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Author(s)	Tanaka, Toshihiro; Gokcen, N.A.; Morita, Z.
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Relationship Between Enthalpy of Mixing and Excess Entropy in Liquid Binary Alloys

Toshihiro Tanaka*, N. A. Gokcen**, and Z. Morita*

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

A thermodynamic solution model for liquid binary alloys has been derived on the basis of free volume theory. This model can evaluate the excess entropy of mixing from the enthalpy of mixing in liquid binary alloys. The calculated values of excess entropy, excess Gibbs energy and activities of the elements are in good agreement with the experimental data of various alloy systems. It is shown from this model that the relationship between enthalpy of mixing and excess entropy in liquid binary alloys is dependent upon temperature.

Zusammenhang zwischen Mischungsenthalpien und Überschußentropien in flüssigen binären Legierungen

Ein thermodynamisches Modell für flüssige binäre Legierungen ist mit der Theorie des freien Volumens abgeleitet worden. Dieses Modell gestattet es, Überschußentropien aus Mischungsenthalpien der flüssigen binären Legierungen zu berechnen. Die theoretische Voraussage von Überschußentropien, freien Überschußmischungsenthalpien und Aktivitäten der Elemente stimmt mit experimentellen Werten in verschiedenen flüssigen binären Systemen überein. Es konnte gezeigt werden, daß die Beziehung zwischen Mischungsenthalpien und Überschußentropien in flüssigen binären Legierungen von der Temperatur abhängig ist.

1 Introduction

A significant amount of research on the thermodynamic properties in liquid alloys has been carried out experimentally and also theoretically. Recently, several empirical attempts^{1) to 8)} have been made to correlate the enthalpy of mixing ΔH_{MIX} and excess entropy ΔS^{Ex} in liquid binary alloys. For example, Kubaschewski⁴⁾ has obtained the following relationship between partial enthalpy ΔH_X^{MIX} and partial entropy ΔS_X^{Ex} of solute elements in dilute solutions.

$$\Delta H_X^{\text{MIX}} = 3400 \Delta S_X^{\text{Ex}} \quad (1)$$

Lupis⁷⁾ has also proposed the following similar relationship:

$$\Delta H_X^{\text{MIX}} = \tau \Delta S_X^{\text{Ex}} \quad (2)$$

In this equation, τ is constant and a value of 3000 ± 1000 K for this parameter has been proposed for ordinary metallic solutions. However, Lupis suggested that τ is not always constant for all types of alloys and it might be dependent upon the nature of the elements involved in the alloy. Figure 1 shows a plot of maximum values of ΔH_{MIX} against ΔS^{Ex} at the same composition. The values of ΔH_{MIX} and ΔS^{Ex} are taken from the compilation by Kubaschewski and Alcock²⁾. As shown in this figure, the relationship between ΔH_{MIX} and ΔS^{Ex} seems to be dependent upon temperature. Kubaschewski¹⁾ considered boiling points of component metals, $T_{b,A}$ and $T_{b,B}$, as one of the physical properties of constituents in alloys and obtained another empirical relationship as follows:

$$\Delta S^{\text{Ex}} = 0.64 \Delta H_{\text{MIX}} / 0.5 (T_{b,A} + T_{b,B}) \quad (3)$$

On the other hand, Williams⁸⁾ considered contributions of the configuration and the vibration of atoms in alloys for excess entropy to explain the relationship between ΔH_{MIX} and ΔS^{Ex} . The coefficients of each contribution, however, were determined by parameter-fitting method with experimental values. Therefore, the physical meanings of each

term are not clear, and the physical properties of elements involved in alloy systems have not been adequately taken into account.

The purpose of this work is to derive a thermodynamic model to evaluate the excess entropy and enthalpy of mixing based on the configuration and vibration of atoms in alloys from the free volume theory⁹⁾ and the first approximation of regular solution model¹⁰⁾. On the basis of the model, the relationship between enthalpy of mixing and excess entropy in liquid binary alloys is discussed together with the physical properties of each element in alloys.

