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## MODELING OF THE THERMODYNAMIC PROPERTIES OF LIQUID Fe-Ni AND Fe-Co ALLOYS FROM THE SURFACE TENSION DATA

### MODELOWANIE WŁAŚCIWOŚCI TERMODYNAMICZNYCH CIEKŁYCH STOPÓW Fe-Ni I Fe-Co W OPARCIU O DANE NAPIĘCIA POWIERZCHNIOWEGO

Recently proposed method of modeling of thermodynamic properties of liquid binary alloys from their surface tension data is described. The method utilizes Melford and Hoar equation, relating surface tension with excess Gibbs free energy, combined with new description of the monatomic surface layer and  $\beta$  parameter. The method is tested on Fe-Ni and Fe-Co alloys and the obtained results show very good agreement with experimental thermodynamic data of other authors. The model allows also to calculate the surface tension from thermodynamic data, and it gives better agreement with experimental results than those modeled with the use of Butler equation and traditionally defined monatomic surface layer and  $\beta = 0.83$ .

*Keywords:* Fe-based alloys; modeling; thermodynamic properties; surface tension

W pracy opisana jest niedawno zaproponowana metoda modelowania właściwości termodynamicznych ciekłych stopów dwuskładnikowych z ich danych napięcia powierzchniowego. Metoda wykorzystuje równanie Melforda i Hoara, wiążące napięcia powierzchniowe z nadmiarową energią swobodną Gibbsa, w połączeniu z nowym opisem monoatomowej warstwy powierzchniowej i parametru  $\beta$ . Metoda została przetestowana na stopach Fe-Ni i Fe-Co, a uzyskane wyniki pokazują bardzo dobrą zgodność z eksperymentalnymi danymi termodynamicznymi innych autorów. Model ten pozwala również na obliczanie napięcia powierzchniowego z danych termodynamicznych i daje lepszą zgodność z wynikami eksperymentalnymi niż modelowanie przy użyciu równania Butlera i tradycyjnie definiowanej monoatomowej warstwy powierzchniowej oraz  $\beta = 0.83$ .

### 1. Introduction

Several experimental methods were successfully applied to thermodynamic properties determination of liquid alloys. They all differ in principles, have their own limitations and consequently may give different, even contradictory results. What they have in common is that they are difficult, generally time-consuming and/or expensive. The obtained thermodynamic data can be later used to evaluate physical properties of liquid alloys such as viscosity or surface tension. For a binary alloy the surface tension is predicted by the Butler equation (1), derived in 1932 [1] under assumption that the monatomic surface layer, considered as a separate phase, is in equilibrium with the bulk phase.

$$\sigma = \sigma_1 + \frac{RT}{S_1^0} \ln \left( \frac{X_1^S}{X_1^B} \right) + \frac{G_{S(1)}^{ex} - G_{B(1)}^{ex}}{S_1^0} = \sigma_2 + \frac{RT}{S_2^0} \ln \left( \frac{X_2^S}{X_2^B} \right) + \frac{G_{S(2)}^{ex} - G_{B(2)}^{ex}}{S_2^0} \quad (1)$$

In 1957 Hoar and Melford [2] derived another equation (2) basing on the formation energy change of the surface on two different ways:

$$\sigma = \sigma_1 \frac{S_1^0}{S_1} + \frac{RT}{S_1} \ln \left( \frac{X_1^S}{X_1^B} \right) + \frac{G_{S(1)}^{ex} - G_{B(1)}^{ex}}{S_1} = \sigma_2 \frac{S_2^0}{S_2} + \frac{RT}{S_2} \ln \left( \frac{X_2^S}{X_2^B} \right) + \frac{G_{S(2)}^{ex} - G_{B(2)}^{ex}}{S_2} \quad (2)$$

The symbols in equations (1) and (2) denote:  $\sigma, \sigma_1, \sigma_2$  – the surface tension of the alloy and its components;  $S_1^0, S_2^0, S_1, S_2$  – the molar surface area and partial molar surface area in the monatomic surface layer of both components,  $G_{S(1)}^{ex}, G_{S(2)}^{ex}, G_{B(1)}^{ex}, G_{B(2)}^{ex}$  – partial excess Gibbs free energy of both components in the surface phase and bulk phase,  $X_1^S, X_2^S, X_1^B, X_2^B$  – mole fractions of both components in surface phase and bulk phase,  $R$  – gas constant,  $T$  – temperature.

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In case, when  $S_i^0 = S_i$ , equation (2) takes the form originally proposed by Butler (Eq. 1) and the surface tension of the alloy can be calculated if the surface layer area  $S_i^0$  and relation between  $G_{S(i)}^{ex}$  and  $G_{B(i)}^{ex}$  is known. According to the proposition of Hoar and Melford [2] the monatomic surface layer area is commonly calculated from the following relation:

$$S_i = LV_i^{2/3} N^{1/3} \quad (3)$$

The excess Gibbs free energy of components in the monatomic surface layer is calculated as follows:

$$G_{S(i)}^{ex} = \beta G_{B(i)}^{ex} \quad (4)$$

Symbols in Eq. 3 and 4 mean:  $V_i$  denotes the molar volume of the component “ $i$ ”,  $N$  is the Avogadro number,  $L = 1.091$  is the geometric factor for close-packed atoms (Fig. 1) of the surface monolayer and  $\beta$  is a factor characterizing the difference in the coordination number of atoms in both phases and its value proposed by Tanaka [3] is 0.83.

The method utilizing Butler equation with traditionally defined surface layer and parameter  $\beta$  (Eqs 1, 3 and 4) will be, in following paragraphs and figures, referred to as BTR.

The BTR method allows one to calculate the surface tension from excess Gibbs free energy of the components, but it was shown earlier in [4] on the basis of binary alloys of silver with bismuth, indium, and tin, and alloys of tin with antimony, bismuth, and lead that the agreement between the calculated surface tension and the experimental data is sometimes very poor.

