Use of Thermodynamic Data to Determine Surface Tension and Viscosity of Metallic Alloys

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Introduction

During the last three decades, various thermodynamic databases have been compiled to be applied mainly to the calculation of phase diagrams of alloys, salts, and oxides.[1] The accumulation and assessment of thermodynamic data and phase-equilibrium information to establish those databases is sometimes called the CALPHAD (calculated phase diagram) approach.[2] The CALPHAD approach has been recognized as useful in various aspects of materials science and engineering.[1,2] In addition to the use of thermodynamic databases for the calculation of phase diagrams, it would be very desirable to apply them to the calculation of other physicochemical quantities, such as surface tension. By doing this, not only can the utility of databases be enlarged, but also a deeper understanding of the physical properties in question can be reached.

On the basis of the concepts just mentioned, we have applied those thermodynamic databases to the calculation of the surface tension of liquid alloys and molten ionic mixtures.[3-7] In these calculations, we have applied Butler's equation[8] for the surface tension of liquid alloys. In addition, we have modified Butler's equation to be extended to molten ionic mixtures by considering the relaxation structure in the surface. These approaches will lead us to develop a multifunctional data-bank system that will be widely applicable in the evaluation of physicochemical properties of liquid alloys and molten ionic mixtures from thermodynamic data.

In this article, we explain some physical models for the surface tension and viscosity of liquid alloys and molten ionic mixtures, in which thermodynamic data can be directly applied to evaluate these physical properties. In addition, the concept for the just-mentioned multifunctional thermodynamic data-bank system will be described by demonstrating the simultaneous calculation of phase diagrams, surface tension, and viscosity of some alloys used for new, Pb-free soldering materials.

Butler's Equation for Calculating Surface Tension of A-B Binary Liquid Alloys

Several authors[3,4,9-17] have proposed calculations of surface tension of liquid alloys by employing thermodynamic data, as shown in Table I. Their principles are based on Butler's equation,[8] which is expressed for surface tension σ of any A-B binary liquid alloy as follows:

$$\sigma = \sigma_A + \frac{RT}{A_A} \ln \frac{(1 - N_B^S)}{(1 - N_B^B)}$$

$$+ \frac{1}{A_A} \overline{G}_A^{E,S}(T, N_B^S) - \frac{1}{A_A} \overline{G}_A^{E,B}(T, N_B^B)$$

$$= \sigma_B + \frac{RT}{A_B} \ln \frac{N_B^S}{N_B^B} + \frac{1}{A_B} \overline{G}_B^{E,S}(T, N_B^S)$$

$$- \frac{1}{A_B} \overline{G}_B^{E,B}(T, N_B^B). \tag{1}$$

Butler derived Equation 1 assuming an equilibrium between a bulk phase and a surface phase, which is regarded as a hypothetical independent phase. In Equation 1, R is the gas constant, T is the temperature, σ_X is the surface tension of pure liquid X, and A_X is the molar surface area in a monolayer of pure liquid X (X = A or B). A_X can be obtained from

$$A_X = L N_0^{1/3} V_X^{2/3}, \tag{2}$$

where N_0 is Avogadro's number, and V_X is the molar volume of pure liquid X. L in Equation 2 is usually set to be 1.091 for liquid metals, assuming close-packed structures. Since no exact information is available for the value of L in Equation 2 for ionic melts, $L = 1$ is used approximately for the fused salts. N_X^S and N_X^B in Equation 1 are mole fractions of a component X in a surface phase and a bulk phase, respectively; $\overline{G}_X^{E,S}(T, N_B^S)$ is the partial excess Gibbs energy of X in the surface phase as a function of T and N_B^S; $\overline{G}_X^{E,B}(T, N_B^B)$ is the partial excess Gibbs energy of X in the bulk phase as a function of T and N_B^B (X = A or B).