2 Derivation of Thermodynamic Equations

In this work, the relationship between the enthalpy of mixing ΔH_{MIX} and the excess entropy ΔS^{Ex} is discussed on the

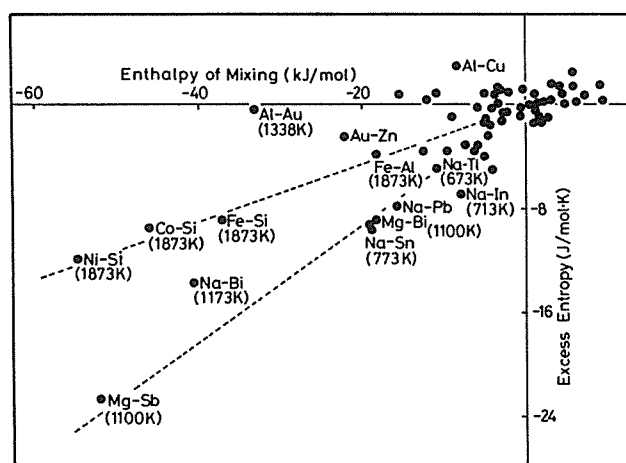


Fig. 1. Relationship between enthalpy of mixing and excess entropy in liquid binary alloys.

basis of the free volume theory advanced by Shimoji and Niwa⁹). Assuming that an atom vibrates harmonically in its cell surrounded by the nearest-neighbour atoms, the partition functions for pure liquid A and B, Q_{AA} and Q_{BB} , are given by the following equations.

$$Q_{AA} = v_A^{N_A} \cdot \exp(-E_A/kT) \\ = \{-\pi R_{AA}^2 kT/U_{AA}\}^{3/2 N_A} \cdot \exp(-N_A \cdot U_{AA}/2 kT) \quad (4)$$

$$Q_{BB} = v_B^{N_B} \cdot \exp(-E_B/kT) \\ = \{-\pi R_{BB}^2 kT/U_{BB}\}^{3/2 N_B} \cdot \exp(-N_B \cdot U_{BB}/2 kT) \quad (5)$$

v_A, v_B : free volumes of A and B atoms in pure liquid.
 R_{AA}, R_{BB} : distance which interatomic potential extends in cells of pure liquid A and B respectively, as shown in Fig. 2.
 U_{AA}, U_{BB} : depth of potential energy in cells of pure liquid A and B respectively, as shown in Fig. 2.
 $U_{AA} = Z \cdot u_{AA}, U_{BB} = Z \cdot u_{BB}$
 u_{AA}, u_{BB} : energies of A – A and B – B pairs, respectively.
 Z : coordination number.
 N_A, N_B : number of A and B atoms.
 k : Boltzmann constant.
 T : temperature in K.

Partition function of A – B binary alloy is

$$Q = g \cdot \{-\pi R_A^2 kT/U_A\}^{3/2 N_A} \{-\pi R_B^2 kT/U_B\}^{3/2 N_B} \\ \cdot \exp\{-(N_A \cdot U_A + N_B \cdot U_B)/2 kT\} \quad (6)$$

g : degeneracy factor.

R_A, R_B : distances which interatomic potential of A and B atoms extend in cells of A – B binary alloy.

U_A, U_B : depth of potential energy of A and B atoms in cell of A – B binary alloy.

The energy $E = (N_A U_A + N_B U_B)/2$ of A – B binary alloy in Eq. (6) can be expressed in terms of pair interaction energy of A – A, B – B and A – B, namely, u_{AA}, u_{BB} and u_{AB} as follows:

$$E = N_A U_{AA}/2 + N_B U_{BB}/2 + N_{AB} \Omega_{AB}/Z \quad (7)$$

$$U_{AA} = Z u_{AA}, U_{BB} = Z u_{BB}$$

N_{AB} : number of A – B pairs.

$$\Omega_{AB} = Z \{u_{AB} - 1/2 \cdot (u_{AA} + u_{BB})\}; \text{ exchange energy} \quad (8)$$

For condensed systems and at ordinary pressure levels, the Gibbs energy may be assumed to be equivalent to the Helmholtz energy, because their difference, the term PV , is usually negligible. Thus, for all practical purposes⁷),

$$G_{AA} \sim F_{AA} = -kT \ln Q_{AA} \quad (9)$$

$$G_{BB} \sim F_{BB} = -kT \ln Q_{BB} \quad (10)$$

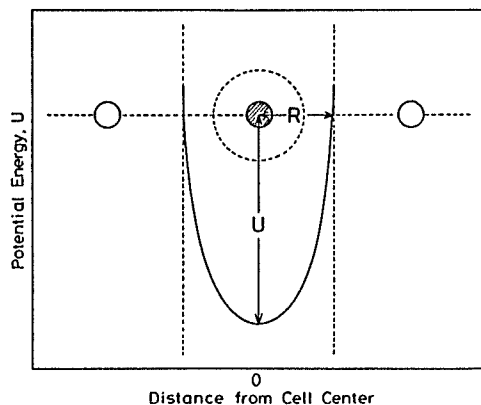


Fig. 2. Interatomic potential in a cell.

