MODELING OF THE THERMODYNAMIC PROPERTIES FROM THE SURFACE TENSION.
PART I. POLARIZED ATOMS MODEL OF THE SURFACE AREA FOR MODELING OF THE SURFACE TENSION

MODELOWANIE WŁAŚCIWOŚCI TERMODYNAMICZNYCH Z NAPIĘCIA POWIERZCHNIOWEGO.
CZĘŚĆ I. MODEL ATOMÓW SPOLARYZOWANYCH MONOATOMOWEJ WARSTWY POWIERZCHNIOWEJ
DLA OBLICZENIA NAPIĘCIA POWIERZCHNIOWEGO

The polarized atoms model of the surface layer, the molar surface layer area correction parameters \(k_{(0)}\) and \(k_{s}\) of the liquid metal and alloys and the new definition of the \(\beta\) parameter describing the relation between the excess Gibbs free energy of the bulk and the surface phase (both dependent on temperature and concentration) are proposed for modeling of the surface tension of the binary liquid alloys. The comparative analyses were conducted for six binary alloys: Ag-Bi, Ag-In, Ag-Sn, Bi-Sn, Pb-Sn and Sb-Sn. It was found that the predicted surface tension using the new, proposed parameters and the Hoar and Melford relation, generally correlates better with the experimental results obtained by the maximum bubble pressure method then by the Butler equation using the constant value of \(\beta = 0.81\) and the monoatomic partial molar surface layer areas equal to those of pure liquid metals.

Zaproponowany model atomów spolaryzowanych monoatomowej warstwy powierzchniowej i współczynniki jej korekcji dla metali i stopów \((k_{(0)}\) i \(k_{s}\)) oraz nowa definicja-parametru \(\beta\), opisującego relację pomiędzy nadmierną energią swobodną fazy objętościowej i powierzchniowej (monoatomowej warstwy), wykorzystano w modelowaniu napięcia powierzchniowego dwuskładnikowych stopów metali dla 6 układów: Ag-Bi, Ag-In, Ag-Sn, Bi-Sn, Pb-Sn oraz Sb-Sn. Stwierdzono, że wyniki obliczeń uzyskane z zastosowaniem nowych parametrów \((k_{s}\) i \(\beta\)) oraz równania Hoar i Melforda, lepiej korelują z eksperymentalnymi wartościami napięcia powierzchniowego zmierzonymi metodą maksymalnego ciśnienia w pęcherzykach gazowych, w porównaniu do tych obliczonych z zależności Butlera przy \(\beta = 0.81\) oraz powierzchni molowej monoatomowej warstwy powierzchniowej równej czystym metalom dwuskładnikowych stopów bez uwzględniania korekcji.

1. Introduction

Prediction of the physical properties, such as the viscosity or the surface tension of the liquid alloys has been conducted in the last years using the excess Gibbs free energy of liquid phase mainly because of the high costs of the experiments. For modeling of the surface tension the Butler equation, derived in 1932 [1], has been commonly used. This equation was derived on the assumption that the surface layer (thought as an individual phase) and the bulk phase are in equilibrium. In this model the partial molar surface layer area of the components is equal to the area of pure components. The resulting equation is as follows:

\[
\sigma = \sigma_1 + \frac{RT}{S_1} \ln \left( \frac{X_1^S}{X_1^B} \right) + \frac{\beta G_{(S1)}^{ex} - G_{(B1)}^{ex}}{S_1} = \\
\sigma_2 + \frac{RT}{S_2} \ln \left( \frac{X_2^S}{X_2^B} \right) + \frac{\beta G_{(S2)}^{ex} - G_{(B2)}^{ex}}{S_2}.
\]

