Estimation of the Surface Tensions of Binary Liquid Alloys

K.S. YEUM, R. SPEISER, and D.R. POIRIER

A simple method to estimate the surface tensions of binary alloys has been developed by assuming that the partial molar excess free energies are proportional to the number of nearest neighbors in both the bulk solution and in the surface itself. In order to estimate the surface tension of the alloys, excess free energies of the alloys and the surface tensions of the pure components are required. This method has been applied to ten alloys exhibiting positive, positive as well as negative, and negative deviations from ideal solution behavior. The method depends upon the reliability of the thermodynamic data for the bulk solutions, and, further, it is important to use an interpolation scheme that is consistent with the Gibbs-Duhem requirement, when the thermodynamic data are presented in tabular form as a function of composition. To accomplish this interpolation, a special calculation technique is presented.

I. INTRODUCTION

VARIOUS models for binary solutions have been developed to predict the surface tension of the alloys. For alloys with weak chemical interactions, Defay and Prigogine[1] applied a regular solution model to describe the surface tension; however, the model cannot be applied to the alloys with strong chemical interactions. Joud *et al.*,[2] based on the "surrounded atom" concept and a surface monolayer introduced by Mathieu *et al.*,[3] developed a partition function of a binary solution and then derived expressions for the surface tensions of binary alloys. Laty *et al.*[4] extended this statistical approach and correlated thermodynamic data with the potential energies varying with coordination number. They considered a surface monolayer, as well as the layer just below the surface layer bridging the surface layer to the bulk solution. The numbers of *A-A*, *B-B*, and *A-B* bonds were correlated to the potential energies and then to the thermochemical data of the alloy. They introduced a "privileged surrounded atom," which represents the preference for certain types of neighbors, and the perturbation energy, which measures the extent of the preference. A number of probabilities involved in their model are functions of the potential energies, perturbation energy, and the privileged surrounded atoms. In their treatment, these probabilities were computed for complete atomic disorder. Because this assumption is in conflict with the probability expressions dependent on potential energy, their chemical potentials do not satisfy the Gibbs-Duhem relation.

Goumiri and Joud[5] enhanced the model to eliminate the inconsistency and computed the probabilities rigorously. Their model can be used to interpret experimental data, if the parameters involved in their model are properly adjusted. However, the parameters, which must be consistent with thermochemical data, cannot be easily obtained.

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This paper presents a simple method of predicting the surface tensions of binary alloys, starting with the surface tensions of pure components and the excess free energies of the alloy. The success of this method is demonstrated by applying it to ten binary alloys that collectively show positive deviations, positive as well as negative deviations, depending on composition, and strong negative deviations from ideal solution behavior. In an earlier paper,[6] we applied the model to two binary alloys. To demonstrate general applicability, this model has been refined and applied to the ten binary alloys in this paper.

II. SURFACE TENSION MODEL

The surface of a multicomponent solution can be treated as a "phase." If the components in the surface and bulk phases are in thermodynamic equilibrium, the chemical potential of each component in the surface phase is equal to the chemical potential of the corresponding component in the bulk solution plus the surface energy. Based on this thermodynamic requirement, Butler[7] showed that the surface tension of a binary solution can be given by

$$\sigma = \sigma_A + \frac{RT}{S_A} \ln \frac{a'_A}{a_A} = \sigma_B + \frac{RT}{S_B} \ln \frac{a'_B}{a_B} \qquad [1]$$

where σ, σ_A, and σ_B are the surface tensions of the solution, pure component A, and pure component B, respectively; S_i is the monolayer of component i (i = A or B); a_i and a'_i are the activities of component i in the bulk and surface phases, respectively; R is the gas constant; and T is the absolute temperature. Note that Eq. [1] is valid only if the standard states for the bulk and surface phases are properly defined. The activity a_i is measured with respect to the pure bulk liquid of component i, whose activity is defined as unity. Similarly, the activity a'_i is measured with respect to the pure liquid surface phase of component i, whose activity is defined as unity. The standard states for the bulk and surface phases do not coincide, because the number of nearest neighbors is different for the pure bulk and surface phases.

By replacing an activity with the product of mole fraction and activity coefficient, Eq. [1] is rewritten as

$$\sigma = \sigma_A + \frac{RT}{S_A} \ln \frac{1 - X'_B}{1 - X_B} + \frac{RT}{S_A} \ln \frac{\gamma'_A}{\gamma_A}$$

$$= \sigma_B + \frac{RT}{S_B} \ln \frac{X'_B}{X_B} + \frac{RT}{S_B} \ln \frac{\gamma'_B}{\gamma_B} \quad [2]$$

where X_B and X'_B are the mole fractions of component B in the bulk and surface phases, respectively, and γ_i and γ'_i are the activity coefficients of component i in the bulk and surface phases, respectively.

The activity coefficients for the bulk phase, derived by Fowler and Guggenheim,[8] using a quasi-chemical model, are

$$\ln \gamma_A = \frac{z}{2} \ln \frac{(\beta - 1 + 2X_B)}{X_B(\beta + 1)} \quad [3]$$

and

$$\ln \gamma_B = \frac{z}{2} \ln \frac{(\beta + 1 - 2X_B)}{(1 - X_B)(\beta + 1)} \quad [4]$$

with

$$\beta = [4X_B(1 - X_B)e^{2w/kT} + (1 - 2X_B)^2]^{1/2} \quad [5]$$

In Eqs. [3] through [5], z is the coordination number of the atoms in the bulk phase, k is the Boltzmann constant, and w is the pair-wise interaction energy defined as

$$w = \frac{\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})}{2}$$

where ε_{ij} is the energy ascribed to the i-j bonds. If we want to match these relations with experimental data, the two parameters w and z must be adjusted; *i.e.*, w and z are functions of X_B. In this work, however, we found that z can be assumed constant without compromising estimates of the surface tensions.

It is assumed that the above relations also apply to the surface phase, and that w for the surface is equal to w for the bulk phase. In effect, therefore, the curve of excess free energy *vs* composition for the surface is the same curve for the bulk phases reduced by the ratio z'/z, where z' is the coordination number for the surface atoms. Then, $\ln \gamma'_A$ and $\ln \gamma'_B$ are proportional to the coordination number, and the activity coefficients for the components in the surface phase are

$$\ln \gamma'_A = \frac{z'}{z} \ln \gamma_A \quad [6]$$

and

$$\ln \gamma'_B = \frac{z'}{z} \ln \gamma_B \quad [7]$$

for $X'_B = X_B$. Thus, the activity coefficients for the surface phase are also functions of composition.

Equation [2], together with Eqs. [6] and [7], is used to calculate the surface tension σ and the composition of the surface phase X'_B for a set of parameters comprising X_B, S_A, S_B, γ_A, and γ_B. The surface monolayer areas for the pure components of the alloy may be computed from their densities and structures.

III. INPUT DATA

Table I gives the data used in the calculations of the surface tensions of ten liquid binary alloys. The surface areas of the pure liquid components were computed from the densities of the pure liquid elements at temperature T, as given by Brandes.[9] The densities were used to calculate the surface monolayer areas per gram atom by the following relationship found in Reference 10:

$$S_i = b\mathrm{N}^{1/3}V_i^{2/3} \quad [8]$$

where b is a geometric factor (1.091 for a close-packed lattice), N is Avogadro's number, and V_i is the molar volume of component i determined from its density. The coordination number for the bulk atoms z is assumed to be 12. If the surface atoms are assumed to be arranged on a close-packed plane, the number of nearest neighbors of an atom in the surface layer is six and three in the layer immediately below. For consistency, we have assumed that the number of nearest neighbors surrounding a central atom in the surface phase z' is nine for all the alloys tested in this work. Then, Eqs. [6] and [7] give $\gamma'_A = \gamma_A^{3/4}$ and $\gamma'_B = \gamma_B^{3/4}$ for the same bulk and surface phase compositions, *i.e.*, for $X'_B = X_B$.