$$G \sim F = -kT \ln Q \quad (11)$$

From the above equations, the change in Gibbs energy of mixing, ΔG_{MIX} , is

$$\Delta G_{MIX} = G - (G_{AA} + G_{BB}) \\ = N_{AB} \Omega_{AB}/Z - kT \ln g \\ - kT \cdot 3/2 \cdot [N_A \ln(-\pi R_A^2 kT/U_A) \\ + N_B \ln(-\pi R_B^2 kT/U_B) \\ - \{N_A \ln(-\pi R_{AA}^2 kT/U_{AA}) \\ + N_B \ln(-\pi R_{BB}^2 kT/U_{BB})\}] \quad (12)$$

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

2.1 Enthalpy Term

From Eq. (12),

$$\Delta H_{MIX}^i = \Delta H^{Ex} = N_{AB} \Omega_{AB}/Z \quad (13)$$

As regards the configuration of atoms in alloys, short range order is taken into account on the basis of the first approximation to the regular solutions proposed by one of the authors¹⁰). According to this model, N_{AB} is given by the following equation for dilute solutions:

$$N_{AB} = Z \cdot N_O x_A x_B (1 - x_A x_B \Omega_{AB}/kT) \quad (14)$$

N_O : Avogadro's number

x_A, x_B : mole fractions of A and B, respectively.

Consequently, the enthalpy of mixing per mole $\Delta H_{MIX} = \Delta H_{MIX}^i/N_O$ can be given by the following equation:

$$\Delta H_{MIX} = \Omega_{AB} x_A x_B (1 - x_A x_B \Omega_{AB}/kT) \quad (15)$$

2.2 Entropy Term

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

$$\Delta S_{CONF} = -k \ln g \\ = \Delta S_{CONF}^{Ideal} + \Delta S_{CONF}^{Ex} \quad (16)$$

In this equation, ΔS_{CONF}^{Ideal} is the ideal entropy of mixing, given by

$$\Delta S_{CONF}^{Ideal} = -k (x_A \ln x_A + x_B \ln x_B) \quad (17)$$

For excess entropy arising from configuration of atoms in alloys, the following equation based on the first approximation to the regular solutions¹⁰) was also adopted

$$\Delta S_{CONF}^{Ex} = -x_A^2 x_B^2 \Omega_{AB}^2 / 2 kT \quad (18)$$

Excess entropy arising from vibration of atoms ΔS_{VIB}^{Ex} can be derived from Eq. (12), i. e.,

$$\Delta S_{VIB}^{Ex} = 3/2 \cdot k N_O \{2x_A \ln(R_A/R_{AA}) \\ + 2x_B \ln(R_B/R_{BB}) \\ + x_A \ln(U_{AA}/U_A) + x_B \ln(U_{BB}/U_B)\} \quad (19)$$

In order to evaluate ΔS_{VIB}^{Ex} in the above equation, it is necessary to have information on R_A, R_B, U_A and U_B in A – B binary alloy. In this work, the simplest relations were adopted from Shimoji and Niwa, i. e., the random distribution of atoms is assumed with the following equations:

$$U_A = x_A U_{AA} + x_A U_{AB}, U_B = x_B U_{BB} + x_A U_{AB} \quad (20)$$

$$U_{AB} = Z \cdot u_{AB}$$

$$R_A = 1/2 \{R_{AA} + (x_A R_{AA} + x_B R_{BB})\} \quad (21)$$

$$R_B = 1/2 \{R_{BB} + (x_A R_{AA} + x_B R_{BB})\} \quad (22)$$

Finally, the excess entropy for vibration of atoms per mole, $\Delta S_{\text{VIB}}^{\text{Ex}} = \Delta S_{\text{VIB}}^{\text{Ex}}/N_O$, is given by

$$\Delta S_{\text{VIB}}^{\text{Ex}} = 3/2 \cdot k x_A x_B [(R_{AA} - R_{BB})^2/R_{AA} R_{BB} + \{2U_{AA}U_{BB} - U_{AB}(U_{AA} + U_{BB})\} U_{AA}U_{BB}] \quad (23)$$

It is quite difficult to evaluate U_{AB} in Eq. (23) from the physical quantities for the components of A - B alloy; hence $\Delta S_{\text{VIB}}^{\text{Ex}}$ cannot be calculated. It is therefore proposed that U_{AB} from Eq. (8) be used for this purpose, i. e.,

$$U_{AB} = \Omega_{AB} + (U_{AA} + U_{BB})/2 \quad (24)$$

Consequently,

$$\begin{aligned} \Delta S_{\text{VIB}}^{\text{Ex}} = & 3/2 \cdot k x_A x_B [(R_{AA} - R_{BB})^2/R_{AA} R_{BB} \\ & + \{4U_{AA}U_{BB} - 2\Omega_{AB}(U_{AA} + U_{BB}) \\ & - (U_{AA} + U_{BB})^2\}/2U_{AA}U_{BB}] \end{aligned} \quad (25)$$

In the preceding equations, all of the quantities except Ω_{AB} belong to the pure elements. Thus, if the value of Ω_{AB} can be obtained from the enthalpy of mixing ΔH_{MIX} , then $\Delta S_{\text{VIB}}^{\text{Ex}}$ can be calculated from Eq. (25). It is obvious from Eq. (14), (15) and (25) that ΔH_{MIX} is related to ΔS^{Ex} through Ω_{AB} .