Another equation allowing to calculate the surface tension from the thermodynamic properties of the liquid was presented in 1957 by Hoar and Melford [2];

\[
\sigma = \frac{S_1^0}{S_1} + \frac{RT}{S_1} \ln \left( \frac{X_1^S}{X_1^B} \right) + \frac{\beta G_{(S1)}^{ex} - G_{(B1)}^{ex}}{S_1} = \\
\frac{S_2^0}{S_2} + \frac{RT}{S_2} \ln \left( \frac{X_2^S}{X_2^B} \right) + \frac{\beta G_{(S2)}^{ex} - G_{(B2)}^{ex}}{S_2}.
\]
The symbols in Eqs (1) and (2) denote: \( \sigma \), \( \sigma_{1(2)} \) – the surface tension of the alloy and of the component 1 or 2, \( S_i(2) \), \( S_{1(2)} \) – the molar surface layer area and the partial molar surface layer area of the component 1 or 2, \( G_{S_i(2)}^{ex} \), \( G_{S_{1(2)}}^{ex} \) – partial excess Gibbs free energy of 1 or 2 component in the surface or in the bulk phase (subscript \( S \) or \( B \)), \( R \) – gas constant and \( T \) – temperature.

The assumption that the molar change of the surface area \( \Delta S \) is equal to zero makes, the partial molar surface layer area equal to the surface molar area of pure components and Eq. (2) becomes identical with the Butler equation (1). Equation (2) is the most common form of the relation which can be used for the calculation of the surface tension from the thermodynamic properties of alloys. However, because of its simplicity, only the Butler equation (1), has been used for the calculation of the surface tension of metallic alloys together with the following relation for the calculation of the surface layer area

\[
S_i = LV_i^{2/3} N_i^{1/3} = LND_i^2
\]

and with the equation describing the relation between the excess Gibbs free energy of the component in the bulk and the surface phase;

\[
G_{S_i}^{ex} = \beta G_{S_{B_i}}^{ex}(X_{S_i}).
\]

In Eqs (3) and (4) \( V \) is the molar volume of the component “\( i \)”, \( N \) is Avogadro number, \( L = 1.091 \) is the geometric factor recalculating the surface layer area into that with the closed-packed structure, \( D_i = (V/N)^{1/3} \) is the approximate value of the atomic radius of component “\( i \)”, \( G_{S_i}^{ex} \) and \( G_{B_i}^{ex} \) is the excess Gibbs free energy of the component “\( i \)” in the surface and the bulk phase, and \( \beta = 0.83 \) is the coefficient proposed by Tanaka and co-workers [3] characterizing the difference between the coordination number of atoms in the bulk and in the surface phase.

The results of experimental investigations performed by the author and co-workers, who used the maximum pressure method [4, 5, 6, 7, 8, 9], enabled comparative analyses of the calculated, from the Butler Equation (1), and the experimental data in the entire range of concentrations and in a wide temperature range. The observed differences between the mentioned two sets of the data are shown in Fig. 1 for the Ag-Bi system (\( G^{ex} \) from [10]) as an example. They concern the curvilinear character of the surface tension, the positive value of the temperature coefficient which is very well visible for alloys with higher Ag concentration (\( X_{Ag} = 0.5, 0.75, 0.9 \)), and great differences between the experimental (symbols) and the calculated (lines) surface tension (low Bi concentrations and lower temperatures).

The sensitivity of Eq. (1) to adjustable parameters: \( \beta \), \( S_i \) and \( G^{ex} \), was analyzed in order to find out which parameter can be responsible for the observed discrepancy.

The results of calculations conducted for the Ag-Bi and Ag-Sn systems (Tables 1–3, Fig. 3) using for the Ag-Sn alloys the thermodynamic data from [10, 11] can be summarized as follows:

1. The values of \( \beta = 0.83 \) and \( L \) calculated from Eq. (3), commonly used for modeling the surface tension by the Butler equation (1), do not always give the results comparable with the experimental data.
2. The change of the value of the \( \beta \) parameter can only increase or decrease the calculated surface tension, but it can not change the temperature coefficient (from positive to negative).
3. The changes of the molar surface layer area of the components, similar to those for the \( \beta \) parameter (about \( \pm 10\% \)), produce greater changes in the calculated surface tension. Accordingly, one may come to the conclusion that the great discrepancies, between the calculated and the experimental values of the surface tension, are probably due to the great difference between the real values of the partial molar surface layer areas of the components and those given by Eq. (3) (used in calculations).
4. The calculated values of the surface tension, using the thermodynamic parameters from different works ([12] and [13]), can differ even by a few dozen mN m\(^{-1}\) as in case of the Ag-Sn system (Table 4).
5. The observed (rather strong) curvilinear dependence of the calculated surface tension on temperature, obtained from calculations using Butler relation (1), often with its maximum, has not been confirmed by experimental results.
Surface tension calculated using Butler’s equation (1) for the Ag-Bi alloy of \( X_{\text{Bi}} = 0.25 \), different \( \beta \) values and \( L = 1.091 \)