Relationship between Excess Gibbs Energy in Bulk and Surface Phases

Since $\overline{G}_X^{E,B}(T, N_B^B)$ in Equation 1 can be obtained directly from thermodynamic databases, we only need the additional information on $\overline{G}_X^{E,S}(T, N_B^S)$ in the surface phase. The authors[3,4,9-17] shown in Table I proposed their own models for $\overline{G}_X^{E,S}(T, N_B^S)$, which can be summarized as follows:

$$\overline{G}_X^{E,S}(T, N_B^S) = \beta^{MIX} \quad \overline{G}_X^{E,B}(T, N_B^S), \tag{3}$$

where β^{MIX} is a parameter corresponding to the ratio of the coordination number in the surface phase Z^S to that in the bulk phase Z^B. Equation 3 means that $\overline{G}_X^{E,S}(T, N_B^S)$, which has the same formula as $\overline{G}_X^{E,B}(T, N_B^B)$, is obtained by replacing N_B^B by N_B^S in $\overline{G}_X^{E,B}(T, N_B^B)$ (X = A or B) and then multiplying β^{MIX} by $\overline{G}_X^{E,B}(T, N_X^S)$. Speiser et al.[12,13] proposed Equation 3 with $\beta^{MIX} = Z^S/Z^B = 9/12 = 3/4$ on the basis of the assumption that the excess Gibbs energy in the bulk phase is proportional to the coordination number Z^B ($Z^B = 12$), and that the coordination num-

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Table I: Information on Calculation of Surface Tension and Viscosity in Liquid Alloys.

(1) Examples of Calculations of Surface Tension of Alloys

Authors	Alloys	β^{MIX} in Eq. 3	Ref.
Hoar et al.	Sn-Pb, Pb-In	1/2–3/4	(9)
Monma et al.	Cu-Ni, Ni-Mo	0.80–0.84	(10, 11)
Speiser et al.	Fe-Cu, Cu-Pb, Sn-Pb, Ag-Pb, Pb-In, Bi-Ag, etc.	3/4	(12, 13)
Hajra et al.	Fe-S, Fe-Ni, Fe-Ti, Cu-Ag-Au, etc.	3/4	(14–17)
Tanaka et al.	a series of Fe-based binary alloys, Fe-Cr-Ni, etc.	2/3; 3/4	(3, 4)

(2) Data for Calculation of Surface Tension of Liquid Bi-Sn Alloys

	Ref.
σ_{Bi} (N m^{-1}) = 0.458 − 0.07 × (T − 544), σ_{Sn} (N m^{-1}) = 0.560 −0.09 × (T − 505)	(19)
V_{Bi} (m^3 mol^{-1}) = 20.8 × 10^{-6} {1 + 1.17 × 10^{-4}(T − 544)}	(19)
V_{Sn} (m^3 mol^{-1}) = 17.0 × 10^{-6} {1 + 0.87 × 10^{-4}(T −505)}	(19)

$G^E(T, N_{Sn}^B)$ (J mol^{-1}) = $N_{Sn}^B(1 - N_{Sn}^B)\{L^0 + (1 - 2N_{Sn}^B)L^1\}$;   (18)

$L^0 = 490 + 0.97\,T,\quad L^1 = -30 - 0.235T$

$\overline{G}_{Bi}^{E,B}(T, N_{Sn}^B)$ (J mol^{-1}) = $(N_{Sn}^B)^2\{L^0 + (3 - 4N_{Sn}^B)L^1\}$

$\overline{G}_{Sn}^{E,B}(T, N_{Sn}^B)$ (J mol^{-1}) = $(1 - N_{Sn}^B)^2\{L^0 + (1 - 4N_{Sn}^B)L^1\}$

$\overline{G}_{Bi}^{E,B}(T, N_{Sn}^S)$ (J mol^{-1}) = $\beta^{MIX}(N_{Sn}^S)^2\{L^0 + (3 - 4N_{Sn}^S)L^1\}$

$\overline{G}_{Sn}^{E,B}(T, N_{Sn}^S)$ (J mol^{-1}) = $\beta^{MIX}(1 - N_{Sn}^S)^2\{L^0 + (1 - 4N_{Sn}^S)L^1\}$

(3) Calculated Results of Surface Tension of Liquid Bi-Sn Alloys

N_{Sn}^B	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
N_{Sn}^S	0.00	0.015	0.031	0.051	0.073	0.100	0.135	0.184	0.262	0.418	1.00
σ (N m^{-1})	0.374	0.380	0.387	0.395	0.403	0.413	0.425	0.439	0.458	0.487	0.551