The surface tensions of the pure components, $\sigma_i(T)$, are taken from the same works for which the measured surface tensions of the alloys are reported. When they are not reported, they are taken from Brandes.[9]

The partial molar excess enthalpy and entropy for component i are defined by

$$\Delta\bar{H}_i^{xs} = \Delta\bar{H}_i - \Delta\bar{H}_i^{(id)} \quad [9]$$

and

$$\Delta\bar{S}_i^{xs} = \Delta\bar{S}_i - \Delta\bar{S}_i^{(id)} \quad [10]$$

respectively, where the overline represents partial quantities and the superscripts *xs* and (*id*) represent excess and ideal quantities, respectively. For an ideal solution, the enthalpy of solution is zero for any composition. Thus,

$$\Delta\bar{H}_i^{(id)} = 0 \quad [11]$$

For an ideal solution,

$$\Delta\bar{S}_i^{(id)} = -\mathrm{R} \ln X_i \quad [12]$$

The partial molar excess enthalpy, defined by Eq. [9], is redundant, because it is equal to the partial molar enthalpy. The partial excess Gibbs free energy at T K is given by

$$\Delta\bar{G}_i^{xs}(T) = \Delta\bar{H}_i - T\Delta S_i^{xs} \quad [13]$$

The partial molar excess free energies for alloys, except for Ag-Pb and Ni-Si alloys, were taken from Hultgren *et al.*;[11] as is often true, the data are given at equal intervals in composition. The number of segments in the composition axis n is ten, and, thus, the step value h is 0.1. The partial molar excess free energies of component B at ten compositions and the partial molar excess free energies of A at infinite dilution are listed in Table I.

The temperatures of the surface tension data and of the thermochemical data were different for some alloys. In these instances, the thermochemical data were extrapolated to the temperatures of the reported surface

Table I. Properties and Partial Molar Excess Free Energies Used for the Calculation of the Surface Tensions of Binary Liquid Alloys

		Alloy (A-B)									
		Fe-Cu	Cu-Pb	Sn-Pb	Ag-Pb*	Pb-In	Bi-Ag	Ag-Sn**	Cu-Al	Fe-Si	Ni-Si†
T (K)		1823	1373	823	1273	723	1233	1250	1373	1823	1823
σ_A (mN · m^{-1})		1754	1301	546	916	450	332	897	1287	1760	1735
σ_B (mN · m^{-1})		1224	380	428	388	531	916	496	793	700	700
$S_A \times 10^{-4}$ (m^2 · g atom^{-1})		3.68	3.67	6.20	4.72	6.72	7.42	4.71	3.67	3.68	3.54
$S_B \times 10^{-4}$ (m^2 · g atom^{-1})		3.79	7.11	6.78	7.05	6.05	4.71	6.36	4.81	4.66	4.66
$\Delta\bar{G}_B^{xs}$ (J · g atom^{-1})	$X_B = 0$	34,142	21,422	6607	4100	1326	9778	−17,405	−69,621	−104,019	−122,286
	0.1	26,045	17,937	5849	4025	1389	4360	−11,150	−54,497	− 91,538	− 95,287
	0.2	19,590	14,201	5134	3833	1305	2197	− 6213	−40,459	− 73,509	− 70,563
	0.3	14,472	10,196	4456	3418	1163	1184	− 2787	−26,878	− 50,735	− 49,070
	0.4	10,581	7130	3816	2791	987	105	− 632	−14,113	− 27,485	− 31,430
	0.5	7657	4845	3146	2025	753	−1038	414	− 7196	− 12,958	− 17,933
	0.6	5397	3042	2427	1259	531	−1640	791	− 3523	− 6280	− 8548
	0.7	3435	1686	1636	619	347	−1506	1025	− 1594	− 2975	− 2912
	0.8	1720	748	862	197	159	− 887	757	− 603	− 1180	− 343
	0.9	477	184	255	17	42	− 305‡	268	− 134	− 264	180
$\Delta\bar{G}_A^{xs}$	$X_A = 0$	35,773	19,949	14,489	5653	3008	−9330‡	4142	−36,280	− 65,304	− 60,338

Partial molar excess free energy data:
*Based on Hager and Wilkomirsky.[16]
**Errors in Hultgren *et al.*[11] were corrected.
†Estimated from the data reported by Martin-Garin *et al.*[20] and Schwerdtfeger and Engell.[21]
‡Extrapolated values.

tension data. Assuming that the partial molar excess enthalpy and the partial molar excess entropy for component A are independent of temperature, we can obtain

$$\Delta\bar{G}_B^{xs}(T_2) = \Delta\bar{G}_B^{xs}(T_1) - (T_2 - T_1)\Delta\bar{S}_B^{xs} \qquad [14]$$

from Eq. [13] applied at T_1 and T_2. T_1 and T_2 are the temperatures for the thermochemical and surface tension data, respectively. The excess Gibbs free energy at T_2 was obtained using the values of $\Delta\bar{G}_B^{xs}$ and $\Delta\bar{S}_B^{xs}$ listed at T_1.

The partial molar excess free energies of components A and B were interpolated with the cubic spline, and $\Delta\bar{G}_A^{xs}$ was obtained from $\Delta\bar{G}_B^{xs}$ by using a special method given in the Appendix. The method is particularly useful when the thermodynamic quantities are given in a tabular form and interpolations, which are consistent with the Gibbs-Duhem relations, are required. Table II shows the excess free energies, ΔG^{xs} and $\Delta\bar{G}_{Cu}^{xs}$, for Cu-Al melts calculated from Eqs. [A25] through [A33] in the Appendix. The data used in the calculations are eleven $\Delta\bar{G}_{Al}^{xs}$ values and the value of $\Delta\bar{G}_{Cu}^{xs}$ at $x = 1$ taken from Hultgren *et al.*[11] The difference between the calculated values and those listed in Hultgren *et al.* are less than 60 J · g atom^{-1} for all compositions.

IV. RESULTS AND DISCUSSION

Figures 1 through 3, 6 through 10, 12, and 13 show the surface tensions of ten binary alloys. The surface compositions obtained as intermediate results are also shown as insets in the figures. The thermochemical data compiled by Hultgren *et al.*[11] are used for most of the alloys. When the data for an alloy were questionable or not listed, pertinent data were derived from other

Table II. Integral and Partial Excess Free Energies (J · g atom^{-1}) for Cu-Al Melts at 1373 K

X_{Al}	$\Delta\bar{G}_{Al}$* Reference 11	ΔG^{xs} Reference 11	ΔG^{xs} Calculated	$\Delta\bar{G}_{Cu}^{xs}$ Reference 11	$\Delta\bar{G}_{Cu}^{xs}$ Calculated
0.0	−69,621	0	0	0	0
0.1	−54,497	− 6167	− 6201	− 799	− 835
0.2	−40,459	−10,719	−10,719	− 3284	− 3284
0.3	−26,878	−13,556	−13,597	− 7845	− 7904
0.4	−14,113	−14,447	−14,452	−14,669	−14,678
0.5	− 7196	−13,715	−13,725	−20,238	−20,254
0.6	− 3523	−11,979	−11,988	−24,669	−24,685
0.7	− 1594	− 9577	− 9581	−28,204	−28,217
0.8	− 603	− 6711	− 6714	−31,137	−31,156
0.9	− 134	− 3498	− 3498	−33,752	−33,777
1.0	0	0	0	−36,280	−36,280

*Input data used for the calculation of self-consistent excess free energies.

available sources. The procedures followed to estimate the data and other measures taken to select an adequate input data are described below.

A. *Alloys with Positive Deviations from Ideality*

The model is applied to five alloy systems exhibiting positive deviations from ideal behavior. These alloys, listed in the order of decreasing extent of the deviation, are Fe-Cu, Cu-Pb, Sn-Pb, Ag-Pb, and Pb-In. Measured surface tensions for the pure components were used for computations, even though large errors seemed to be involved in some of the measurements.