<table>
<thead>
<tr>
<th>( \beta )</th>
<th>( \sigma_{973K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{973K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1073K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1173K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1273K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1373K} ) [mN.m(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>470.87</td>
<td>478.47</td>
<td>484.68</td>
<td>489.56</td>
<td>493.15</td>
<td></td>
</tr>
<tr>
<td>0.83</td>
<td>470.59</td>
<td>478.1</td>
<td>484.23</td>
<td>489.03</td>
<td>492.56</td>
<td></td>
</tr>
<tr>
<td>0.9</td>
<td>470.35</td>
<td>477.78</td>
<td>483.84</td>
<td>488.57</td>
<td>492.04</td>
<td></td>
</tr>
</tbody>
</table>

Surface tension calculated using Butler’s equation (1) for the Ag-Sn alloy of \( X_{\text{Sn}} = 0.3 \), different \( \beta \) values and \( L = 1.091 \)

<table>
<thead>
<tr>
<th>( \beta )</th>
<th>( \sigma_{973K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{973K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1073K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1173K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1273K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1373K} ) [mN.m(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>653.87</td>
<td>659.80</td>
<td>662.47</td>
<td>662.01</td>
<td>659.01</td>
<td>654.04</td>
</tr>
<tr>
<td>0.83</td>
<td>653.95</td>
<td>659.73</td>
<td>662.09</td>
<td>661.20</td>
<td>657.75</td>
<td>652.37</td>
</tr>
<tr>
<td>0.9</td>
<td>654.01</td>
<td>659.69</td>
<td>661.73</td>
<td>660.45</td>
<td>656.61</td>
<td>650.87</td>
</tr>
</tbody>
</table>

The influence of the molar surface layer area on the calculated surface tension from the Butler equation (1) for the Ag-Bi alloy with \( X_{\text{Bi}} = 0.25 \)

<table>
<thead>
<tr>
<th>( S ) [m(^2).mol(^{-1})]</th>
<th>( \sigma_{973K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{973K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1073K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1173K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1273K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1373K} ) [mN.m(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9*S</td>
<td>480.35</td>
<td>488.36</td>
<td>494.81</td>
<td>499.78</td>
<td>503.35</td>
<td></td>
</tr>
<tr>
<td>1.0*S</td>
<td>470.59</td>
<td>478.10</td>
<td>484.23</td>
<td>489.03</td>
<td>492.56</td>
<td></td>
</tr>
<tr>
<td>1.1*S</td>
<td>462.50</td>
<td>469.68</td>
<td>475.63</td>
<td>480.37</td>
<td>483.93</td>
<td></td>
</tr>
</tbody>
</table>

Surface tension calculated for the Ag-Sn liquid alloy with \( X_{\text{Sn}} = 0.3 \), using thermodynamic parameters Xie et al. [12] and Chevalier [13]

<table>
<thead>
<tr>
<th></th>
<th>( \sigma_{973K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{973K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1073K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1173K} ) [mN.m(^{-1})]</th>
<th>( \sigma_{1273K} ) [mN.m(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xie et al. [12]</td>
<td>582</td>
<td>596</td>
<td>589</td>
<td>590</td>
<td>591</td>
</tr>
<tr>
<td>Chevalier [13]</td>
<td>674</td>
<td>680</td>
<td>683</td>
<td>682</td>
<td>678</td>
</tr>
</tbody>
</table>

Hence, the main aim of this work (Part 1) is to propose a new model of the surface layer, a new definition of the \( \beta \) parameter for metals and alloys and finally to carry out the calculations of the surface tension for 6 binary metallic systems [4–9] using the Hoar and Melford equation (2), and to compare the results with those obtained from Butler relation (1).