(4) Data for Calculation of Viscosity of Liquid Bi-Sn Alloys in Eqs. 16 and 17

	Ref.
ρ_{Bi} (kg m^{-3}) = 10.05 × 10^3 + 1.18 × (T − 544), ρ_{Sn}/kg m^{-3} = 6.98 × 10^3 + 0.61 × (T − 505)	(19)
M_{Bi} (kg mol^{-1}) = 208.98 × 10^{-3} M_{Sn}/kg mol^{-1} = 118.6 × 10^{-3}	(19)
ΔG_{Bi}^* = (J mol^{-1}) = 6437 + 25.836T ΔG_{Sn}^*/J mol^{-1} = 6780 + 24.013T	(34)

ΔG^* (J mol^{-1}) = $N_{Bi}\Delta G_{Bi}^* + N_{Sn}\Delta G_{Sn}^* + 3RTN_{Bi}N_{Sn} + RT(N_{Bi}\ln N_{Bi} + N_{Sn}\ln N_{Sn}) + G^E(T, N_{Sn}^B)$

(5) Calculated Results of Viscosity of Liquid Bi-Sn Alloys

N_{Sn}	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
η (mPa s)	1.38	1.32	1.38	1.45	1.51	1.53	1.52	1.48	1.42	1.36	1.44

ber in the surface phase is reduced by the ratio $Z^S/Z^B = 9/12$, compared with that in the bulk phase, because atoms in the surface lose some of their bonds with their nearest-neighbor atoms. For example, the partial excess Gibbs energy in the bulk phase using a regular alloy model is expressed as follows:

$$\overline{G}_X^{E,B}(T, N_B^B) = (1 - N_B^B)^2 Z^B \Omega_{AB},$$

$$\Omega_{AB} = e_{AB} - \frac{1}{2}(e_{AA} + e_{BB}),\quad (4)$$

where Ω_{AB} is the interaction parameter, and e_{AB}, e_{AA}, and e_{BB} are the bond energies of A–B, A–A, and B–B pairs. When these bond energies are assumed to be constant in the surface and in the bulk, the excess Gibbs energy in the surface depends only on the coordination number. Then,

$$\overline{G}_X^{E,S}(T, N_B^S) = (1 - N_B^S)^2 Z^S \Omega_{AB}.\quad (5)$$

Thus we can obtain the following equation:

$$\overline{G}_X^{E,S}(T, N_B^S) = \frac{Z^S}{Z^B}\overline{G}_X^{E,B}(T, N_B^S).\quad (6)$$

The value of β^{MIX} in Equation 3, however, might be affected by other factors in addition to Z^S/Z^B; for example, the relaxation of surface structure. Furthermore, when applying Equations 1 and 3 to ionic mixtures, no information on Z^S/Z^B was available. We therefore have determined β^{MIX} as follows:[4–7] after the ideal surface is created from the bulk for pure substance X, some of the binding energy in the ideal surface U_X^S is assumed to be consumed to form the relaxation structure in the surface, and the difference

between the rest of the energy in the surface and the binding energy in the bulk U_X^B can be seen as the surface tension σ_X multiplied by the molar surface area A_X. Then,

$$\sigma_X A_X = (U_X^S - \Delta E_X) - U_X^B,\quad (7)$$

where U_X^S is assumed to be $U_X^S = (Z^S/Z^B)$ U_X^B. In addition, the binding energy U_X^B is replaced by the heat of evaporation $-\Delta H_{Eva,X}$. The energy to form the relaxation structure in the surface ΔE_X in Equation 7 is assumed to be $\Delta E_X = \lambda(U_X^S - U_X^B)$. Then, Equation 7 is

$$\sigma_X A_X = \{1 - \beta^{Pure}\}\Delta H_{Eva,X},\quad (8)$$

where $\beta^{Pure} = \{Z^S + \lambda(Z^B - Z^S)\}/Z^B = (Z^S)/Z^B$ is the apparent ratio of the coordination number in the surface to that in the bulk for pure substances, considering the relaxation of the surface, and λ is a proportionality factor.

