



Title	Thermodynamic Evaluation of the Surface Tension of Molten Salt Mixtures in Common Ion Alkali-Halide Systems
Author(s)	Tanaka, Toshihiro; Hara, Shigeta; Ogawa, Mahoba et al.
Citation	Zeitschrift für Metallkunde. 1998, 89(5), p. 368-374
Version Type	VoR
URL	https://hdl.handle.net/11094/26515
rights	©Carl Hanser Verlag, München
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

Toshihiro Tanaka, Shigeta Hara, Mahoba Ogawa and Tamotsu Ueda

Osaka University, Japan

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

A thermodynamic model has been derived for the surface tension of molten salt mixtures in common ion alkali-halide systems considering the relaxation structure of the surface and the ionic sizes. The composition dependence of the surface tension of those systems has been discussed on the basis of the calculated results which have been obtained using thermodynamic databases.

1 Introduction

Various thermodynamic databases have been constructed in some countries so far. Usually these databases have been used for the calculation of phase diagrams, which is sometimes called the CALPHAD (computer CALculation of PHase Diagrams) approach [92Nis]. This CALPHAD approach has been recognized to be useful in various aspects of metallurgical engineering and materials science. In addition to the use of thermodynamic databases for the calculations of phase diagrams, it would be rather desirable to apply them to the calculation of other physico-chemical quantities, such as surface tensions. Performing this, not only the utility of databases can be enlarged, but also a deeper understanding of the physical properties in question can be reached.

The authors have already applied those thermodynamic databases to the calculation of the surface tension of molten alloys, molten salt mixtures, and molten oxide mixtures [94Tan, 96Tan]. In those calculations, we have applied Butler's equation [32But] and the approach proposed by Speiser et al. [87Spe, 89Yeu] to evaluate the excess Gibbs energy in the surface. Although the calculated results of the surface tension of molten alloys usually agree well with the experimental results, some calculated results for molten salt mixtures show discrepancies with the literature values [94Tan, 96Tan].

The molten salt mixtures generally have the tendency to show large downward curvature of the composition dependence of the surface tension [80Goo, 96Tan]. In addition, there have not been any thermodynamic models which can provide good agreement of the calculated surface tension with the literature values even for alkali-halide systems [80Goo, 96Tan].

The purpose of the present work is to derive the thermodynamic model to evaluate the surface tension of molten salt mixtures in common ion alkali-halide systems, and to discuss the composition dependence of the surface tension of those systems.

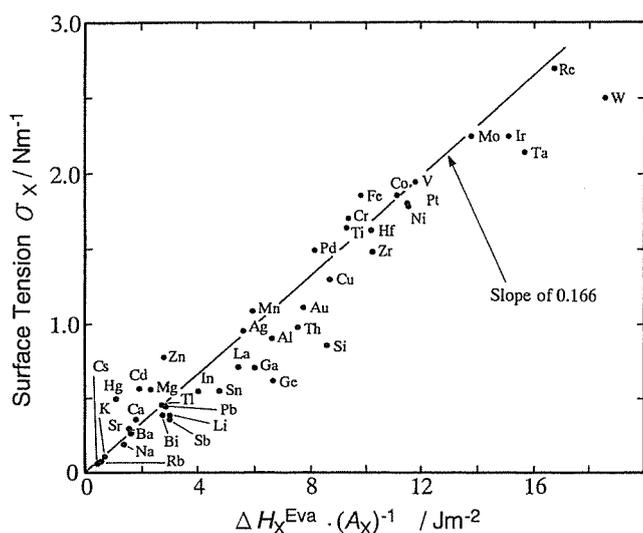


Fig. 1. Correlation of surface tension σ_X with $\Delta H_X^{Eva}/A_X$ for various liquid metals.

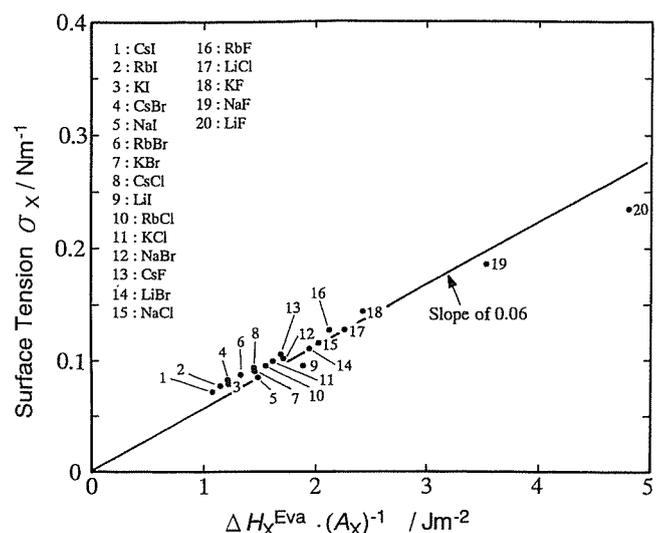


Fig. 2. Correlation of surface tension σ_X with $\Delta H_X^{Eva}/A_X$ for pure alkali-halide molten salts.