In this work, we correlate the depth of potential energy in each cell of pure elements, U_{AA} and U_{BB} in Eq. (25), with other physical quantities. If an atom vibrates harmonically in its cell of a pure element, then the free volumes v_{AA} and v_{BB} are expressed by⁷⁾

$$v_{AA} = (-\pi R_{AA}^2 k T / U_{AA})^{3/2} \quad (26)$$

$$v_{BB} = (-\pi R_{BB}^2 k T / U_{BB})^{3/2} \quad (27)$$

On the other hand, the free volumes v_{AA} and v_{BB} can also be given by the following equations¹¹⁾:

$$v_{AA} = (kT/2\pi M_{AA} v_{AA}^2)^{3/2} \quad (28)$$

$$v_{BB} = (kT/2\pi M_{BB} v_{BB}^2)^{3/2} \quad (29)$$

M_{AA} and M_{BB} : atomic weights of A and B.

v_{AA} and v_{BB} : frequencies of A and B in pure liquid.

From Eqs. (26) to (29)

$$U_{AA} = -2\pi^2 R_{AA}^2 M_{AA} v_{AA}^2 \quad (30)$$

$$U_{BB} = -2\pi^2 R_{BB}^2 M_{BB} v_{BB}^2 \quad (31)$$

Substitution of Eqs. (30) and (31) into Eq. (25) gives

$$\begin{aligned} \Delta S_{\text{VIB}}^{\text{Ex}} = & 3/2 k x_A x_B \{(R_{AA} - R_{BB})^2/R_{AA} R_{BB} + 2 \\ & + \Omega_{AB} (R_{AA}^2 M_{AA} v_{AA}^2 + R_{BB}^2 M_{BB} v_{BB}^2) \\ & / 2\pi^2 R_{AA}^2 R_{BB}^2 M_{AA} M_{BB} v_{AA}^2 v_{BB}^2 \\ & - (R_{AA}^2 M_{AA} v_{AA}^2 + R_{BB}^2 M_{BB} v_{BB}^2)^2 \\ & / 2R_{AA}^2 R_{BB}^2 M_{AA} M_{BB} v_{AA}^2 v_{BB}^2\} \end{aligned} \quad (32)$$

From the foregoing equation, $\Delta S_{\text{VIB}}^{\text{Ex}}$ can be calculated from Ω_{AB} obtained from ΔH_{MIX} when the values of R_{AA} , R_{BB} , M_{AA} , M_{BB} , v_{AA} and v_{BB} are known. M_{AA} and M_{BB} are the atomic weights and R_{AA} and R_{BB} , the distances in the cells for the potential energy and assumed to be half of the nearest-neighbour distance, r_{AA} and r_{BB} ¹²⁾, thus, $R_{AA} = 1/2 r_{AA}$ and

$R_{BB} = 1/2 r_{BB}$. The values of r_{AA} and r_{BB} can be obtained from molar volumes of pure elements V_{AA} and V_{BB} in the following way if a closepacked structure can be assumed in liquid metal.

$$r_{AA} = (2^{1/2} V_{AA}/N_O)^{1/3} \quad (33)$$

$$r_{BB} = (2^{1/2} V_{BB}/N_O)^{1/3} \quad (34)$$

Values of v_{AA} and v_{BB} can be obtained from the following revised Lindemann's equations¹²⁾ if frequency at temperature T could be assumed to be equal to that at the melting point of each pure element.

$$v_{AA} = 2.8 \cdot 10^{12} \beta_A (T_{m,A}/M_{AA} V_{AA}^{2/3})^{1/2} \quad (35)$$

$$v_{BB} = 2.8 \cdot 10^{12} \beta_B (T_{m,B}/M_{BB} V_{BB}^{2/3})^{1/2} \quad (36)$$

$T_{m,A}$ and $T_{m,B}$: melting points of pure elements A and B. β_A and β_B : correction coefficients to transform the frequency in solid into that in liquid at the melting point.