In the same work [4] it was suggested, that in the case of great discrepancies between excess Gibbs free energy values, calculated from the thermodynamic parameters available in the literature, the good agreement between the experimental surface tension and the calculated can be a good criterion of their reliability. In order to improve this agreement a new model of the surface layer and new definition of  $\beta$  were proposed [4]. This model was verified by comparing the results of calculation with experimental data and values obtained from BTR model for six above mentioned binary alloys. In the following work [5] it was shown that it is possible to carry out the calculation in the opposite direction i.e. to calculate the thermodynamic properties of liquid binary alloys from the surface tension data.

The surface tension is the physical property sensitive to the impurities in metals and the atmosphere in which the experiment is conducted. Hence, its measurements should be performed using metals of high purity and in the noble gas atmosphere with a very low concentration of gas contaminations which could react with the

metals. Otherwise, such results should not be treated as characteristic of the metal and rather for the binary or multi-component system because in the case of significant difference between the surface tension of metal and contamination (reaction product), its much lower value causes considerable decrease of the surface tension.

Generally, the measurements of the thermodynamic properties are thought to be less sensitive to the contaminations, although, in the case of electrochemical methods, the influence can be significant.

It should be emphasized that the calculation of the excess free energy based on the surface tension depends on the assumed surface monolayer structure and the  $\beta$  parameter. However, the integral excess free energy of bulk phase calculated from the surface tension should reveal similar deviations from the ideality and it should be comparable with these obtained from the experimental investigations or calculated from the optimized parameters for the liquid phase. Otherwise, it means that the equations for  $\beta$  and the surface monolayer area used in calculations were wrong or the experimental investigations of the surface tension were incorrectly conducted (contaminated protective atmosphere or metals, wrong procedure of measurements).

The aim of this work is to show applicability of the model proposed in [4, 5] for the determination of the surface tension from thermodynamic data as well as thermodynamic properties of liquid Fe-Ni and Fe-Co binary alloys from surface tension data.

## 2. The new approach to surface tension calculation

It was shown earlier in [4] that for the same set of thermodynamic data there are two parameters in equation (1) i.e.  $\beta$  and  $S_i^0$  that can affect the result of the surface tension calculation. Preliminary tests showed that it is the surface layer area  $S_i^0$  that has stronger influence on calculated surface tension.

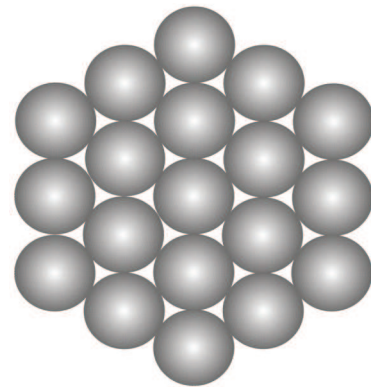


Fig. 1. Top view of the surface monolayer of close-packed atoms

In order to obtain the results close to the experimental data, the new model of the surface layer [4] was proposed. In comparison to the surface monolayer structure presented in Fig. 1 and assumed in Eq. (3), another locations of atoms were postulated (Fig. 2a, 2b) due to the influence of the interaction of atoms of the gas and bulk phase with atoms of the monatomic layer and the very high pressure (compressive stress) in the monolayer (according to the Laplace definition of the surface tension  $\sigma\delta h$ , where:  $h$  is the thickness and  $\delta$  is the compressive stress in the monolayer). Additionally, the following assumptions were made:

1. Due to the absence of atoms above the surface layer and asymmetrical arrangement of forces, the force directed towards the bulk phase acts on electrons of atoms in the surface layer.
2. This force shifts the valence electrons towards the bulk phase causing the polarization of atoms in the surface layer and the change of the inter-atomic distance with respect to that in the bulk phase (see Fig. 1 and 2b).
3. The inter-atomic distance is equal to that given in Eq. (3)  $((V_i/N)^{1/3})$  only at certain characteristic temperature  $T_C$ , at which the value of the vapor pressure of metal is equal to 0.001atm. The temperature  $T_C$  is different for different metals.
4. The inter-atomic distance is lower than that in Eq. (3) because the influence of pressure predominates at temperatures lower than  $T_C$ , while at higher temperatures it is the interaction of atoms of the gas and bulk phase with the atoms of the monolayer which prevails.

Thus it was assumed that the atoms in the monatomic surface layer can be shifted (Fig. 2a), polarized (Fig. 2b) and the inter-atomic distance and the monatomic surface layer area is decreased (or increased when  $T > T_C$ ) in comparison with that calculated using Eq. (3).

It can be seen from Eq. (3) under assumption that the doubled atomic radius is the inter-atomic distance, that the relation between the surface areas and inter-atomic distances is as follows:

$$S_S = \frac{(R_S)^2}{(R_B)^2} S_B = (k_r)^2 S_B \quad (5)$$

where:  $R_S$  and  $R_B$  are the half average inter-atomic distances (i.e. atomic radii) of the metal  $((V_{i(S,B)}/N)^{1/3}/2)$  in the surface and bulk phase,  $S_S$  and  $S_B$  are the monatomic molar surface areas of the metal in the surface and the bulk phase (Eq. 3),  $k_r$  is temperature dependant correction parameter. It was assumed, basing on the analyses of calculated and experimental values of the surface tension

of binary alloys that parameter  $k_r$  is a linear function of temperature. It can be determined [4] provided that at room temperature its value is equal to proportion of the average atomic radius and the effective ionic radius of the element for coordination number 6. It is also equal to 1 at such temperature  $T_C$  at which the vapor pressure of the metal is 0.001 atm. In the vicinity of  $T_C$  a fast increase of the partial pressure of metals is observed. The valence of the ion is assumed to be equal to the number of electrons in the last electronic sub-shell (s, p). The calculated equations describing temperature dependence of  $k_r$  for Co, Fe, Ni are shown in Table 1.

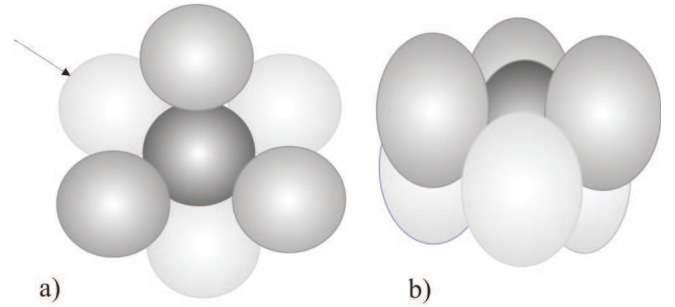


Fig. 2. The possible displacement of the atom because of the interaction with atoms of the bulk phase and atoms of gas phase (Fig. 2a, 2b) and because of the asymmetrical electrostatic interaction (lack of atoms above the monolayer) and the high pressure in the monatomic layer

TABLE 1  
Temperature dependences of  $k_r$  parameters for Co, Fe and Ni

Metal	$k_r = a + bT$
Co	$k_r(Co) = 0.47491 + 0.000224037T$
Fe	$k_r(Fe) = 0.42035 + 0.000253737T$
Ni	$k_r(Ni) = 0.51146 + 0.000213137T$

It was shown by Tanaka [3] that the value of  $\beta$  slightly differs from one metal to the other, and so this fact should be considered in calculation. When  $\beta$  is considered to be a function of concentration, it is necessary to use another mathematical description of excess Gibbs free energy in the surface phase, because instead of being multiplied by constant value of  $\beta$  it is multiplied, in the simplest case, by linear function of composition varying from  $\beta_1$  to  $\beta_2$ . Obviously for metals which slightly differ in  $\beta$  and the surface tension the difference in calculated alloy surface tension will be small, however for the other the difference becomes significant. Temperature independence of  $\beta$  is another simplification and it was suggested [4], that  $\beta$  should be linear function of temperature. The

$\beta$  parameter for each metal is defined by two points: a) at critical temperature (where  $\sigma_i = 0$ )  $\beta$  is equal to zero, b) at melting temperature  $\beta$  is defined by the relation (6).

$$S_i \sigma_i = (1 - \beta) (G_g^0 - G_l^0) \quad (6)$$

Where:  $G_g^0 - G_l^0$  is the change of standard free energy of the transformation of 1 mole of liquid metal atoms into mono-atomic gas at its melting point. It should be mentioned that Tanaka [3] used the heat of vaporization in place of  $G_g^0 - G_l^0$ . Table 2 shows the equations of parameter  $\beta$  for cobalt, iron and nickel.

TABLE 2  
Temperature dependencies of  $\beta$  parameters for Co, Fe and Ni

Metal	$\beta = a + bT$
Co	$\beta_{Co} = 0.964 - 0.000147T$
Fe	$\beta_{Fe} = 0.928 - 0.000145T$
Ni	$\beta_{Ni} = 1.000 - 0.000149T$

As a result of the above, the following relation for the molar surface layer area was proposed [4] for binary alloys:

$$S_m = 1.091 \left[ (k_{r1})^2 (1 - X_2^S) + (k_{r2})^2 X_2^S \right] \cdot \left[ V_1 (1 - X_2^S) + V_2 X_2^S \right]^{2/3} N^{1/3} \quad (7)$$

Where:  $V_1$  and  $V_2$  are the molar volume and  $k_{r1}$  and  $k_{r2}$  are the correction parameters for both metals,  $X_2^S$  is the concentration of the second metal in the surface layer.

Using this equation the partial molar surface areas of different metals were calculated.

In [4] it was shown in the case of Ag-In alloys, that the dependence of  $\beta$  both on temperature and concentration has influence on calculated surface tension, therefore the following equation was proposed for the excess Gibbs free energy calculation of the surface phase:

$$G_S^{ex} = \left[ \beta_1 (1 - X_2^S) + \beta_2 X_2^S \right] G_B^{ex} \quad (8)$$

### 3. Calculation of the thermodynamic properties

Calculation of the excess Gibbs free energy of liquid binary alloys at constant temperature is possible with the use of either Hoar and Melford [2] or Butler [1] equation system and the double stage optimization procedure. First, applying fixed values of thermodynamic parameters the surface concentration  $X_1^S$  is calculated, next the optimization of the goal function as a sum of squared differences between calculated and experimental surface tension is performed. The method described in

paragraphs 2 and 3, utilizing Hoar and Melford equation (eq. 2) with newly defined surface layer (eq. 7) and parameter  $\beta$  (eq. 8) will be, in the rest of this paper, referred to as HMNP.

The experimental surface tension data described with Eq. 9, are the input data.

$$\sigma = \sigma_1 X_1^B + \sigma_2 X_2^B + \sum_{i=1}^n Z_i X_2^i, \quad Z_1 = - \sum_{i=2}^n Z_i \quad (9)$$

A procedure of calculation of the excess Gibbs free energy from the surface tension is performed as follows:

1. Working out the relation (9) describing the dependence of the surface tension on  $X_2$  and  $T$  basing on the experimental data. Parameters  $Z_i$  are placed in input file
2. Reading from the input file the data necessary in calculations: surface tensions, densities, parameters  $W_i, \beta, k_r$  etc. (after starting the procedure)
3. Simulation of the thermodynamic parameters of  $G_B^{ex}$  ( $P_i$ ,  $i=1, n$ )
4. Calculation of the surface tension for many concentrations using the equation (9)
5. Modeling the surface tension using BTR (Eqs 1, 3, 4) or HMNP (Eqs 2, 7, 8) relation
6. Determination of the goal function  $D = \sum (\sigma_{ex} - \sigma_{cal})^2$
7. Checking whether  $D$  reached the minimum value:
  - a) If  $D \neq D_{min}$  the sequence of calculations is repeated from point 3
  - b) If  $D = D_{min}$  the calculations at fixed temperature are stopped and  $G_B^{ex}$  is calculated in the entire range of concentrations  $X_i^B$  and written in output file

Stages from 2 to 7 are performed by the software, specially developed to solve the presented problem using BTR and HMNP model. In our program the excess Gibbs free energy is described by the following equation:

$$G^{ex} = \sum_{i=1}^n P_i X_2^i = \sum_{i=2}^n P_i (X_2^i - X_2), \quad P_1 = - \sum_{i=2}^n P_i \quad (10)$$

Parameters  $P_i$  can be easily converted into  $L_i$  parameters of Redlich-Kister [6] equation and vice versa. The partial excess Gibbs free energy values of components were calculated using Eq. 8 and known relations between partial molar functions and one mole function of the binary alloy.

### 4. Results and discussion

Two iron based metallic systems, namely Fe-Ni and Fe-Co, were chosen to test the applicability of the model [4, 5] to alloys of high melting temperatures. Because of their high melting temperature a lot more difficulties

arise in experimental determination of their surface tension and thermodynamic properties, compared to lower melting alloys tested in [4, 5]. In this paper surface tension data obtained using two methods that is oscillating drop method and sessile drop method are used for excess Gibbs free energy calculation.

#### 4.1. Iron-nickel system

The surface tension of Fe-Ni alloys have been determined by many researchers [7-12]. The oscillating droplet method was used by [7, 8] and the others applied sessile drop method. Fig. 3 shows compositional dependence of the surface tension of Fe-Ni alloys at 1823 K from different authors. Great differences between their results may be observed. From all of these data only the results of Lee and coworkers [7] and Brillo and Egrý [8] show slightly positive deviation from additive behavior, which is thermodynamically most probable due to negative values of the excess Gibbs free energy of liquid Fe-Ni alloys [14, 15, 21]. In addition their data show relatively good compatibility, except the surface tension value for Ni.

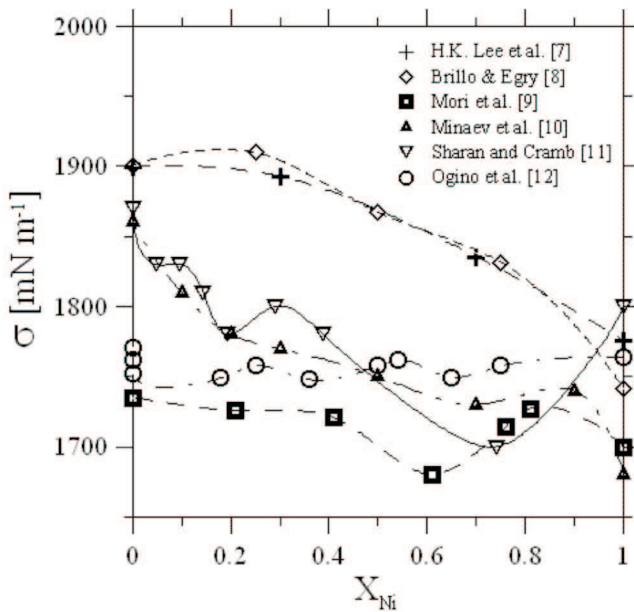


Fig. 3. Surface tension dependence on composition in Fe-Ni system. Data of [7,8,12] at 1873K and data of [9-11] at 1823K. Lines are used to suggest the trends only

In the case of nickel the surface tension data of [8] are about  $40 \text{ mN}\cdot\text{m}^{-1}$  lower than the data of [7] at 1873K. These differences are not great in comparison with the value of the surface tension of metals and alloys. There is also, some inconsistency in Brillo and Egrý's work [8] between the data given in figure and those calculated using equations describing the surface

tension temperature dependence for respective compositions. It concerns the alloy of  $X_{Fe} = 0.25$  for which the calculated surface tension from equation is about  $140 \text{ mN}\cdot\text{m}^{-1}$  lower than that in figure. It should be noted that the deviations of the experimental data from the linear changes are higher for the data of Brillo [8] than for Lee [7]. This means that the calculated excess Gibbs free energy will be characterized by the much lower values in comparison to that calculated from the data of Lee [7]. As in the process of calculations of the excess Gibbs free energy the experimental data of the surface tension are used in the form of the equation (9) (to have many points  $(X, \sigma)$  as input data), first the parameters  $Z_i$  and  $\sigma_i$  were calculated basing on the experimental data. Because of inconsistency regarding Brillo and Egrý's work [8], the experimental values of the surface tension presented in figures by [7] and [8] were digitized. Then by the least squares method the coefficients of equations  $\sigma = a + bT$  with the errors  $E_i$  at any temperature for the given alloy [23] were determined. These coefficients and errors were next used in the procedure of calculating the parameters of Eq. (9) by applying the weights defined by the following relation:  $W_i = E_{max}/E_i$ , where:  $W_i$  is the weight of the surface tension at the point  $(T_i, \sigma_i)$ ,  $E_i$  is the error in the point  $(T_i, \sigma_i)$  and  $E_{max}$  is the maximal error obtained in the set of points  $(T, \sigma)$ . In effect, the points with the lower errors  $E_i$  influence much more the goal function (sum of squared differences between calculated and experimental values) and finally the value of the parameters in Eq. (9). It ensures that the values calculated from Eq. (9) are close to those from the experiment characterizing lower value of error.

The obtained linear equations of the investigated alloys showed very good agreement with those presented in publications except that cited earlier. The worked out relations (11) and (12) for Lee [7] and Brillo [8] results, respectively, are as follows:

$$\sigma_{FeNi} = (2579 - 0.3601T) X_{Fe} + (2349 - 0.3055T) X_{Ni} + 94(X_{Ni} - X_{Ni}^2) \quad (11)$$

$$\sigma_{FeNi} = (2450 - 0.2927T) X_{Fe} + (2180 - 0.2381T) X_{Ni} + 204(X_{Ni} - X_{Ni}^2) \quad (12)$$

The calculated standard deviations are 6 and  $8 \text{ mN}\cdot\text{m}^{-1}$ , respectively.

The comparison of the experimental data with those calculated from Eqs (11) and (12) is presented in Figs 4a and 4b. In these figures points represent experimental data, while lines show values calculated using equation (11) and (12), respectively.

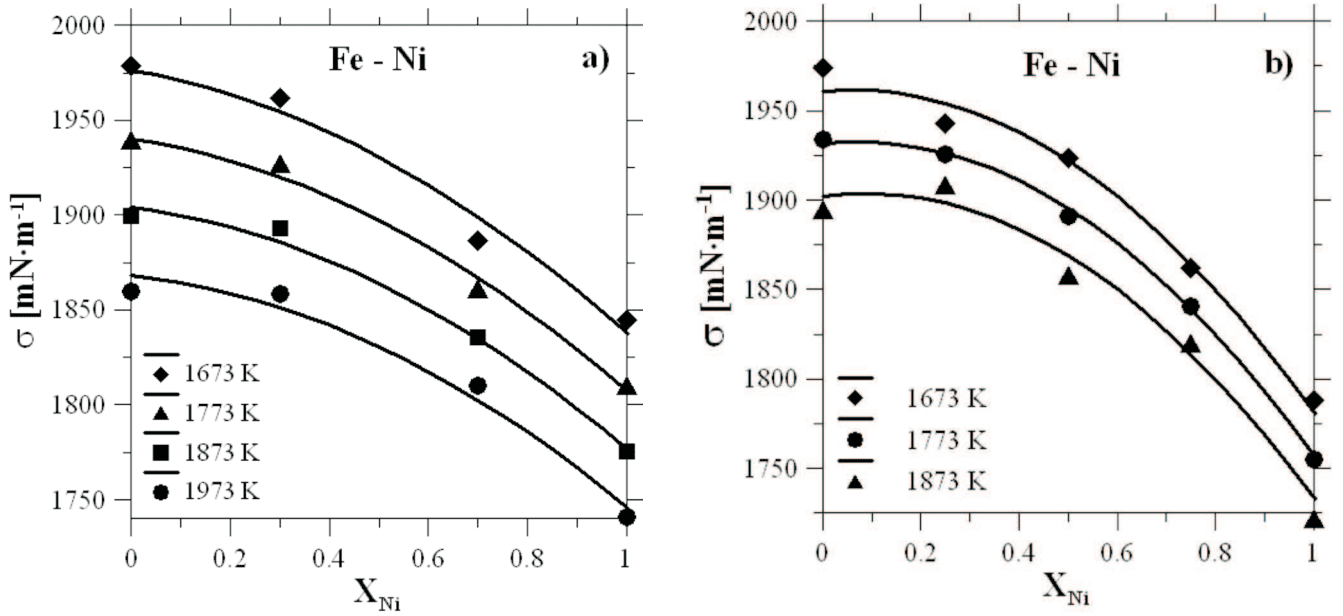


Fig. 4. Surface tension dependence on composition in Fe-Ni system. Data of a) Lee et al. [7], b) Brillo and Egly [8], respectively

The surface tension was first modeled with the use of thermodynamic data of Lee [14] and Speiser [15] and compared to experimental data of [7] (Fig. 5a) and [8] (Fig. 5b). Such a procedure gives the possibility to estimate whether the experimental surface tension data are well reproduced by thermodynamic properties and at the same time to estimate if the excess Gibbs free energy calculated from the surface tension data will be similar to those used in modeling.

According to the Butler [1] and Hoar-Melford [2] equations such a mutual relation between the thermodynamic and physical properties ( $G^{ex}$ ,  $\sigma$ ) measured in the same conditions is expected when  $\beta$  and  $S$  are suitably defined and measurements correctly conducted. This fact is very easy to notice, especially for systems with the low difference of the surface tension. It may be expected, that basing on the well worked out and checked thermodynamic parameters (excess Gibbs free energy) the measured surface tension should well agree with the modeled surface tension and vice versa [4, 5]. If the mutual corre-

lation is not observed the experimental method, probably for the surface tension, should be revised.

In calculations of the surface tension of Fe-Ni alloys the density data of pure components given in table 3 were adopted from Smithells Metals Reference Book [22] to calculate molar surface area. Values of  $k_r$  and  $\beta$  for pure components are given in tables 1 and 2, respectively. Surface tension values for Fe and Ni were taken from Eqs 11 and 12, respectively. The calculated surface tension of Fe-Ni alloys together with the experimental values is presented in Figure 5a) and 5b).

TABLE 3

Density of Co, Fe, Ni [22]

Metal	$\rho_i$ , g·cm <sup>3</sup>
Co	= 9.685 - 0.00109T
Fe	= 8.622 - 0.00088T
Ni	= 9.960 - 0.00119T

TABLE 4

Redlich-Kister polynomial parameters for Fe-Ni system determined from thermodynamic data

R-K parameters Lee [14]	R-K parameters Speiser [15]	R-K parameters Hultgren [21]
$L_0 = -16911 + 5.1622T$	$L_0 = -20292.4 + 5.14894T$	$L_0 = -11227, L_2 = -599.494$
$L_1 = 10180 - 4.146656$	$L_1 = 11924.4 - 6.16329T$	$L_1 = 6757.97, L_3 = -2452.49$

In these figures continuous lines denote the values calculated from HMNP model while dotted lines those calculated from BTR model. Thin lines represent the results of calculations using the excess Gibbs free energy data of Lee [14] and thick line the data of Speiser [15], respectively (see table 4). As can be seen in figure 5a), HMNP gives better agreement with experimental surface tension data regardless which thermodynamic data were used. In case of data of Brillo and Egry (see Fig 5b) the situation is different. Here, for both models, the agreement is better for Speiser's [15] data used in calculations. Most importantly, although the agreement is quite good at 1673 K there is no agreement with experimental data at 1873 K. It suggests that the data of Brillo [8] will give much lower values of the excess Gibbs free energy than the data of Lee [7].

In the following step the excess Gibbs free energy for Fe-Ni alloys was calculated with the use of surface

tension data given by Lee [7] and Brillo [8] applying both BTR and HMNP model. Table 5 presents parameters  $P_i$  calculated for Fe-Ni system from surface tension data. Calculated Gibbs free energy was compared to the data of different investigators, as can be seen in Fig. 6. From this figure it is clear that the agreement between the experimental data [7] is much better for HMNP than for BTR model. The values of excess Gibbs free energy calculated with HMNP are very close to the average of experimental results, although they slightly differ depending on surface tension data used. It is interesting to note that the excess Gibbs free energy calculated from the BTR model is up to 2.5 times lower than that calculated from HMNP. The excess Gibbs free energy calculated from the surface tension data of Brillo et al. [8] shows about twice lower values in comparison with those calculated using Lee [7] data. Disagreement is observed for both models of calculations.

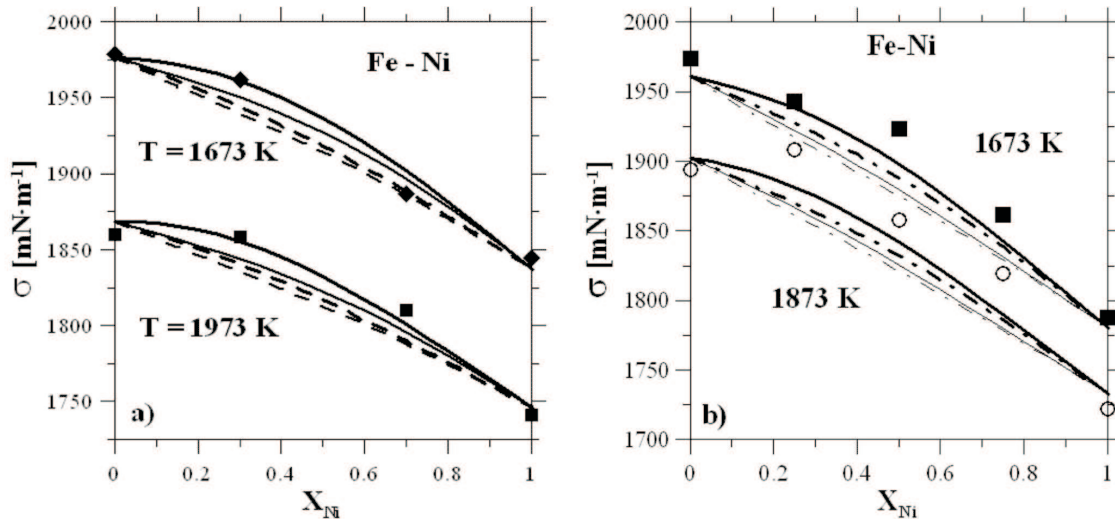


Fig. 5. Values of the surface tension in Fe-Ni system: a) calculated [7] and b) experimental [8]

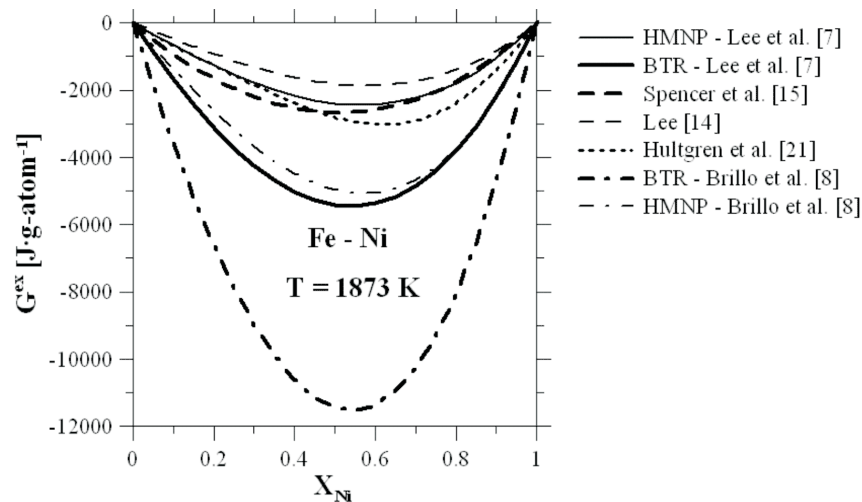


Fig. 6. Calculated and experimental [14, 15, 21] thermodynamic properties of the Fe-Ni system at 1873K

Parameters  $P_i$  (Eq. 10) of the excess Gibbs free energy of liquid Fe-Ni alloys calculated from the surface tension data at 1873 K

Surface tension data	$P_i$	$P_i$
	Model BTR	Model HMNP
Lee [7], Eq. (11)	$P_1 = -18014.65$ $P_2 = 10807.60$ $P_3 = 7207.06$	$P_1 = -6876.42$ $P_2 = 1511.49$ $P_3 = 5364.94$
Brillo [8], Eq. (12)	$P_1 = -38100.05$ $P_2 = 22723.72$ $P_3 = 15376.33$	$P_1 = -13864.92$ $P_2 = 1853.66$ $P_3 = 12011.26$

## 4.2. Iron-cobalt system

Iron and cobalt have similar melting temperature and surface tension at melting point, and so one could expect surface tension composition dependence of Fe-Co alloys to be linear. The surface tension of Fe-Co alloys was investigated by many authors including [10, 12, 13]. Figure 7 shows a comparison between the data of Eichel and Egry [13] and Ogino et al. [12], who covered the whole concentration range, at the same temperature 1873 K. It can be seen that the data obtained with the oscillating drop method [13] are generally higher than the data obtained with the sessile drop method [12]. Moreover, they also differ in general trend i.e. there is a strong minima between 0.6 and 0.8 mole fraction of iron in the data of [13] while no such thing occurs in the data of [12]. The experimental surface tension data were described with the equation (9):

$$\sigma_{CoFe} = 1809.5X_{Co} + 1761.4X_{Fe} - 15.1037X_{Fe} - 123.4839X_{Fe}^2 + 138X_{Fe}^3 \quad (13)$$

$$\sigma_{CoFe} = (2501.3 - 0.34659T)X_{Co} + (2597.8 - 0.39210T)X_{Fe} + (-348.6 + 0.0183)(X_{Fe} - X_{Fe}^2) \quad (14)$$

for the Ogino [12] and Eichel [13] data, respectively. Comparison of experimental and calculated from Eqs (11) and (14) values is shown in Fig. 7. It was impossible to use the same procedure of calculations of the equation (11) parameters, because the Ogino data [12] were given only for one temperature (1873 K) while Eichel [13] reported data for many concentrations at 4 temperatures, calculated from the worked out earlier linear equations ( $\sigma = a + bT$ ), so their weights were assumed to be 1.

Using the thermodynamic data of [16-18], two sets of Redlich-Kister polynomial parameters were worked out for Fe-Co system (see table 6) and finally excess Gibbs free energy at 1873K was determined. As can be seen in Fig. 8, those two sets of data give similar dependences of the excess Gibbs free energy vs. composition,

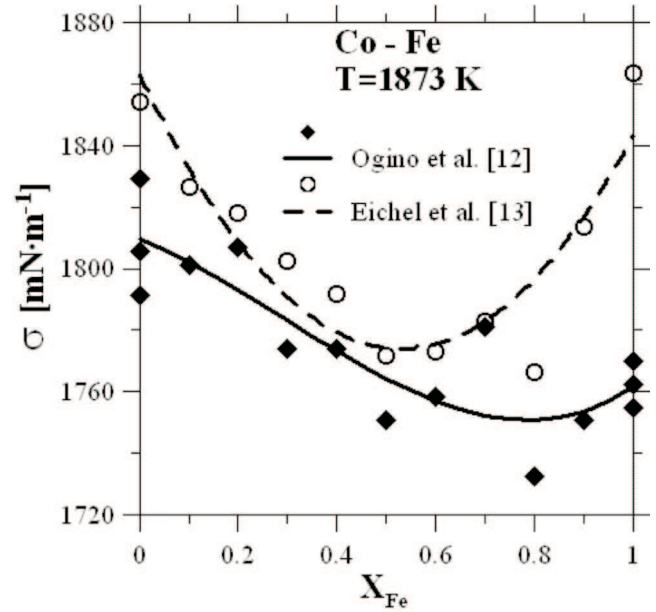


Fig. 7. Surface tension of Fe-Co alloys at 1873K

however, they differ in maxima location. In the case of  $G^{ex}$  calculated from the data of Belton and Predel [16, 18] it is  $X_{Fe} = 0,3$  and in case of  $G^{ex}$  calculated from the data of Batalin and Predel [17,18] it is  $X_{Fe} = 0,6$ . It is worth noting that these sets of data are quite similar to those of Morachevskii [20] and Tomiska & Neckel [19], respectively. For this reason both sets [12, 13] were used in the surface tension calculation at 1873 K using the surface tension data for iron and cobalt from Eq. 13 and 14.

TABLE 6  
Redlich-Kister polynomial parameters for Fe-Co system determined from thermodynamic data. (SD-average standard deviation)

R-K parameters Reference [16,18]	R-K parameters Reference [17,18]
$L_0 = -10146 + 8.41903T$	$L_0 = -9962.28 + 8.01428T$
$L_1 = -2916.21 + 3.90722T$	$L_1 = -2825.69 - 0.244203T$
$L_2 = 308.196$	$L_2 = 308.196$
SD=21 J/g-atom	SD=63 J/g-atom



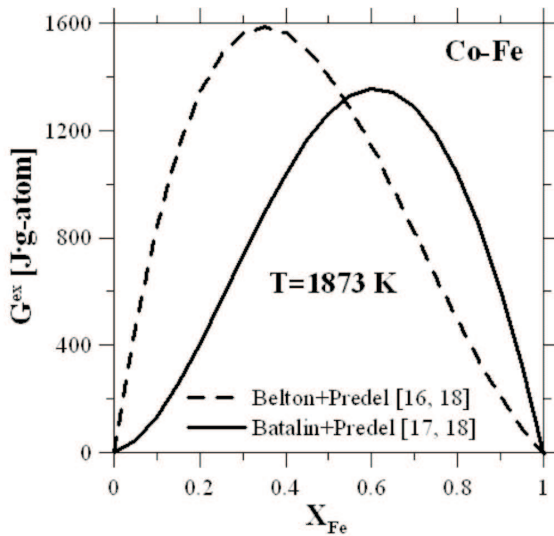


Fig. 8. Determined thermodynamic properties for Fe-Co alloys

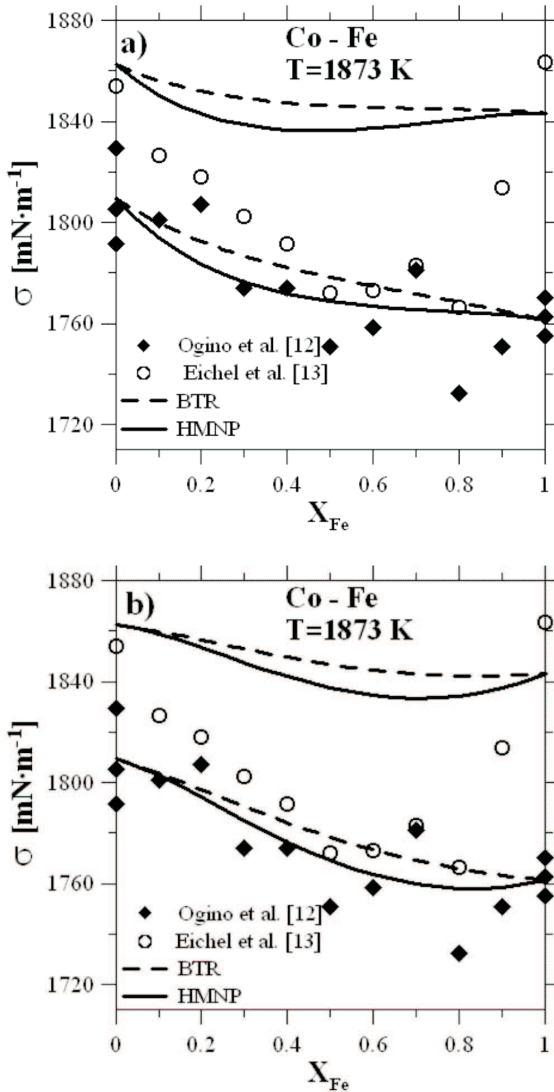


Fig. 9. Calculated and experimental surface tension [12, 13] at 1873K.  $G^{ex}$  used in surface tension modeling was calculated from the data of a) Belton and Predel [16,18] and b) Batalin and Predel [17,18], respectively

As can be seen from Fig. 9a and 9b, calculated surface tension deviates negatively from linear trend as it is in case of experimental data. The agreement between calculated surface tension (both using BTR and HMNP model) is much better in case of Ogino's [12] data. It is also clear that new model (HMNP) gives better agreement than the BTR model.

Weak agreement between results of calculation and the data of Eichel and Egly [13] suggest that these data are less reliable than the data of Ogino [12] and that the excess Gibbs free energy calculated from theirs [13] surface tension will show much higher values than that obtained from Ogino data [12].

Later, using the algorithm presented in section 3 and the data of [12] and [13] described with equations (13) and (14), respectively, the excess Gibbs free energy for this alloy was calculated at 1873K with the use of HMNP model and compared with the result of calculation with the use of BTR. Table 7 presents parameters  $P_i$  calculated for Co-Fe system from surface tension data. As can be seen in Fig. 10, using Ogino surface tension data [12], the results of calculation with the use of HMNP agree well with the experimental data of other authors, while the data calculated with BTR equation are more than three times higher than the average of the other values. The values of  $G^{ex}$  calculated from the Eichel and Egly surface tension data [13] show over twice higher values in comparison with those obtained from Ogino values [12] and from other thermodynamic investigation methods [16-20].

TABLE 7

Parameters  $P_i$  (Eq.10) of the excess Gibbs free energy of liquid Co-Fe alloys calculated from the surface tension data at 1873 K

Surface tension data	$P_i$	
	Model BTR	Model HMNP
Ogino [12], Eq. (13)	$P_1 = 371.98$ $P_2 = 30089.52$ $P_3 = -30461.50$	$P_1 = 646.28$ $P_2 = 11126.96$ $P_3 = -11773.24$
Eichel [13], Eq. (14)	$P_1 = 37570.59$ $P_2 = -37669.26$ $P_3 = 98.67$	$P_1 = 24732.59$ $P_2 = -24797.11$ $P_3 = 64.52$

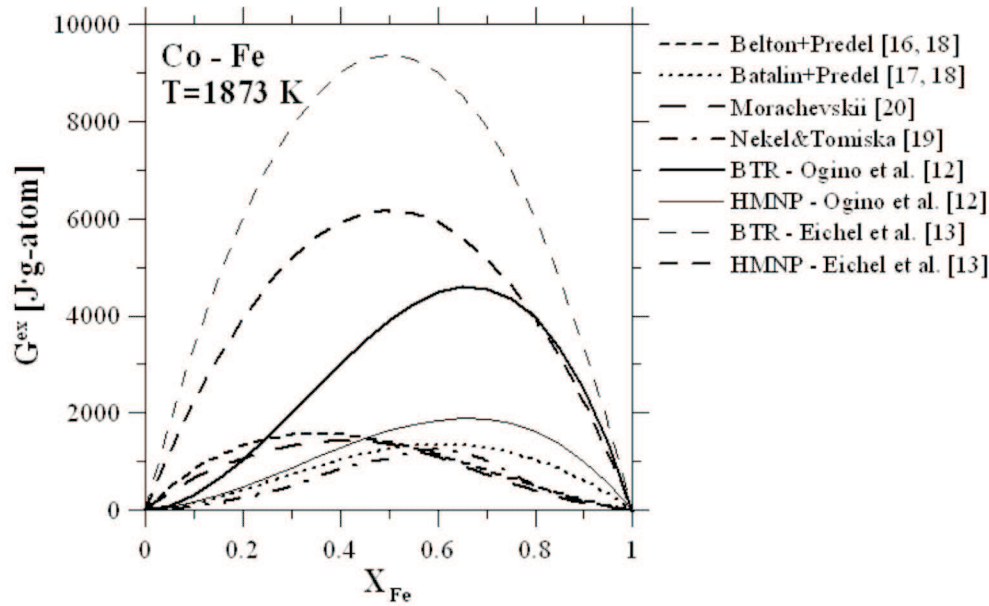


Fig. 10. Excess Gibbs free energy of the Fe-Co system calculated from the models and obtained from the experiments [16-20]

## 5. Conclusion

Recently put forward model [4, 5] including new definition of both surface layer and parameter  $\beta$  was described. It was shown that the model can be successfully applied to surface tension modeling from thermodynamic data as well as modeling of thermodynamic properties (excess Gibbs free energy) from surface tension data in case of high temperature systems.

Among surface tension data for Fe-Ni system available in literature two sets [7, 8], most justified thermodynamically, were selected. Both sets of data were obtained by the oscillating droplet method and show relatively good agreement one with another. However, it was shown that the data of Brillo and Egry [8] are less reliable than the data of Lee and coworkers [7]. Data [7] were compared to surface tension calculated with the use of BTR and HMNP models using two sets of thermodynamic data taken from literature [14, 15]. The results of calculations show that HMNP model gives better agreement between calculated surface tension and experimental data than it is possible in the case of BTR model, regardless which thermodynamic data were used in calculations. Next the excess Gibbs free energy was calculated and the values obtained from HMNP are close to the average of experimental data of different authors, while the values calculated from BTR are up to 2.5 times lower. This proves that not only is the HMNP model much better tool for surface tension modeling compared to BTR model, but also it is the only acceptable tool for excess Gibbs free energy modeling from surface tension data.

Also in the case of Fe-Co system two sets of surface tension data were investigated, one obtained from oscillating drop method [13] and the other from sessile drop method [12]. The surface tension of Fe-Co alloys was modeled with the use of two sets of thermodynamic data assessed in this work and it was shown that HMNP gives improved agreement with experimental surface tension data compared to BTR model. It was also shown that HMNP can be used as a tool to assess the reliability of experimental surface tension data with the difference between calculated and experimental data being the criteria. The excess Gibbs free energy calculated using Ogino surface tension data [12] agrees well and is only slightly higher than experimental data of other authors while results from BTR model are up to three times higher. Analogical calculations of the excess Gibbs free energy conducted basing on Eichel and Egry surface tension values [13] show complete disagreement either with those from Ogino results [12] or from different thermodynamic investigation methods.

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