The relations between σ_X and $\Delta H_{Eva,X}/A_X$ for pure liquid metals and fused salts are shown in Figure 1. From the linear re-
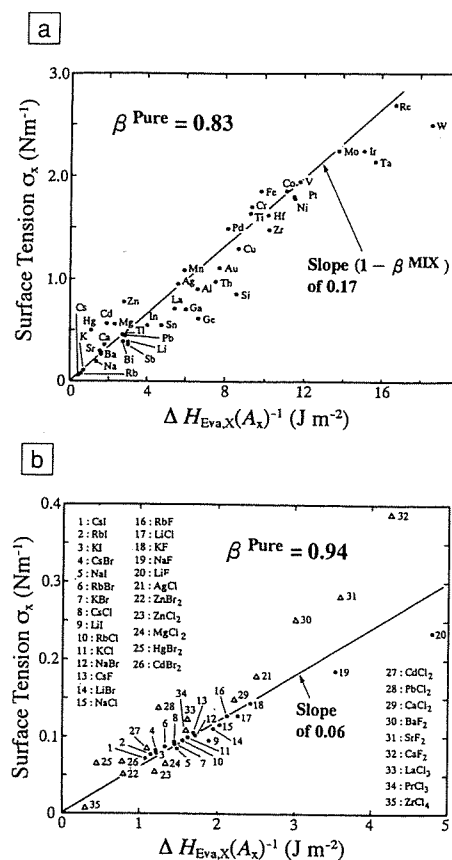
Figure 1. Relationship between σ_X and $\Delta H_{Eva,X}/A_X$ in (a) pure liquid metals and (b) pure molten salts.

lations between σ_X and $\Delta H_{Eva,X}/A_X$ in this figure, the following values for $\beta^{Pure} = (Z^S)/Z^B$ were obtained:

$\beta^{Pure} = 0.83$ for liquid metals
and 0.94 for ionic melts. (9)

Consequently, we assume the following relation:

β^{MIX} in Equation 3 = β^{Pure} in Equation 9. (10)

Procedure for Calculating Surface Tension of Liquid Alloys

The surface tension σ of liquid alloys can be calculated as follows:
(1) Set temperature T and composition N_B^B of an alloy.
(2) Insert the values for surface tension σ_X and molar volume V_X of pure liquid substances at the chosen temperature in Equations 1 and 2.
(3) Determine excess Gibbs energies in the bulk phase at the chosen temperature and composition, and substitute them in Equation 1.
(4) Then, the two equations on the right-hand side of Equation 1 become an equation with unknown N_B^S. This equation is solved for N_B^S, and the value of N_B^S is substituted again into, for example, the first equation of the right-hand side of Equation 1 to calculate the surface tension σ of the liquid alloy on the left-hand side of Equation 1.

Evaluating Surface Tension of Liquid Alloys

As an exercise in evaluating the surface tension of liquid alloys, let us calculate the surface tension of liquid Bi-Sn alloys from a set of thermodynamic data[18] in Table I, which have been assessed to give accordance with the phase diagram for this alloy system. The data of σ_X, V_X,[19] and the excess Gibbs energy $G^E(T, N_B^B)$[18] are given in Table I. Partial excess Gibbs energies $\bar{G}_A^{E,B}(T, N_B^B)$ and $\bar{G}_B^{E,B}(T, N_B^B)$ of components A and B are obtained from the following relations:

$$\bar{G}_A^{E,B}(T, N_B^B) = G^E(T, N_B^B) - N_B^B \frac{\partial G^E(T, N_B^B)}{\partial N_B^B}$$
(11)

$$\bar{G}_B^{E,B}(T, N_B^B) = G^E(T, N_B^B) + (1 - N_B^B) \frac{\partial G^E(T, N_B^B)}{\partial N_B^B}.$$
(12)