1. *Fe-Cu*

The surface tensions of pure liquid iron reported by many authors are not in agreement. Noting that its reported value at 1823 K ranges from 1720 to 1865 $mN \cdot m^{-1}$, Dyson[12] measured the surface tensions of Fe-S alloys, showed that 100 ppm of sulfur lowers the surface tension more than 300 $mN \cdot m^{-1}$, and attributed this disagreement to the difference in the content of highly surface-active sulfur in iron. He also pointed out that researchers used different values of the density of liquid iron for the estimation of the surface tension from sessile-drop measurements.

In the calculation of the surface tensions of the Fe-Cu alloy, the surface tension of pure iron was taken from Dyson[12] and that of liquid copper from Brandes.[9] Figure 1 compares the calculated curve with the surface tensions measured by Dyson.[12]

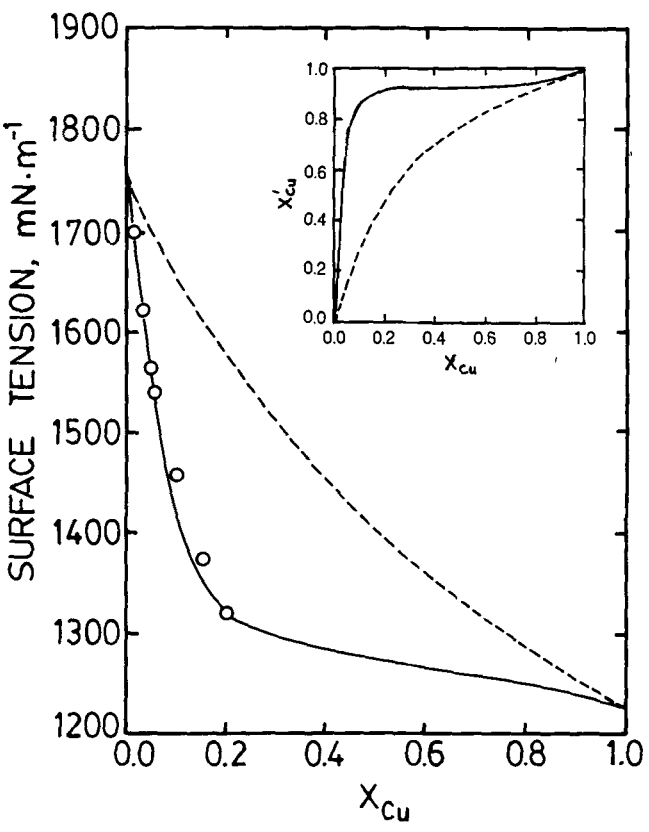

Fig. 1—Surface tensions of Fe-Cu alloys at 1823 K: ○ = Dyson;[12] --- = ideal solution; and —— =calculated.

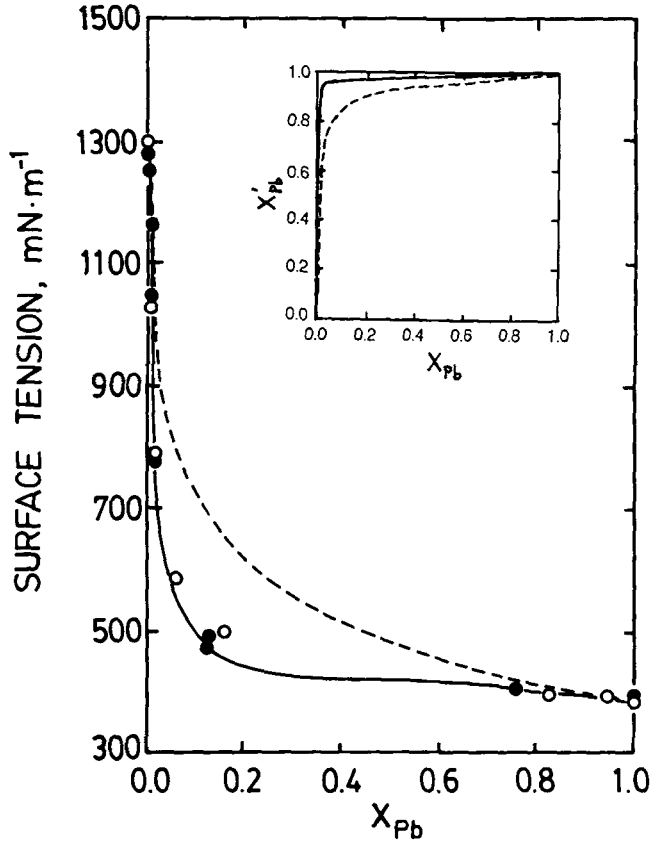

Fig. 2—Surface tensions of Cu-Pb alloys at 1373 K: ○ = Metzger;[13] ● = Joud *et al.*;[14] --- = ideal solution; and —— = calculated.

2. *Cu-Pb*

Figure 2 compares the calculated curve with the surface tension data obtained by Metzger[13] and Joud *et al.*[14] Our calculated surface tensions are in excellent agreement with the experimental data in the full range of composition.

3. *Sn-Pb*

Figure 3 compares the calculated curve with the surface tension data obtained by Hoar and Melford.[15] Our calculated surface tensions are in good agreement with the experimental data.

4. *Ag-Pb*

Thermodynamic data at infinite dilution are often values extrapolated from the data measured at other adjacent compositions. The thermodynamic data compiled by Hultgren *et al.*[11] contain an improbable discontinuity near $X_{Pb} = 0$. These compiled data are based on emf measurements obtained using a chloride electrolyte. Hager and Wilkomirsky[16] selected an oxide electrolyte for emf measurements, because the displacement reactions between the alloys and the chloride electrolyte are liable to cause substantial errors in emf measurements. Hence, we chose to rely on the data of Hager and Wilkomirsky[16] and determined the often used parameter

$$\alpha_{Pb} = \frac{\ln \gamma_{Pb}}{(1 - X_{Pb})^2} \qquad [15]$$

for extrapolation and interpolation purposes.

The plot of α_{Pb} *vs* X_{Pb} at 1273 K is shown in Figure 4.

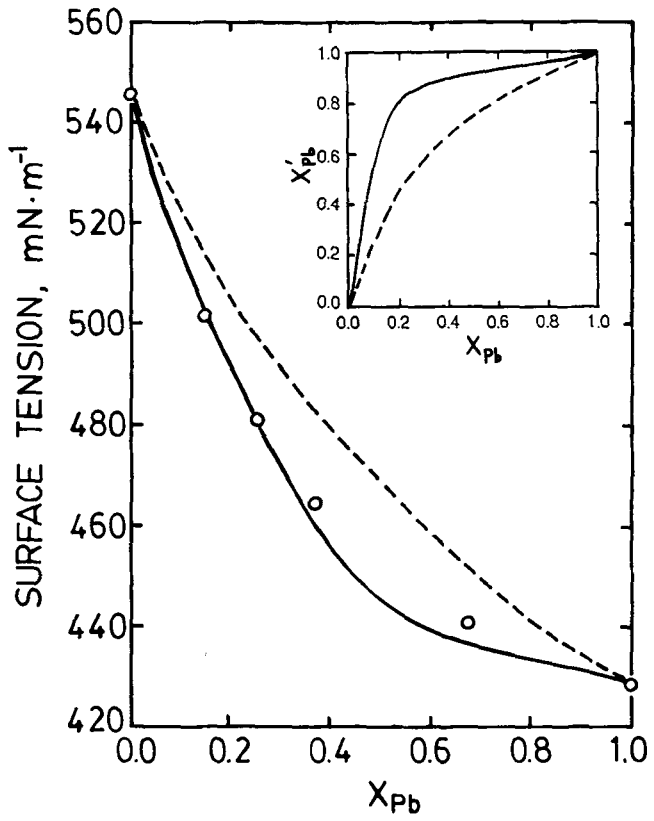

Fig. 3—Surface tensions of Sn-Pb alloys at 823 K: ○ = Hoar and Melford;[15] --- = ideal solution; and —— = calculated.