2 Butler's Equation

In order to use the thermodynamic databases directly in the previous work [94Tan, 96Tan], Butler's equation [32But] has been selected to calculate the surface tension of liquid solutions. Butler derived the equation of surface tension of liquid solutions assuming an equilibrium between a bulk phase and a hypothetical surface phase [32But]. The surface phase consists of the outermost monolayer at the surface. Butler's equation for an A-B binary solution is given in Eq. (1)

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

In the above equation, σ_X ($X = A$ or B) is the surface tension of the pure liquid X , A_X ($X = A$ or B) is the molar surface area of a pure liquid, and these are obtained from the molar volume V_X of the pure liquid X using Eq. (2).

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

where N_0 is the Avogadro number.

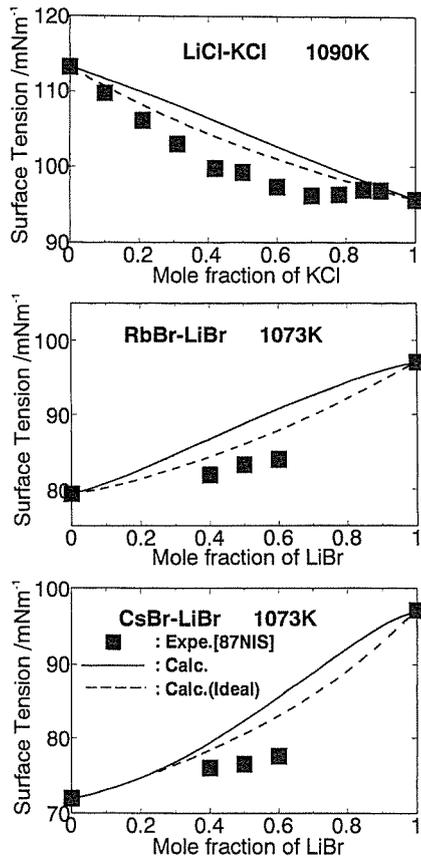


Fig. 3. Comparison of calculated results from Eq. (1) for surface tension of some molten salt mixtures in alkali-halide systems with the experimental results.

Table 1. Relationship between sign of excess Gibbs energy and deviation of surface tension from ideal solution based on Eqs (1) to (3) and (9) in liquid alloys

Liquid Alloys		
Sign of Excess Gibbs Energy in Bulk		Deviation of Surface Tension from ideal Solution
Positive	↔	Negative
Negative	↔	Positive

In Eq. (1), superscripts S and B denote the surface phase and the bulk phase, respectively. $\bar{G}_A^{E,P}(T, N_B^P)$ and $\bar{G}_B^{E,P}(T, N_B^P)$ ($P = S$ or B) are the partial excess Gibbs energies of the components A and B. These are functions of temperature T and mole fraction N_B in the parentheses.

The partial excess Gibbs energies in the bulk phase $\bar{G}_A^{E,B}(T, N_B^B)$ and $\bar{G}_B^{E,B}(T, N_B^B)$ can be obtained directly from thermodynamic databases. For the excess Gibbs energy in the surface phase, we have used Eq. (3).

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

Equation (3) was based on the models proposed by Speiser and coworkers [87Spe, 89Yeu]. This equation means that the partial excess Gibbs energy in the surface phase has the same function of T and N_B as that in the bulk phase, but the mole fraction N_B^B in the bulk phase is replaced by the mole fraction N_B^S in the surface phase. In addition, a coefficient β^{MIX} is multiplied to the right-hand side. This β^{MIX} comes mainly from the difference between the coordination number in the bulk phase and that in surface phase. The value of β^{MIX} was determined in the previous work [96Tan] as follows:

The thermodynamic relation is given for the equilibrium between the bulk phase and the surface phase for a pure substance X in Eq. (4) [96Tan]

$$\sigma_X A_X = U_X^S - U_X^B \quad (4)$$

where $U_X^S < 0$, $U_X^B < 0$ are the binding energy of the pure substance X in the surface and that in the bulk.

The following relation is assumed:

$$U_X^S = \frac{Z^S}{Z^B} U_X^B \quad (5)$$

where Z^S and Z^B are the coordination numbers in the surface and the bulk, respectively.

Here, the binding energy U_X^B is replaced by the heat of evaporation $-\Delta H_X^{\text{Eva}}$ as follows:

$$U_X^B = -\Delta H_X^{\text{Eva}} \quad (6)$$

Finally, the following relation is obtained:

$$\sigma_X = \left(1 - \frac{Z^S}{Z^B}\right) \frac{\Delta H_X^{\text{Eva}}}{A_X} \quad (7)$$

When σ_X is plotted against $\Delta H_X^{\text{Eva}}/A_X$, the gradients of the relations for liquid metals and molten salts are not satisfied with the above Eq. (7) assuming $(Z^S/Z^B)_{\text{metal}} = 9/12 = 3/4$ and $(Z^S/Z^B)_{\text{salt}} = 5/6$. We have, therefore, introduced β^{pure}

as the apparent ratio of the coordination number in the surface phase to that in the bulk phase instead of Z^S/Z^B as follows

$$\sigma_X = (1 - \beta^{\text{pure}}) \frac{\Delta H_X^{\text{Eva}}}{A_X} \quad (8)$$

As shown in Figs. 1 and 2, $\beta^{\text{pure}} = 0.83$ and $\beta^{\text{pure}} = 0.94$ were obtained on the basis of Eq. (8) for pure liquid metals and for pure molten salts, respectively. In addition, we assumed the following relation for molten salt mixtures as well as liquid alloys [96Tan]

$$\beta^{\text{pure}} \text{ in Eq. (8)} = \beta^{\text{MIX}} \text{ in Eq. (3)} \quad (9)$$

3 Calculated Results Obtained from Butler's Equation

When all of the informations are put into Eq. (1), 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).