The partial excess Gibbs energies in the surface are obtained from Equations 3 and 10. Figure 2 and Table I show the cal-
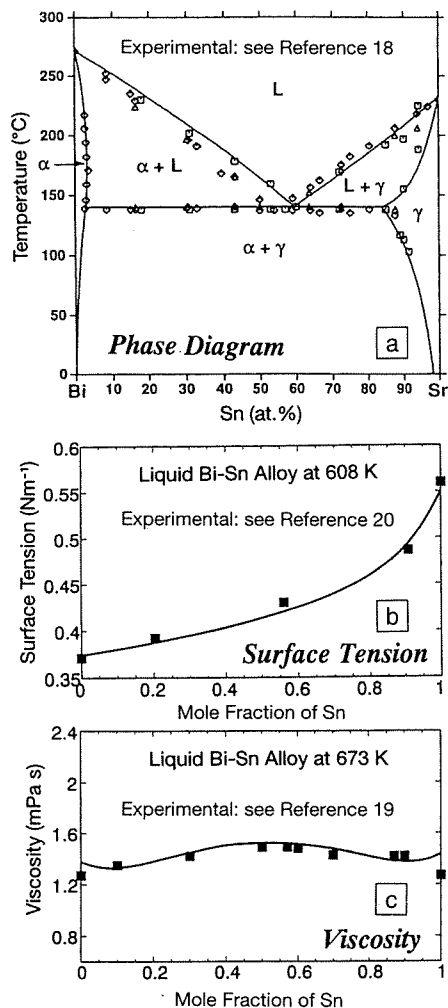

Figure 2. (a) Calculated phase diagram, (b) surface tension, and (c) viscosity in Bi-Sn binary alloys obtained from a set of thermodynamic data.[18]

culated results of the surface tension σ of liquid Bi-Sn alloys with the calculated results for the phase diagram and the viscosity of these alloys, which are described later. The calculated results of the surface composition N_{Sn}^S of the liquid Bi-Sn alloy are shown in Table I.

We have also calculated the surface tension of liquid Cu-Pb and Fe-Si alloys from Equations 1, 2, and 3 with the various values for β^{MIX} shown in Table I and $\beta^{MIX} = 0.83$, based on the assumption in Equation 10. Thermodynamic data for Cu-Pb alloys were taken from the assessment by Hayes et al.,[21] and for Fe-Si alloys, from Lacaze and Sundman.[22] These data are part of the Scientific Group Thermo-

data Europe (SGTE) database.[23] Figure 3a shows the calculated results of σ in liquid Cu-Pb alloys for which activities of the components indicate large positive deviation from Raoult's law.[21] The relation between N_{Pb}^B and N_{Pb}^S in this alloy is also shown in this figure. Figure 3a shows that the calculated results of σ with all of the previously mentioned β^{MIX} values agree well with the experimental results[24-28] and that the difference between the calculated σ for $\beta^{MIX} = 1$ and that for $\beta^{MIX} = 1/2$ is smaller than 30 mN m^{-1}. On the other hand, from the calculated results of σ in liquid Fe-Si alloys in Figure 3b, we found that the curves of σ calculated for each β^{MIX} value can be distinguished from each other, and the calculated result with $\beta^{MIX} = 0.83$ agrees well with the experimental data. In this alloy, the activities of the components show large negative deviation from Raoult's law.[22] From these calculations, it is observed that in alloys with negative excess Gibbs energy in the bulk, the surface tension deviates positively from that of the ideal alloy[3] as shown in Figure 3b. On the other hand, in alloys with positive excess Gibbs energy in the bulk, the surface tension has the tendency to show negative deviations from that of the ideal alloy (Figure 3a). We found that this rule can be generally applied to liquid alloys on the basis of Equations 1–3 and 10.[3]

Thermodynamic Evaluation of the Surface Tension of Molten Ionic Mixtures in Common Ion Alkali-Halide Systems