It should be noted that when taking into account the remarkable discrepancy in the excess Gibb’s free energy calculated from the thermodynamic parameters of different studies on the optimization and the calculation of the phase diagrams, it seems that a good agreement in a wide concentration and temperature range between the calculated and the experimental surface tension could be a good criterion of their reliability. Then, the measurements of the surface tension could be used to obtain the thermodynamic properties, giving additional data for application in the thermodynamics of alloys, which is the main subject of the second part of this work (Part 2, this Journal).
2. Polarized atoms model of the monoatomic surface layer

As it has been shown earlier, it is impossible to improve the results of modeling of the surface tension, by correction of the $\beta$ parameter. To obtain data close to those from measurements, another model of the monoatomic surface layer, different from that described by the Eq. (3) should be introduced because the molar surface layer area is the second parameter influencing strongly the calculated surface tension of alloys.

The following assumptions for the derivation of a new model of the surface layer area were made:

1. Nonsymmetrical arrangement of forces around the atoms in the surface layer, due to absence of atoms above them, creates a resultant force acting on the electrons and directed towards the bulk phase.

2. This force causes a shift of the most outer valence electrons in the direction of the bulk phase which involves the polarization of the surface atoms and the change of the interatomic distance $D_i$ contrary to that in the bulk phase (Eq. 3).

3. The interatomic distance $D_i$ is equal to that in Eq. (3) only at a certain temperature $T_c$, characterizing the constant and identical value of the vapor pressure for all metals.

4. At temperatures lower than $T_c$, the interatomic distance $D_i$ is lower and at temperatures higher than $T_c$ the interatomic distance is greater than that in Eq. (3).

5. The increase of $D_i$, at temperature higher than $T_c$, over that in Eq. (3), is the result of very intense interaction of atoms of the surface layer with atoms of the vapor and the bulk phase in comparison with these interactions at temperatures lower than $T_c$.

Basing on the above assumptions, one can derive a relation allowing to calculate the surface layer area from the molar volume of the liquid alloys and .

Using Eq. (3) one can show that the relation between two surface areas of different atomic radii is described by the relation:

$$S_1 = \frac{R_1^2}{R_2^2} S_2 = k_2^2 S_2,$$

(5)

where: $R_1$ and $R_2$ are the half average interatomic distances (atomic radii) of metals of $V_1$ and $V_2$ molar volumes and $S_1$, $S_2$ are the molar surface layer areas of the metal 1 and 2, $k_r$ is the correction parameter.

Equation (5) is true when the metal transforms from the surface to the bulk with the same structure and the different interatomic distances (diameter).

Marking with the subscript "S" the real molar surface layer area of the monoatomic surface phase and with "B" the molar surface layer area calculated from the molar volume of the liquid metal when the atomic radius in the surface phase is known, the real surface layer (phase) area can be calculated according to the relation:

$$S_S = \frac{R_S^2}{R_B^2} S_B = k_2^2 S_B,$$

(6)

where: $R_S$ and $R_B$ are the atomic radii (half of the interatomic distances) of the metal in the surface and bulk phase.

Thus, knowing $k_r$ and calculating $S_B$ from Eq. (3), the molar surface layer area of the metal can be easily calculated from Eq. (6).

The determination of the correction parameter $k_r$ is based on the following assumptions:
1. The correction parameter \( k_c \) is the linear function of temperature.

2. \( T_C \) is the temperature at which the vapor pressure of the metal is equal to \( p_m = 0.001 \text{atm} \). This value was assumed from the analyses of the differences between the experimental and the calculated surface tension of the binary alloys [4–9] with the new \( S_c \) and \( \beta \) values (new value of \( S_c \) involves new value of \( \beta \), see [3] and next chapter) proposed in this work.

3. At room temperature (undercooled liquid metal), the atomic radius of the metal in the surface layer is approximately equal to the effective ionic radius of this metal in the ionic crystal, for the coordination number equal to 6 (as for surface layer), and for the valence of the ion equal to the number of valence electrons \( n_e \) filling the last electronic subshell (s, p) of the atom of this metal. For most metals \( n_e \) is equal to 2, for Sb and Bi \( n_e = 3 \) and for Po \( n_e = 4 \) (the effective ionic radius depends on the coordination number and the valence of the ion).