In the previous work [96Tan], the surface tensions of liquid alloys and molten salt mixtures were calculated from Eqs. (1) to (3) and the assumption of Eq. (9). As described in the previous work [96Tan], the calculated results

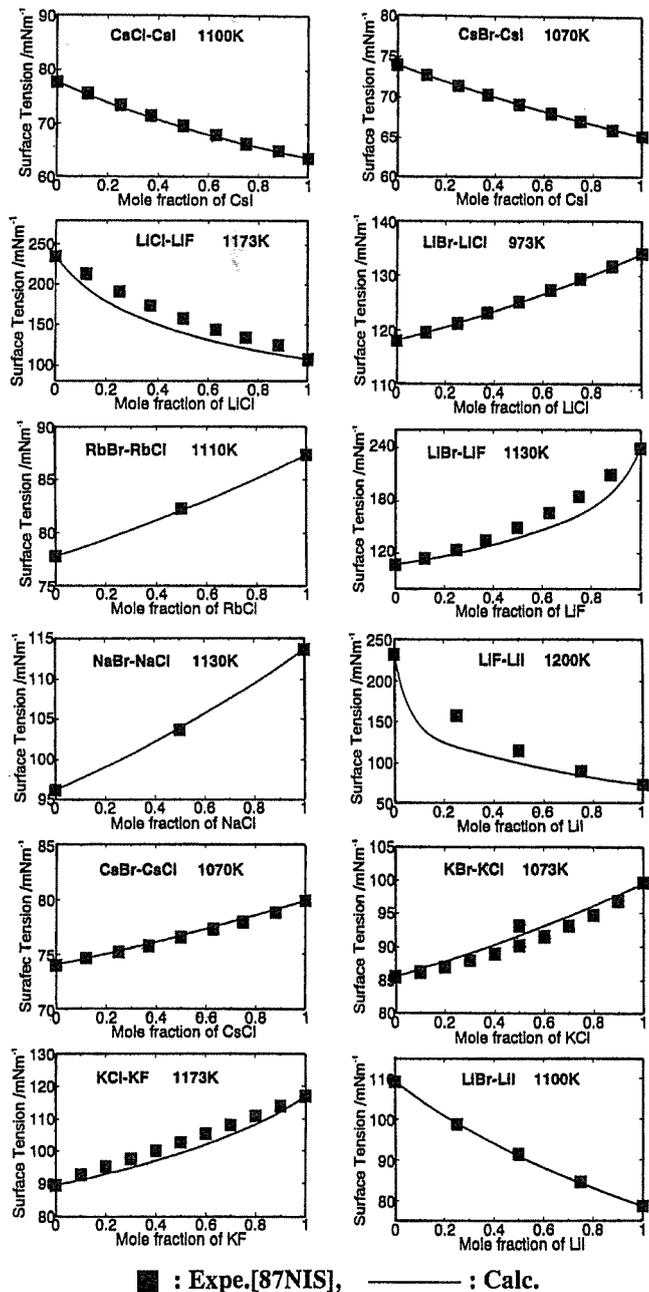


Fig. 4a. Comparison of calculated results from Eq. (20) for surface tension of various molten salt mixtures in common cation alkali-halide systems with the experimental results