Since Lindemann's equation gives the frequency at the melting point in solid, coefficients β_A and β_B are necessary to obtain the frequency in liquid state. To a good approximation, β can be set to 0.5 for elements¹²⁾ having no data for β .

As mentioned above, if the value of Ω_{AB} can be estimated by any method, e. g. Miedema's semi-empirical rules¹³⁾, all the thermodynamic quantities can be calculated from the preceding equations. However, we focus on the relationship between ΔH_{MIX} and $\Delta S^{\text{Ex}} (= \Delta S_{\text{CONF}}^{\text{Ex}} + \Delta S_{\text{VIB}}^{\text{Ex}})$ in this work and the obtain Ω_{AB} from measured values of ΔH_{MIX} . Thus, from Eq. (15), Ω_{AB} can be expressed as

$$\Omega_{AB} = kT \{1 - (1 + 4\Delta H_{\text{MIX}}/kT)^{1/2}\}/2x_A x_B \quad (37)$$

In Eq. (37), the value of Ω_{AB} can be obtained from measured values of ΔH_{MIX} at each composition. Then, $\Delta S_{\text{CONF}}^{\text{Ex}}$ and $\Delta S_{\text{VIB}}^{\text{Ex}}$ can be calculated from Eqs. (32) to (37). Furthermore, excess Gibbs energy ΔG^{Ex} and activity of element X, a_x , may also be evaluated. However, Ω_{AB} for alloys with $\Delta H_{\text{MIX}} > 0$ can be obtained from

$$1 > 4 \cdot \Delta H_{\text{MIX}}/kT \quad (38)$$

Therefore, for these alloys, the configuration of atoms is assumed to be random and the calculation of ΔS^{Ex} and ΔG^{Ex} is carried out by the following equations:

$$\Omega_{AB} = \Delta H_{\text{MIX}}/x_A x_B \quad (39)$$

$$\Delta S^{\text{Ex}} = \Delta S_{\text{VIB}}^{\text{Ex}}; (\Delta S_{\text{CONF}}^{\text{Ex}} = 0) \quad (40)$$

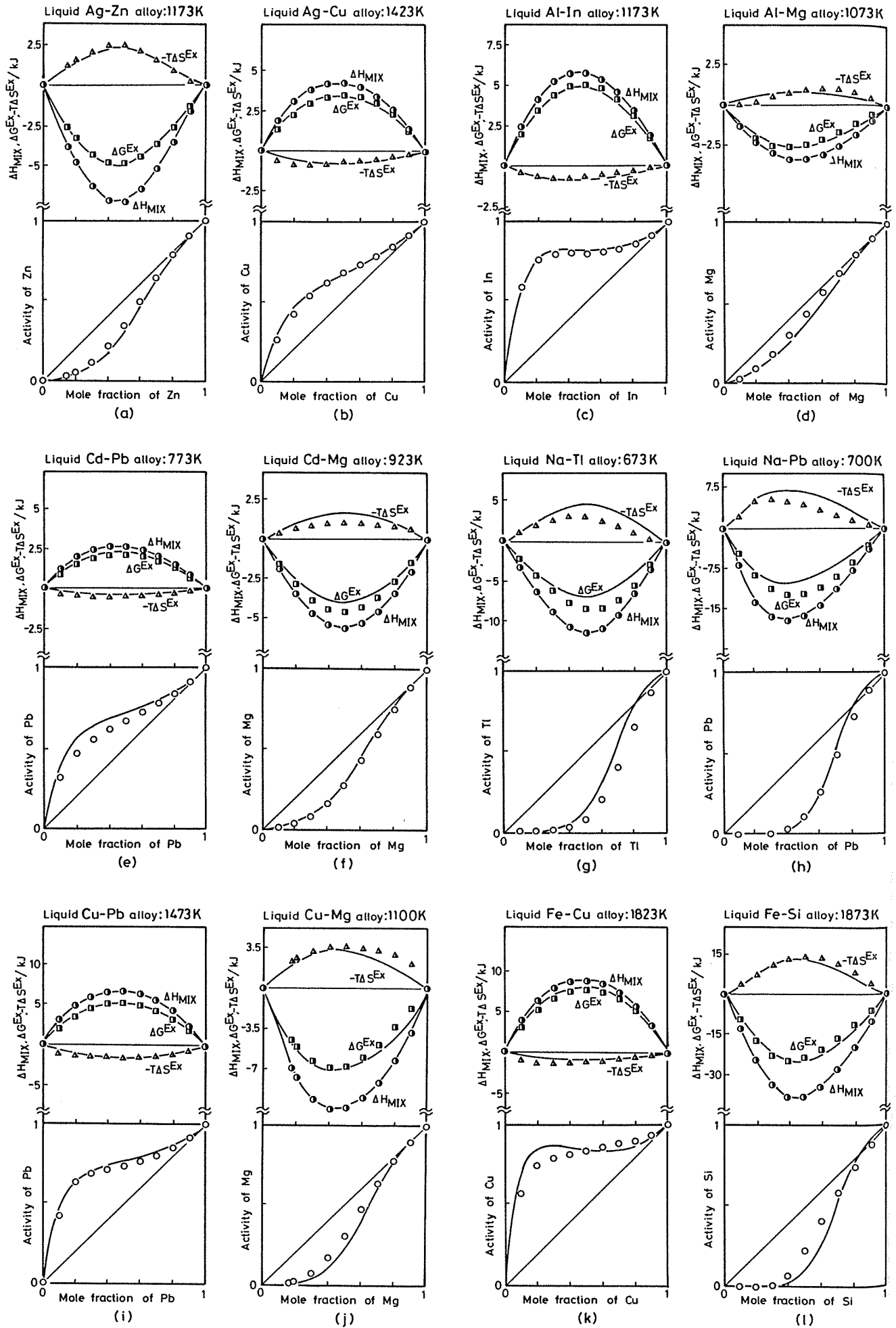
$$\Delta G^{\text{Ex}} = \Delta H_{\text{MIX}} - T \Delta S_{\text{VIB}}^{\text{Ex}} \quad (41)$$

