_{\text{AB}} &= k T \{1 - (1 - 4 \Delta H_{\text{MIX}} / k T)^{1/2}\} \\ &\quad / 2 x_{\text{A}} x_{\text{B}} \end{aligned}$$

4) Eqs. (28) and (29)

$$\begin{aligned} \text{(Wrong)} \quad v_{\text{AA}} &= (k T / 2 \pi M_{\text{AA}} \nu_{\text{AA}}^2)^{3/2} & (28) \\ v_{\text{BB}} &= (k T / 2 \pi M_{\text{BB}} \nu_{\text{BB}}^2)^{3/2} & (29) \end{aligned}$$

7) Table 2

$$\begin{aligned} \text{(Wrong)} \quad \text{The values of } \Delta S^{\text{Ex}}: & -1.84 (x_{\text{Zn}} = 0.80), \\ & -1.36 (x_{\text{Zn}} = 0.90) \\ \text{(Right)} \quad \text{The values of } \Delta S^{\text{Ex}}: & -0.84 (x_{\text{Zn}} = 0.80), \\ & -0.36 (x_{\text{Zn}} = 0.90) \end{aligned}$$