As shown in the preceding sections, the calculated results of σ for liquid alloys from Equations 1–3 and the assumption of Equation 10 agree well with the experimental data. As shown in Figure 4, however, the calculated results (chain curves) from these equations for molten ionic mixtures show some discrepancies with the experimental data.[29] As indicated in Figure 3, we found that there exists a general relationship between the composition dependence of the excess Gibbs energy in the bulk and that of the surface tension σ in liquid alloys. However, as shown in Figure 4, the experimental results of the surface tension of those molten ionic mixtures, of which excess Gibbs energies are negative, show negative deviations from that of the ideal mixture (dotted curves). The calculated results of the surface tension of those ionic mixtures cannot satisfy the experimental results when Equations 1–3 and 10 are used, because the calculated results (chain curves) based on these equations deviate positively from those of the
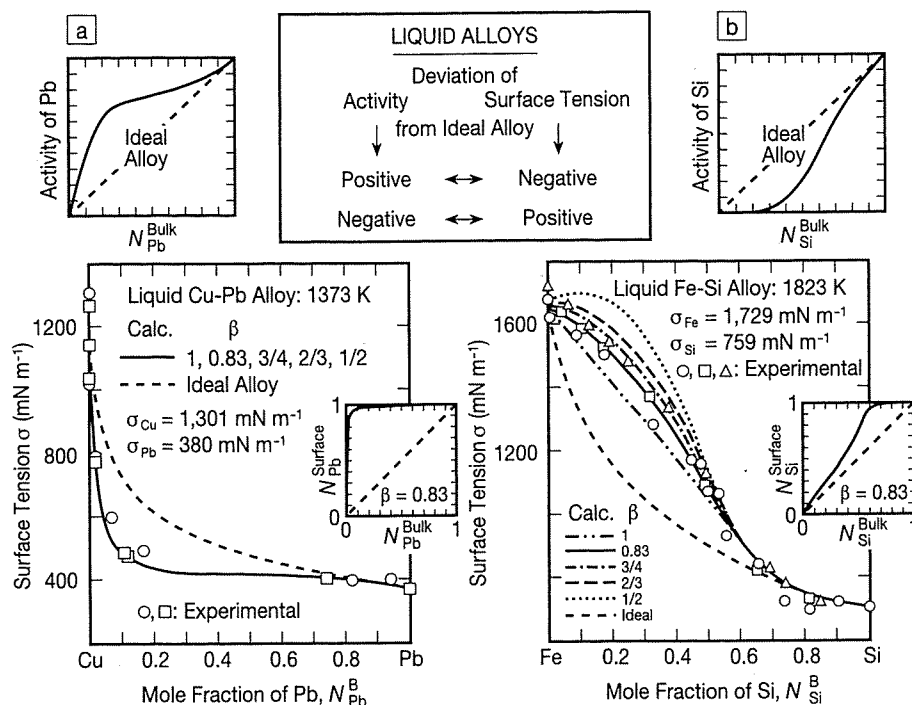
Figure 3. Calculated results of surface tension with experimental values in (a) liquid Cu-Pb and (b) Fe-Si alloys.
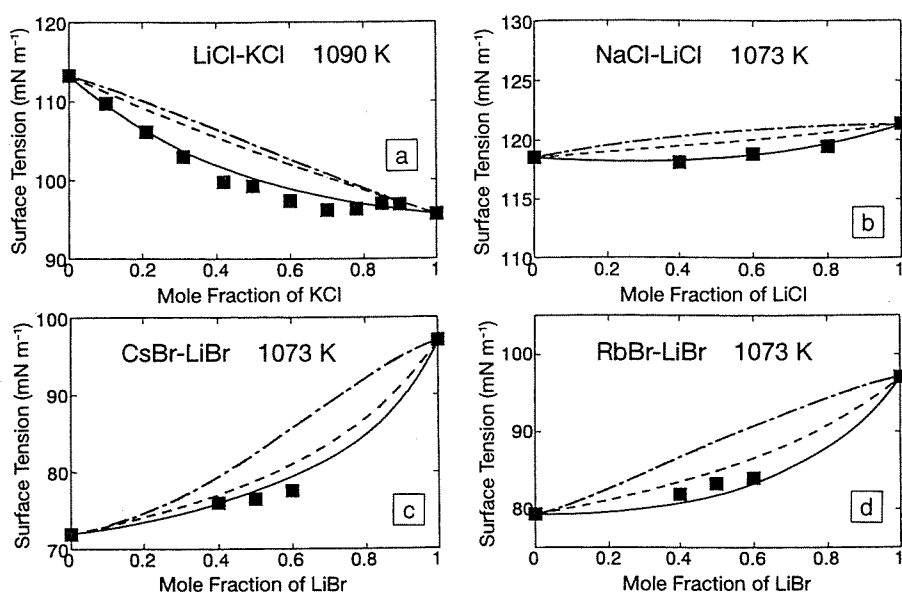