3 Calculation of ΔS^{Ex} , ΔG^{Ex} and a_x in Liquid Binary Alloys and Discussion on Validity of the Present Model

In this section, ΔS^{Ex} , ΔG^{Ex} and a_x in various liquid binary alloys were calculated from measured values of ΔH_{MIX} on the basis of the present thermodynamic model and then the validity of this model is discussed.

Table 1 shows physical quantities of several elements needed for calculation of ΔS^{Ex} . For ΔH_{MIX} , values selected by Hultgren et al.¹⁴⁾ were adopted. Measured values of ΔS^{Ex} , ΔG^{Ex} and a_x presented in Hultgren et al. were also used for comparison with the calculated results in this work.

As an example, the calculated results for ΔS^{Ex} , ΔG^{Ex} and a_x in liquid binary Ag-Zn system are shown in Table 2. First, the



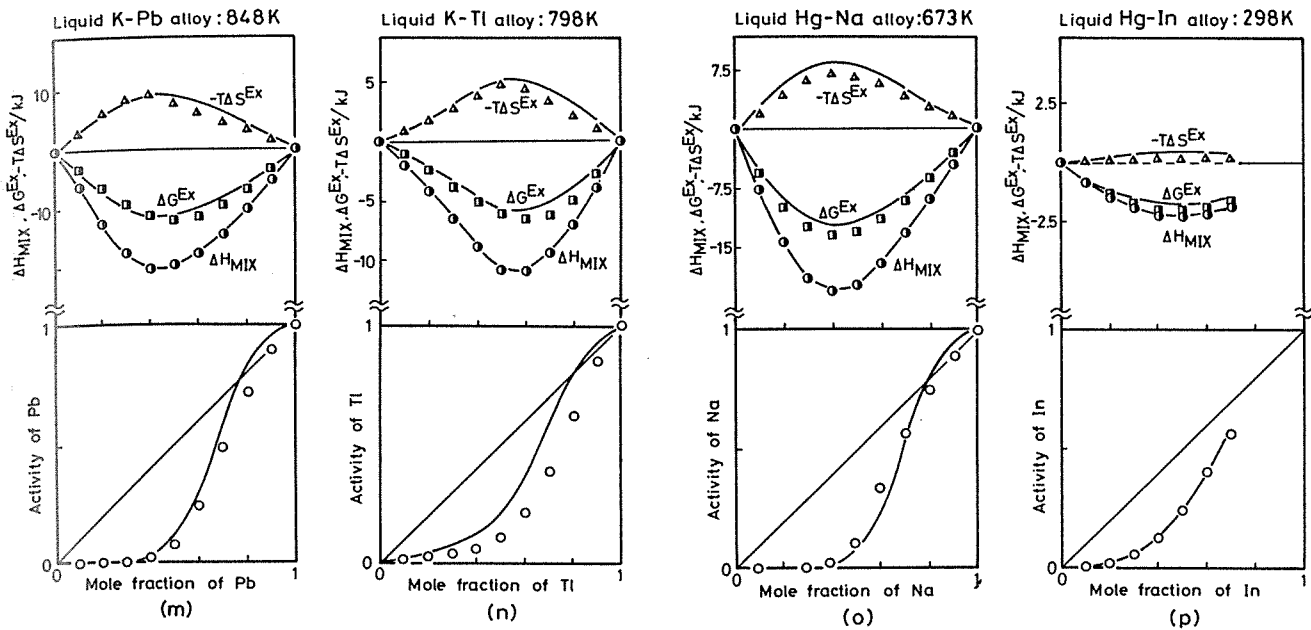


Fig. 3a to p. Comparison of calculated results for excess entropy, excess Gibbs energy and activity with experimental data in liquid binary alloys at the temperature indicated. (—: calc. ●, □, ▲, ○: exp.)

