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**MODELING OF THE THERMODYNAMIC PROPERTIES FROM THE SURFACE TENSION.
PART 2. CALCULATIONS AND THE COMPARATIVE STUDIES**

**MODELOWANIE WŁAŚCIWOŚCI TERMODYNAMICZNYCH Z NAPIĘCIA POWIERZCHNIOWEGO.
CZĘŚĆ II. OBLICZENIA I STUDIA PORÓWNAWCZE**

Using the polarized atoms model of the surface monoatomic layer of metals and alloys, presented in Part I, there has been calculated the molar excess Gibbs free energy from the experimental data of the surface tension determined by the maximum bubble pressure method. The calculations were conducted for 6 liquid alloys: Ag-Bi, Ag-In, Ag-Sn, Bi-Sn, Pb-Sn and Sb-Sn in a wide range of temperatures. New definition of β parameter describing the relation between the excess Gibbs free energy of the bulk and the surface phase, and the new relation describing the monoatomic molar surface layer area of liquid alloys were used in the calculations. The obtained results were compared at two temperatures with those measured by a different experimental method in many laboratories. It has been shown that the data calculated in this work are located between those from the other experimental studies and those calculated from the thermodynamic parameters used for the calculations of the phase diagram.

Model atomów spolaryzowanych monoatomowej warstwy powierzchniowej przedstawiony w części I, zastosowano w obliczeniach molowej nadmiarowej energii swobodnej Gibbsa z pomiarów napięcia powierzchniowego, uwzględniając nowe (zapropozowane w części I) zależności dla obliczania parametru β , opisującego relację pomiędzy nadmiarową energią swobodną Gibbsa fazy objętościowej i powierzchniowej oraz powierzchni molowej monoatomowej warstwy powierzchniowej metali i stopów. W obliczeniach korzystano z napięcia powierzchniowego zmierzonego w szerokim zakresie temperatur metodą maksymalnego ciśnienia w pęcherzykach gazowych dla 6 dwuskładnikowych układów: Ag-Bi, Ag-In, Ag-Sn, Bi-Sn, Pb-Sn oraz Sb-Sn. Wartości nadmiarowej energii swobodnej Gibbsa, uzyskane z obliczeń, mieszczą się pomiędzy wyznaczonymi eksperymentalnie różnymi metodami badawczymi oraz obliczonymi ze zoptymalizowanych parametrów termodynamicznych, opracowanych przez różnych badaczy do obliczania równowag fazowych w cytowanych powyżej układach dwuskładnikowych.

1. Introduction

The calculations of the surface tension, presented in Part I (this Journal), using the temperature dependence of the new β parameters correlating the excess Gibbs free energy of the bulk and the surface phase, and the correction parameters k_r for the metals and alloys showed that the calculated and the measured data of the surface tension of some binary alloys are in good agreement. The discussion of the influence of the different quantities on the calculated surface tension showed that in the case of a good agreement between the calculated and the measured surface tension of alloys, the last one can be used for modeling of the excess free energy in the bulk phase from the measured values of the surface tension. Such data could enriched the data base of these proper-

ties, and next they could be used for critical evaluation of the phase equilibria. The method could be very convenient for systems characterized by the high liquidus temperature when due to the long time of measurements a reaction of the alloys with the elements of the experimental equipment is possible. It should be added that the surface tension measurements could be conducted for a short time of the contact of the liquid with other materials or without any contact by the levitation method, for example.

Thus, a good model for the prediction of the surface tension of alloys could be very helpful to work out the procedure for a verses process, i.e. for the calculation of the excess free energy from the surface tension data. The main aim of this work is to present a comparative study of the calculated excess Gibbs free energy

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from the surface tension data, obtained by the maximum bubble pressure method, and those measured by various experimental methods as well as those calculated from the optimized thermodynamic parameters, worked out by different authors. The new parameters for the modeling of the surface tension from the thermodynamic properties (presented in Part I – this Journal) will be used.