Figure 4. Calculated results of surface tension of molten ionic mixtures in common ion alkali-halide systems. (a) is LiCl-KCl, (b) is NaCl-LiCl, (c) is CsBr-LiBr, and (d) is RbBr-LiBr. — · — · — · —: Equation 1 + β^{MIX} = 0.94 in Equation 9; ■: experimental results[29]; — — — — —: ideal alloys in Equation 1; ————: Equation 2 + Equation 13 + Equation 14.

ideal mixture (dotted curves). Thus the results in Figures 3 and 4 show that some additional factors have to be considered in Equations 1 and 3 for molten ionic mixtures. We have, therefore, derived new equations for the surface tension of molten ionic mixtures, considering the effect of the surface-relaxation structure on the excess Gibbs energy and the size effect on the mixing entropy as follows:[5-7]

$$\sigma = \sigma_A + \frac{RT}{A_A} \ln \frac{D_A^S}{D_A^B} + \frac{1}{A_A} \overline{G}_A^{E,S}(T, N_B^S)$$

$$- \frac{1}{A_A} \overline{G}_A^{E,B}(T, N_B^B)$$

$$= \sigma_B + \frac{RT}{A_B} \ln \frac{D_B^S}{D_B^B} + \frac{1}{A_B} \overline{G}_B^{E,S}(T, N_B^S)$$

$$- \frac{1}{A_B} \overline{G}_B^{E,B}(T, N_B^B), \qquad (13)$$

where

$$D_X^S = \frac{N_X^S d_X}{N_A^S d_A + N_B^S d_B} \quad \text{and}$$

$$D_X^B = \frac{N_X^B d_X}{N_A^B d_A + N_B^B d_B} \quad (X = A \text{ or } B).$$

$$\frac{\overline{G}_X^{E,S}(T, N_B^S)}{\overline{G}_X^{E,B}(T, N_B^S)} = \left\{ \frac{(Z^S)'}{Z^B} \right\} \frac{1}{\zeta^4} = 1.1, \qquad (14)$$

where d_A and d_B are the ionic distances of the substances A and B, which are assumed here to be the sum of the radii of the cation and anion for pure salts A and B. $\zeta(= d_X^S/d_X^B)$ is the ratio of the ionic distance in the surface phase d_X^S to that in the bulk phase d_X^B. The change in the ionic distance in the surface is caused by relaxation at the surface. ζ has been evaluated to be 0.97 by Sawada and Nakamura,[30] from their theoretical work on the displacement of ions at the surface. $(Z^S)'/Z^B = \beta^{Pure} = 0.94$ has been obtained in Equation 8. Figure 4 shows the calculated results (solid curves) from Equations 2, 13, and 14 by using thermodynamic data of $G^{E,B}(T, N_B^S)$ stored in the databases,[31,32] which permit the calculation of phase diagrams of ionic mixtures. As shown in this figure, the calculated results (solid curves) agree well with the experimental data.[29]

Evaluating Viscosity of Liquid Alloys and Its Application to Soldering Materials

Some models for evaluating the viscosity of liquid alloys have been proposed, in which thermodynamic data can be applied directly. Two models are represented in this section.

Hirai[33] has presented an equation for the viscosity of liquid alloys as follows:

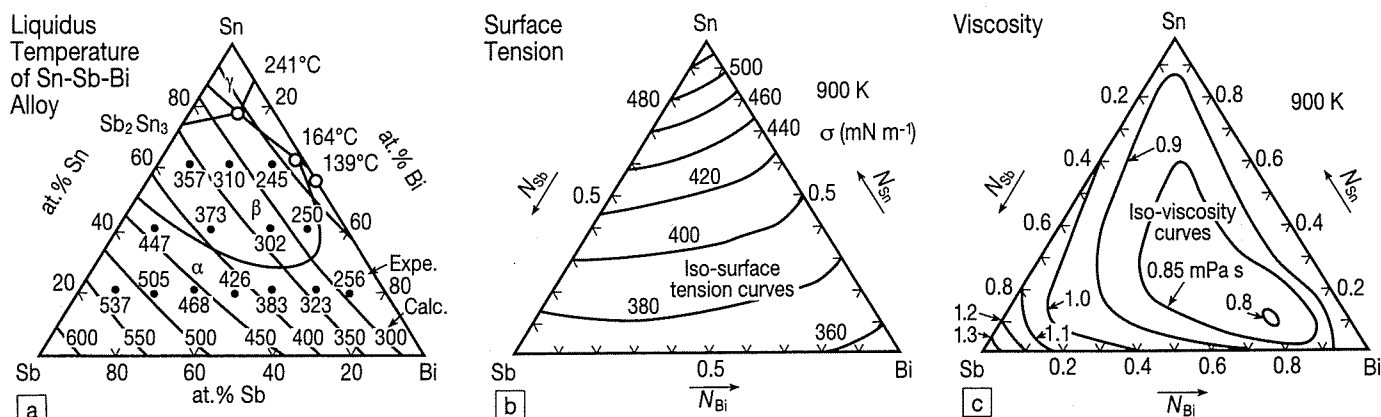# Use of Thermodynamic Data to Determine Surface Tension and Viscosity of Metallic Alloys

Figure 5. Calculated results of (a) liquidus, (b) surface tension, and (c) viscosity in Sn-Sb-Bi ternary alloys obtained from a set of thermodynamic data.[18]

$$\eta = A \exp\left(\frac{B}{RT}\right),$$

$$A = \frac{1.7 \times 10^{-7}\rho^{2/3}T_L M^{-1.6}}{\exp\left(\frac{B}{RT_L}\right)},$$

$$B = 2.65T_L^{1.27}, \tag{15}$$

where M and ρ are atomic weight and density of liquid alloys. Equation 15 shows that the viscosity of liquid alloys is a function of liquidus temperature T_L, which can be obtained from the phase diagram, calculated using thermodynamic data.

Seetharaman et al.[34,35] proposed another equation for the viscosity of liquid alloys as follows:

$$\eta = A^* \exp\left(\frac{\Delta G^*}{RT}\right),$$

$$A^* = 39.9 \times 10^{-11}\frac{\rho}{M}, \tag{16}$$

where $\rho = \Sigma N_i \rho_i$ (ρ_i is the density of pure component i), $M = \Sigma N_i M_i$ (M_i is the atomic weight of pure component i), and

$$\Delta G^* = \Sigma N_i \Delta G_i^* + 3RT\Sigma N_i N_j$$
$$+ \{RT\Sigma N_i \ln N_i + G^E(T, N_B^B)\}, \tag{17}$$

where ΔG_i^* is the activation energy of pure component i. In this model, the activation energy of the viscosity of the liquid alloy, ΔG^*, consists of the activation energy of the pure components ΔG_i^* and the excess Gibbs energy of the alloy $G^E(T, N_B^B)$, which also can be obtained from the data in the thermodynamic databases.

Based on the equations of the surface tension and the viscosity of liquid alloys described here, we can evaluate the phase diagram, the surface tension, and the viscosity in alloys simultaneously from thermodynamic data. As an example, Figure 2 and Table I show the calculated results of the viscosity of liquid Bi-Sn binary alloys, obtained from a set of thermodynamic data,[18] and some physical properties.[19] Figure 5 shows the calculated results of the liquidus temperature, the surface tension, and the viscosity of Sn-Sb-Bi ternary alloys, in which Butler's Equation 1 and Equations 16 and 17 have been extended to ternary systems. Since this alloy is one of the candidates for Pb-free soldering materials, the simultaneous calculation of these properties is very useful in searching for suitable compositions for these new soldering materials.

Concluding Remarks

Thermodynamic models have been presented for the surface tension and the viscosity of liquid alloys and molten ionic mixtures, in which thermodynamic data can be applied directly. Based on the present approach, a multifunctional thermodynamic data-bank system can be developed that will be widely applicable in the evaluation of physicochemical properties of the liquid phases with the simultaneous calculation of the phase diagrams in alloys and ionic mixtures from thermodynamic data, as shown in Figures 2 and 5.

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