values of $\Omega_{\text{Ag-Zn}}$ were calculated from ΔH_{MIX} at each composition in Hultgren et al. with Eq. (37). Then, using Eqs. (15) and (32) to (37), ΔS^{Ex} was evaluated from $\Omega_{\text{Ag-Zn}}$ and other quantities shown in Table 1. Further, ΔG^{Ex} and a_x were also calculated. Figure 3a shows a comparison of the calculated results for ΔS^{Ex} , ΔG^{Ex} and a_x with the experimental data for this system. As is obvious from this figure, the calculated results are in good agreement with the experimental data. In the same way, ΔS^{Ex} , ΔG^{Ex} and a_x in other liquid bin-

ary alloys were calculated and the results are shown in Figs. 3b to p together with the experimental values. It is obvious from these figures that the calculated and experimental values are in good agreement in various alloys. Especially, for alloys which show $\Delta H_{\text{MIX}} > 0$, it seems to be sufficient to consider the vibrational contribution to ΔS^{Ex} . On the other hand, some of the alloys indicating large negative values of ΔH_{MIX} show strange activity curves in the high solute concentration region. Thus, more strict equations for short range order configuration of atoms have to be used for these alloys.

Table 1. Physical quantities used in the calculation of excess entropy. M_x : atomic weight (g/mol), V_x : molar volume (cm^3/mol), $T_{m,x}$: melting point (K), and β_x : correction factor.

Elements	M_x	V_x	$T_{m,x}$	β_x
Ag	107.9	10.27	1234	0.47
Al	27.0	10.00	993	0.52
Cd	112.4	13.00	594	0.55
Cu	63.5	7.11	1356	0.45
Fe	55.9	7.09	1809	0.49
Hg	200.6	14.09	234	0.84
In	114.8	15.73	430	0.68
K	39.1	45.61	336	0.46
Mg	24.3	14.00	922	0.45
Na	22.5	23.79	371	0.49
Pb	207.2	18.27	600	0.55
Si	28.1	12.07	1685	0.50
Tl	204.4	17.22	577	0.56
Zn	65.4	9.17	693	0.54

4 Relationship Between ΔH_{MIX} and ΔS^{Ex}

As stated above, ΔH_{MIX} and ΔS^{Ex} are related to each other by Eqs. (14), (15) and (25). Figure 4 shows the relationship between ΔH_{MIX} and ΔS^{Ex} at $x_A = x_B$ obtained by the present calculation. This figure appears to show a temperature dependence of the relationship between ΔH_{MIX} and ΔS^{Ex} . This temperature dependence can be confirmed by the following treatment. Thus, considering the alloys with small absolute values of $\Omega_{\text{A-B}}$ and small differences of atomic weights and nearest-neighbour distances, Eqs. (15), (18) and (32) can be transformed into the following approximate equations:

$$\Delta H_{\text{MIX}} = x_A x_B \Omega_{\text{A-B}} \quad (42)$$

$$\Delta S_{\text{CONF}}^{\text{Ex}} = 0 \quad (43)$$

Table 2. Calculated results for excess entropy, excess Gibbs energy and activity in liquid Ag-Zn binary alloy at 1173 K.

x_{Zn}	ΔH_{MIX} (J/mol)	$\Omega_{\text{Ag-Zn}}$ (J/mol)	$\Delta S_{\text{VIB}}^{\text{Ex}}$ (J/mol · K)	$\Delta S_{\text{CONF}}^{\text{Ex}}$ (J/mol · K)	ΔS^{Ex} (J/mol · K)	ΔG^{Ex} (J/mol)	a_{Zn}
0.15	-3800	-22900	-0.53	-0.37	-0.90	-2750	0.02
0.20	-4810	-22000	-0.64	-0.55	-1.19	-3420	0.04
0.30	-6370	-20900	-0.80	-0.84	-1.64	-4440	0.09
0.40	-7230	-20100	-0.88	-1.02	-1.90	-4990	0.17
0.50	-7300	-19400	-0.90	-1.04	-1.94	-5030	0.30
0.60	-6560	-18700	-0.83	-0.88	-1.71	-4550	0.46
0.70	-5220	-17900	-0.70	-0.62	-1.32	-3670	0.62
0.80	-3500	-17000	-0.51	-0.33	-1.84	-2510	0.77
0.90	-1620	-15600	-0.27	-0.09	-1.36	-1200	0.90

