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NEW CONSIDERATIONS REGARDING THE THERMODYNAMIC OF BINARY ALLOY SYSTEMS

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În lucrare este prezentat un nou model de interacţiune, aplicabil sistemelor de aliaje binare, fiind o generalizare a modelelor Hardy (soluţie subregulară) şi Sharkey (soluţie subsubregulară). Entropia de amestec, diferită de cea a soluţiei ideale, este calculată luându-se în considerare probabilitatea apariţiei în topituri a elementelor de ordine datorită neaditivităţii legăturilor dintre atomii de natură diferită.

The paper presents a new model of interaction, applicable to systems of binary alloys. This model is a generalisation of Hardy (for sub-regular solution) and Sharkey (for sub-sub-regular solution) models. The entropy of mixture, different of that for ideal solution, was calculated taking into consideration the probability of order elements to appear in molten melts because of the non-additivity of bonds between atoms of different species.

Introduction

In the last decades, a highly performant informational system has been created, the calculus technics have developped in an alert rithm and several expert programs have been developped. All these have permitted to intensify the thermodynamical studies on alloy systems. The results obtained in the research activity through the large scale utilisation of mathematical models are astonishing.

In parallel with empirical models of interactions (*Margules relationships* [1,3], *Redlich-Kister equations* [3,4], *spline functions* [5-8], *orthogonal polynoms Legendre* [3], etc.), useful to solve different practical problems where the focus is on the agreement between the calculated and the real, experimental values, a series of theoretical models were developed and perfected (*the model of regular solution, the model of sub-regular solution, the model of sub-sub-regular, the quasi-chemical model*, etc.) trying to establish a link between the thermodynamic properties of alloys and their structure.

In former work, two new models (*sub-regular partially-ordered solution* - SRPOS [9] and *sub-sub-regular partially-ordered solution* – SSRPOS [10]) which take into consideration the issue in many liquid alloys of some elements of order due to the non-addivity of bonds between atoms of different

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nature were presented. Further research in this direction, presented here, try to generalise the utilised calculus method.

As it is well known, the regular solution model considers that the bond energy for pairs of different atoms (1-2) is ε_{12}. According to the new proposed model, the interraction energy for the pair of atoms 1-2 is different of ε_{12} when the atom type 1 is found in the neighborhood of two atoms type 2, disposed in a certain way in the net nodes, the probability of this kind of groups being equal to $x_1 x_2^2$; also, the energy of interaction differs of ε_{12} when the atom of type 1 lies in the vicinity of three atoms of type 2, the probability of such groups being $x_1 x_2^3$. By generalisation, we can say that the energy of interaction differs of ε_{12} when the atom of type 1 is in the vicinity of *n* atoms of type 2, the probability of such groups being equal to $x_1 x_2^n$.

In this case, from the total number of bonds P_{12}

$$P_{12} = 2x_1 x_2 \left(0.5 z N_0\right) = x_1 x_2 z N_0 \tag{1}$$

are subdued

$$P_{12}^{(1)} = 2x_1 x_2^2 \left(0.5 z N_0\right) = x_1 x_2^2 z N_0 \tag{2}$$

bonds having the energy $\varepsilon_{12}^{(1)} \neq \varepsilon_{12}$ and

$$P_{12}^{(2)} = 2x_1 x_2^3 \left(0.5 z N_0\right) = x_1 x_2^3 z N_0 \tag{3}$$

bonds having the energy $\varepsilon_{12}^{(2)} \neq \varepsilon_{12}$,

.....

$$P_{12}^{(n)} = 2x_1 x_2^{k+1} \left(0.5 z N_0\right) = x_1 x_2^{n+1} z N_0 \tag{4}$$

bonds having the energy $\varepsilon_{12}^{(k)} \neq \varepsilon_{12}$, the difference $P_{12} - \sum_{i=1}^{n} P_{12}^{(i)}$ referring to the bonds with the energy ε_{12}. On this basis, the molar heat of mixture will be given by the relationship:

$$\Delta H_m^M = \left(P_{12} - \sum_{i=1}^{n} P_{12}^{(i)} \right) \left(\varepsilon_{12} - 0.5 \sum_{i=1}^{n} \varepsilon_{ii} \right) + \sum_{i=1}^{n} P_{12}^{(i)} \left(\varepsilon_{12}^{(i)} - 0.5 \sum_{i=1}^{n} \varepsilon_{ii} \right) \tag{5}$$

respectively,

$$\Delta H_m^M = P_{12} \left(\varepsilon_{12} - 0.5 \sum_{i=1}^{n} \varepsilon_{ii} \right) + \sum_{i=1}^{n} P_{12}^{(i)} \left(\varepsilon_{12}^{(i)} - \varepsilon_{12} \right), \tag{6}$$

where:

ε_{ii} - represents the bonding energies corresponding to the pairs of atoms *i*-*i*;

x_1, x_2 - molar (atomic) fractions of the alloy components;

N_0 - Avogadro's number.

With the aid of relationships (1)-(4) and with the notations:

$$Q_1 = zN_0\left(\varepsilon_{12} - 0.5\sum_{i=1}^{n}\varepsilon_{ii}\right),\quad Q_{i+1} = zN_0\left(\varepsilon_{12}^{(i)} - \varepsilon_{12}\right),\quad i = 1,2,...,n, \tag{7}$$

the relationship (6) becomes (Q_1, Q_{i+1}-mixture energies)

$$\Delta H_m^M = \sum_{i=1}^{n+1} Q_i x_1 x_2^i\ . \tag{8}$$

According to the proposed model, the molar entropy of mixture is calculated with:

$$\Delta S_M^{am} = k\ ln\, w, \tag{9}$$

$$w = \frac{\left[N_1 + N_2 - \sum_{i=1}^{n}\left(m_1^{(i)} + m_2^{(i)}\right)\right]!}{\left[N_1 - \sum_{i=1}^{n} m_1^{(i)}\right]!\left[N_2 - \sum_{i=1}^{n} m_2^{(i)}\right]!} \cdot \frac{\prod_{i=1}^{n}\left[m_1^{(i)} + m_2^{(i)}\right]!}{\prod_{i=1}^{n} m_1^{(i)}!\, m_2^{(i)}!}, \tag{10}$$

where

$N_1 = x_1 N_0$, $N_2 = x_2 N_0$-represent the total number of atoms of type 1 and 2, respectively;

$m_1^{(i)}$, $m_2^{(i)}$- is the number of atoms of type 1 and 2, respectively, forming groups with the probability $x_1 x_2^{i+1}$ ($i = 1,2,...,n$), their bonding energy being $\varepsilon_{12}^{(i)}$;

Considering that

$$m_1^{(i)} = \lambda_i N_1 = \lambda_i x_1 N_0\ , \tag{11}$$

where λ_i are structural parameters ($\lambda_i \in [0,1]$), and between $m_1^{(i)}$ and $m_2^{(i)}$ there are dependencies having the form supposed to be:

$$\frac{m_2^{(i)}}{m_1^{(i)}} = \frac{x_2^{i+1}}{x_1},\quad m_2^{(i)} = \lambda_i x_2^{i+1} N_0,\qquad i = 1,2,...,n. \tag{12}$$

To calculate the molar entropy of mixture with relationships (9)-(12) we recall the approximation of Stirling:

$$ln\, N! \cong N\, ln\, N - N, \tag{13}$$

$$\Delta S_m^M = k \ln w = R\left\{\left[1 - x_1 \sum_{i=1}^{n} \lambda_i - \sum_{i=1}^{n} \lambda_i x_2^{i+1}\right] \ln\left[1 - x_1 \sum_{i=1}^{n} \lambda_i - \sum_{i=1}^{n} \lambda_i x_2^{i+1}\right] + \right.$$

$$+ \sum_{i=1}^{n} \lambda_i \left(x_1 + x_2^{i+1}\right) \ln\left[\lambda_i \left(x_1 + x_2^{i+1}\right)\right] - x_1 \left(1 - \sum_{i=1}^{n} \lambda_i\right) \ln\left[x_1 \left(1 - \sum_{i=1}^{n} \lambda_i\right)\right] - \quad (14)$$

$$\left. - x_2 \left(1 - \sum_{i=1}^{n} \lambda_i x_2^i\right) \ln\left[x_2 \left(1 - \sum_{i=1}^{n} \lambda_i x_2^i\right)\right] - x_1 \sum_{i=1}^{n} \lambda_i \ln\left(\lambda_i x_1\right) - x_2 \sum_{i=1}^{n} \lambda_i x_2^i \ln\left(\lambda_i x_2^{i+1}\right)\right\}$$

The Gibbs free energy of the binary system containing p_1 moles of component 1 and p_2 moles of component 2 is given by the relationship:

$$G = H - TS = p_1 H_1^0 + p_2 H_2^0 + \Delta H^M - T\left(p_1 S_1^0 + p_2 S_2^0 + \Delta S^M\right), \quad (15)$$

where: H_1^0, H_2^0- represent the enthalpies of pure components 1 and 2 respectively;

S_1^0, S_2^0- are the entropies of pure components 1 and 2, respectively;

$\Delta H^M = \left(p_1 + p_2\right)\Delta H_m^M$, $\Delta S^M = \left(p_1 + p_2\right)\Delta S_m^M$ - are the enthalpy of mixture and, respectively, the entropy of mixture.

After calculations, the relationship (15) becomes:

$$G = -RT\left\{\left[1 - p_1 \sum_{i=1}^{n} \lambda_i - p_2 \sum_{i=1}^{n} \lambda_i x_2^i\right] \ln\left[1 - x_1 \sum_{i=1}^{n} \lambda_i - x_2 \sum_{i=1}^{n} \lambda_i x_2^i\right] - p_1 \sum_{i=1}^{n} \lambda_i \ln\left(\lambda_i x_1\right) - \right.$$

$$- p_2 \sum_{i=1}^{n} \lambda_i x_2^i \ln\left(\lambda_i x_2^{i+1}\right) + \sum_{i=1}^{n} \lambda_i \left(p_1 + p_2 x_2^i\right) \ln\left[\lambda_i \left(x_1 + x_2^{i+1}\right)\right] - p_1 \left(1 - \sum_{i=1}^{n} \lambda_i\right) \ln\left[x_1 \left(1 - \sum_{i=1}^{n} \lambda_i\right)\right] - \quad (16)$$

$$\left. - p_1 \left(1 - \sum_{i=1}^{n} \lambda_i x_2^i\right) \ln\left[x_2 \left(1 - \sum_{i=1}^{n} \lambda_i x_2^i\right)\right]\right\} + p_1 G_1^0 + p_2 G_2^0 + p_1 \sum_{i=1}^{n+1} x_2^i Q_i$$

Deriving the relationship (16) with respect to p_1 and p_2, we obtain the chemical potentials of components and, respectively, their activity coefficients:

$$\left(\frac{\partial G}{\partial p_1}\right)_{p_2,P,T} = \mu_1 = G_1^0 + RT\ln x_1 + \sum_{i=1}^{n} i\left(Q_i - Q_{i+1}\right)x_2^{i+1} + \left(n+1\right)Q_{n+1}x_2^{n+2} +$$

$$+ RT\left\{\left(1-\sum_{i=1}^{n}\lambda_i\right)\ln\left[\frac{1-\sum_{i=1}^{n}\lambda_i}{1-\sum_{i=1}^{n}\lambda_i + x_2\sum_{i=1}^{n}\lambda_i\left(1-x_2^i\right)}\right] - \sum_{i=1}^{n}\lambda_i\left(1-ix_2^{i+1}\right)\ln\left(1-x_2+x_2^{i+1}\right) +\right.$$

$$\left. + \sum_{i=1}^{n} i\lambda_i x_2^{i+1}\ln\left[\frac{1-\sum_{i=1}^{n}\lambda_i x_2^i}{x_2^i\left(1-\sum_{i=1}^{n}\lambda_i + x_2\sum_{i=1}^{n}\lambda_i\left(1-x_2^i\right)\right)}\right]\right\} \qquad (17)$$

$$\ln\gamma_1 = \sum_{i=1}^{n} i\left(\omega_i - \omega_{i+1}\right)x_2^{i+1} + \left(n+1\right)\omega_{n+1}x_2^{n+2} + \sum_{i=1}^{n} i\lambda_i x_2^{i+1}\ln\left[\frac{1-\sum_{i=1}^{n}\lambda_i x_2^i}{x_2^i\left(1-\sum_{i=1}^{n}\lambda_i + x_2\sum_{i=1}^{n}\lambda_i\left(1-x_2^i\right)\right)}\right] -$$

$$- \sum_{i=1}^{n}\lambda_i\left(1-ix_2^{i+1}\right)\ln\left(1-x_2+x_2^{i+1}\right) + \left(1-\sum_{i=1}^{n}\lambda_i\right)\ln\left[\frac{1-\sum_{i=1}^{n}\lambda_i}{1-\sum_{i=1}^{n}\lambda_i + x_2\sum_{i=1}^{n}\lambda_i\left(1-x_2^i\right)}\right] \qquad (18)$$

$$\left(\frac{\partial G}{\partial p_2}\right)_{n_1,P,T} = \mu_2 = G_2^0 + RT\ln x_2 + x_1^2\sum_{i=1}^{n+1} iQ_i\left(1-x_1\right)^{i-1} + RT\left\{\ln\left[\frac{1-\sum_{i=1}^{n}\lambda_i\left(1-x_1\right)^i}{1-x_1\sum_{i=1}^{n}\lambda_i - \sum_{i=1}^{n}\lambda_i\left(1-x_1\right)^{i+1}}\right] +\right.$$

$$\left. + \sum_{i=1}^{n}\lambda_i\left(1-x_1\right)^i\left(1+ix_1\right)\ln\frac{\left[1-x_1\sum_{i=1}^{n}\lambda_i - \sum_{i=1}^{n}\lambda_i\left(1-x_1\right)^{i+1}\right]\left(1-x_1\right)^i}{\left[1-\sum_{i=1}^{n}\lambda_i\left(1-x_1\right)^i\right]\left[x_1+\left(1-x_1\right)^{i+1}\right]}\right\} \qquad (19)$$

$$\ln\gamma_2 = x_1^2\sum_{i=1}^{n+1} i\omega_i\left(1-x_1\right)^{i-1} + \ln\left[\frac{1-\sum_{i=1}^{n}\lambda_i\left(1-x_1\right)^i}{1-x_1\sum_{i=1}^{n}\lambda_i-\sum_{i=1}^{n}\lambda_i\left(1-x_1\right)^{i+1}}\right] +$$

$$+\sum_{i=1}^{n}\lambda_i\left(1-x_1\right)^i\left(1+ix_1\right)\ln\frac{\left[1-x_1\sum_{i=1}^{n}\lambda_i-\sum_{i=1}^{n}\lambda_i\left(1-x_1\right)^{i+1}\right]\left(1-x_1\right)^i}{\left[1-\sum_{i=1}^{n}\lambda_i\left(1-x_1\right)^i\right]\left[x_1+\left(1-x_1\right)^{i+1}\right]} \tag{20}$$

where: $\omega_i = Q_i/RT;\quad i=1,2,...,n+1$ (ω_i - interaction parameters).

Relationships (18) and (20) allow to calculate the activity coefficients in binary systems when the quantities $\omega_i\ \left(i=1,2,...,n+1\right)$ and $\lambda_i\ \left(i=1,2,...,n\right)$ are known. These quantities can be established on the basis of experimental values of activities or of the activity coefficients for different compositions of the considered alloy.

a) For $\lambda_i = 0,\ i=1,2,...,n$, $\omega_1 \neq 0$ and $\omega_i = 0,\ i=2,3,...,n+1$ these relationships transform into the equations of the *regular model* having the aspect:

$$\ln\gamma_1 = \omega_1 x_2^2, \tag{21}$$

$$\ln\gamma_2 = \omega_1 x_1^2. \tag{22}$$

b) For $\lambda_i = 0,\ i=1,2,...,n$, $\omega_1 \neq 0, \omega_2 \neq 0$ and $\omega_i = 0,\ i=3,4,...,n+1$ the equations of the *subregular model* are obtained, they having the aspect

$$\ln\gamma_1 = \left(\omega_1-\omega_2\right)x_2^2 + 2\omega_2 x_2^3, \tag{23}$$

$$\ln\gamma_2 = \left(\omega_1+2\omega_2\right)x_1^2 - 2\omega_2 x_1^3,. \tag{24}$$

c) For $\lambda_i = 0,\ i=1,2,...,n$, $\omega_1 \neq 0, \omega_2 \neq 0, \omega_3 \neq 0$ and $\omega_i = 0,\ i=4,5,...,n+1$ the equations of the *sub-subregular model* are resulting

$$\ln\gamma_1 = \left(\omega_1-\omega_2\right)x_2^2 + 2\left(\omega_2-\omega_3\right)x_2^3 + 3\omega_3 x_2^4, \tag{25}$$

$$\ln\gamma_2 = \left(\omega_1+2\omega_2+3\omega_3\right)x_1^2 - 2\left(\omega_2+3\omega_2\right)x_1^3 + 3\omega_3 x_1^4,. \tag{26}$$

d) For $\lambda_1 \neq 0, \lambda_i = 0,\ i=2,3,...,n$, $\omega_1 \neq 0, \omega_2 \neq 0$ and $\omega_i = 0,\ i=3,4,...,n+1$ the equations of *SRPOS model* are obtained having the aspect

$$\ln\gamma_1 = (\omega_1 - \omega_2)x_2^2 + 2\omega_2 x_2^3 + (1-\lambda)\ln\frac{1-\lambda}{1-\lambda(x_1+x_2^2)} + \lambda x_2^2 \ln\frac{1-\lambda x_2}{x_2\left[1-\lambda(x_1+x_2^2)\right]} -$$
$$-\lambda(1-x_2^2)\ln(x_1+x_2^2) \tag{27}$$

$$\ln\gamma_2 = (\omega_1 + 2\omega_2)x_1^2 - 2\omega_2 x_1^3 + (1-\lambda+\lambda x_1^2)\ln\frac{1-\lambda x_2}{1-\lambda(x_1+x_2^2)} + \lambda(1-x_1^2)\ln\frac{x_2}{x_1+x_2^2} \tag{28}$$

e) For $\lambda_1 \neq 0,\ \lambda_2 \neq 0,\ \lambda_i = 0,\ \ i = 3,4,...,n,\ \omega_1 \neq 0,\ \omega_2 \neq 0,\ \omega_3 \neq 0$ and $\omega_i = 0,\ \ i = 4,5,...,n+1$ the equations of the *SSRPOS model* are obtained with the aspect:

$$\ln\gamma_1 = (\omega_1-\omega_2)x_2^2 + 2(\omega_2-\omega_3)x_2^3 + 3\omega_3 x_2^4 + (1-\lambda-\lambda')\ln\frac{1-\lambda-\lambda'}{1-(\lambda+\lambda')x_1-\lambda x_2^2-\lambda' x_2^3} -$$
$$-2x_2^2(\lambda+3\lambda' x_2)\ln x_2 - \lambda(1-x_2^2)\ln(x_1+x_2^2) + (\lambda x_2^2 + 2\lambda' x_2^3)\ln\frac{x_2-\lambda x_2^2-\lambda' x_2^3}{1-(\lambda+\lambda')x_1-\lambda x_2^2-\lambda' x_2^3} - \tag{29}$$
$$-\lambda'(1-2x_2^3)\ln(x_1+x_2^3)$$

$$\ln\gamma_2 = \omega_1 x_1^2 + 2\omega_2 x_1^2 x_2 + 3\omega_3 x_1^2 x_2^2 + \ln\frac{1-\lambda x_2-\lambda' x_2^2}{1-(\lambda+\lambda')x_1-\lambda x_2^2-\lambda' x_2^3} - \lambda x_2(2-x_2)\ln\left(\frac{x_1}{x_2^2}+1\right) -$$
$$-\lambda' x_2^2(3-2x_2)\ln\left(\frac{x_1}{x_2^3}+1\right) + \left[\lambda x_2(2-x_2) + \lambda' x_2^2(3-2x_2)\right]\ln\frac{1-(\lambda+\lambda')x_1-\lambda x_2^2-\lambda' x_2^3}{x_2-\lambda x_2^2-\lambda' x_2^3} \tag{30}$$

In what follows we proposed to apply this new model of interaction to the study of the thermodynamic properties of alloys from the system Fe-Mn.

I. System Fe-Mn.

The experimental values of activity coefficients for different molar fractions of manganese are given in Table 1.

Table 1.

Values of activity coefficients in the system Fe-Mn (solid alloys –1450 K) [11]

$x_{Mn}=x_2$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$\gamma_{Fe}=\gamma_1$	1.000	1.004	1.015	1.037	1.069	1.113	1.172	1.250	1.361	1.521	1.765
$\gamma_{Mn}=\gamma_2$	1.543	1.441	1.350	1.269	1.199	1.141	1.094	1.057	1.027	1.008	1.000

We determined the quantities $\omega_i \ (i=1,2,...,n+1)$ and $\lambda_i \ (i=1,2,...,n)$ by applying the method of the smallest squares to the relationship (18). For this purpose we employed the function:

$$\Phi_1 = \sum_{j=1}^{N=11} \left(\tilde{y}_{1,j} - y_{1,j}\right)^2 , \tag{31}$$

where:

$y_{1,j} = \ln \gamma_{1,j}$ - ($\gamma_{1,j}$ - experimental value in the point "*j*"),

$\tilde{y}_{1,j} = \ln \tilde{\gamma}_{1,j}$ - ($\tilde{\gamma}_{1,j}$ - the value calculated with the relation (18) in the point "*j*"),

N – number of experimental points, taking into account the particular cases (a)-(e).

By considering the partial derivatives of the function (31) with respect to the interactions parameters $\omega_i \ (i=1,2,...,n+1)$ and with the structural parameters $\lambda_i \ (i=1,2,...,n)$ equal to zero and solving the obtained systems, the following mathematical models were establishes, tested with Gauss criterion (Ω):

[$\Omega_k = \dfrac{1}{N-l} \sum_{j=1}^{N} \left(\tilde{y}_{k,j} - y_{k,j}\right)^2$, $k=1,2$, $Fe=1$, $Mn=2$, l – unknown parameters from the respective model].

I. Regular solution.

$$\ln \gamma_1 = 0.5183\left(1-x_1\right)^2, \tag{32}$$

$$\ln \gamma_2 = 0.5183\left(1-x_2\right)^2. \tag{33}$$

$$\Omega_1 = 1.215 \cdot 10^{-3}, \qquad \Omega_2 = 2.754 \cdot 10^{-3}, \qquad \Omega_1 + \Omega_2 = 3.969 \cdot 10^{-3} .$$

II. Subregular solution.

$$\ln \gamma_1 = 0.2446\left(1-x_1\right)^2 + 0.3139\left(1-x_1\right)^3, \tag{34}$$

$$\ln \gamma_2 = 0.7155\left(1-x_2\right)^2 - 0.3139\left(1-x_2\right)^3. \tag{35}$$

$$\Omega_1 = 8.649 \cdot 10^{-5}, \qquad \Omega_2 = 3.420 \cdot 10^{-4}, \qquad \Omega_1 + \Omega_2 = 4.285 \cdot 10^{-4} .$$

III. Sub-subregular solution.

$$\ln\gamma_1 = 0.4975(1-x_1)^2 - 0.3672(1-x_1)^3 + 0.4365(1-x_1)^4, \tag{36}$$

$$\ln\gamma_2 = 0.4594(1-x_2)^2 - 0.0762(1-x_2)^3 + 0.4365(1-x_2)^4. \tag{37}$$

$$\Omega_1 = 5.403\cdot10^{-6}, \qquad \Omega_2 = 2.166\cdot10^{-4}, \qquad \Omega_1+\Omega_2 = 2.22\cdot10^{-4}.$$

IV. SRPOS model.

$$\ln\gamma_1 = 0.1849(1-x_1)^2 + 0.3767(1-x_1)^3 + 0.938\ln\frac{0{,}938}{0.938+0.062x_1x_2} + \\ + 0.062x_2^2\ln\frac{0.938+0.062x_1}{x_2[0.938+0.062x_1x_2]} - 0.062(1-x_2^2)\ln(x_1+x_2^2), \tag{38}$$

$$\ln\gamma_2 = 0.7499(1-x_2)^2 - 0.3767(1-x_2)^3 + 0.062x_2(2-x_2)\ln\frac{x_2}{x_1+x_2^2} \\ + (1-0.124x_2+0.062x_2^2)\ln\frac{1-0.062x_2}{0.938+0.062x_1x_2}. \tag{39}$$

$$\omega_1 = 0.3733, \qquad \omega_2 = 0.1883 \qquad \lambda = 0.062.$$

$$\Omega_1 = 4.414\cdot10^{-5}, \quad \Omega_2 = 3.172\cdot10^{-5}, \qquad \Omega_1+\Omega_2 = 7.586\cdot10^{-5}.$$

V. SSRPOS model.

$$\ln\gamma_1 = 0.01335x_2^2 + 0.54298x_2^3 + 0.865\ln\frac{0.865}{0.865+0.135x_2-0.0596x_2^2-0.0754x_2^3} + \\ + 0.01181x_2^4 + (0.0596x_2^2+0.1508x_2^3)\ln\frac{x_2-0.0596x_2^2-0.0754x_2^3}{0.865+0.135x_2-0.0596x_2^2-0.0754x_2^3} - \\ - 0.0754(1-2x_2^3)\ln(x_1+x_2^3) - 2x_2^2(0{,}0596+0.2262x_2)\ln x_2 - 0.0596(1-x_2^2)\ln(x_1+x_2^2) \tag{40}$$

$$\ln\gamma_2 = 0.55085x_1^2x_2 + 0.01181x_1^2x_2^2 + \ln\frac{1-0.0596x_2-0.0754x_2^2}{0.865+0.135x_2-0.0596x_2^2-0.0754x_2^3} -$$
$$-0.0596x_2(2-x_2)\ln\left(\frac{x_1}{x_2^2}+1\right)-0.0754x_2^2(3-2x_2)\ln\left(\frac{x_1}{x_2^3}+1\right)+0.28878x_1^2+$$
$$+\left[0.0596x_2(2-x_2)+0.0754x_2^2(3-2x_2)\right]\ln\frac{0.865+0.135x_2-0.0596x_2^2-0.0754x_2^3}{x_2-0.0596x_2^2-0.0754x_2^3} \tag{41}$$

$$\omega_1 = 0.28878,\quad \omega_2 = 0.27543,\quad \omega_3 = 3.937\cdot10^{-3},\quad \lambda_1 = 0.0596,\quad \lambda_2 = 0.0754$$
$$\Omega_1 = 1.774\cdot10^{-7},\qquad \Omega_2 = 4.524\cdot10^{-7},\qquad \Omega_1+\Omega_2 = 6.298\cdot10^{-7}.$$

VI. SSSRPOS model (sub-sub-subregular partially-ordered solution)

$$\ln\gamma_1 = x_2^2\left(-0.08318+1.5238x_2-1.6856x_2^2+0.8132x_2^3\right)+0.893\ln\frac{0.893}{0.893+0.107x_1x_2}+$$
$$+0.107x_2^2\ln\frac{1-0.107x_2}{x_2(0.893+0.107x_1x_2)}-0.107\left(1-x_2^2\right)\ln\left(x_1+x_2^2\right) \tag{42}$$

$$\ln\gamma_2 = x_1^2\left(0.32013+0.8066x_2-1.0757x_2^2+0.8132x_2^3\right)+\ln\frac{1-0.107x_2}{0.893+0.107x_1x_2}+$$
$$+0.107\left(1-x_1^2\right)\ln\frac{x_2(0.893+0.107x_1x_2)}{(1-0.107x_2)\left(x_1+x_2^2\right)} \tag{43}$$

$$\omega_1 = 0.32013,\quad \omega_2 = 0.4033,\quad \omega_3 = -0.35857,\quad \omega_4 = 0.2033,\quad \lambda_1 = 0.107,$$
$$\lambda_2 = \lambda_3 = 0$$
$$\Omega_1 = 2.875\cdot10^{-6},\qquad \Omega_2 = 5.963\cdot10^{-6},\qquad \Omega_1+\Omega_2 = 8.839\cdot10^{-6}.$$

In Table 2 the experimental values of the activity coefficients for Fe and Mn are compared with the values calculated with the established models relationships:

Table 2.

Comparison between calculated and experimental values of activity coefficients in the system of solid alloys Fe-Mn at 1450 K

$x_{Mn}=x_2$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Experimental values											
$\gamma_{Fe}=\gamma_1$	1.000	1.004	1.015	1.037	1.069	1.113	1.172	1.250	1.361	1.521	1.765
$\gamma_{Mn}=\gamma_2$	1.543	1.441	1.350	1.269	1.199	1.141	1.094	1.057	1.027	1.008	1.000
Values calculated with relationships (32) - (33)											
$\gamma_{Fe}=\gamma_1$	1.000	1.005	1.021	1.048	1.086	1.138	1.205	1.289	1.393	1.522	1.679
$\gamma_{Mn}=\gamma_2$	1.679	1.522	1.393	1.289	1.205	1.138	1.086	1.048	1.021	1.005	1.000
Values calculated with relationships (34) - (35)											
$\gamma_{Fe}=\gamma_1$	1.000	1.003	1.012	1.031	1.061	1.106	1.169	1.256	1.373	1.533	1.748
$\gamma_{Mn}=\gamma_2$	1.494	1.420	1.346	1.275	1.209	1.150	1.099	1.058	1.026	1.007	1.000
Values calculated with relationships (36) - (37)											
$\gamma_{Fe}=\gamma_1$	1.000	1.005	1.018	1.039	1.070	1.112	1.169	1.249	1.362	1.524	1.763
$\gamma_{Mn}=\gamma_2$	1.583	1.447	1.344	1.263	1.197	1.142	1.096	1.057	1.027	1.007	1.000
Values calculated with relationships (38) - (39)											
$\gamma_{Fe}=\gamma_1$	1.000	1.004	1.015	1.035	1.065	1.108	1.168	1.253	1.369	1.530	1.753
$\gamma_{Mn}=\gamma_2$	1.548	1.431	1.343	1.269	1.204	1.147	1.098	1.058	1.027	1.007	1.000
Values calculated with relationships (40) - (41)											
$\gamma_{Fe}=\gamma_1$	1.000	1.004	1.015	1.037	1.069	1.113	1.172	1.250	1.360	1.521	1.765
$\gamma_{Mn}=\gamma_2$	1.543	1.442	1.351	1.269	1.199	1.141	1.094	1.057	1.027	1.008	1.000
Values calculated with relationships (42) - (43)											
$\gamma_{Fe}=\gamma_1$	1.000	1.004	1.015	1.035	1.067	1.112	1.171	1.251	1.361	1.521	1.765
$\gamma_{Mn}=\gamma_2$	1.542	1.435	1.349	1.269	1.200	1.142	1.095	1.056	1.027	1.008	1.000

Conclusions

- The work proposes a new model of interaction applicable to binary metallic systems. Taking into consideration the apparition of certain elements of order in liquid alloys due to non-additivity of bonds between atoms of different nature, the model establishes a new relationship to calculate the entropy of mixture; in this context, new thermodynamic quantities were defined: $\lambda_i \in [0,1]$, $\sum \lambda_i < 1$, named *structural parameters*.

- The proposed model represents a generalisation of certain known models: *regular, sub-regular, sub-sub-regular solutions,* SRPOS, SSRPOS [9,10]. It reduces to these when one or more structural parameters are null.

- The equations of the model, (18) and (20) have been verified for the solid alloys (1450 K) from the system Fe-Mn and a good agreement was found between calculated and experimental values, in the case of the model SSRPOS. In the case of liquid alloys (1863 K), the best agreement was obtained for the regular model.

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