The regression of the 19 data points to a third-order polynomial is given by

$$\alpha_{Pb} = 0.3874 + 0.6912X_{Pb} + 1.5827X_{Pb}^2 - 2.9054X_{Pb}^3 \quad [16]$$

and the excess integral energy ΔG^{xs} and excess partial molar free energies of Ag and Pb are as follows (see Eqs. [A4] through [A6] in the Appendix):

$$\Delta G^{xs} = RTX_{Pb}(1 - X_{Pb})\,(0.3874 + 0.3456X_{Pb} + 0.5276X_{Pb}^2 - 0.7264X_{Pb}^3) \quad [17]$$

$$\Delta \bar{G}_{Ag}^{xs} = RTX_{Pb}^2(0.0418 - 0.1820X_{Pb} + 1.3540X_{Pb}^2 - 0.7264X_{Pb}^3) \quad [18]$$

$$\Delta \bar{G}_{Pb}^{xs} = RT(1 - X_{Pb})^2\,(0.3874 + 0.6912X_{Pb} + 1.5827X_{Pb}^2 - 2.9054X_{Pb}^3) \quad [19]$$

Figure 5 shows the free energy plots given as functions of mole fractions. The partial molar excess free energies of the Ag-Pb alloys listed in Table I were calculated from these polynomials. Finally, Figure 6 compares the calculated surface tensions with the measured values reported by Metzger[13] and Joud *et al.*[14]

5. *Pb-In*

Figure 7 compares the calculated curve with the surface tension data obtained by Hoar and Melford.[15] The excess free energies reported for 673 K were extrapolated to 773 K by applying Eq. [14]. Our calculated surface tensions are in good agreement with the experimental data.

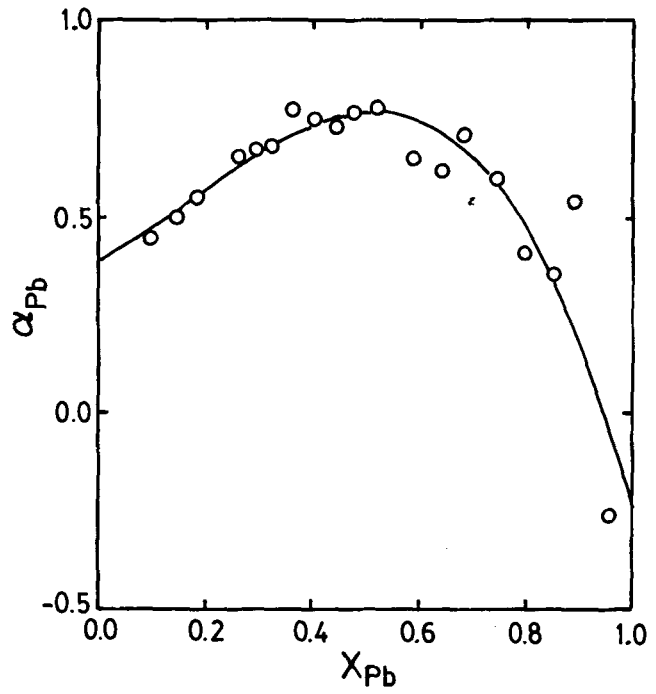

Fig. 4—α_{Pb} in Ag-Pb alloys at 1273 K estimated from the data given by Hager and Wilkomirsky.[16]

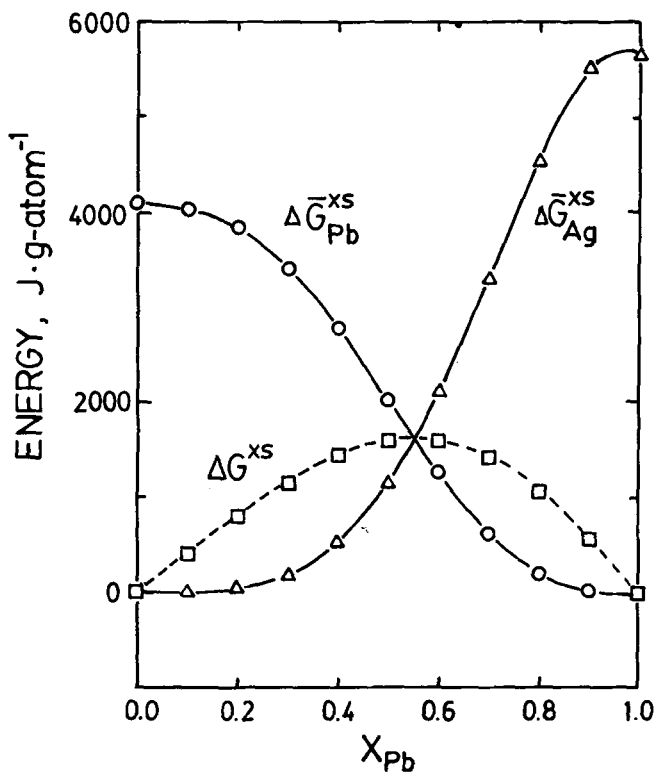

Fig. 5—Integral and partial molar excess free energies of Ag-Pb alloys at 1273 K.

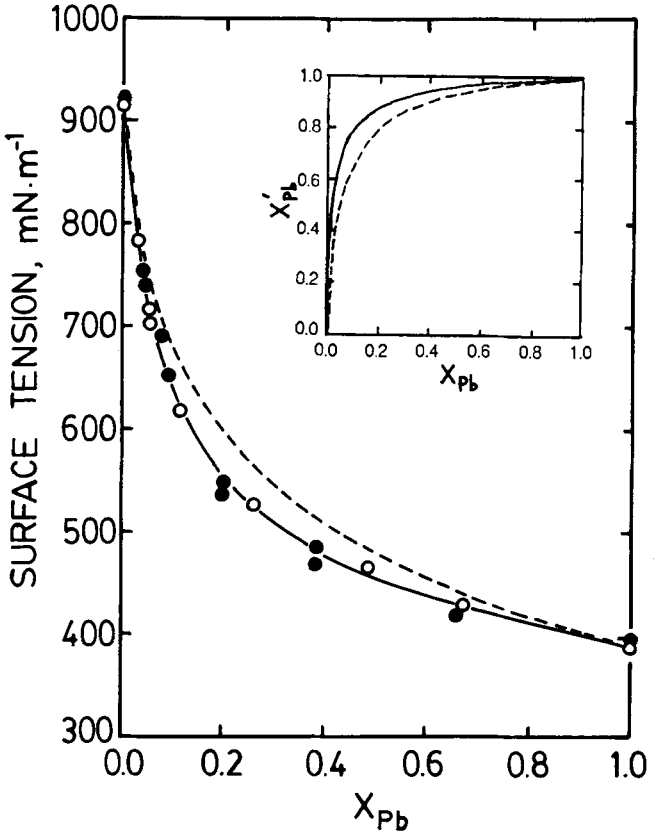

Fig. 6—Surface tensions of Ag-Pb alloys at 1273 K: ○ = Metzger;[13] ● = Joud *et al.*;[14] --- = ideal solution; and —— = calculated.