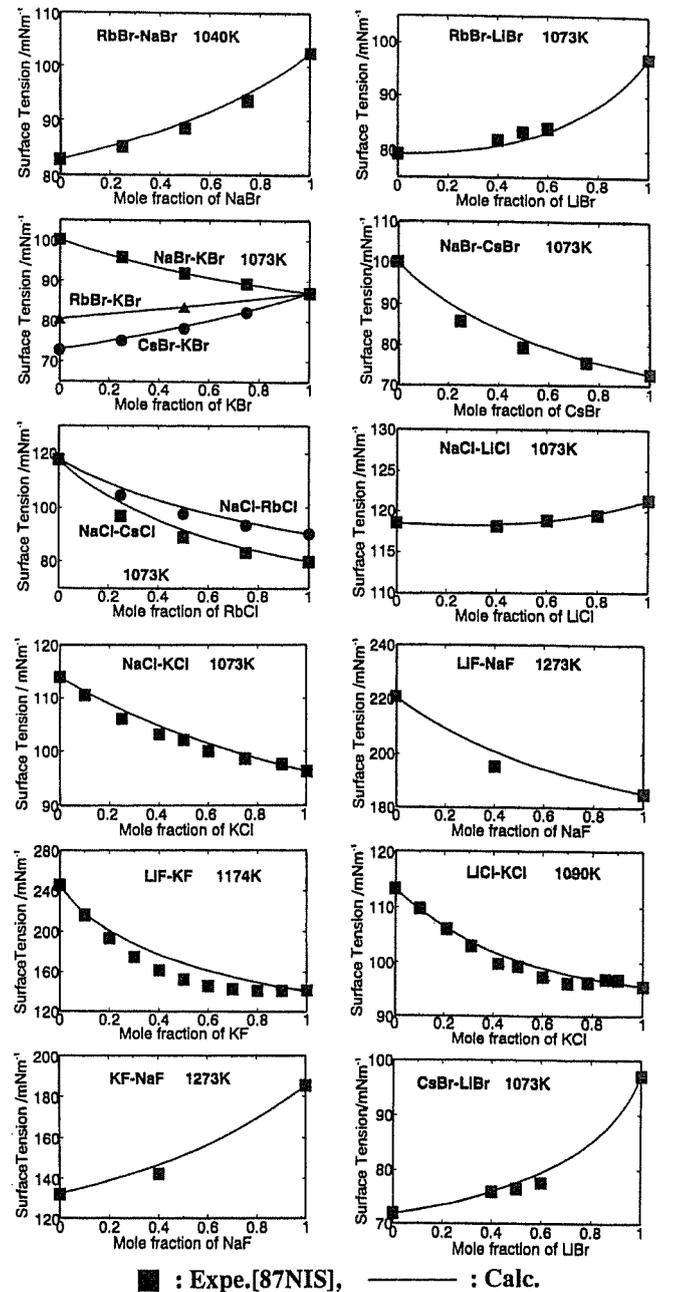


Fig. 4b. Comparison of calculated results from Eq. (20) for surface tension of various molten salt mixtures in common anion alkali-halide systems with the experimental results.

for liquid alloys agree well with the experimental data. However, the calculated results for some molten salt mixtures show some discrepancies with the experimental data as shown in Fig. 3. Those molten salt mixtures have the tendency to show large downward curvature in the composition dependence of the surface tension. In addition, as shown in Table 1, we noticed that in alloys with negative excess Gibbs energy in the bulk, the surface tension deviates positively from that of the ideal solution [94Tan]. On the other hand, in alloys with positive excess Gibbs energy in the bulk, the surface tensions have the tendency to show negative deviations from that of the ideal solution. We found that this rule can be generally applied to liquid alloys on the basis of Eqs (1) to (3) and (9) [94Tan]. However, as shown in Fig. 3, the experimental results of the surface tension of those molten salt mixtures, of which excess Gibbs energies are negative, show negative deviations from that of the ideal solution. Then, the calculated results of the surface tension of those molten salt mixtures cannot satisfy the experimental results so far as Eqs (1) to (3) and (9) are used because the calculated results based on these equations deviate positively from that of the ideal solution. Thus, the results in Fig. 3 and Table 1 show that we need to consider some additional factors to the Eqs (1) to (3) and (9) for molten salt mixtures. In the present works, we will introduce two factors to derive a new equation for the surface tension of those mixtures. One of them is the consideration of the relaxation of the surface, which is explained in the following Section 4.1 and 4.2. The other is the mixing entropy considering the ionic sizes described in the Section 4.3.

4 Derivation of Equations of Surface Tension of Molten Salt Mixtures

4.1 Surface Tension of Pure Molten Salts

In order to elucidate the apparent ratio β^{pure} in Eq. (8), we have considered the relaxation effect in the surface on the relationship among U_X^S , U_X^B and σ_X as described below.

Since the real surface has a higher energy than the ideal surface, which is created by dividing the bulk, it is assumed that some parts of the energy in the surface are consumed to form the relaxation structure, and the rest of the difference between the energy in the surface and that in the bulk can be seen as the real surface energy

$$\sigma_X A_X = (U_X^S - \Delta E_X) - U_X^B \quad (10)$$

where $\Delta E_X > 0$ is the energy to form the relaxation structure.

The relation in Eq. (5) is introduced again. In addition, the energy to form the relaxation structure in the surface is assumed to be proportional to U_X^B as follows

$$\Delta E_X = -\frac{\xi}{Z^B} U_X^B \quad (11)$$

The binding energy U_X^B is replaced by the heat of evaporation $-\Delta H_X^{\text{Eva}}$ again as shown in Eq. (6).

Then,

$$\begin{aligned} \sigma_X &= \left[1 - \frac{(Z^S + \xi)}{Z^B} \right] \frac{\Delta H_X^{\text{Eva}}}{A_X} \\ &= \left[1 - \frac{(Z^S)'}{Z^B} \right] \frac{\Delta H_X^{\text{Eva}}}{A_X} \\ &= [1 - (\beta^{\text{pure}})'] \frac{\Delta H_X^{\text{Eva}}}{A_X} \end{aligned} \quad (12)$$

where $(\beta^{\text{pure}})' = \frac{(Z^S)'}{Z^B} = \frac{(Z^S + \xi)}{Z^B}$, and $(Z^S)' = (Z^S + \xi)$ is the apparent coordination number in the surface under consideration of surface relaxation.