To obtain the temperature dependence of the \( k_c \) parameter its value should be known at least at two different temperatures. The first value, at room temperature, is calculated from Eq. (6) \( (R_S/R_B = R_S/R_A) \) and from the data given in Table 5. The second, based on the assumption of this model, that \( k_c = 1 \) at the characteristic temperature \( T_C \) (the vapor pressure of the metal is equal to 0.001 atm). The average values of the atomic radii were used in the calculations basing on the data of B o j a r s k i et al. [14], T e a u t u m et al. [15] and G o l d s c h m i d t given in [16]. The values of ionic radii were taken from S h a n o n [17] for \( L_k = 6 \) (Table 5).

The characteristic temperatures \( T_C \) for metals were calculated basing on the thermodynamic data and the vapor pressure of B a r i n and K n a c k e [18]. The obtained equations for the temperature dependence of \( k_c \) for metals are shown in Table 6.

### TABLE 5

<table>
<thead>
<tr>
<th>Metal</th>
<th>( V )</th>
<th>( R_A, R_B ) [m(^{-1})]</th>
<th>( R_S/R_A )</th>
<th>( R_A, R_B ) [m(^{-1})]</th>
<th>( R_S/R_A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0</td>
<td>1.38</td>
<td>0.8478</td>
<td>0.8478</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>0</td>
<td>1.71</td>
<td>1.03</td>
<td>0.6023</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>+3</td>
<td>1.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>0</td>
<td>1.57</td>
<td>1.18</td>
<td>0.8408</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>1.18</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The average atomic radii \( R_A \) and the ionic radii \( R_S \) of some metals for the coordination number \( L_k = 6 \) and their quotient \( R_S/R_A \) at \( T = 298 \text{K} \). (\( V \) – valency)

### TABLE 6

<table>
<thead>
<tr>
<th>Metal</th>
<th>( k_c = a + bT )</th>
<th>Metal</th>
<th>( k_c = a + bT )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.81246 + 0.00011885T</td>
<td>Pb</td>
<td>0.61487 + 0.00031337T</td>
</tr>
<tr>
<td>Bi</td>
<td>0.46392 + 0.00046414T</td>
<td>Sb</td>
<td>0.27835 + 0.00072165T</td>
</tr>
<tr>
<td>In</td>
<td>0.80084 + 0.00013402T</td>
<td>Sn</td>
<td>0.53284 + 0.00025143T</td>
</tr>
</tbody>
</table>

### 3. The dependence of the \( \beta \) parameter on the temperature and the metal

It was shown by T a n a k a et al. [3], that the value of the \( \beta \) parameter changes slightly from one metal to the other. Thus, this fact should be taken into consideration and accepted in the calculation. Using a constant value of \( \beta \) for metals the calculation procedure becomes simpler because the same shape of the mathematical function can be used in the calculations of the excess G i b b s free energy for the bulk and the surface phase. When \( \beta \) is assumed to be the function of concentration, it implies another mathematical description of the excess G i b b s free energy in the surface phases because that one for the bulk is multiplied not by the constant value of \( \beta \) but in the simplest case by the linear function of the composition, which varies from \( \beta_1 \) to \( \beta_2 \) according to the concentration of the surface phase. For a small difference between \( \beta_1 \) and \( \beta_2 \), and the surface tensions of the metals, the discrepancies between the calculated values could be very small. In other cases the differences become significant, which will be shown in the next part of this work. Therefore, the use of the different values of the \( \beta \) parameter is proposed in this work.

The temperature independence of the \( \beta \) parameter is another simplification. It seems however that it should depend on the temperature, because with the temperature increase the influence of the square correction factor \( k_c \) on the surface layer area becomes greater and after reaching the temperature \( T_C \) the increase of the surface layer area is much higher than that calculated from Eq. (3) \( (k_c > 1) \). As a result the interatomic distances in the surface layer become greater and the thermodynamic properties of the surface layer approach the ideal solution faster.

Assuming, that with the temperature increase the solutions become closer to the ideal one and the approach of the thermodynamic properties of the surface layers to the ideal solutions is faster, one comes to the conclusion, that there should exist such a temperature \( T_{cr} \) at which the bulk phase would be characterized by a certain deviation from the ideal one while the surface phase (layer) is already ideal. Additionally, taking into consideration the relation (4), one comes to the conclusion that at \( T_{cr} \) the
\( \beta \) parameter must be equal to zero. It was assumed that the temperature \( T_{cr} \) is this one at which \( \sigma = A + BT_{cr} = 0 \). Thus, in such a way, the coordinates of the first point to be used for the calculation of the temperature dependences of \( \beta \) were determined.

The coordinates of the second point will be established from the relations:

\[
S \sigma = (1 - \beta)(G_S^\infty - G_S^2),
\]

where: \( S \) and \( \sigma \) are the molar surface layer area and the surface tension of metal, and \( G_S^\infty - G_S^2 \) is the standard free energy change of the transformation of 1 mole of metal atoms into its monoatomic gas at its melting temperature (Tanaka et al. [3] assumed the heat of vaporization).

Supposing that \( \beta \) is the linear function of temperature, the equations were worked out basing on the thermodynamic data from Barin and Knacke [18], the author’s data on the surface tension published in [4–9], the density listed in Table 7 and the correction parameter \( k \), from Table 6. They are shown in Table 8 together with the other data used in the calculations.

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \rho = a + b \cdot T )</th>
<th>Ref.</th>
<th>Metal</th>
<th>( \rho = a + b \cdot T )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>10.470 - 0.000912T</td>
<td>[4]?</td>
<td>Pb</td>
<td>11.471 - 0.001318T</td>
<td>[16]</td>
</tr>
<tr>
<td>Bi</td>
<td>10.692 - 0.001190T</td>
<td>[19]</td>
<td>Sb</td>
<td>6.981 - 0.000563T</td>
<td>[20]</td>
</tr>
<tr>
<td>In</td>
<td>7.315 - 0.0006795T</td>
<td>*</td>
<td>Sn</td>
<td>7.312 - 0.000615T</td>
<td>[21]</td>
</tr>
</tbody>
</table>

* New unpublished data from the dilatometric measurements

**Table 7**

Physical and thermodynamic properties and the temperature dependences of \( \beta = A + BT \) for Ag, Bi, In, Pb, Sb and Sn. \( \beta_i \) is the \( \beta \) value calculated at melting temperature.

<table>
<thead>
<tr>
<th>Metal</th>
<th>( T_c ) [K]</th>
<th>( \sigma ) [mN m(^{-1})]</th>
<th>( S ) [m(^2) mol(^{-1})]</th>
<th>( G_S^\infty - G_S^2 ) [J mol(^{-1})]</th>
<th>( \beta_i )</th>
<th>( T_{cr} ) [K]</th>
<th>( \beta ) = A + BT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>1233.95</td>
<td>898.9</td>
<td>42475.82</td>
<td>128272</td>
<td>0.6969</td>
<td>5953</td>
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<tr>
<td>Bi</td>
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<td>377.7</td>
<td>36842.56</td>
<td>13883</td>
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<td>In</td>
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<tr>
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<tr>
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<td>56326.05</td>
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<td>7475</td>
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<tr>
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<td>540.7</td>
<td>27338.93</td>
<td>246692</td>
<td>0.942</td>
<td>6988</td>
<td>= 1.015 - 0.000145T</td>
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**Table 8**

4. The molar surface layer area and the surface excess Gibbs free energy of alloys

In this work the following relation for the molar surface layer area has been proposed for the binary alloys:

\[
S_m = 1.091[k_1^2(1 - X_5) + k_2X_5][V_1(1 - X_5) + V_2X_5]^{1/2},
\]

where: \( V_1, V_2 \) are the molar volume and \( k_1, k_2 \) are the correction parameters (Table 6) of metals, \( X_5 \) is the concentration of the second metal in the surface phase (monoatomic layer). Using (8) the partial molar surface layer areas of different metals were calculated and used in the modeling of the surface tension of alloys.

To estimate the influence of the \( \beta \) parameters on the surface tension calculations were conducted for the Ag-In system using three different expressions of \( \beta \) for alloys; the results are presented in Table 9. The conclusion is, that the dependence of \( \beta \) on either the concentration or on the concentration and temperature, results in the surface tension greater than that calculated using the average value of this parameter, especially for alloys with lower In concentration and at higher temperatures. The differences are greater than 10 mN m\(^{-1}\) and some mN m\(^{-1}\) are observed even for \( X_{In} = 0.5 \). Thus, in the surface tension modeling the following equation will be applied for calculation of the excess Gibbs free energy of the surface phase:

\[
G_S^{ex} = [\beta_1(T)(1 - X_5) + \beta_2(T)X_5]G_B^{2k}(X_5)
\]

(9)

together with the equations describing the dependence of the \( \beta \) parameters on temperature from Table 8.
### Table 9

<table>
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<tr>
<th>T [K]</th>
<th>(X_{In} = 0.1)</th>
<th>(X_{Sn} = 0.3)</th>
<th>(X_{Sn} = 0.5)</th>
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<th>(X_{Sn} = 0.3)</th>
<th>(X_{Sn} = 0.5)</th>
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<th>(X_{Sn} = 0.3)</th>
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<td>575.2</td>
<td>818.1</td>
<td>707.4</td>
<td>581.1</td>
</tr>
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</table>

### 5. Results and discussion

The presented temperature dependences for \(\beta\) and \(k_r\) parameters were used to calculate the temperature dependences of the surface tension for 6 binary liquid alloys in the whole range of concentration, and compared with the experimental data obtained by the maximum bubble pressure method. The data of the molar volume were calculated from the equations given in Table 6 and the optimized thermodynamic parameters of the excess Gibbs free energy of alloys were taken from the following papers: Ag-Bi [4], Ag-In [5], Ag-Sn [12], Bi-Sn [24], Pb-Sn [22], Sb-Sn [23].

The calculations of the surface tension were conducted in two variants. The first: using the Butler relation (1) with \(\beta = 0.83\), and the partial molar surface layer areas of components calculated from Eq. (3). The second: using the Hoar and Melford equation (2), new values of \(\beta\) parameter (Table 8), partial molar surface layer areas and excess Gibbs free energies of components calculated using Eq.(8) and Eq. (9), respectively. Results of the calculations according to the first variant are shown in Figs 3a–8a, and according to the second one – in Figs 3b–8b, both shown as solid lines. The experimental data in Figs 3–8 are from [4–9], and they are designated by different symbols.

The calculated results of the surface tension for the Ag-Bi system, presented in Fig. 3a, show that the data calculated by Butler equation (1) differ from the experimental values not only in the values but also in the character of changes. While the experimental data show a steady decrease with decreasing temperature, the calculated surface tension, specially for alloys with lower Bi concentration (\(X_{Bi} < 0.5\)), demonstrates the opposite tendency. A much better agreement was obtained for the modeling using the Hoar and Melford relation (2) and corrected \(\beta\) and \(k_r\) parameters (Fig. 3b). For most alloys the observed temperature dependences for the experimental and the calculated data are almost the same, and the calculated and the experimental values of the surface tension are generally similar.

Results of calculations for Ag-In (Figs 4a, 4b), Bi-Sn (Figs 6a, 6b) and Sb-Sn (Figs 8a, 8b) according to second variant (new \(\beta, k_r\), Eq. (1)) show a better agreement, with the data obtained by the maximum bubble pressure method than those obtained by Butler equation (1).

Data of the surface tension for the Ag-Sn system, calculated from the thermodynamic parameters presented in a recent study on the critical evaluation of this system [12], are shown in Figs 5a and 5b. Results of the calculations according to variant I (Eq. (1)) are generally lower than the experimental values. When the new parameters \(\beta\) and \(k_r\) proposed in this work are applied, the obtained data (Eq. 2) are a bit lower for the alloys with \(X_{Sn} > 0.3\) and almost identical for higher Sn concentration. It seems that a slight correction of thermodynamic parameters may cause the observed weak maximum (\(X_{Sn} = 0.3\)) and the curvilinearity of some alloys can be reduced.