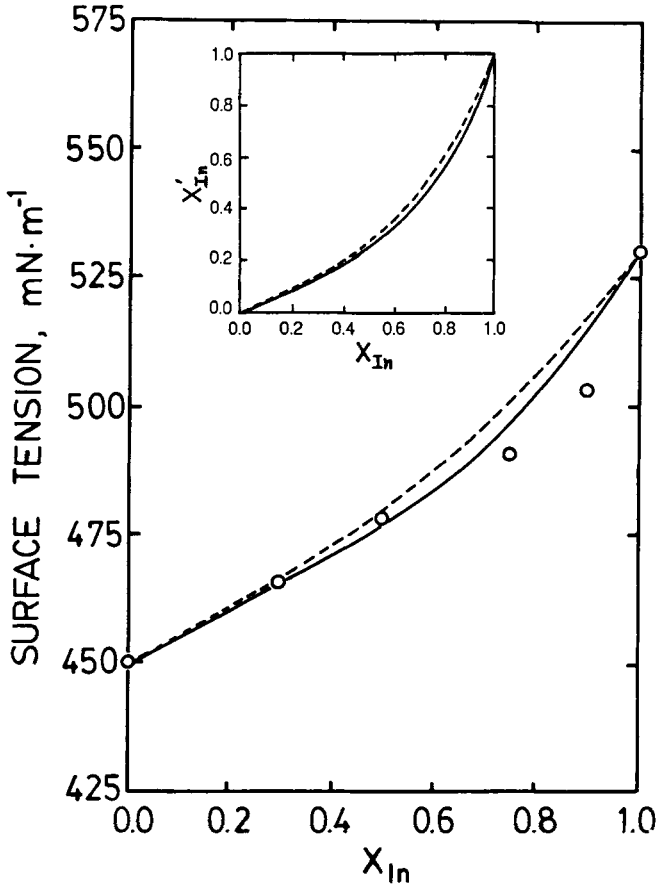

Fig. 7—Surface tensions of Pb-In alloys at 723 K: ○ = Hoar and Melford;[15] --- = ideal solution; and —— = calculated.

B. *Alloys with Positive and Negative Deviations from Ideality*

1. *Bi-Ag*

Figure 8 compares the calculated curve with the experimental data reported by Metzger.[13] The surface tension increases sharply in the range of $0.7 < X_{Ag} < 1.0$, and the difference between the experimental data and calculated curve is greater than that for other alloys. This might be caused by the additional uncertainties involved in the thermochemical data for this alloy. The data compiled by Hultgren *et al.*[11] for 1000 K do not include the partial molar excess free energies between $X_{Ag} = 0.812$ and $X_{Ag} = 1.0$, because alloys of these compositions are solid. Hence, in this work, the data at $X_{Ag} = 0.9$ and $X_{Ag} = 1.0$ were obtained by extrapolation. Furthermore, the thermodynamic data were extrapolated to 1233 K by assuming that the partial molar excess enthalpies and entropies are independent of composition. Comparison of the curve based on ideal solution behavior and the curve calculated from this model shows that ΔG^{xs} is negative at the Ag-rich region and positive at the Bi-rich region.

2. *Ag-Sn*

The integral quantities and partial molar quantities for liquid alloys at 1250 K listed in Hultgren *et al.*[11] are not consistent. By careful examination of the data and comparison with cited references, we found that the labels for the partial molar quantities were reversed. The corrections to be made to the table are (a) "X_{Sn}" must be read as "X_{Ag}"; (b) "Ag Component" must be read as "Sn Component"; and (c) "Sn Component" must be read as "Ag Component." The data shown in Table I are the values taken after making the above corrections. Figure 9 shows the experimental data reported by Lauermann *et al.*[17] and the curve calculated from our model. Our calculated surface tensions are in fairly good agreement with the experimental data.

C. *Alloys with Negative Deviations from Ideality*

1. *Cu-Al*

The calculated surface tensions are shown in Figure 10. The data of Laty *et al.*,[18] by two methods: the maximum bubble pressure (open squares) and the sessile drop (open circles), and earlier measurements by Eremko *et al.*[19] (open triangles) are distributed along our calculated curve. Laty *et al.* postulated that when the attraction between unlike pairs of atoms is strongly negative, there is short-range order in the liquid, and this is manifested in the curve for surface tension at Cu_3Al.

2. *Ni-Si*

Because the thermochemical data for this alloy are not given in Hultgren *et al.*,[11] we had to use other data. The chemical potentials of silicon in Ni-Si alloys reported by Martin-Garin *et al.*[20] and Schwerdtfeger and Engell[21] in the range of $0.05 < X_{Si} < 0.65$ were used to estimate

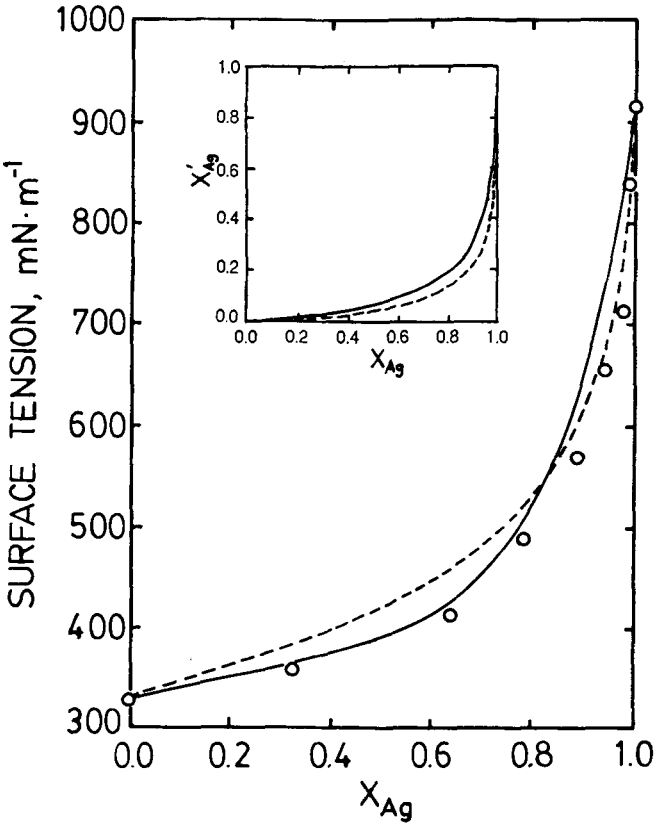

Fig. 8—Surface tensions of Bi-Ag alloys at 1233 K: ○ = Metzger;[13] --- = ideal solution; and —— = calculated.

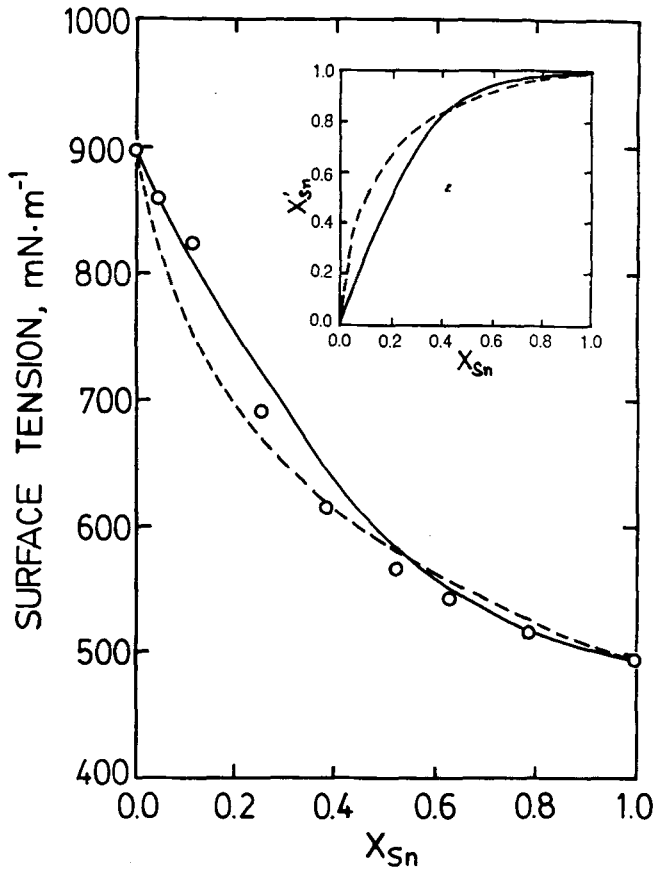

Fig. 9—Surface tensions of Ag-Sn alloys at 1250 K: ○ = Lauermann *et al.*;[17] --- = ideal solution; and —— = calculated.

the excess free energies. A second-order polynomial was used for $\xi(x)$ in Eq. [A1], and then $\Delta\bar{G}^{xs}_{Si}$ is written as

$$\frac{\Delta\bar{G}^{xs}_{Si}}{RT} = (1 - X_{Si})^2 (a_0 + 2a_1X_{Si} + 3a_2X^2_{Si}) \quad [20].$$

Figure 11 shows a plot of $\alpha_{Si} = \Delta\bar{G}^{xs}_{Si}/RT(1 - X_{Si})^2$ *vs* X_{Si} for the data in the range of $0.05 < X_{Si} < 0.65$ at 1853 K. A regression of the data to Eq. [20] gives the coefficients $a_0 = -8.031$, $a_1 = 3.105$, and $a_2 = 7.177$. The partial molar excess free energy of nickel is then given by

$$\frac{\Delta\bar{G}^{xs}_{Ni}}{RT} = X^2_{Si}[(a_0 - a_1) + (a_1 - a_2)X_{Si} + a_2X^2_{Si}] \quad [21]$$

from Eq. [A5] in the Appendix.