When a plot of σ_X is made with $\Delta H_X^{\text{Eva}}/A_X$, the value of $(\beta^{\text{pure}})'$ is determined from the gradient of the linear relation as shown in Figs 1 and 2. That is to say, $(\beta^{\text{pure}})' = 0.83$ for liquid metals and $(\beta^{\text{pure}})' = 0.94$ for molten salts. Data of σ_X and ΔH_X^{Eva} are described in Ref. [96Tan]. Even when we assume $\beta^{\text{MIX}} = (\beta^{\text{pure}})'$, in which the surface relaxation for pure molten salts is considered, the calculated results of the surface tension of molten salt mixtures based on Eqs (1) to (3) and (9) do not agree with the experimental data as shown in Fig. 3. Therefore, in the molten salt mixtures, we should consider that the relaxation structure in the surface affects the additional change in the excess Gibbs energy in the surface except the change in the apparent coordination number $(Z^S)' = (Z^S + \xi)$.

4.2 Relationship Between the Excess Gibbs Energy in the Bulk Phase and that in the Surface Phase of Molten Salt Mixtures

The excess Gibbs energy $\bar{G}_X^{\text{Ex,B}}(T, N_B^B)$ in the bulk phase is assumed to be mainly determined by the polarization which is generated by the different ions having the same charge sign. $\bar{G}_X^{\text{Ex,B}}(T, N_B^B)$ can be expressed by the following equation on the basis of the thermodynamic model of molten mixtures of alkali-metal halides by Lumsden [61Lum] although we ignore the effect of the London force on the excess Gibbs energy $\bar{G}_X^{\text{Ex,B}}(T, N_B^B)$

$$\bar{G}_X^{\text{Ex,B}}(T, N_B^B) \propto \alpha Z^B \left(\frac{1}{d_A^2} - \frac{1}{d_B^2} \right)^2 \quad (13)$$

where α is the polarization factor, d_A and d_B are the ionic distances of the substances A and B, and they are assumed here to be the sum of the radius of the cation and that of the anion for pure salts A and B, respectively. For example, in the case of NaF–LiF system,

$$d_A = (\text{ionic radius of Na}^+) + (\text{ionic radius of F}^-) \quad (14)$$

$$d_B = (\text{ionic radius of Li}^+) + (\text{ionic radius of F}^-) \quad (15)$$

We assume the following equation for the excess Gibbs energy in the surface $\bar{G}_X^{\text{Ex,S}}(T, N_B^S)$ corresponding to Eq. (13) for the bulk

$$\begin{aligned} \bar{G}_X^{\text{Ex,S}}(T, N_B^S) &\propto \alpha (Z^S)' \left\{ \frac{1}{(\zeta d_A)^2} - \frac{1}{(\zeta d_B)^2} \right\}^2 \\ &= \alpha (Z^S)' \left\{ \frac{1}{d_A^2} - \frac{1}{d_B^2} \right\}^2 \frac{1}{\zeta^4} \end{aligned} \quad (16)$$