2. Description of the procedure

Calculation of the thermodynamic parameters describing the excess Gibbs free energy of binary alloys is possible using the Hoar and Melford equation [1] written in the following form:

$$\sigma = \frac{\sigma_1 S_1^0}{S_1} + \frac{RT}{S_1} \ln \left(\frac{X_S}{X_B} \right) + \frac{\beta G_1^{\text{ex}}(X_S, T) - G_1^{\text{ex}}(X_B, T)}{S_1} \quad (1)$$

$$\sigma = \frac{\sigma_2 S_2^0}{S_2} + \frac{RT}{S_2} \ln \left(\frac{1 - X_S}{1 - X_B} \right) + \frac{\beta G_2^{\text{ex}}(X_S, T) - G_2^{\text{ex}}(X_B, T)}{S_2} \quad (2)$$

The symbols in Eqs (1) and (2) denote; σ , $\sigma_{1(2)}$ – the surface tension of the alloy and the component 1 or 2, $S_{1(2)}^0$, $S_{1(2)}$ – the molar surface area and partial molar surface area of the component 1 or 2, $G_{S(1),(2)}^{\text{ex}}$, $G_{B(1),(2)}^{\text{ex}}$ – the excess Gibbs free energy of the component 1 or 2 in the surface or bulk phase (subscript S or B), R – gas constant, T – the temperature and β is the parameter correlating the excess free energy in the bulk and in the surface phase.

The system of equations (1) and (2) can be solved at $T = \text{const}$ by the procedure of the double stage optimization. At first, the optimization of the surface concentration X_S with the fixed values of the thermodynamic parameters a_i is conducted, and next, the optimization of the destination function as a sum of squares differences between the experimental and the calculated values of the surface tension is performed. The surface tension calculated from the equation describing the experimental data is applied as the experimental value. In such a way it was possible to use in the optimization procedure, a much greater number of data (about 20) than the number of experimental points. For interpretation of the experimental surface tension data of the Ag-Bi system the Eberhart relation [2] was used (3):

$$\sigma_{A-B} = \sigma_A \left(1 - \frac{X_B}{X_A R + X_B} \right) + \sigma_B \frac{X_B}{X_A R + X_B} \quad (3)$$

and for the other systems the following equations were used:

$$\sigma_{A-B} = \sigma_A X_A + \sigma_B X_B + \Delta \sigma_{A-B} \quad (4)$$

$$\sigma = \sigma_A X_A + \sigma_B X_B + X_A X_B \sum_{i=0}^n c_i (X_A - X_B)^i, \quad (5)$$

where: σ and $\sigma_{A(B)}$ are the surface tensions of the alloy and of the components, $X_{A(B)}$ is the mole fraction of the component A or B , R is the enrichment factor (it can depend on T and on concentration), $\Delta \sigma_{A-B}$ is the equation proposed by Redlich-Kister [3] for the interpretation of the thermodynamic properties of the binary alloys and the coefficients c_i are the functions of temperature.

A short description of the calculation procedure is presented in Fig. 1.

The test of the procedure has shown that starting from the surface tension data, calculated for the given thermodynamic parameters and the other data necessary in the calculations, the obtained values of the molar excess Gibbs free energy were almost the same and the observed differences were less than a few dozen $\text{J} \cdot \text{mol}^{-1}$ as long as the number of thermodynamic parameters was less than one, the same, or higher than the number of the thermodynamic parameters applied in the test procedure.

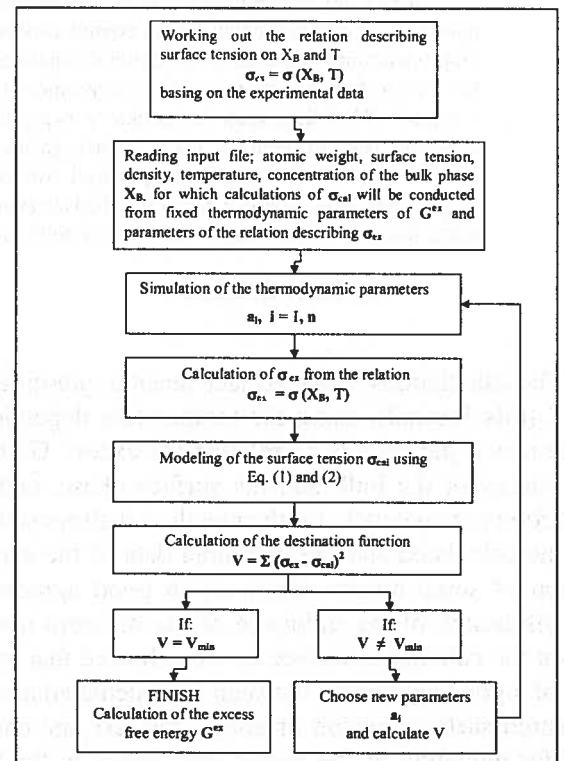


Fig. 1. The scheme of the procedure for the calculation of the thermodynamic properties from the surface tension

3. Results and Discussion

At first, the equations describing the dependence of the surface tension on the temperature and concentration for six binary systems: Ag-Bi [4], Ag-In [5], Ag-Sn [6], Bi-Sn [7], Pb-Sn [8] and Sb-Sn [9] presented earlier in Part I (this Journal) were worked out.

The calculations were conducted with a different number of the thermodynamic coefficients and the optimization was completed when the standard deviations of the surface tension were about $2 \text{ mN}\cdot\text{m}^{-1}$. The obtained excess Gibbs free energies for the mentioned above systems are drawn in Figs 2–9 as a continuous line, together with the data recalculated from the partial excess Gibbs free energy measured by the various experimental methods. The experimental thermodynamic data for the systems presented in this work were described by the Redlich-Kister equation [3] with the standard deviation varying from a few to about $500 \text{ J}\cdot\text{mole}^{-1}$. Care was taking that the description repeated well the experimental data, but without the local extremes and many inflection points.

In the case of two systems, namely Ag-Bi and Ag-Sn, the remarkable differences between the thermo-

dynamic properties calculated from the thermodynamic parameters are observed. Thus, the comparative presentations of the calculated excess Gibbs free energies calculated from the surface tension are shown separately from those obtained from the experimental investigations and those calculated from thermodynamic parameters worked out by various authors. For the other systems, the mentioned three kinds of the excess Gibbs free energies are shown in the same Figures.

The excess Gibbs free energies of the Ag-Bi liquid alloys, calculated from the experimental studies [10–13] and from Hultgren [13], are shown in Figs 2 and 3, at two temperatures, 873 K and 1273 K. It is easy to notice that the values calculated from the surface tension are located between those obtained from experiments and those calculated from the optimized thermodynamic parameters [4, 14, 15]. Only for high concentrations of Bi the values calculated in this work are lower than those obtained from the direct measurements. The excess free energies calculated, and that measured by [11], are positive in the entire range of concentrations, while the other measurements yield negative values for lower Bi concentrations.

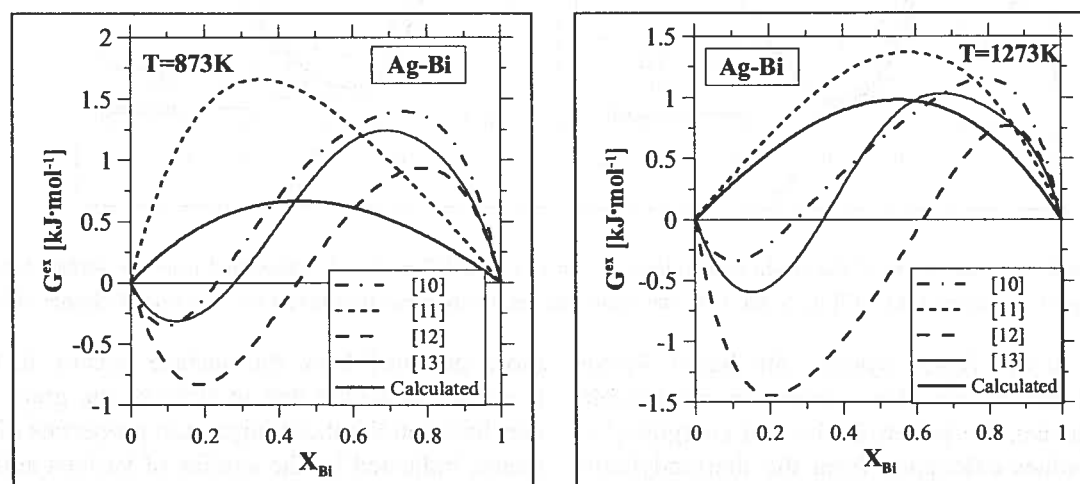


Fig. 2. Excess Gibbs free energy of the Ag-Bi liquid alloys calculated at a) $T = 873 \text{ K}$ and b) $T = 1273 \text{ K}$ from the surface tension, from the partial experimental values [10], [11], [12] and from [13]

Comparison of the excess Gibbs free energies for the Ag-In liquid alloys is shown in Fig. 4 at 873 K and 1273 K. The system is characterized by the negative deviations from the ideal behaviour in the entire range of concentrations as well as the great discrepancy of the data [5, 13, 16–19]. The values obtained by Nozaki et al. [18] and proposed by Hultgren and co-authors [13]

are definitely different from others [16, 17, 19], and also from those calculated from the surface tension data, and those from the optimized thermodynamic parameters [5]. The observed differences between the lowest and the highest experimental values of the excess Gibbs free energy reach about $7 \text{ kJ}\cdot\text{mol}^{-1}$ at the minimal values from -8 to $-9 \text{ kJ}\cdot\text{mol}^{-1}$.

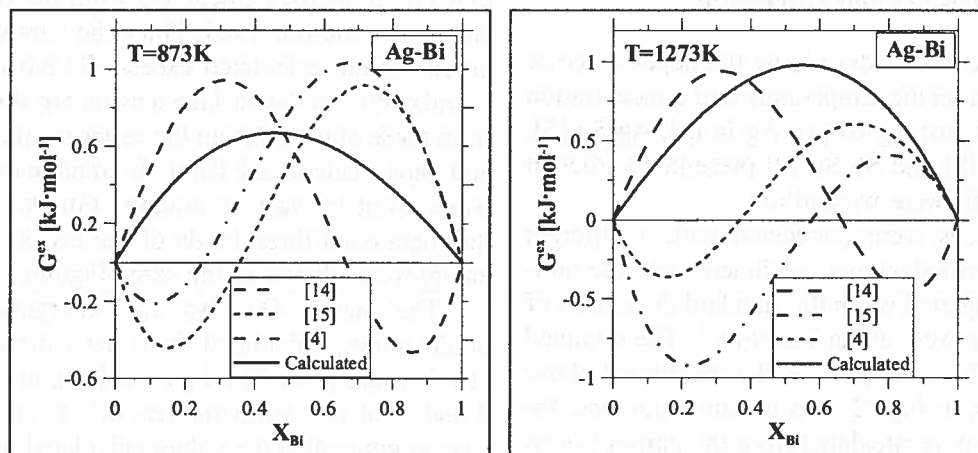


Fig. 3. Excess Gibbs free energy of the Ag-Bi liquid alloys calculated at a) $T = 873\text{ K}$ and b) $T = 1273\text{ K}$ from surface tension and from the optimized thermodynamic parameters given by [4], [14] and [15]

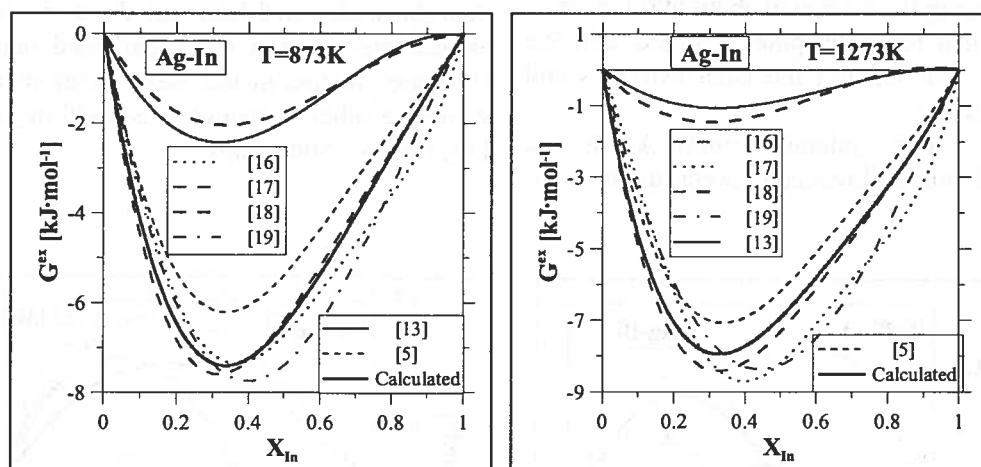


Fig. 4. Excess Gibbs free energy of the Ag-In liquid alloys at $T = 873\text{ K}$ and $T = 1273\text{ K}$, calculated from the surface tension, the experimental data of [16], [17], [18] and [19], the optimized thermodynamic parameters [5] and from Hultgren [13]

Similarly to the Ag-Bi system, the liquid Ag-Sn alloys (Figs 5 and 6) are characterized by remarkable differences between the excess Gibbs free energies [13, 15, 20–27]. Values calculated from the thermodynamic parameters, worked out by the different authors [15, 25–27], change from about $-3.5\text{ kJ}\cdot\text{mol}^{-1}$ to almost $2\text{ kJ}\cdot\text{mol}^{-1}$. The data obtained in this work show positive values for alloys with higher Sn concentrations, whereas for low Sn alloy concentrations they are slightly negative. The excess free energy, obtained from the experimental data [24] and [23] for the Sn – rich alloys, is characterized by positive values at 873 K , too, but lower than

those obtained from the surface tension in this work. It should be added that in spite of the great discrepancies between the thermodynamic properties of the liquid phase, indicated by the studies of various authors, good reproduction of the calculated equilibrium lines in comparison with those obtained by the different experimental method can be observed. This fact indicates, on the one hand, the big flexibility of the special software used in the calculations and on the other hand, the lack of the exact procedures for the measurement methods or of the other standard tests concerning the kind and the approximate range of the deviations from the ideal solutions.

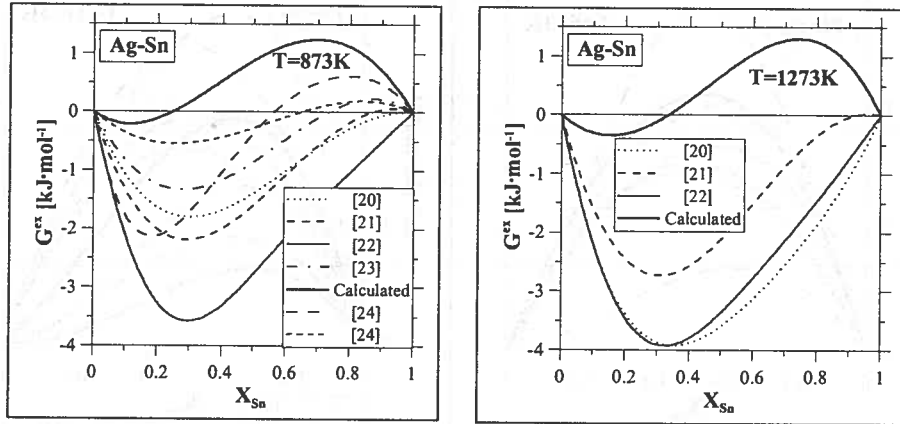


Fig. 5. Excess Gibbs free energy of the Ag-Sn liquid alloys at $T = 873 \text{ K}$ and $T = 1273 \text{ K}$, calculated from surface tension, the experimental data of [20], [21], [22], [23], [24] and from Hultgren [13]

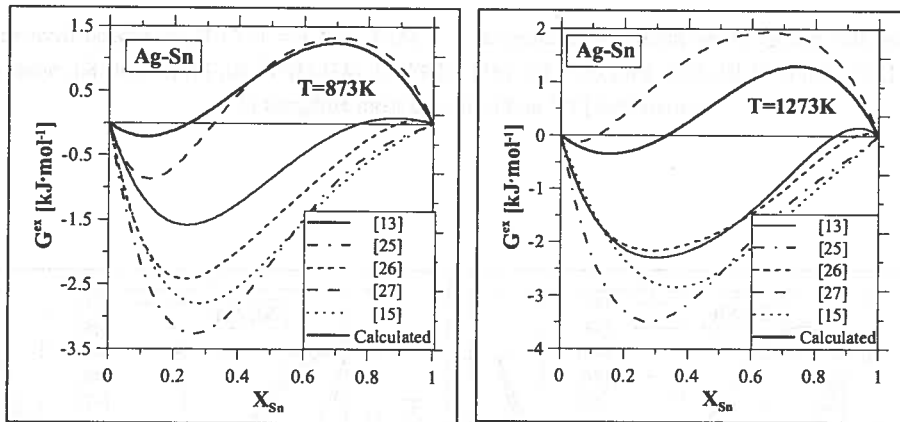


Fig. 6. Excess Gibbs free energy of the Ag-Sn liquid alloys at $T = 873 \text{ K}$ and $T = 1273 \text{ K}$, calculated from surface tension, the optimized thermodynamic parameters [25], [26], [27] and [15], and from Hultgren [13]

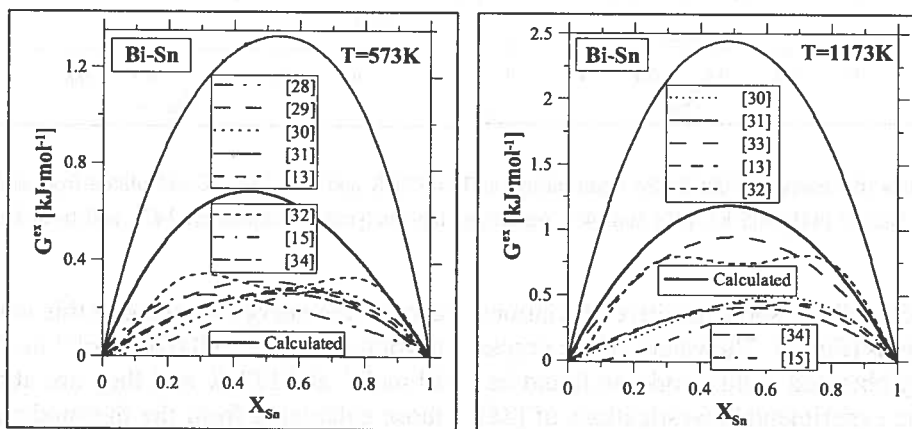


Fig. 7. Excess Gibbs free energy of the Bi-Sn liquid alloys at $T = 573 \text{ K}$ and $T = 1173 \text{ K}$, calculated from surface tension, the experimental data of [28] (602 K), [29] (608 K), [30], [31] and [32], [33] (1373 K), optimized thermodynamic parameters [15] and [34], and from Hultgren [13]

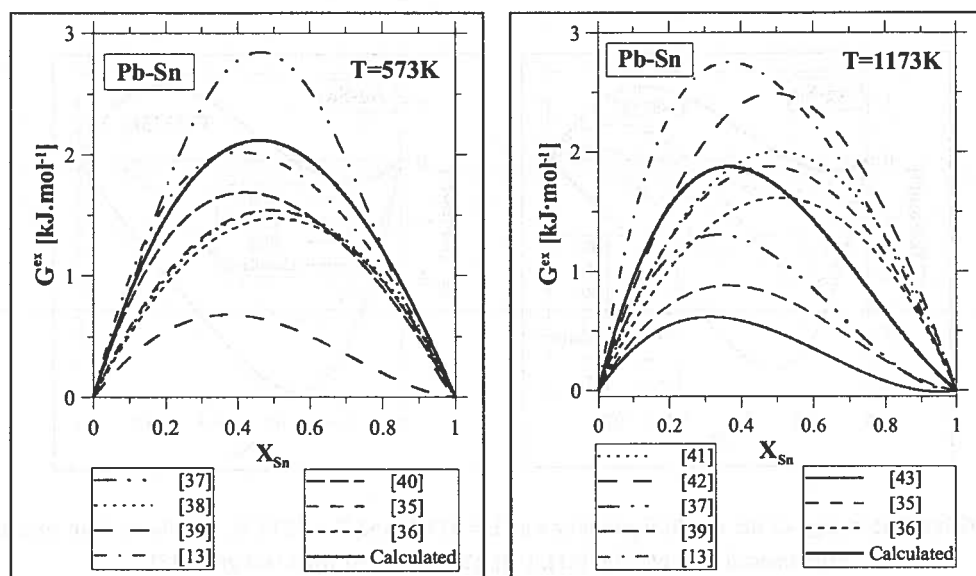


Fig. 8. Excess Gibbs free energy of the Pb-Sn liquid alloys at $T = 573$ K and $T = 1173$ K, calculated from surface tension, the experimental data of [37], [38] (773 K), [39], [40] (823 K), [41] (1048 K), [42] (1007 K), [43] (1050 K), optimized thermodynamic parameters [35] and [36], and from Hultgren [13]

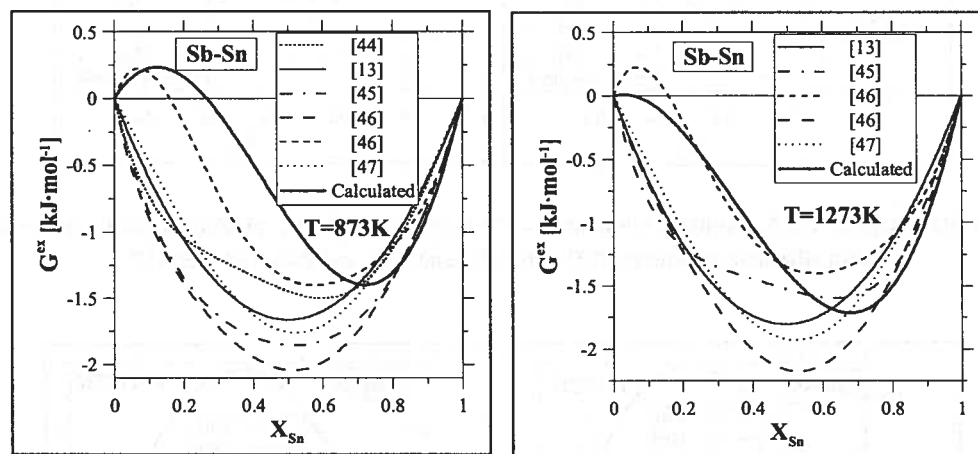


Fig. 9. Excess Gibbs free energy of the Sb-Sn liquid alloys at $T = 873$ K and $T = 1273$ K, calculated from surface tension, the experimental data of [44] (905 K), [45] and [46], optimized thermodynamic parameters [47], and from Hultgren [13]

The liquid Bi-Sn alloys show positive deviations from the ideal solutions (Fig. 7). The values of the excess Gibbs free energy obtained in this work are found between those from the experimental investigations of [28] (602 K), [29] (608 K), [30], [31], [32] and [34] (1373 K), and they are higher than those calculated from the optimized thermodynamic parameters given by [15] and [34]. The differences between the maximal values of G^{ex} of the cited authors are about $1 \text{ kJ}\cdot\text{mol}^{-1}$ at 573 K and almost $2 \text{ kJ}\cdot\text{mol}^{-1}$ at 1173 K. The maximal values of the

excess free energy obtained in this work from the surface tension are equal to $0.67 \text{ kJ}\cdot\text{mol}^{-1}$ at 573 K and about $1.2 \text{ kJ}\cdot\text{mol}^{-1}$ at 1173 K and they are about twice as big as those calculated from the thermodynamic parameters.

A comparison of the excess free energy of the Pb-Sn liquid alloys at 573 K and 1173 K is presented in Fig. 8. As it is seen, the differences between the data of G^{ex} measured in the various laboratories and by various methods are significant and they are bigger than $2 \text{ kJ}\cdot\text{mol}^{-1}$. Both, the excess Gibbs free energy of the

liquid Pb-Sn alloys calculated from the optimized parameters [35], [36] and those derived from the surface tension, are between the values obtained by [37], [38] (773K), [39], [40], [41], [42], [43], and from [13]. The excess free energy at 573 K obtained from optimization [35], [36] is lower than that calculated from the surface tension in the entire concentration range, and that at 1173 K only for $X_{\text{Sn}} < 0.45$ and the maximal differences are not higher than $0.5 \text{ kJ}\cdot\text{mol}^{-1}$.

The results of calculations for Sb-Sn liquids alloys are shown in Fig. 9 together with the other data of the excess Gibbs free energy [13, 44–47]. According to the results of the calculations based on the optimized thermodynamic parameters [47] the liquid Sb-Sn are characterized by the negative deviations from the ideal behavior. A relatively good agreement of all data is observed at the temperature 1273 K. The excess Gibbs free energies recalculated from the experimental studies differ from one another by about $0.7 \text{ kJ}\cdot\text{mol}^{-1}$ for the middle and for the low Sn concentrations. The data calculated in this work and those taken from [46] show positive deviations from the ideal solutions. At the temperature 873 K, low discrepancies between presented data are observed for alloys with high Sn concentration. Similar values are shown by the excess Gibbs free energies calculated in this work and those taken from [46]. The differences are about $0.5 \text{ kJ}\cdot\text{mol}^{-1}$.

Basing on the presented comparative studies of the excess Gibbs free energy of liquid alloys of 6 systems obtained from the experimental investigations and those calculated using Eq. (1) and (2), new values of β and the polarized atoms model of the monoatomic surface layer area (see Part I), it can be concluded, that the excess Gibbs free energies of alloys calculated from the data of the surface tension, measured by the maximum bubble pressure method, are comparable with the values obtained from the experimental data of the partial excess Gibbs free energy, and this implies that they could be accepted in the future critical evaluations of the thermodynamic properties of the liquid phase.

4. Summarizing remarks

The procedure enabling the calculation of the thermodynamic properties of the liquid alloys from measurements of the surface tension has been presented and used for the calculation of the excess Gibbs free energy of liquid alloys for 6 systems: Ag-Bi, Ag-In, Ag-Sn, Bi-Sn, Pb-Sn and Sb-Sn. In the calculation the new values of the β parameter and the new relation describing the monoatomic surface layer area (Part I – this Journal) were applied.

The excess Gibbs free energies calculated from the surface tension were compared with those obtained using different experimental methods. It has been shown that the data calculated using the surface tension determined by the maximum bubble method are located between those derived from the partial excess Gibbs free energy measured by different experimental methods. It seems that the thermodynamic properties of the liquid alloys, which can be calculated from the surface tension measurements, may be used as additional information for application in the critical evaluation of the thermodynamics of liquid alloys.

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