The data listed in Table I were computed from Eqs. [20] and [21]. Because the data in the range of $0.05 < X_{Si} < 0.65$ were extrapolated to $X_{Si} = 1$, there are uncertainties. Furthermore, with Eq. [14], the excess free energies were also extrapolated to 1823 K, the temperature at which surface tensions were measured. Nevertheless, our calculated surface tensions are in good agreement with the experimental measurements of Shergin *et al.*,[22] except possibly in the compositional range of $0.15 < X_{Si} < 0.35$ (Figure 12).

3. *Fe-Si*

Our calculated surface tensions are in excellent agreement with the experimental data measured by Popel *et al.*[23] in the full range of composition (Figure 13).

D. *Discussion*

Independent calculations of the compositions of the surface were obtained by consideration of the Gibbs adsorption isotherm.[24] At constant temperature and pressure, the Gibbs adsorption is given by the following equation, which is applicable for any position of the dividing surface:

$$-\left(\frac{1}{RT}\right) d\sigma = \Gamma_A \, d \ln a_A + \Gamma_B \, d \ln a_B \quad [22]$$

where Γ_i is the surface excess of component i defined by

$$\Gamma_i = \frac{X'_i - X_i}{S_i} \quad [23]$$

This equation defines the excess measured with reference to the composition in the bulk liquid. Equation [22] cannot be solved for Γ_A and Γ_B, unless an additional constraint is imposed on the system.

For example, with $\Gamma_A = -\Gamma_B$, Eq. [22] becomes

$$\Gamma_B = -\frac{X_A}{RT} \frac{d\sigma}{d \ln a_B} \quad [24]$$

Guggenheim and Adam[25] considered the monolayer model of the dividing surface and defined the surface excess quantities, $\Gamma^{(u)}_A$ and $\Gamma^{(u)}_B$, such that they are the

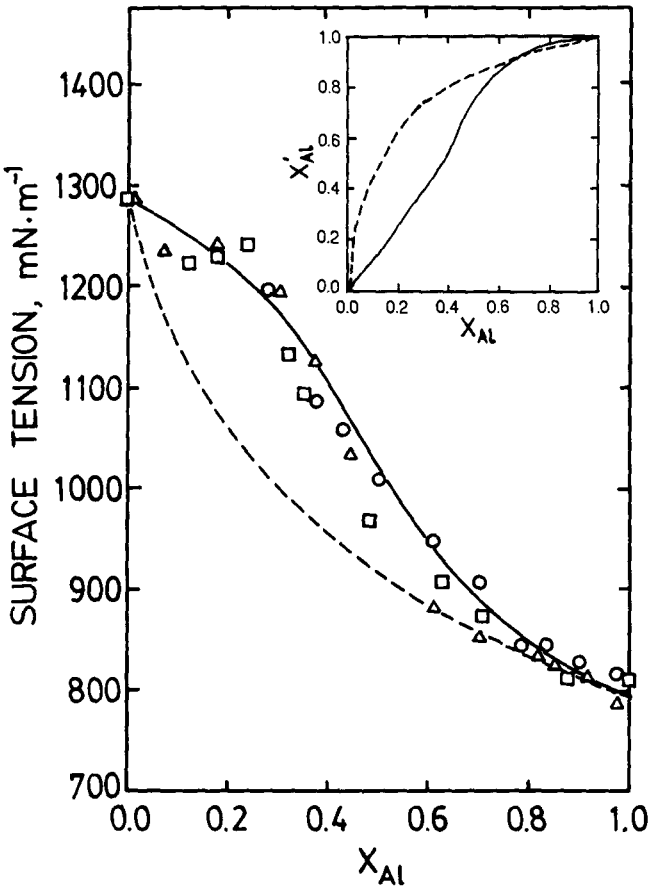

Fig. 10—Surface tensions of Cu-Al alloys at 1373 K: ○ = Laty *et al.*,[18] sessile drop; △ = Laty *et al.*,[18] maximum bubble pressure; □ = Eremko *et al.*;[19] --- = ideal solution; and —— = calculated.

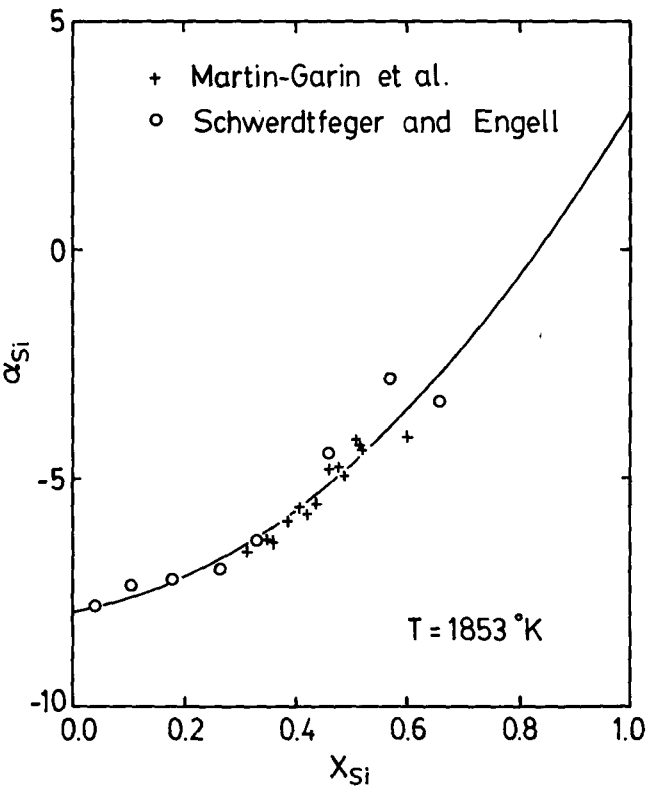

Fig. 11—Least-square fit of α_{Si} function to a second-order polynomial: + = Ref. 20; ○ = Ref. 21.

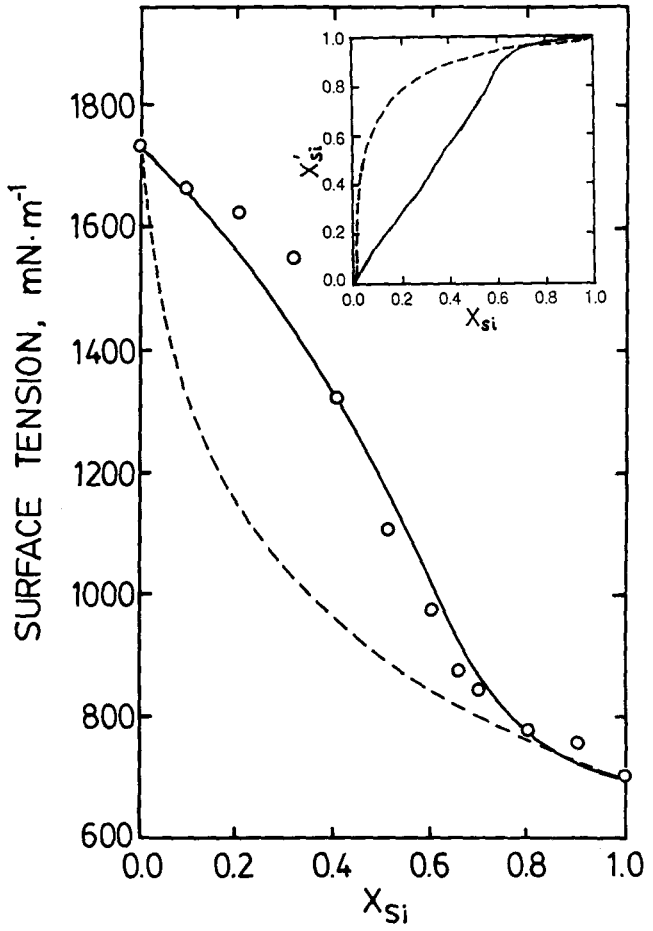

Fig. 12—Surface tensions of Ni-Si alloys at 1823 K: ○ = Shergin *et al.*;[22] --- = ideal solution; and —— = calculated.

number of moles of A and B, respectively, in unit areas of the monolayer. From their treatment, we can get

$$\Gamma_B^{(u)} = \frac{X_B + S_A\Gamma_B}{X_A S_A + X_B S_B} \qquad [25]$$

and

$$X'_B = \frac{X_B + S_A\Gamma_B^{(u)}}{1 + \Gamma_B(S_A - S_B)} \qquad [26]$$

From Eqs. [24] through [26], the compositions of the surface layers are estimated based on available surface tension data, but our model adopts additional assumptions to estimate the surface tension, as well as the composition of the surface layer. It was found that the difference between the surface layer composition, obtained during a calculation of surface tension, and that estimated from Eqs. [24] through [26] was always less than 5 pct for all bulk compositions tested herein. The difference is within the error involved in the numerical estimation of the first derivative $d\sigma/d \ln a_B$ in Eq. [24], and such a small difference indicates that the surface concentrations predicted by the model are valid.

There may be some short-range order in the alloy systems exhibiting very large negative deviations from ideality. The large deviations observed in some solutions are explained in terms of "associated complexes" first

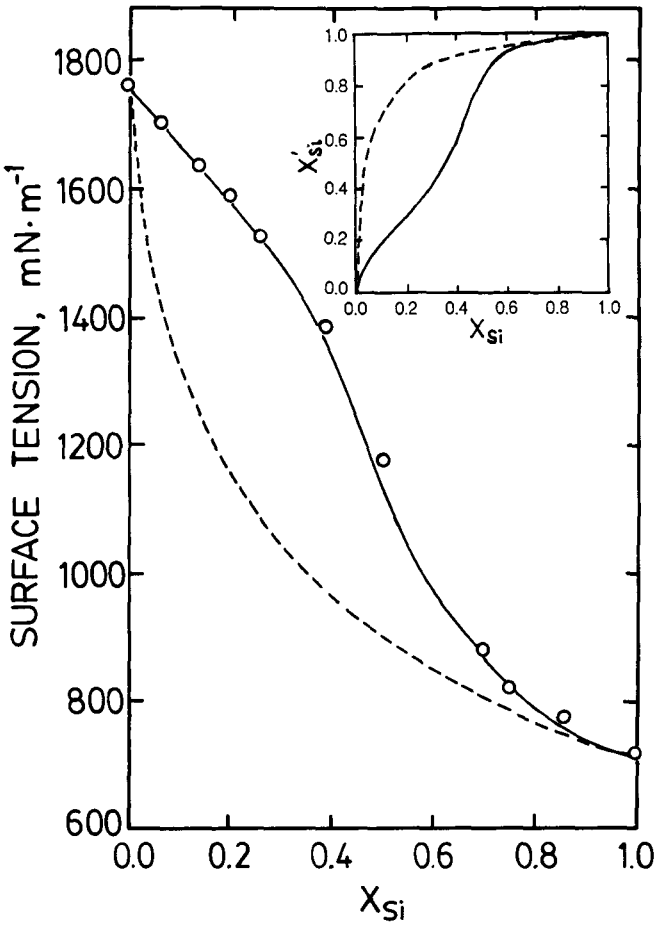

Fig. 13—Surface tensions of Ni-Si alloys at 1823 K: o = Popel *et al.*;[23] --- = ideal solution; and —— = calculated.

proposed by Dolezalek[26] in 1908. These complexes are equivalent to compound-like species whose concentrations in solution depend upon the equilibrium constants of the species. Jordan[27] has effectively applied this concept to the study of bulk alloy phases.

The Cu-Al, Fe-Si, and Ni-Si alloys may be the candidates for the application of the above ideas. In the Cu-Al system, there is the sequence of species: Al_2Cu, AlCu, Al_2Cu_3, and Al_4Cu_9; in Fe-Si: Fe_2Si, Fe_5Si_3, FeSi, $FeSi_2$, and $FeSi_{2.33}$; and in Ni-Si: Ni_3Si, Ni_5Si_2, Ni_2Si, Ni_3Si_2, NiSi, and $NiSi_2$.

The question should be asked: just how many of the species listed in the alloy systems cited above contribute to the anomalies found in the experimental σ *vs* X_B curves for the Cu-Al, Fe-Si, and Ni-Si systems? Certainly, the greater the ratio of the temperature and the melting point of the alloy, the lesser is the short-range order and/or the stability of a stoichiometric "compound" in the liquid. A binary metallic solution is really a ternary system of positive ions immersed in a sea of neutralizing electrons. The Cu-Al alloys form electron compounds in the solid state and if the electrons occupy states within Brillouin-like zones with diffuse boundaries, the tendency to form compound-like complexes will be minimal. The Ni-Si alloy is a more difficult case to interpret, because Si is a nonmetal. The outer electron shell of the Ni atom is 3d 4s, and the outer shell of Si is 3s 4p. If the 4s shell of Ni and the 4p shell of Si contributed two electrons each to the electron sea, there would be no compound formation. But less symmetrical ionizations may be possible.

However, Laty *et al.*[18] claim structure anomalies in the case of the Cu-Al and Ni-Si alloy systems, and Kaufman and Whalen[28] claim there are extrema in the Au-Sn system. On the other hand, Faber[29] cites the research of Pokrovsky *et al.*,[30] who measured the surface tension of Au-Sn alloys between the temperatures 773 and 523 K and found no extrema. It is still uncertain whether or not the anomalies are real or just the experimental scatter of data, but the fact that the systems with negative deviations from ideal behavior consistently exhibit these anomalies seems to indicate that they are real.

APPENDIX

Self-consistent thermodynamic data

The partial molar quantity of a component can be obtained from the partial molar quantity of the other component by integrating the Gibbs-Duhem relation. The integral property is then estimated from the partial molar quantities. The integration required in the reduction of the data can be avoided, if the partial molar quantities are interpolated with a function.

An integral thermodynamic quantity, $W(x)$, may be expressed as

$$W(x) = x(1 - x)\xi(x) \qquad [A1]$$

where x is the mole fraction of component B in the bulk solution (equal to X_B in the text), and $\xi(x)$ is a smooth and continuous function. Notice that the symbol x is used instead of X_B in the Appendix, as a matter of convenience. The partial quantities of component A, $\bar{W}_A(x)$, and of component B, $\bar{W}_B(x)$, derived from their definitions are

$$\bar{W}_A(x) = x^2[\xi(x) - (1 - x)\xi'(x)] \qquad [A2]$$

and

$$\bar{W}_B(x) = (1 - x)^2 [\xi(x) + x\xi'(x)] \qquad [A3]$$

respectively. The thermodynamic quantity W may be enthalpy, entropy, or free energy functions.