Table 2. Values of surface tension and density of pure molten salts and excess Gibbs energy $G^{E,B}(T, N_A^B, N_B^B)$ of molten salt mixtures in the bulk phase. $G^{E,B}(T, N_A^B, N_B^B)$ in Eqs (21) and (22) 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/mN · m ⁻¹	Density of pure molten salts $\rho_X/10^{-3}$ kg · m ⁻³	$G^{E,B}(T, N_A^B, N_B^B)$ of molten salt mixtures in the bulk phase/J · mol ⁻¹
CsCl–CsI	1100	CsCl: 77.6	2.60	$N_{CsCl}N_{CsI}(745 - 167N_{CsCl})$
		CsI: 63.5	2.95	
LiCl–LiF	1173	LiCl: 107.5	1.38	$N_{LiCl}N_{LiF}(-1000)$
		LiF: 234.5	1.78	
RbBr–RbCl	1110	RbBr: 77.8	2.55	$N_{RbBr}N_{RbCl}(121 + 46N_{RbCl})$
		RbCl: 87.4	2.14	
NaBr–NaCl	1130	NaBr: 96.2	2.25	$N_{NaBr}N_{NaCl}(293 + 105N_{NaCl})$
		NaCl: 113.7	1.53	
CsBr–CsCl	1070	CsBr: 74.0	2.94	$N_{CsBr}N_{CsCl}(63)$
		CsCl: 79.9	2.63	
KCl–KF	1173	KCl: 89.4	1.45	$N_{KCl}N_{KF}\{3066 - 10621N_{KF} + 9125(N_{KF})^2\}$
		KF: 117.0	1.88	
CsBr–CsI	1070	CsBr: 74.0	2.94	$N_{CsBr}N_{CsI}(364 - 15 N_{CsBr})$
		CsI: 65.2	2.99	
LiBr–LiCl	973	LiBr: 118.0	2.43	$N_{LiBr}N_{LiCl}(80 + 113 N_{LiCl})$
		LiCl: 134.0	1.46	
LiBr–LiF	1130	LiBr: 107.1	2.33	$N_{LiBr}N_{LiF}\{(1677 - 9.431 T) + (8567 - 0.812 T)N_{LiF}\}$
		LiF: 238.8	1.80	
LiF–LiI	1200	LiF: 231.9	1.77	$N_{LiF}N_{LiI}\{(-1391 + 10.286 T) - 16.836 TN_{LiI} + 8.065 T(N_{LiI})^2\}$
		LiI: 72.9	2.69	
KBr–KCl	1073	KBr: 85.5	2.07	$N_{KBr}N_{KCl}(146 + 109 N_{KCl})$
		KCl: 99.4	1.51	
LiBr–LiI	1100	LiBr: 109.2	2.35	$N_{LiBr}N_{LiI}(818 + 17 N_{LiBr})$
		LiI: 78.6	2.78	
RbBr–NaBr	1040	RbBr: 82.8	2.62	$N_{NaBr}N_{RbBr}(-3452 - 460 N_{NaBr})$
		NaBr: 102.5	2.33	
NaBr–KBr	1073	NaBr: 100.2	2.30	$N_{NaBr}N_{KBr}(-2134 - 251 N_{NaBr})$
		KBr: 87.1	2.07	
RbBr–KBr	1073	RbBr: 80.4	2.59	0
		KBr: 87.1	2.07	
CsBr–KBr	1073	CsBr: 72.7	2.93	$N_{CsBr}N_{KBr}(377)$
		KBr: 87.1	2.07	
NaCl–RbCl	1073	NaCl: 117.9	1.56	$N_{NaCl}N_{RbCl}\{(-3222 + 5.922 T) + (-335 - 5.245 T)N_{NaCl}\}$
		RbCl: 90.1	2.17	
NaCl–CsCl	1073	NaCl: 117.9	1.56	$N_{NaCl}N_{CsCl}\{(-4310 + 5.764 T) + (418 - 5.901 T)N_{NaCl}\}$
		CsCl: 79.8	2.63	
NaCl–KCl	1073	NaCl: 114.0	1.56	$N_{NaCl}N_{KCl}(-2050 - 272 N_{NaCl})$
		KCl: 96.3	1.51	
LiF–KF	1174	LiF: 245.7	1.78	$N_{LiF}N_{KF}\{(-19251 + 4.521 T) - (1205 + 3.146 T)N_{KF} + 4732(N_{KF})^2\}$
		KF: 141.7	1.88	
KF–NaF	1273	KF: 132.1	1.82	$N_{KF}N_{NaF}(-335 + 2.541 T)$
		NaF: 185.2	1.95	
RbBr–LiBr	1073	RbBr: 79.4	2.59	$N_{LiBr}N_{RbBr}\{-16067 - 4018 N_{LiBr} - 4686 N_{LiBr}N_{RbBr}\}$
		LiBr: 97.0	2.37	
NaBr–CsBr	1073	NaBr: 100.2	2.30	$N_{NaBr}N_{CsBr}(-4728 - 209 N_{NaBr})$
		CsBr: 72.7	2.93	
NaCl–LiCl	1073	NaCl: 118.5	1.56	$N_{NaCl}N_{LiCl}(-4686)$
		LiCl: 121.4	1.42	
LiF–NaF	1273	LiF: 220.7	1.73	$N_{LiF}N_{NaF}\{(-7565 + 1.607 T) + (368 + 1.124 T)N_{NaF}\}$
		NaF: 185.2	1.95	
LiCl–KCl	1090	LiCl: 113.3	1.41	$N_{LiCl}N_{KCl}\{(-17570 + 7.627 T) + (-377 - 4.958 T)N_{LiCl}\}$
		KCl: 95.7	1.50	
CsBr–LiBr	1073	CsBr: 71.9	2.93	$N_{CsBr}N_{LiBr}\{(-18661 + 15.171 T) - (10376 + 7.010 T)N_{LiBr} + (3891 - 15.051 T)(N_{LiBr})^2\}$
		LiBr: 97.0	2.37	

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, I/126.904

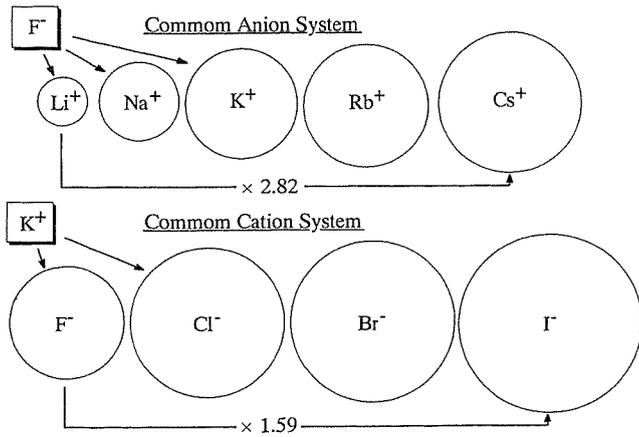


Fig. 5. Comparison of ionic radii of alkali cations and halide anions.

ζ is the ratio of the ionic distance in the surface phase, which is caused by the relaxation in the surface, to that in the bulk phase. ζ has been evaluated to be 0.97 by Sawada and Nakamura [79Saw] from their theoretical work on the displacement of ions at the surface. When the ratio of $\bar{G}_X^{Ex,S}(T, N_B^S)$ in Eq. (13) to $\bar{G}_X^{Ex,B}(T, N_B^B)$ in Eq. (16) is expressed by replacing N_B^B in Eq. (16) by N_B^S , we have obtained the following equation

$$\frac{\bar{G}_X^{Ex,S}(T, N_B^S)}{\bar{G}_X^{Ex,B}(T, N_B^B)} = \left\{ \frac{(Z^S)'}{Z^B} \right\} \frac{1}{\zeta^4} \quad (17)$$