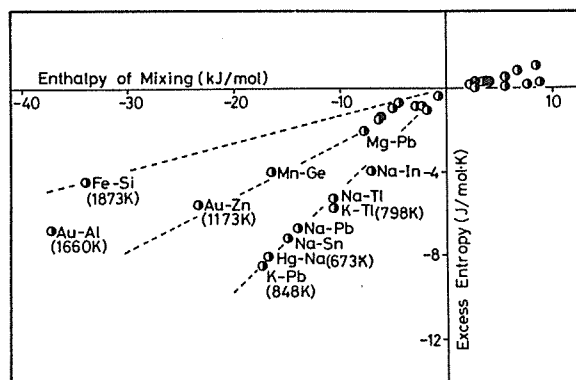


Fig. 4. Relationship between ΔH_{MIX} and ΔS^{Ex} in liquid binary alloys, calculated from the present model.

$$\Delta S_{\text{VIB}}^{\text{Ex}} \propto x_A x_B \Omega_{A-B} (1/T_{m,A} + 1/T_{m,B}) \quad (44)$$

From the above equations, ΔH_{MIX} and ΔS^{Ex} are related by

$$\Delta S^{\text{Ex}} \propto \Delta H_{\text{MIX}} (1/T_{m,A} + 1/T_{m,B}) \quad (45)$$

Then, Fig. 4 can be reconstructed by using Eq. (45) as shown in Fig. 5, wherein most of the alloys seem to fall onto a linear relation. This means that the relationship between ΔH_{MIX} and ΔS^{Ex} are dependent upon melting points of the components. Thus, the temperature dependence of the empirical relationship shown in Fig. 1 can be explained thermodynamically by the present model.

5 Some Problems in Present Model

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

- 1) A more satisfactory treatment of alloys which show complicated behaviour of thermodynamic properties versus compositions.
- 2) In alloys showing large negative values of ΔH_{MIX} , more appropriate short range order configuration of atoms have to be considered.
- 3) A better treatment of alloys exhibiting the different signs between ΔH_{MIX} and ΔS^{Ex} is necessary. However, this problem also requires careful experimental investigation. Such alloys are near the origin of $\Delta H_{\text{MIX}} - \Delta S^{\text{Ex}}$ maps. Therefore, considering the difficulties of thermodynamic experiments, some unreliable experimental values might pose unexpected obstacles in correlating ΔH_{MIX} and ΔS^{Ex} .

7 Summary

In this work, a thermodynamic model was derived on the basis of the free volume theory and the first approximation to the regular solutions. The model is capable of evaluating the excess entropy from the enthalpy of mixing of liquid

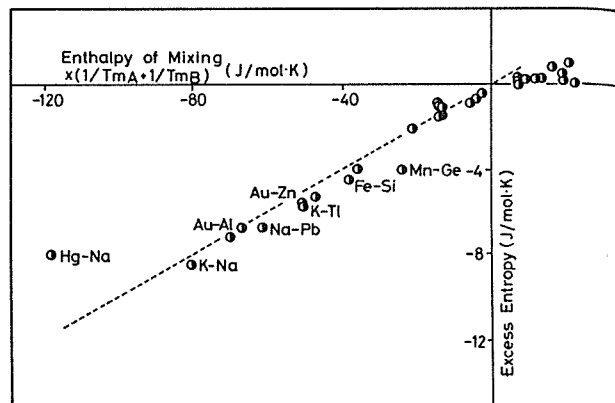


Fig. 5. Relationship between ΔH_{MIX} , $(1/T_{m,A} + 1/T_{m,B})$ and ΔS^{Ex} in liquid binary alloys, calculated from the present model.

binary alloys. The calculated results were discussed and compared with the experimental data. The results obtained are summarized as follows.

- 1) Values of ΔS^{Ex} could be estimated from ΔH_{MIX} , and the ΔG^{Ex} and a_x were obtained in various liquid binary alloys. The calculated results for ΔS^{Ex} , ΔG^{Ex} and a_x were in good agreement with the experimental data on various liquid binary alloys.
- 2) The relationship between ΔH_{MIX} and ΔS^{Ex} was explained by considering configuration and vibration of atoms in alloys on the basis of the present model. It was shown that the relationship between ΔH_{MIX} and ΔS^{Ex} in liquid binary alloys depends on the melting points of component elements.

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