In the case of the Pb-Sn system (Fig. 7a, 7b) the agreement between the calculated data of the surface tension for the first and the second variant and those from the experimental investigations is good. At higher temperatures, the results obtained for the variant II of calculations agree a little better with those obtained from the maximum bubble pressure measurement and, at lower temperatures, than those for the I variant.

It can be concluded from a comparison of the calculated (in two variants) and the experimental data that the agreement between the experimental surface tension data and those calculated using the Hoar and Melford equation (2), together with \(k_r\) and \(\beta\) parameters (Table 6, and 8), proposed in this work, is much better than using the values calculated from the Butler relation (1) with the constant value of \(\beta = 0.83\), and the partial molar surface layer areas of the components equal to those for pure metals (Eq. (3)).
Fig. 3. Temperature dependences of the surface tension of the Ag-Bi liquid alloys obtained by: a) Butler, and b) Hoar and Melford relation (Eqs (1) and (2))

Fig. 4. Temperature dependences of the surface tension of the Ag-In liquid alloys obtained by: a) Butler, and b) Hoar and Melford relation (Eqs (1) and (2))

Fig. 5. Temperature dependences of the surface tension of the Ag-Sn liquid alloys obtained by: a) Butler, and b) Hoar and Melford relation (Eqs (1) and (2))
Fig. 6. Temperature dependences of the surface tension of the Bi-Sn liquid alloys obtained by: a) Butler, and b) Hoar and Melford relation (Eqs (1) and (2))

Fig. 7. Temperature dependences of the surface tension of the Pb-Sn liquid alloys obtained by: a) Butler, and b) Hoar and Melford relation (Eqs (1) and (2))

Fig. 8. Temperature dependences of the surface tension of the Sb-Sn liquid alloys obtained by: a) Butler, and b) Hoar and Melford relation (Eqs (1) and (2))
6. Conclusions

It was shown that the use of the parameters $\beta = 0.83$ and $S^0$ (molar surface layer area of pure metal) for the modeling of the surface tension by the Butler method gives the values which sometimes are not in agreement with the experimental data concerning the values and the temperature coefficient (positive from modeling, negative from experiment). To improve the agreement between the experimental and the calculated values of the surface tension an analysis of the influence of the $\beta$ parameter and the molar surface monoatomic layer area was performed. It has been found that the influence of the $\beta$ parameter, describing the relation between the excess Gibbs free energy of the bulk and the surface phase is much lower on the calculated values of the surface tension in comparison with the molar surface layer area of the components.

A new model of the surface monoatomic layer, assuming the polarization of the surface atoms has been proposed and a way of the calculation of the new correction coefficient for the molar surface layer area has been presented. It is next applied in the calculations of the partial molar surface layer areas of the components for some binary alloys.

A new expression for the $\beta$ parameter has been proposed, and considering to the correction parameter of the molar monoatomic surface layer area $k_r$, the linear temperature dependences of $\beta$ parameter for some metals were calculated.

A comparative analysis of the calculated and the experimental data of the surface tension showed that a much better agreement between the calculated values of the surface tension and those obtained from the measurements by the maximum bubble pressure method was observed when the $\beta$ and $k_r$ parameters, proposed in this work, were accepted in the calculations using the Hooar and Melford relation (2). The Butler equation (1) with $\beta = 0.83$ and the partial molar monoatomic surface layer areas equal to those for pure components (metals) gave poor agreement.

The new proposed expressions for the $\beta$ and the monoatomic molar surface layer areas of metals and alloys were used for 6 metals and 6 binary alloys. The future comparative studies of the experimental and the calculated surface tension for other systems will allow, perhaps, to specify better the characteristic temperature $T_c$ and the temperature dependence of the correction coefficient $k_r$ and the $\beta$ parameter or to confirm the assumptions and the polarized atoms model of the monoatomic surface layer, presented in this work.

REFERENCES


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