When $(\beta^{pure})' = (Z^S)'/Z^B = 0.94$ and $\zeta = 0.97$ are assumed, we finally obtain:

$$\frac{\bar{G}_X^{Ex,S}(T, N_B^S)}{\bar{G}_X^{Ex,B}(T, N_B^B)} = 1.1 \quad (18)$$

4.3 Revised Butler's Equation for the Surface Tension of the Molten Salt Mixtures

Recently, Ye and Sahai [96Ye] reported that the consideration of the volume fraction in Guggenheim's equation for the surface tension of ideal solutions results in the good agreement of the calculated results with the experimental data in some molten salt systems on the basis of the approach by Grjothheim et al. [72Grj]. As described above, the ionic distances d_A and d_B affect the excess Gibbs energy in the molten salt mixtures. We have, therefore, considered the size effects in the term of mixing entropy in Butler's equation (1) by using d_A and d_B . Then, Butler's equation of the surface tension of A-B binary molten salt mixture is expressed as follows

$$\begin{aligned} \sigma &= \sigma_A + \frac{RT}{A_A} \ln \frac{D_A^S}{D_A^B} + \frac{1}{A_A} \bar{G}_A^{E,S}(T, N_B^S) - \\ &\quad - \frac{1}{A_A} \bar{G}_A^{E,B}(T, N_B^B) \\ &= \sigma_B + \frac{RT}{A_B} \ln \frac{D_B^S}{D_B^B} + \frac{1}{A_B} \bar{G}_B^{E,S}(T, N_B^S) - \\ &\quad - \frac{1}{A_B} \bar{G}_B^{E,B}(T, N_B^B) \end{aligned} \quad (19)$$

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

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

That is to say,

$$\begin{aligned} \sigma &= \sigma_A + \frac{RT}{A_A} \ln \frac{(1 - N_B^S)}{(1 - N_B^B)} + \frac{1}{A_A} \bar{G}_A^{E,S}(T, N_B^S) - \\ &\quad - \frac{1}{A_A} \bar{G}_A^{E,B}(T, N_B^B) + \frac{RT}{A_A} \ln \frac{(1 - N_B^B)d_A + N_B^B d_B}{(1 - N_B^S)d_A + N_B^S d_B} \\ &= \sigma_B + \frac{RT}{A_B} \ln \frac{N_B^S}{N_B^B} + \frac{1}{A_B} \bar{G}_B^{E,S}(T, N_B^S) - \\ &\quad - \frac{1}{A_B} \bar{G}_B^{E,B}(T, N_B^B) + \frac{RT}{A_B} \ln \frac{(1 - N_B^B)d_A + N_B^B d_B}{(1 - N_B^S)d_A + N_B^S d_B} \end{aligned} \quad (20)$$

The final terms in the right hand side of Eq. (20) are the difference between the mixing entropy considering the ionic distances d_A and d_B in the surface phase and these ones in the bulk phase.

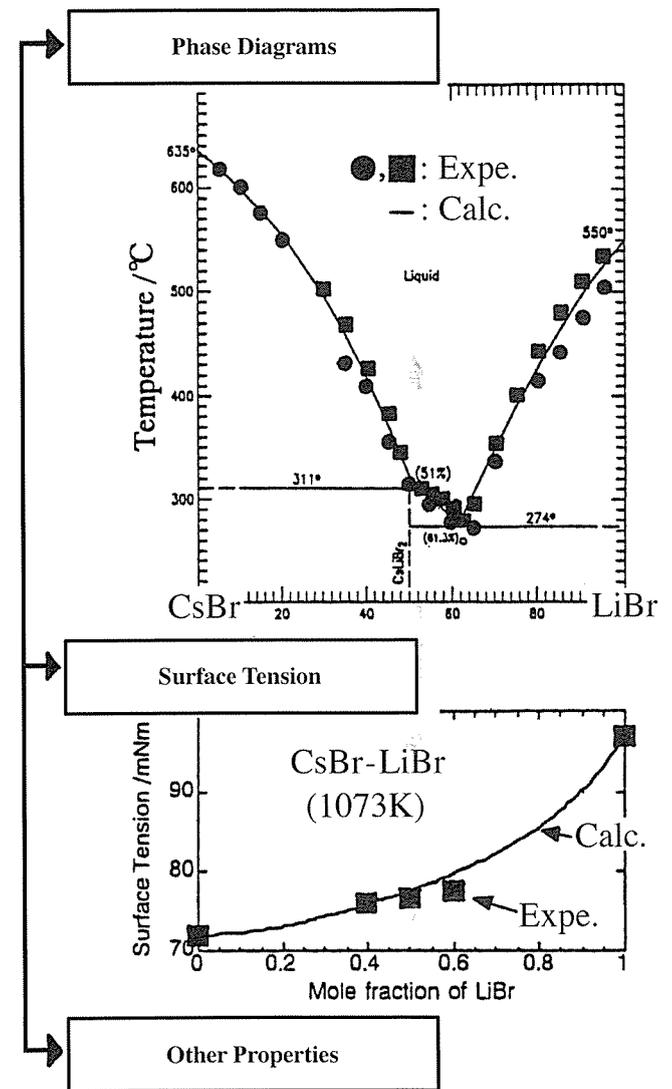


Fig. 6. Concept of multi-functional thermodynamics databank systems.

