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Citation	Zeitschrift für Metallkunde. 1996, 87(5), p. 380-389
Version Type	VoR
URL	https://hdl.handle.net/11094/26520
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Application of Thermodynamic Databases to the Evaluation of Surface Tensions of Molten Alloys, Salt Mixtures and Oxide Mixtures

The authors discuss the application of thermodynamic solution databases, which have been constructed so far to calculate thermodynamic properties and phase diagrams, to the evaluation of surface tensions of molten alloys, salt mixtures and oxide mixtures. In particular, the relationship between the excess Gibbs energy in the bulk phase and that in the "surface phase" which are used in Butler's equation for surface tension was derived for molten ionic solutions as well as molten alloys. In this work, the surface tensions of some liquid binary alloys, various molten salt mixtures, which mainly consist of alkali cations and halide anions, and some molten oxide mixtures, in particular binary silicate systems, were calculated and compared with experimental values.

1 Introduction

During the last three decades, various thermodynamic databases have been compiled to be mainly applied to the calculation of phase diagrams of alloys, salts and oxides [90Bal]. The accumulation and assessment of thermodynamic data and phase equilibrium information to establish those databases is sometimes called CALPHAD (Computer **Cal**culation of **Pha**se **D**iagrams) approach [92Nis]. The CALPHAD approach has been recognized to be useful in various aspects of materials science and engineering [90Bal, 92Nis]. If it would be possible to use the thermodynamic databases to evaluate physical properties of liquid solutions as well as phase equilibria, we could not only widen the applicability of those thermodynamic databases but also further the understanding of the physical properties of molten alloys, salt mixtures and oxide mixtures. In a previous work [94Tan], the authors discussed the application of the thermodynamic solution databases, which have been generated by Kaufman et al. [77Kau] for the calculation of phase diagrams of iron base alloys, to the evaluation of the surface tension of liquid iron alloys. In the calculation of the surface tension of those liquid alloys, we applied a procedure presented by Speiser et al. [87Spe, 89Yeu] which is based on Butler's equation [32But] with a model for activity coefficients in a hypothetical "surface phase". In order to extend the above procedure to the calculation of the surface tension of molten salts and oxide mixtures, we need information on the excess Gibbs energy in the surface phase of those ionic melts. In the present work, we derive some relationships between the excess Gibbs energy in the bulk phase and that in the surface phase for molten ionic mixtures as well as molten alloys. Then, we discuss the application of some thermodynamic solution databases to calculate the surface tension of some molten alloys and ionic mixtures.

2 Butler's Equation for the Surface Tension of A–B Binary Liquid Solutions

Several authors have proposed calculations of the surface tension of liquid solutions by employing thermodynamic data; for example 1) Hoar and Melford: [57Hoa]; 2) Monma and Sudo: [61Mon1, 61Mon2]; 3) Kasama: [78Kas]; 4) Speiser et al.: [87Spe, 89Yeu].

All of the above authors carried out the calculations for only liquid binary alloys, although their principles are based on Butler's equation [32But], which is expressed for the surface tension σ of any A–B binary liquid solution as follows:

$$\begin{aligned}\sigma &= \sigma_A + \frac{RT}{A_A}\ln\frac{(1-N_B^S)}{(1-N_B^B)} + \frac{1}{A_A}\overline{G}_A^{E,S}(T,N_B^S) - \\ &\quad - \frac{1}{A_A}\overline{G}_A^{E,B}(T,N_B^B) \\ &= \sigma_B + \frac{RT}{A_B}\ln\frac{N_B^S}{N_B^B} + \frac{1}{A_B}\overline{G}_B^{E,S}(T,N_B^S) - \\ &\quad - \frac{1}{A_B}\overline{G}_B^{E,B}(T,N_B^B) \qquad (1)\end{aligned}$$

where R is the gas constant, T: temperature, σ_X: surface tension of pure liquid X, A_X: surface area in a monolayer of pure liquid X ($X = A$ or B). A_X can be obtained from the following equation:

$$A_X = L N_0^{1/3} V_X^{2/3} \qquad (2)$$

where N_0: Avogadro number, V_X: molar volume of pure liquid X. L in Eq. (2) is usually set to be 1.091 for liquid metals assuming closed packed structures. N_X^S and N_X^B in Eq. (1) are mole fractions of a component X in a surface phase and a bulk phase, respectively; $\overline{G}_X^{E,S}(T,N_B^S)$: partial excess Gibbs energy of X in the surface phase as a function of T and N_B^S; $\overline{G}_X^{E,B}(T,N_B^B)$: partial excess Gibbs energy of X in the bulk phase as a function of T and N_B^B ($X = A$ or B).

Table 1. List of liquid solutions for which surface tensions have been calculated so far from Eqs. (1) to (3) with the value of β.

	β	liquid solutions
Hoar and Melford [57Hoa]	1/2 to 3/4	Sn–Pb and Pb–In
Monma and Sudo [61Mon1, 61Mon2]	0.80 to 0.84 for alloys	Cu–Ni and Ni–Mo
	0.90 to 0.94 for ionic solutions	$Cu-Cu_2O$, $Cu-Cu_2S$
Kasama [78Kas]	1	Ag–Au, Fe–Mn, Sn–Pb, Ag–Pb, Cu–Pb, Cu–Sn and Fe–Si
Speiser et al. [87Spe, 89Yeu]	3/4	Fe–Cu, Cu–Pb, Sn–Pb, Ag–Pb, Pb–In, Bi–Ag, Cu–Al, Fe–Si and Ni–Si
Tanaka and Iida [94Tan]	2/3, 3/4	Ag–Pb, Sn–Pb, Cu–Pb, Cu–Fe, Cu–Al, Ni–Si, a series of iron base binary alloys and Fe–Cr–Ni ternary alloy

3 Relationship between Partial Excess Gibbs Energy in Bulk Phase and that in Surface Phase

Butler derived Eq. (1) assuming an equilibrium between a bulk phase and a surface phase, which is regarded as a hypothetical independent phase. Since $\overline{G}_X^{E,B}(T,N_B^B)$ 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. Speiser et al. [87Spe, 89Yeu], Hoar and Melford [57Hoa], Monma and Sudo [61Mon1, 61Mon2] and Kasama [78Kas] proposed their own models for $\overline{G}_X^{E,S}(T,N_B^S)$, which can be summarized as follows [94Tan]:

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

where β is a parameter corresponding to the ratio of the coordination number Z in the surface phase to that in the bulk phases, Z^S/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 to $\overline{G}_X^{E,B}(T,N_B^S)$. The above four groups have reported calculations of surface tension of the liquid binary alloys shown in Table 1. Using the respective value for β also shown in Table 1, the results agreed well with the measured values, though Hoar and Melford [57Hoa], and Monma and Sudo [61Mon1, 61Mon2] applied only a regular solution model for the excess Gibbs energy in Eq. (3). For example, Speiser et al. [87Spe, 89 Yeu] proposed Eq. (3) with $\beta = Z^S/Z^B$ on the basis of the assumption that the excess Gibbs energy is proportional to the coordination number, and that the coordination number in the surface phase is reduced by the ratio Z^S/Z^B compared with that in the bulk phase because atoms in the surface lose some of their bonds with their nearest-neighbor atoms. The value of β, however, might be affected by other factors except Z^S/Z^B, for example, a change in binding energy in the surface phase, rearrangement of atom configurations and so on. Furthermore, when applying Eqs. (1) and (3) to ionic mixtures, no information on Z^S/Z^B has been available. We, therefore, have determined β as follows:

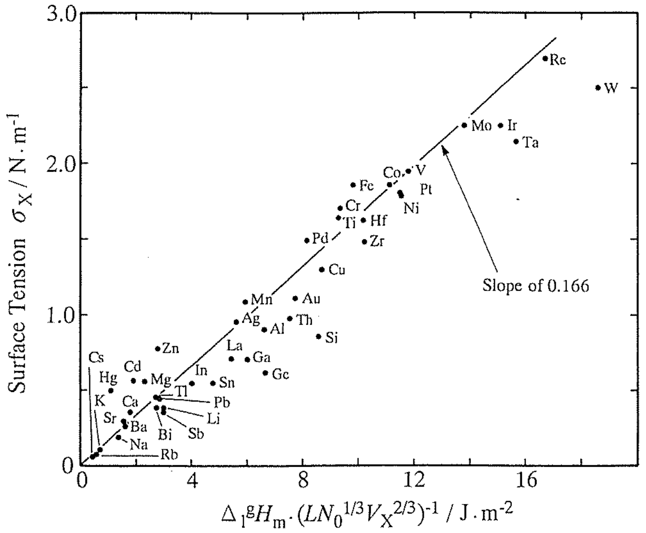


Fig. 1. Correlation of surface tension σ_X with $\Delta_l^g H_m \cdot (LN_0^{1/3} V_X^{2/3})^{-1}$ for various liquid metals ($L = 1.091$).

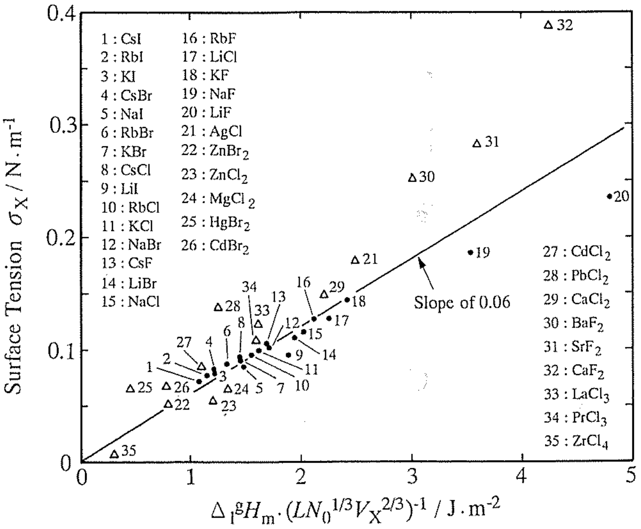


Fig. 2. Correlation of surface tension σ_X with $\Delta_l^g H_m \cdot (LN_0^{1/3} V_X^{2/3})^{-1}$ for various ionic melts ($L = 1$).

Table 2. Data for the determination of β for liquid metals.

X	$\Delta_l^g H_{m,X}$ [kJ · mol^{-1}]	T_m [K]	V_X [10^{-6}m^3 mol^{-1}]	$\Delta_l^g H_{m,X}/(LN_0^{1/3}V_X^{2/3})$ [J · m^{-2}]	σ_X [N · m^{-1}]
Li	157	452	13.4	3.02	0.398
Na	107	371	24.8	1.37	0.191
Mg	133	923	15.3	2.35	0.559
Al	306	933	11.3	6.60	0.914
Si	392	1687	11.1	8.56	0.865
K	88	337	47.1	0.73	0.115
Ca	158	1124	29.5	1.80	0.361
Ti	438	1998	11.6	9.29	1.650
V	485	1973	9.5	11.75	1.950
Cr	351	2178	8.27	9.33	1.700
Mn	246	1517	9.54	5.94	1.090
Fe	357	1808	7.94	9.75	1.872
Co	396	1765	7.60	11.13	1.873
Ni	400	1728	7.43	11.42	1.778
Cu	318	1356	7.94	8.68	1.303
Zn	119	693	9.94	2.80	0.782
Ga	280	303	11.4	6.01	0.718
Ge	340	1232	13.2	6.62	0.621
Rb	85	312	57.7	0.62	0.085
Sr	160	1070	37.0	1.57	0.303
Zr	581	2130	15.4	10.20	1.480
Mo	600	2895	10.3	13.77	2.250
Pd	351	1828	10.1	8.14	1.500
Ag	266	1234	11.6	5.64	0.966
Cd	104	594	14.0	1.95	0.570
In	239	430	16.3	4.04	0.556
Sn	294	505	17.0	4.83	0.560
Sb	195	904	18.8	3.00	0.367
Cs	77	302	72.2	0.48	0.070
Ba	178	1263	41.4	1.62	0.277
La	409	1193	23.3	5.45	0.720
Hf	571	2480	14.9	10.25	1.630
Ta	761	3123	12.1	15.69	2.150
W	823	3655	10.5	18.65	2.500
Re	711	3440	9.96	16.69	2.700
Ir	628	2727	9.61	15.10	2.250
Pt	504	2047	10.3	11.56	1.800
Au	358	1336	11.3	7.73	1.169
Hg	61	234	14.7	1.11	0.498
Tl	173	576	18.0	2.74	0.464
Pb	189	601	19.4	2.84	0.458
Bi	194	544	20.8	2.79	0.378
Th	544	2088	22.1	7.51	0.978

$\Delta_l^g H_m, T_m, V_X, \sigma_X$: [88Iid]

1) We assume that the surface tension σ_X of pure liquid metals and pure ionic melts at their melting points is determined by the following relation:

$$\begin{aligned} A_X \cdot \sigma_X &= LN_0^{1/3}V_X^{2/3} \cdot \sigma_X \\ &= (-U_X^B) - (-U_X^S) \\ &= (-U_X^B) - \beta^* \cdot (-U_X^B) \\ &= \Delta_l^g H_{m,X} - \beta^* \cdot \Delta_l^g H_{m,X} = (1 - \beta^*) \cdot \Delta_l^g H_{m,X} \quad (4) \end{aligned}$$

where U_X^B and U_X^S are binding energies in the bulk phase and the surface phase, respectively, and $\beta^* = U_X^S/U_X^B$. In the above equation, surface entropy terms are neglected, and $(-U_X^B)$ is assumed to be approximately equal to evaporation energy at melting points, $\Delta_l^g H_{m,X}$, which is obtained from the relation [88Iid]: $\Delta_l^g H_{m,X} = \Delta_S^g H_{m,X} - \Delta_S^l H_{m,X}$ where $\Delta_S^g H_{m,X}$ and $\Delta_S^l H_{m,X}$ are sublimation energy and enthalpy of fusion of substance X at its melting point.

2) The relations between σ_X and $\Delta_l^g H_m/(LN_0^{1/3}V_X^{2/3})$ for pure liquid metals and fused salts are shown in Figs. 1 and 2. The data [78Ogi, 79Kub, 86Gok, 87NIS, 88Iid] necessary to obtain these relations are listed in Tables 2 and 3. We applied $L = 1.091$ in Eq. (4) for liquid metals. Since there has not been any exact information on the value of L in Eqs. (2) and (4) for ionic melts, we used approximately $L = 1$ for the fused salts. From the linear relations between σ_X and $\Delta_l^g H_m/(LN_0^{1/3}V_X^{2/3})$ in Figs. 1 and 2, the following values for β^* were obtained:

$$\beta^* = 0.83 \text{ for liquid metals} \quad (5)$$

$$\beta^* = 0.94 \text{ for ionic melts} \quad (6)$$

The linear relation between σ_X and $\Delta_l^g H_m/(LN_0^{1/3}V_X^{2/3})$ in Fig. 1 has been determined to correspond to a similar relation between σ_X and $\Delta_l^g H_m/V_X^{2/3}$ for liquid metals in "Fig. 5.13" on page 132 in [88Iid]. On the other hand,

Table 3. Data for the determination of β for ionic melts.

X	$\Delta_S^g H_{m,X}$ [kJ · mol^{-1}]	$\Delta_S^l H_{m,X}$ [kJ · mol^{-1}]	d_X [g · cm^{-3}]	M_X [g · mol^{-1}]	T_m [K]	$\frac{\Delta_l^g H_{m,X}}{LN_0^{1/3}V_X^{2/3}}$ [Jm^{-2}]	$\frac{T_m}{LN_0^{1/3}V_X^{2/3}}$ [10^3 Km^{-2}]	σ_X [Nm^{-1}]
LiF	265.7	26.8	1.809	25.9	1121	4.80	22.5	0.236
LiCl	196.6	19.9	1.502	42.4	883	2.26	11.3	0.128
LiBr	190.8	17.7	2.529	86.8	823	1.94	9.2	0.110
LiI	210.5	14.6	3.109	133.8	742	1.89	7.2	0.094
NaF	264.8	33.5	1.950	42.0	1265	3.54	19.4	0.186
NaCl	219.7	28.0	1.556	58.4	1074	2.03	11.4	0.114
NaBr	205.9	26.2	2.339	102.9	1023	1.71	9.7	0.101
NaI	203.3	23.6	2.742	149.9	933	1.48	7.7	0.086
KF	227.6	28.2	1.910	58.1	1130	2.43	13.7	0.144
KCl	207.9	26.6	1.527	74.6	1045	1.61	9.3	0.099
KBr	203.8	25.5	2.122	119.0	1013	1.44	8.2	0.090
KI	194.6	24.1	2.444	166.0	958	1.21	6.8	0.079
RbF	218.0	23.0	2.925	104.5	1048	2.13	11.5	0.127
RbCl	203.3	18.4	2.248	120.9	988	1.54	8.2	0.095
RbBr	187.0	15.5	2.718	165.4	953	1.32	7.3	0.087
RbI	179.9	12.6	2.906	212.4	913	1.14	6.2	0.077
CsF	192.0	21.8	3.649	151.9	976	1.68	9.6	0.106
CsCl	203.3	15.9	2.792	168.4	918	1.45	7.1	0.092
CsBr	193.3	23.6	3.134	212.8	908	1.21	6.5	0.083
CsI	192.5	23.8	3.197	259.8	894	1.07	5.6	0.072
AgCl	214.2	13.0	4.872	143.3	728	2.50	9.1	0.179
$MgCl_2$	209.2	43.1	1.682	95.2	987	1.34	7.9	0.062
CaF_2	383.3	29.7	2.518	78.1	1691	4.25	20.3	0.387
$CaCl_2$	292.9	28.5	2.085	111.0	1045	2.22	8.8	0.148
SrF_2	361.9	29.7	3.470	125.6	1750	3.60	19.0	0.282*
BaF_2	334.7	28.5	4.214	175.3	1563	3.02	15.4	0.253*
$ZnCl_2$	155.2	10.3	2.525	136.3	591	1.20	4.9	0.054
$ZnBr_2$	124.7	15.6	3.466	225.2	675	0.80	5.0	0.051
$CdCl_2$	162.8	30.1	3.388	183.3	841	1.10	7.0	0.085
$CdBr_2$	140.2	33.5	4.076	272.2	840	0.77	6.1	0.067
$HgBr_2$	82.8	18.0	5.119	360.3	511	0.45	3.6	0.065
$PbCl_2$	175.7	23.0	4.954	278.1	772	1.24	6.2	0.138
$LaCl_3$	298.3	54.4	3.213	245.3	1128	1.61	7.4	0.123
$PrCl_3$	291.8	50.6	3.227	247.3	1059	1.59	7.0	0.107
$ZrCl_4$	103.3	37.7	1.643	233.0	710	0.29	3.1	0.007

$\Delta_S^g H_{m,X}, \Delta_S^l H_{m,X}, T_m$: [79Kub] d_X (density), σ_X: [87NIS] $^*\sigma_X$: 78Ogi] M_X (= $M_{cation} + M_{anion}$) (molecular weight): [88Iid, 86Gok] $V_X = M_X/d_X$, $L = 1$ $\Delta_l^g H_{m,X} = \Delta_S^g H_{m,X} - \Delta_S^l H_{m,X}$

the value $\beta^* = 0.94$ for ionic melts has been determined by a least-square regression method for the linear relation in Fig. 2.

3) We assume the following relation;

$$\beta = \beta^* (= U_X^S / U_X^B) \text{ : for pure liquid metals or ionic melts}$$
$$= \overline{G}_X^{E,S}(T, N_B^S) / \overline{G}_X^{E,B}(T, N_B^S) \text{ : for solutions} \quad (7)$$

4) Figure 3 shows the relationship between σ_X and $T_m/(LN_0^{1/3}V_X^{2/3})$ for pure molten oxides as well as the ionic melts shown in Fig. 2. The values [93Ike] of σ_X, T_m and V_X for pure molten oxides are listed in Table 4. Although the information on $\Delta_l^g H_m$ for molten oxides is not available, $\Delta_l^g H_m$ can be associated to T_m as pointed out in [88Iid] for liquid metals. Consequently, Fig. 3 shows that molten oxides belong to the same category as the above ionic melts. Thus, from the above assumption 3), we have determined β in Eq. (3) as follows:

$$\beta = 0.83 \text{ for liquid alloys} \quad (8)$$

$$\beta = 0.94 \text{ for molten ionic mixtures including oxide mixtures} \quad (9)$$

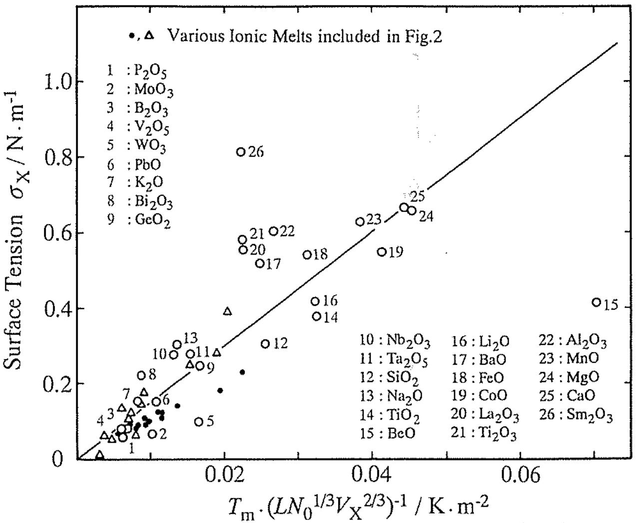


Fig. 3. Correlation of surface tension σ_x with $T_m \cdot (LN_0^{1/3}V_X^{2/3})^{-1}$ for various ionic melts ($L = 1$).

Table 4. Data for the calculation of the relation between σ_X and $T_m/(LN_0^{1/3}V_X^{2/3})$ for molten oxides.

X	T_m [K]	V_X [cm^3 mol^{-1}]	$\frac{T_m}{LN_0^{1/3}V_X^{2/3}}$ [10^3 Km^{-2}]	σ_X [Nm^{-1}]
Li_2O	2000	19.9	32.3	0.420
BeO	2843	10.5	70.3	0.415
B_2O_3	723	45.8	6.7	0.080
Na_2O	1193	33.5	13.6	0.308
MgO	3073	22.9	45.2	0.660
Al_2O_3	2320	33.3	26.6	0.606
SiO_2	1993	28.2	25.5	0.307
P_2O_5	836	63.8	6.2	0.060
K_2O	980	52.0	8.3	0.156
CaO	2860	21.1	44.4	0.670
TiO_2	2143	21.9	32.5	0.380
Ti_2O_3	2090	36.8	22.4	0.584
V_2O_5	943	78.4	6.1	0.080
MnO	2058	16.0	38.4	0.630
FeO	1641	15.6	31.2	0.545
CoO	2078	14.5	41.4	0.550
GeO_2	1389	30.9	16.7	0.250
Nb_2O_5	1773	62.2	13.4	0.279
MoO_3	1068	44.3	10.1	0.070
BaO	2196	34.2	24.7	0.520
La_2O_3	2573	50.1	22.5	0.560
Sm_2O_3	2593	51.3	22.3	0.815
Ta_2O_5	2150	67.5	15.4	0.280
WO_3	1743	44.2	16.5	0.100
PbO	834	27.6	10.8	0.153
Bi_2O_3	1098	58.2	8.7	0.213

T_m, V_X, σ_X: [93Ike] $L = 1$

Monma and Sudo [60Mon, 61Mon1] have already carried out treatments similar to points 1) to 3), given above and they obtained β-values of 0.80 to 0.84 for liquid metals and 0.90 to 0.94 for ionic melts. They applied Eqs. (1) to (3) to some liquid alloys [61Mon2], of which the excess Gibbs energies were expressed by a regular solution model. Skapski [48Ska] and Oriani [50Ori] also investigated the above treatments 1) and 2) for pure liquid metals.

4 Procedure of Calculation of Surface Tensions of Liquid Solutions

The surface tension σ of liquid solutions can be calculated as follows:

1) Setting temperature T and composition N_B^B of a solution.

2) Inserting the values for surface tension σ_X and molar volume V_X of pure liquid substances at the above temperature in Eqs. (1) and (2).

3) Determining excess Gibbs energies in the bulk phase at the above temperature and composition, and substituting them in Eq. (1).

4) Then, one pair between the two equations on the right-hand side of Eq. (1) becomes the 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, e.g., the first equation of the right-hand side of Eq. (1) to calculate the surface tension σ of the liquid solution on the left-hand side of Eq. (1). It should be emphasized here, that the solution for N_B^S can be carried out in two ways: (1) mathematically explicit or (2) applying a numerical method. A mathematically explicit method has been used in the following applications whenever explicit polynomial expressions were available for the (partial) excess Gibbs energies, i.e. for liquid metals and salts. A numerical procedure was used for the case of the Gaye model which provides implicitly results for the (partial) Gibbs energies, i.e. for liquid oxides.

Table 5. Data for the calculation of surface tensions of liquid Cu–Pb and Fe–Si alloys.

Elements	Surface Tension of pure substance σ_X [mNm^{-1}]	Molar Volume of pure substance [88Iid] $V_X = V_{m,X}\{1 + \alpha_X \cdot (T - T_{m,X})\}[10^{-6}\mathrm{m}^3 \cdot \mathrm{mol}^{-1}]$		
		$V_{m,X}$ [10^{-6} m$^3 \cdot$ mol^{-1}]	α_X [10^{-4} K^{-1}]	$T_{m,X}$ [K]
Cu	1301* (1373 K)	7.94	1.0	1356
Pb	380* (1373 K)	19.42	1.24	601
Fe	1729* (1823 K)	7.94	1.3	1808
Si	759* (1823 K)	11.1	1.4	1687

* The values of σ at pure compositions reported in literature, which are quoted to be compared with the calculated results for σ, have been selected as σ_X.

Excess Gibbs Energy

Liquid Cu–Pb Alloys: [86Hay]
$G^{E,B}(T, N_{Pb}) = (1 - N_{Pb}) N_{Pb} \{A_0 - B_0T + (A_1 - B_1T)(1 - 2N_{Pb}) + (A_2 - B_2T)(1 - 2N_{Pb})^2 + (A_3 - B_3T)(1 - 2N_{Pb})^3\}$
A_i: $A_0 = 27190.2$, $A_1 = 2229.2$, $A_2 = -7029.2$, $A_3 = -7397.6$
B_i: $B_0 = 4.21329$, $B_1 = 0.53584$, $B_2 = -6.48832$, $B_3 = -5.07992$

Liquid Fe–Si Alloys: [91Lac]
$G^{E,B}(T, N_{Si}) = (1 - N_{Si}) N_{Si} \{L_0 + L_1(1 - 2N_{Si}) + L_2(1 - 2N_{Si})^2 + L_3(1 - 2N_{Si})^3\}$
$L_0 = -164434.6 + 41.9773\,T$
$L_1 = -21.523\,T$
$L_2 = -18821.542 + 22.07\,T$
$L_3 = 9695.8$

5 Application of Thermodynamic Databases to the Evaluation of Surface Tension of Liquid Alloys

In the previous work [94Tan], we investigated the dependence of surface tension of liquid alloys upon the value of β in Eq. (3). In the present work, we recalculated the surface tension of liquid Cu–Pb and Fe–Si alloys with $L = 1.091$ in Eq. (2) and with various values for β shown in Table 1 and Eq. (8). The data of σ_X, V_X and $G^E(T, N_B^B)$ are given in Table 5. Thermodynamic data for Cu–Pb alloys were taken from the assessment by Hayes et al. [86Hay] and for Fe–Si alloys from Lacaze and Sundman [91Lac]. These data are part of the SGTE (Scientific Group Thermodata Europe) database [87Ans]. Partial excess Gibbs energies $\overline{G}_A^{E,B}(T, N_B^B)$ and $\overline{G}_B^{E,B}(T, N_B^B)$ of components A and B are obtained from the following relations;

$$\overline{G}_A^{E,B}(T, N_B^B) = G^E(T, N_B^B) - N_B^B \frac{\partial G^E(T, N_B^B)}{\partial N_B^B} \tag{10}$$

$$\overline{G}_B^{E,B}(T, N_B^B) = G^E(T, N_B^B) + (1 - N_B^B) \frac{\partial G^E(T, N_B^B)}{\partial N_B^B} \tag{11}$$

As can be seen in Figs. 4 and 5, the calculated results for the surface tension in the two alloys are in good agreement with the experimental values [59Met, 73Jou, 64Dzh, 74Kaw, 71She] using $\beta = 0.83$ in Eq. (8). The curves in small squares in the above figures show the relation between N_B^B and N_B^S of the solute element B in the above alloys.

6 Application of Thermodynamic Databases to the Evaluation of Surface Tensions of Molten Salt Mixtures

Pelton et al. [83Pel, 88Pel] have assessed a thermodynamic database which permits calculation of thermodynamic properties and phase diagrams of salt mixtures according to the CALPHAD approach. In the present section, we discuss the application of this database to the evaluation of the surface tension of molten salt mixtures. Common ion systems considering the following ions have been treated:

Cations : $Li^+, Na^+, K^+, Rb^+, Cs^+$;

Anions : F^-, Cl^-, Br^-, NO_3^-

Surface tension data of pure component salts, σ_X in Eq. (1), were taken from the NIST database [87NIS]. We obtained V_X in Eq.(2) from the selected density ρ_X of pure ionic melt in the NIST database [87NIS] and the molar weight M_X of the cations and anions as follows;

$$V_X = \frac{M_{cation} + M_{anion}}{\rho_X} \tag{12}$$

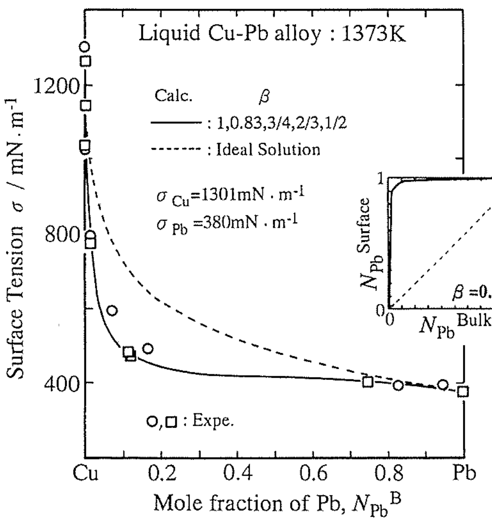


Fig. 4. Comparison of calculated results for the surface tension of liquid Cu–Pb alloys with literature values, ○: Metzger [59Met], □: Joud et al. [73Jou].

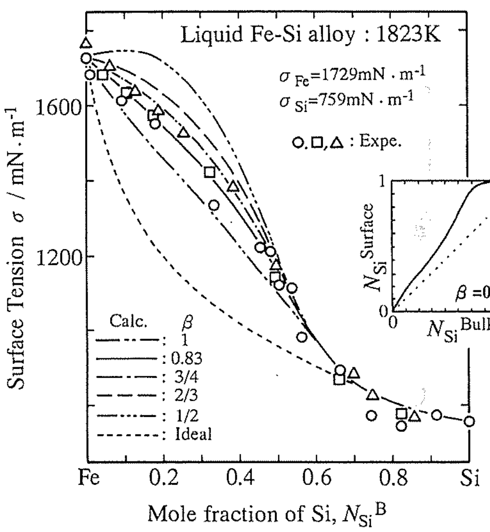


Fig. 5. Comparison of calculated results for surface tension of liquid Fe–Si alloys with literature values, ○: Dzhemilev et al. [64Dzh], □: Kawai et al. [74Kaw], △: Shergin et al. [71She].

Table 6. Values of surface tension and molar volume of pure molten salts and excess Gibbs energy $G^{E,B}(T, N_A^B, N_B^B)$ of molten salt mixtures in bulk phase. $G^{E,B}(T, N_B^B)$ in Eqs. (10) and (11) can be obtained from $G^{E,B}(T, N_A^B, N_B^B)$ with $N_A^B = 1 - N_B^B$.

Molten salt mixtures	Temp. [K]	Surface tension of pure molten salts σ_X [mN · m^{-1}]	Density of pure molten salts ρ_X [10^{-3} kg · m^{-3}]	$G^{E,B}(T, N_A^B, N_B^B)$ of molten salt mixtures in bulk phase [J · mol^{-1}]
NaCl–LiCl	1073	NaCl: 118.5 LiCl: 121.4	1.56 1.42	$N_{NaCl}N_{LiCl}\ (-4686)$
NaCl–KCl	1073	NaCl: 114.0 KCl: 96.3	1.56 1.51	$N_{NaCl}N_{KCl}\ (-2050 - 272\ N_{NaCl})$
LiCl–KCl	1073	LiCl: 114.5 KCl: 97.0	1.42 1.51	$N_{LiCl}N_{KCl}\ \{(-17570 + 7.627\ T)$ $+ (-377 - 4.958\ T)\ N_{LiCl}\}$
NaCl–RbCl	1073	NaCl: 117.9 RbCl: 90.1	1.56 2.17	$N_{NaCl}N_{RbCl}\ \{(-3222 + 5.922\ T)$ $+ (-335 - 5.245\ T)\ N_{NaCl}\}$
NaCl–CsCl	1073	NaCl: 117.9 CsCl: 79.8	1.56 2.63	$N_{NaCl}N_{CsCl}\ \{(-4310 + 5.764\ T)$ $+ (418 - 5.901\ T)\ N_{NaCl}\}$
LiF–KF	1073	LiF: 256.5 KF: 147.1	1.83 1.95	$N_{LiF}N_{KF}\ \{(-19251 + 4.521\ T)$ $+ (-1205 - 3.146\ T)\ N_{KF} + 4732\ (N_{KF})^2\}$
LiF–NaF	1200	LiF: 227.9 NaF: 191.2	1.77 1.99	$N_{LiF}N_{NaF}\ \{(-7565 + 1.607\ T)$ $+ (368 + 1.124\ T)\ N_{NaF}\}$
KF–NaF	1073	KF: 149.0 NaF: 201.6	1.95 2.07	$N_{KF}N_{NaF}\ (-335 + 2.541\ T)$
NaBr–KBr	1073	NaBr: 100.2 KBr: 87.1	2.30 2.07	$N_{NaBr}N_{KBr}\ (-2134 - 251\ N_{NaBr})$
RbBr–KBr	1073	RbBr: 80.4 KBr: 87.1	2.59 2.07	0
CsBr–KBr	1073	CsBr: 72.7 KBr: 87.1	2.93 2.07	$N_{CsBr}N_{KBr}\ (377)$
NaBr–CsBr	1073	NaBr: 100.2 CsBr: 72.7	2.30 2.93	$N_{NaBr}N_{CsBr}\ (-4728 - 209\ N_{NaBr})$
$LiNO_3$–KNO_3	623	$LiNO_3$: 110.6 KNO_3: 111.4	1.73 1.86	$N_{LiNO_3}N_{KNO_3}\{(-7360 - 5.334T)$ $-2301N_{LiNO_3} + 1937(N_{LiNO_3})^2\}$
$NaNO_3$–KNO_3	623	$NaNO_3$: 116.6 KNO_3: 111.3	1.87 1.86	$N_{NaNO_3}N_{KNO_3}(-1640$ $-280N_{NaNO_3})$
LiCl–LiF	1073	LiCl: 128 LiF: 244.4	1.42 1.83	$N_{LiCl}N_{LiF}\ (-1000)$
KCl–KF	1173	KCl: 92 KF: 117	1.45 1.88	$N_{KCl}N_{KF}\{3066 - 10621\ N_{KF}$ $+ 9125\ (N_{KF})^2\}$
NaCl–NaF	1273	NaCl: 109 NaF: 185.2	1.45 1.95	$N_{NaCl}N_{NaF}\ (1416 + 1283\ N_{NaF})$

Atomic weights: Element/M_X [10^{-3} · kg · mol^{-1}]: Li/6.94, Na/22.99, K/39.09, Rb/85.47, Cs/132.91, F/18.998, Cl/35.453, Br/79.904, N/14.0067, O/15.999
σ_X, ρ_X: [87NIS], $G^{E,B}(T, N_A^B, N_B^B)$: [83Pel, 88Pel]

Excess Gibbs energies in the bulk phase of the common ion systems are listed with the values of σ_X, ρ_X and ($M_{cation} + M_{anion}$) in Table 6. Figure 6 shows the calculated results for the surface tension σ of a few molten salt mixtures which have large negative excess Gibbs energies, using $\beta = 0.94$, 0.83 and 3/4 with $L = 1$. The hatched zones in Fig. 6 show the uncertainties of the reported values [87NIS] for the surface tension of molten salt mixtures. The uncertainties have been determined from the scatter of the reported values of σ_X for pure substances in the NIST database [87NIS]. As shown in this figure, the values 3/4 and 0.83 for β, which are adequate for liquid alloys, are unsuitable for the calculation of the surface tension of some molten salt mixtures. Figure 7 shows the comparison of the calculated results for the surface tension σ of various molten salt mixtures with the values stored in the NIST database[87NIS]. It has been reported that the composition dependence of the surface tension of some molten salt mixtures shows large downward curvatures from the linearity [80Goo]. As shown in Fig. 7, some mixtures, for which calculated results have deviations from the literature values, show such composition dependences. It is, therefore, necessary to accumulate further information on the surface structures of molten salt mixtures in order to derive the excess Gibbs energy in the surface phase, which gives us more precise composition dependence of the surface tension of those mixtures.

7 Application of Thermodynamic Databases to the Evaluation of the Surface Tension of Molten Oxide Mixtures

We have applied the procedures described in the preceding sections to the evaluation of surface tensions of molten oxide mixtures. Equations (1), (2) and (3) have been

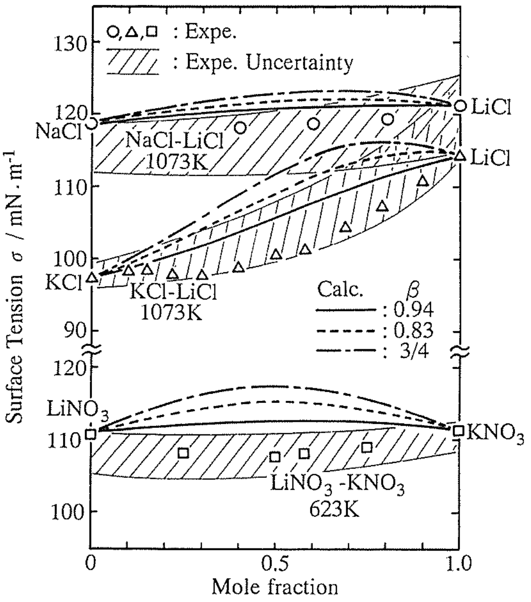


Fig. 6. Calculated results for surface tensions of some molten salt mixtures with various values of β, ○, △, □: [87NIS].

used with the conditions $L = 1$ and $\beta = 0.94$. Here, we have used the cell model developed by Gaye and Welfringer [84Gay] to obtain partial excess Gibbs energies of the components. Since in the cell model the Gibbs energy is not given in the form of a polynomial formula, one has to calculate numerically the partial excess Gibbs energies as well as the surface tension of molten oxide mixtures as follows:

1) At a given temperature and composition, the surface tensions σ_X and molar volumes V_X of the components are determined. In addition, the partial Gibbs energies of the components are calculated numerically in the cell model for a given N_B^B in the bulk phase.

2) Then, changing the value of N_B^S in the surface phase by a numerical procedure, $\overline{G}_A^{E,S}(T, N_B^S)$ and $\overline{G}_B^{E,S}(T, N_B^S)$ are calculated using the cell model and applying Eq. (3). Finding $\overline{G}_A^{E,S}(T, N_B^S)$ and $\overline{G}_B^{E,S}(T, N_B^S)$ to satisfy Eq. (1) for a certain N_B^S, the values of $N_B^S, \overline{G}_A^{E,S}(T, N_B^S)$ and $\overline{G}_B^{E,S}(T, N_B^S)$ are substituted again into Eq. (1) to determine σ of the molten oxide mixture.

In this work, we have calculated the surface tension of molten $CaO-SiO_2$ (1873 K) and $MnO-SiO_2$ (1843 K) binary mixtures. The values of surface tension, molar volume of pure substances and energy parameters W_{ij} and E_{ij} in the cell model are shown in Table 7 [56Bon, 84Gay, 87Mil, 87NIS, 88Har, 93Ike]. Since the values for σ_X of pure liquid CaO and MnO have not been obtained experimentally, we determined σ_{CaO} and σ_{MnO} in Table 7 considering estimated values reported by Boni and Darge [56Bon], Mills and Keene [87Mil], Hara et al. [88Har] and Ikemiya et al. [93Ike]. Figures 8 and 9 show the comparison of the calculated results for the surface tension of the above molten oxide mixtures with the experimental value ranges, which were determined from the reported values [51Kin, 67Muk, 69Ono, 71Sha, 74Gun, 81Muk]. In those figures, the dotted curves indicate those calculations, for which concentrations of the components in the surface phase exceed the composition range of the liquid phase, as shown in Table 8, for which the parameters of the cell model have been assessed. As can be seen in these figures, the composition dependence of the calculated values agree with the experimental results. However, when calculating the surface tension of molten oxide mixtures, one has to consider the following issues which result from the high melting points of pure oxides:

1) The provision of reliable information on the surface tension of pure molten oxides below their melting points.

2) The limitation of the composition range in the liquid in which the thermodynamic data and functions can be applied.

8 Concluding Remarks

In this paper, some relationships between the excess Gibbs energy in the bulk phase and that in the surface phase of molten alloys and ionic mixtures have been discussed. Furthermore, surface tensions of molten alloys, salt mixtures and oxide mixtures have been calculated using the thermodynamic properties of these phases. The thermody-

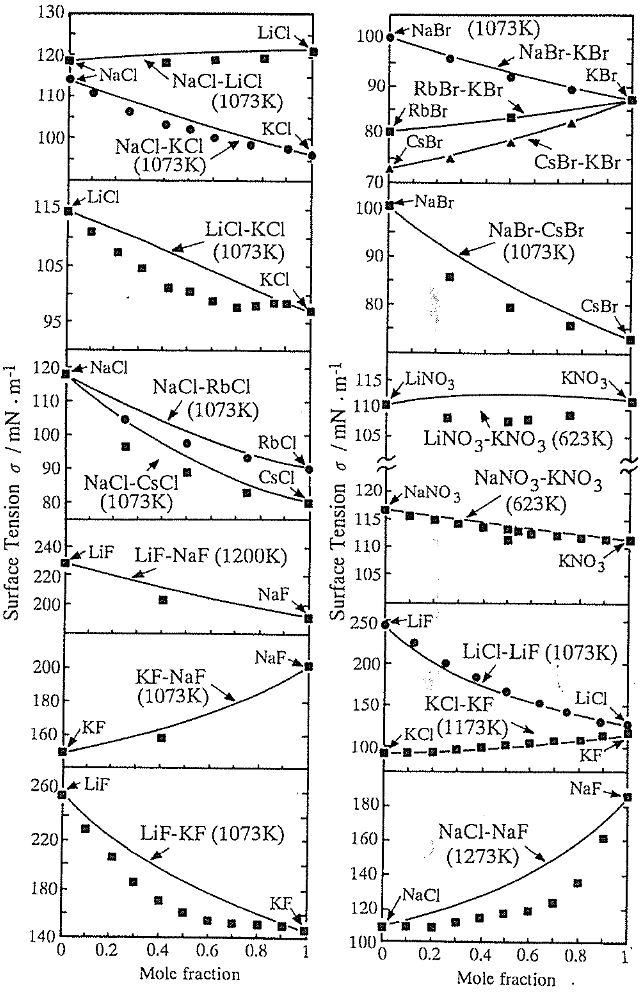
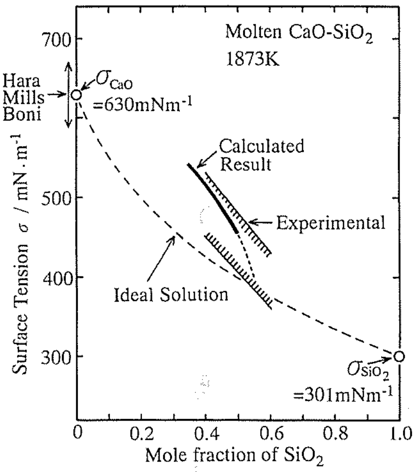


Fig. 7. Comparison of calculated results for surface tensions of various molten salt mixtures with the literature values [87NIS]. Calculated results: ——; literature values: ●, ■, ▲.



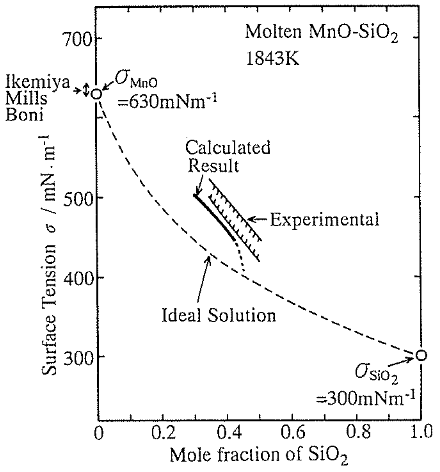


Fig. 8. (left) Comparison of calculated results for surface tension of molten CaO–SiO$_2$ mixtures with the experimental results [51Kin, 69Ono, 71Sha, 74Gun, 81Muk].

Fig. 9. (right) Comparison of calculated results for surface tension of molten MnO–SiO$_2$ mixtures with the experimental results [51Kin, 67Muk].

Table 7. Values for the calculation of surface tensions of molten oxide mixtures.

X	Molar Volume [m^3 · mol^{-1}] [87Mil]
CaO	$20.7 \cdot \{1 + 0.01 \cdot 10^{-2} \cdot (T - 1773)\} \cdot 10^{-6}$
MnO	$15.6 \cdot \{1 + 0.01 \cdot 10^{-2} \cdot (T - 1773)\} \cdot 10^{-6}$
SiO$_2$	$27.516 \cdot \{1 + 0.01 \cdot 10^{-2} \cdot (T - 1773)\} \cdot 10^{-6}$

X	σ_X: Surface Tension [mNm^{-1}]	
	Literature values	Present work
CaO	670 (1823 K) [88Har], 586 (1773 K) [56Bon], 625 (1773 K) [87Mil]	630 (1873 K)
MnO	630 (m.p.) [93Ike], 641 (1773 K) [56Bon], 645 (1773 K) [87Mil]	630 (1843 K)
SiO$_2$	$243.2 + 0.031 \cdot T$ [87NIS]	$243.2 + 0.031 \cdot T$

Energy parameters used in the cell model [84Gay]

system	cation		Cells Formation: W_{ij}/cal		Cells Interaction: E_{ij}/cal	
	i	j	$(W_{ij})_1$	$(W_{ij})_2$	$(E_{ij})_1$	$(E_{ij})_2$
SiO$_2$–CaO	Si	Ca	– 12500	0	– 4500	7500
SiO$_2$–MnO	Si	Mn	– 4500	0	– 1000	5200

$W_{ij} = (W_{ij})_1 + (W_{ij})_2 \cdot N_i$
$E_{ij} = (E_{ij})_1 + (E_{ij})_2 \cdot N_i$

Table 8. Calculated results for surface tensions of molten oxide mixtures and concentration of SiO$_2$ in surface phase.

CaO–SiO$_2$ at 1873 K						
$N^B_{SiO_2}$	0.35	0.40	0.45	0.50	0.51	0.55
σ/mNm^{-1}	545	521	493	461	446	388
$N^B_{SiO_2}$	0.365	0.446	0.540	0.693	0.976**	0.994**
MnO–SiO$_2$ at 1843 K						
$N^B_{SiO_2}$	0.30	0.35	0.40	0.43	0.44	0.45
σ/mNm^{-1}	505	485	461	444	423	407
$N^S_{SiO_2}$	0.362	0.426	0.518	0.622	0.984**	0.988**

The composition with ** is beyond the range where the thermodynamic data and functions are defined in the bulk phase.

namic data have been taken from several databases containing data that have been assessed according to the CALPHAD approach. The application of the present method to a wider range of systems and fine tuning of the general model parameter β as well as the general critical compilation of such properties as σ_X and V_X of the pure substances will enable us to develop a multi-functional thermodynamic databank system. This will be of wide applicability in the evaluation of physico-chemical properties of alloys and other solution-phase-forming systems in conjunction with the simultaneous calculation of the phase equilibria in such systems.

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(Received October 23, 1995)