A. *Polynomial Interpolation*

A simple power series expansion may be used for $\xi(x)$. Then, the integral and partial properties become

$$W(x) = x(1 - x) \sum_{i=0}^{n} a_i x^i \qquad [A4]$$

$$\bar{W}_A(x) = x^2 \sum_{i=0}^{n} (a_i - a_{i+1})x^i \qquad [A5]$$

and

$$\bar{W}_B(x) = (1 - x)^2 \sum_{i=0}^{n} (i + 1)a_i x^i \qquad [A6]$$

The representations of the thermodynamic properties with $\xi(x)$ are useful for compiling thermodynamic properties

of binary alloys. The function $\xi(x)$ gives interdependent properties, $W(x)$, $\bar{W}_A(x)$, and $\bar{W}_B(x)$, which satisfy the Gibbs-Duhem relation and the definitions of the partial quantities of components A and B.

Bale and Pelton[31] studied various series expressions and recommended the Legendre polynomial for $\xi(x)$; however, one problem of the series expansion is the difficulty in expressing the properties of a system which exhibits strong ordering tendencies for which as many as 20 terms may not be sufficient.

B. *Cubic Spline Interpolation*

Thermodynamic data are often compiled in a tabular form with data at equal intervals between successive compositions; *e.g.*,

$$x_i = \frac{i}{n} \quad (i = 0, 1, \ldots, n)$$

Degtyarev and Voronin[32] suggested that a cubic spline would be adequate for interpolating this type of data. For the $\xi(x)$ in Eq. [A1], they used a cubic spline associated with a number of coefficients, which could be estimated successively from a set of formulas. Because some errors were detected in their formulas, derivations are given below.

They expressed the integral and partial thermodynamic properties with

$$W(x) = x(1 - x)Sp(x) \qquad [A7]$$

$$\bar{W}_A(x) = x^2[Sp(x) - (1 - x)Sp'(x)] \qquad [A8]$$

and

$$\bar{W}_B(x) = (1 - x)^2\,[Sp(x) + xSp'(x)] \qquad [A9]$$

The steps in the composition h are constant, and for each segment $x_i \le x \le x_{i+1}$ $(i = 0, 1, 2, \ldots, n - 1)$, the spline $Sp(x)$ can be written as

$$Sp(x) = A_i + B_i(x - x_i) + C_i(x - x_i)^2 + D_i(x - x_i)^3 \qquad [A10]$$

where A_i, B_i, C_i, and D_i are the coefficients associated with the segment.

The cubic spline function must be smooth and continuous. A necessary condition for the smoothness of the function is the continuity of its first derivative. At the nodal point x_{i+1}, $Sp(x)$ and its derivative $Sp'(x)$, estimated from the equations for the (i)th and $(i + 1)$th segments, must be equal; *i.e.*,

$$Sp(x_{i+1} - 0) = Sp(x_{i+1} + 0) \qquad [A11]$$

and

$$Sp'(x_{i+1} - 0) = Sp'(x_{i+1} + 0) \qquad [A12]$$

Inserting Eq. [A10] into Eqs. [A11] and [A12], we arrive at

$$A_{i+1} = A_i + B_ih + C_ih^2 + D_ih^3 \qquad [A13]$$

and

$$B_{i+1} = B_i + 2C_ih + 3D_ih^2 \qquad [A14]$$

respectively. The solution of these equations for C_i and D_i gives

$$C_i = \frac{[3(A_{i+1} - A_i) - (2B_i + B_{i+1})h]}{h^2} \qquad [A15]$$

and

$$D_i = \frac{[(B_i + B_{i+1})h - 2(A_{i+1} - A_i)]}{h^3} \qquad [A16]$$

Equations [A15] and [A16] give C_i and D_i in terms of A_i and B_i. Thus, the coefficients A_i and B_i are sufficient to define $Sp(x)$.

The partial quantities, Eqs. [A8] and [A9], have terms containing $Sp'(x)$. The continuity and smoothness of these functions impose an additional constraint of the second derivative given by

$$Sp''(x_i - 0) = Sp''(x_i + 0) \qquad [A17]$$

and the combination of this equation with Eq. [A10] leads to

$$C_{i-1} + 3D_{i-1}h = C_i \qquad [A18]$$

When Eqs. [A15] and [A16] are substituted into Eq. [A18], it gives

$$3(A_i - A_{i-2}) = (B_i + 4B_{i-1} + B_{i-2})h \quad (i = 2, 3, \ldots, n) \qquad [A19]$$

Additional boundary conditions are required to fully describe a curve. Degtyarev and Voronin[32] selected the following conditions for the third derivatives of the spline function:

$$Sp'''(x_1 - 0) = Sp'''(x_1 + 0) \qquad [A20]$$

$$Sp'''(x_{n-1} - 0) = Sp'''(x_{n-1} + 0) \qquad [A21]$$

These conditions give

$$A_1 = \frac{(B_0 - B_2)h}{4} + \frac{(A_0 + A_2)}{2} \qquad [A22]$$

and

$$B_n = \frac{B_{n-2} + 2(A_n - 2A_{n-1} + A_{n-2})}{h} \qquad [A23]$$

respectively.

Coefficients A_0 and A_n are obtained from the boundary conditions at $x = 0$ and $x = 1$ given by

$$A_0 = \bar{W}_B(x_0) = \bar{W}_B(0); \qquad A_n = \bar{W}_A(x_n) = \bar{W}_A(1) \qquad [A24]$$

It is easy to see that $Sp(x) = A_i$ and $Sp'(x) = B_i$ at $x = x_i$. Then, Eq. [A9] gives

$$B_i = \frac{1}{ih}\left[\frac{\Delta\bar{G}_2^{xs}}{(1 - x_i)^2} - A_i\right] \qquad [A25]$$

Combining Eqs. [A19] through [A25] and rearranging, we finally obtain the following sets of formulas for all of the coefficients that define $Sp(x)$:

$$A_0 = \bar{W}_B(0) \qquad [A26]$$

$$B_0 = \bar{W}_B(0) + \frac{1}{2}\bar{W}_B'(0) \qquad [A27]$$

$$A_2 = \frac{\left[4\frac{\bar{W}_B(x_1)}{(1-x_1)^2} + \frac{\bar{W}_B(x_2)}{(1-x_2)^2} + A_0\right]}{6} \quad [A28]$$

$$B_i = \frac{1}{hi}\left[\frac{\bar{W}_B(x_i)}{(1-x_i)^2} + A_i\right] \qquad (i = 1, 2, \ldots, n-1) \quad [A29]$$

$$A_1 = \frac{h(B_0 - B_2)}{4} + \frac{(A_0 + A_2)}{2} \quad [A30]$$

$$A_i = \frac{i}{3i+1}\left[3A_{i-2} + \frac{\bar{W}_B(x_i)}{(1-x_i)^2}\frac{1}{i} + h(B_{i-2} + 4B_{i-1})\right] \quad (i = 3, 4, \ldots, n-1) \quad [A31]$$

$$A_n = 2h(B_{n-2} + 2B_{n-1}) - 4A_{n-1} + 5A_{n-2} = \bar{W}_A(1) \quad [A32]$$

$$B_n = \frac{B_{n-2} + 2(A_n - 2A_{n-1} + A_{n-2})}{h} \quad [A33]$$

Equation [A28] was obtained by combining Eq. [A19] for $i = 2$ with Eq. [A22] and then eliminating B_1 and B_2 using Eq. [A25]. Similarly, Eq. [A32] was obtained by combining Eq. [A19] for $i = n$ with Eq. [A28]. Equation [A31] was obtained from Eqs. [A19] and [A25]. The coefficients are estimated in the order A_0, B_0, A_2, B_2, A_1, B_1, A_3, B_3, . . ., A_n, B_n. However, note that $\bar{W}'_B(0)$ is not known. The value of A_n, estimated with a $\bar{W}'_B(0)$, may be different from that estimated with $\bar{W}_A(1)$. Therefore, a unique solution must be obtained by adjusting the $\bar{W}'_B(0)$ value until Eq. [A32] is satisfied.

Equations [A26] through [A33] were used for cubic spline interpolations. Degtyarev and Voronin[32] showed results, but because their expressions for Eqs. [A29] and [A31] were found to be incorrect, the above derivation is presented.

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