5 Final Calculated Results and Discussion

Figures 4a and b show the final calculated results from Eqs (2), (18) and (20) based on the consideration of the relaxation in the surface and on the ionic sizes by using thermodynamic data of $G^{\text{Ex},B}(T, N_B^B)$ stored in the databases [83Pel, 88Pel], which permit the calculation of phase diagrams. From the information on $G^{\text{Ex},B}(T, N_B^B)$ in Table 2, the partial excess Gibbs energies of components A and B are obtained from the following equations:

$$\bar{G}_A^{\text{E},B}(T, N_B^B) = G^{\text{E}}(T, N_B^B) - N_B^B \frac{\partial G^{\text{E}}(T, N_B^B)}{\partial N_B^B} \quad (21)$$

$$\bar{G}_B^{\text{E},B}(T, N_B^B) = G^{\text{E}}(T, N_B^B) + (1 - N_B^B) \frac{\partial G^{\text{E}}(T, N_B^B)}{\partial N_B^B} \quad (22)$$

The data on the surface tension and the density of pure component salts in Table 2 are taken from the NIST molten salt database [87NIS]. As σ_X ($X = A$ or B) of pure component salts, we used the value of σ_X compiled for each binary system in the NIST database to compare the calculated result of σ in Eq. (20), which depends upon σ_X , with experimental data [87NIS]. The selected values for σ_X of pure salts in the NIST database are not always the same as those compiled for each binary system because the data source on the surface tension of binary systems are different from each other. Some different values of σ_X are, therefore, found in Table 2 even for the same component salts at the same temperature. The information on the ionic radii in Table 3 have been taken from the compilation by Janz [67Janz]. As shown in Figs 4a and 4b, the calculated results agree well with the experimental data [87NIS] in both common cation and common anion systems. In addition, we found that in common cation systems, the composition dependence of the surface tension is only slightly deviating from linearity. On the other hand, in common anion systems, they have the large downward curvature of the composition dependence of the surface tension. The different tendency of the composition dependence of the surface tension in the common cation and the common anion systems is based on that the radii of cations in the common anion alkali-halide systems change more largely from Li^+ with a minimum radius to Cs^+ with maximum radius among cations (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) compared with the change in the radii of anions for (F^- , Cl^- , Br^- and I^-) in the common cation alkali-halide systems as shown in Fig. 5.

6 Concluding Remarks

A thermodynamic model has been derived for the surface tension of molten salt mixtures considering the surface relaxation structure and the ionic sizes. Based on the present

Table 3. Ionic radii in Å of alkali cations and halide anions

Li	0.60	F	1.36
Na	0.95	Cl	1.81
K	1.33	Br	1.95
Rb	1.48	I	2.16
Cs	1.69		

approach, the surface tension can be evaluated for the molten salt mixtures in the common ion alkali-halide systems by using the thermodynamic databases which have been constructed for the calculation of the phase diagrams of salt systems. In addition, we can develop a multi-functional thermodynamic databank system, which will be of wide applicability in the evaluation of physico-chemical properties of molten salt mixtures with the simultaneous calculation of the phase diagrams in salt mixtures as well as in metals and alloys as shown in Fig. 6.

Literature

- 32But *Butler, J.A.V.*: Proc. Roy. Soc. A135 (1932) 348–375.
 61Lum *Lumsden, J.*: Discussions of the Faraday Society 32 (1961) 138–146.
 67Janz *Janz, G.J.*: Molten Salts Handbook, Academic Press, New York (1967) 1.
 72Grj *Grjotheim, K.; Holm, J.L.; Lillebuen, B.; Oye, H.A.*: Acta Chemica Scand. 26 (1972) 2050–2062.
 79Saw *Sawada, S.; Nakamura, K.*: J. Phys. C 12 (1979) 1183–1193.
 80Goo *Goodisman, J.*: J. Colloid & Interf. Sci. 73 (1980) 115–123.
 83Pel in: L.P. Cook (ed.), Phase Diagrams for Ceramists, Vol. VII, Amer. Ceram. Soc. Westerville, (1983).
 87Spe *Speiser, R.; Poirier, D.R.; Yeum, K.S.*: Script Metall. 21 (1987) 687–692.
 87NIS NIST Molten Salt Database, National Institute of Standards and Technology, Gaithersburg (1987).
 88Pel *Pelton, A.*: CALPHAD 12 (1988) 127–142.
 89Yeu *Yeum, K.S.; Speiser, R.; Poirier, D.R.*: Metall. Trans. B 20B (1989) 693–703.
 92Nis *Nishizawa, T.*: Mater. Trans. JIM 33 (1992) 713–722.
 94Tan *Tanaka, T.; Iida, T.*: Steel Research 65 (1994) 21–28.
 96Tan *Tanaka, T.; Hack, K.; Iida, T.; Hara, S.*: Z. Metallkd. 87 (1996) 380–389.
 96Ye *Ye, J.; Sazhai, Y.*: Mater. Trans JIM 37 (1996) 170–174.

(Received December 2nd, 1997)

Correspondence Address

T. Tanaka, S. Hara, M. Ogawa, T. Ueda
 Department of Materials Science & Processing
 Graduate School of Engineering
 Osaka University
 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan.