THERMODYNAMIC STUDY OF BINARY Pb-Sb SYSTEM USING THE POSS MODEL

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A fost aplicat modelului soluțiilor subsubregulare parțial ordonate (SSPO) pentru a interpreta termodinamic datele experimentale în sistemul Pb-Sb la temperatura de lucru de 923K. S-a obținut o concordanță bună între valorile activității determinate experimental şi valorile activității calculate pentru ambele componente Pb şi Sb pe întreg domeniu investigat.

The partial ordonated subsubregular solutions model (POSS) has been applied to interpret the experimental thermodynamic data in the Pb-Sb system at 923K. A very good agreement has been obtained between experimental and calculated activity values for both components Pb and Sb in the whole investigated range.

Keywords: activity coefficients, thermodynamic model, binary alloys

1. Introduction

Among the most important and widely used thermodynamic models either theoretical or empirical (regular solution model, subregulare solution model, subsubregulare solutions model, partial ordonate subsubregulare solutions model, generalized thermodynamic model, Miedema model, model of coordination spheres, etc.) [1-3]. The partial ordonated subsubregular solutions model (POSS) has been chosen to be applied to interpret our experimental thermodynamical data in the Pb-Sb system.The alloys in the Pb-Sb system have practical interest and they find application in the electrical industry, for cable sheathing, in automotive industry, as antifriction alloys, in prynting industry, as fusible alloys and solders.

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2. Experimental procedure

The experimental thermodynamic data for the Pb-Sb alloys intended to be validated by the POSS model consisted in activity values derived from electromotive force mesurements

Measurements were made at a working temperature of 923K and measuring of electromotive force produced by the galvanic cell was performed in the concentration range 0.05 ÷ 0.09 for Sb, the atomic fractions X_{Sb} being changed at 0.1 step.

The experiment began with making several controling measurements at 905 K for balancing the laboratory installation for testing and comparing the obtained results with existing results from literature (with a deviation of ± 0.5%).

In each experimental point two parallel determinations were performed. We have worked with average values of electromotive force E_i by calculating the statistical parameters (arithmetic mean, dispersion and standard deviation).

Checking of dispersion was made by means of the Cochran criterion. Cochran criterion calculated value is $G_c = 0{,}205$ lower than the table value $G_T = G_{0.05(1\_10)} = 0.602$. This value indicates a good accuracy of the measurements, the average relative error of only 4.09% gives sufficient confidence of used values. A Mathcad software was used in the calculations.

3. Theoretical model applied (POSS model)

As the aim of the study was to compare the experimental activity values in the Pb-Sb sistem with the theoretical ones, a brief outline of the POSS model is given in what follows.

This model considers the emergence of order in a subsubregular solution (POSS). It is considered that the appropriate pair interaction energy of atoms different from 1 and 2 is different from ε_{12} if the atom type 1 is found in the vicinity of two atoms of type 2 arranged in a specifie way in the network nodes, the probability of such groups being equal,.

Also, the energy of interaction differs from that atom type 1 is found in the vicinity of three atoms of type two, be likelihood of such groups being equal with $x_1 x_2^3$. In this case, from the total number of links P_{12}.

$$P_{12} = 2x_1x_2\left(0{,}5zN_0\right) = x_1x_2zN_0 \tag{1}$$

less

$$P_{12}^{'} = 2x_1x_2^2\left(0{,}5zN_0\right) = x_1x_2^2zN_0 \tag{2}$$

bonds that have energy $\varepsilon_{12}^{'} \neq \varepsilon_{12}$ and:

$$P_{12}^{''} = 2x_1x_2^3\left(0{,}5zN_0\right) = x_1x_2^3zN_0 \tag{3}$$

bonds that have energy $\varepsilon_{12}^{''} \neq \varepsilon_{12}$, the difference $P_{12} - P_{12}^{'} - P_{12}^{''}$ referring to the bonds with ε_{12} energy. The given molar heat of mixing is given by:

$$\begin{aligned}\Delta H_m^M &= \left(P_{12} - P_{12}^{'} - P_{12}^{''}\right)\left(\varepsilon_{12} - 0{,}5\varepsilon_{11} - 0{,}5\varepsilon_{22}\right) + \\ &+ P_{12}^{'}\left(\varepsilon_{12}^{'} - 0{,}5\varepsilon_{11} - 0{,}5\varepsilon_{22}\right) + P_{12}^{''}\left(\varepsilon_{12}^{''} - 0{,}5\varepsilon_{11} - 0{,}5\varepsilon_{22}\right)\end{aligned} \tag{4}$$

respectively,

$$\Delta H_m^M = P_{12}\left(\varepsilon_{12} - 0{,}5\varepsilon_{11} - 0{,}5\varepsilon_{22}\right) + P_{12}^{'}\left(\varepsilon_{12}^{'} - \varepsilon_{12}\right) + P_{12}^{''}\left(\varepsilon_{12}^{''} - \varepsilon_{12}\right), \tag{5}$$

where:

ε_{11} şi ε_{22} - are energies corresponding to connecting pairs of atoms 1-1 and 2.2;

x_1, x_2 - molar fraction (atomic) constituents of the alloy; N_0 - Avogadro's number. With relations and notations:

$$Q_1 = zN_0\left(\varepsilon_{12} - 0{,}5\varepsilon_{11} - 0{,}5\varepsilon_{22}\right),\ Q_2 = zN_0\left(\varepsilon_{12}^{'} - \varepsilon_{12}\right),\ Q_3 = zN_0\left(\varepsilon_{12}^{''} - \varepsilon_{12}\right) \tag{6}$$

relationship (5) becomes

$$\Delta H_m^M = Q_1x_1x_2 + Q_2x_1x_2^2 + Q_3x_1x_2^3. \qquad (Q_1, Q_2, Q_3 \text{ - mixing energy}) \tag{7}$$

With the proposed model, the molar entropy of mixing is calculated as follows

$$\Delta S_m^M = k\ln w, \tag{8}$$

$$w = \frac{\left(N_1 + N_2 - m_1 - m_1^{'} - m_2 - m_2^{'}\right)!}{\left(N_1 - m_1 - m_1^{'}\right)!\left(N_2 - m_2 - m_2^{'}\right)!} \cdot \frac{\left(m_1 + m_2\right)!}{m_1!\cdot m_2!} \cdot \frac{\left(m_1^{'} + m_2^{'}\right)!}{m_1^{'}!\cdot m_2^{'}!}, \tag{9}$$

where: $N_1 = x_1N_0$, $N_2 = x_2N_0$ - represents the total number of atoms type 1 and 2; m_1, m_2 - number of atoms type 1 and 2 which form clusters with probability $x_1x_2^2$, the energy $\varepsilon_{12}^{'}$ in these groups are linked. It is considered that:

$$m_1 = \lambda N_1 = \lambda x_1N_0 \text{ and } m_1^{'} = \lambda^{'}N_1 = \lambda^{'}x_1N_0, \tag{10}$$

λ and $\lambda^{'}$ are the structural parameters ($\lambda, \lambda^{'} \in [0,1]$), and between m_1 and m_2, respectively m_1 and m_2, are dependencies that are assumed to be of the form:

$$\frac{m_2}{m_1} = \frac{x_2^2}{x_1}, m_2 = \lambda x_2^2N_0, \tag{11}$$

$$\frac{m_2^{'}}{m_1^{'}} = \frac{x_2^3}{x_1},\ \ m_2^{'} = \lambda^{'}x_2^3N_0. \tag{12}$$

To calculate the molar entropy of mixing with the relations (8) - (12) we resort to Stirling's approximation:

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

$$\begin{aligned}\Delta S_m^M = k\ln w = R\{&\left[1-\left(\lambda+\lambda'\right)x_1-\lambda x_2^2-\lambda' x_2^3\right]\ln\left[1-\left(\lambda+\lambda'\right)x_1-\lambda x_2^2-\lambda' x_2^3\right]+\\ &+\lambda\left(x_1+x_2^2\right)\ln\left[\lambda\left(x_1+x_2^2\right)\right]+\lambda'\left(x_1+x_2^3\right)\ln\left[\lambda'\left(x_1+x_2^3\right)\right]-x_1\left(1-\lambda-\lambda'\right)\ln\left[x_1\left(1-\lambda-\lambda'\right)\right]-\\ &-\left(x_2-\lambda x_2^2-\lambda' x_2^3\right)\ln\left[\left(x_2-\lambda x_2^2-\lambda' x_2^3\right)\right]-\lambda x_1\ln\left(\lambda x_1\right)-\lambda' x_1\ln\left(\lambda' x_1\right)-\\ &-\lambda x_2^2\ln\left(\lambda x_2^2\right)-\lambda' x_2^3\ln\left(\lambda' x_2^3\right)\end{aligned} \tag{14}$$

The Gibbs free energy of binary system containing n_1 atoms-gram component atoms 1 and n_2 2-gram component is given by:

$$G = H - TS = n_1 H_1^0 + n_2 H_2^0 + \Delta H^M - T\left(n_1 S_1^0 + n_2 S_2^0 + \Delta S^M\right), \tag{15}$$

$\Delta H^M = \left(n_1+n_2\right)\Delta H_m^M$, $\Delta S^M = \left(n_1+n_2\right)\Delta S_m^M$ - enthalpy and entropy of mixing.

$$\begin{aligned}G=&n_1G_1^0+n_2G_2^0+\frac{n_1n_2}{n_1+n_2}Q_1+\frac{n_1n_2^2}{(n_1+n_2)^2}Q_2+\frac{n_1n_2^3}{(n_1+n_2)^3}Q_3-\\ &-RT\left\{\left[1-(\lambda+\lambda')n_1-\frac{\lambda n_2^2}{n_1+n_2}-\frac{\lambda' n_2^3}{(n_1+n_2)^2}\right]\ln\left[1-(\lambda+\lambda')x_1-\lambda x_2^2-\lambda' x_2^3\right]-\lambda n_1\ln(\lambda x_1)-\right.\\ &-\lambda' n_1\ln(\lambda' x_1)-\frac{\lambda n_2^2}{n_1+n_2}\ln(\lambda x_2^2)-\frac{\lambda' n_2^3}{(n_1+n_2)^2}\ln(\lambda' x_2^3)+\left[\lambda\left(n_1+\frac{n_2^2}{n_1+n_2}\right)\ln\left[\lambda(x_1+x_2^2)\right]\right]+\\ &+\left[\lambda'\left(n_1+\frac{n_2^3}{(n_1+n_2)^2}\right)\ln\left[\lambda'\left(x_1+x_2^3\right)\right]\right]-n_1\left(1-\lambda-\lambda'\right)\ln\left[x_1\left(1-\lambda-\lambda'\right)\right]-\\ &\left.-\left(n_2-\frac{\lambda n_2^2}{n_1+n_2}-\frac{\lambda' n_2^3}{(n_1+n_2)^2}\right)\ln\left(x_2-\lambda x_2^2-\lambda' x_2^3\right)\right\}\end{aligned} \tag{16}$$

where: H_1^0, H_2^0 - enthalpy of pure components 1 and 2; S_1^0, S_2^0, G_1^0, G_2^0 - entropy and the Gibbs free energies of pure components

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2,P,T} = \mu_1 = G_1^0 + RT\ln x_1 + (Q_1 - Q_2)x_2^2 + 2(Q_2 - Q_3)x_2^3 + 3Q_3x_2^4 +$$
$$+ RT\left\{\lambda x_2^2 \ln\left(\frac{x_1}{x_2^2}+1\right) + (1-\lambda-\lambda')\ln(1-\lambda-\lambda') - \lambda\ln(x_1+x_2^2) + 2\lambda' x_2^3 \ln\left(\frac{x_1}{x_2^3}+1\right) - \right. \quad (17)$$
$$-(1-\lambda-\lambda'+\lambda x_2^2+2\lambda' x_2^3)\ln[1-(\lambda+\lambda')x_1-\lambda x_2^2-\lambda' x_2^3] -$$
$$\left. -\lambda'\ln(x_1+x_2^3) + (\lambda x_2^2 + 2\lambda' x_2^3)\ln(x_2-\lambda x_2^2-\lambda' x_2^3)\right\}$$

4. Results

By means of the relationship 1-17 theoretical values according to the POSS model namely the activity coefficients, the interaction parameters and the mixing energies in the Pb-Sb system have been calculated as follous:

$$\ln\gamma_1 = (1-\lambda-\lambda')\ln(1-\lambda-\lambda') - (1-\lambda-\lambda'+\lambda x_2^2+2\lambda' x_2^3)\ln[1-(\lambda+\lambda')x_1-\lambda x_2^2-\lambda' x_2^3] +$$
$$+\lambda x_2^2\ln\left(\frac{x_1}{x_2^2}+1\right) + 2\lambda' x_2^3\ln\left(\frac{x_1}{x_2^3}+1\right) - \lambda\ln(x_1+x_2^2) - \lambda'\ln(x_1+x_2^3) + (\omega_1-\omega_2)x_2^2 + 3\omega_3 x_2^4 +$$
$$+2(\omega_2-\omega_3)x_2^3 + (\lambda x_2^2+2\lambda' x_2^3)\ln(x_2-\lambda x_2^2-\lambda' x_2^3),$$

$$\left(\frac{\partial G}{\partial n_2}\right)_{n_1,P,T} = \mu_2 = G_2^0 + RT\ln x_2 + Q_1x_1^2 + 2Q_2x_1^2x_2 - RT\left\{\lambda x_2(2-x_2)\ln\left(\frac{x_1}{x_2^2}+1\right) - \right. \quad (19)$$
$$-[1-\lambda x_2(2-x_2)-\lambda' x_2^2(3-2x_2)]\ln[1-(\lambda+\lambda')x_1-\lambda x_2^2-\lambda' x_2^3] - \ln(1-\lambda x_2-\lambda' x_2^2) +$$
$$\left. +\lambda' x_2^2(3-2x_2)\ln\left(\frac{x_1}{x_2^3}+1\right) + [\lambda x_2(2-x_2)+\lambda' x_2^2(3-2x_2)]\ln(x_2-\lambda x_2^2-\lambda' x_2^3)\right\} + 3Q_3x_1^2x_2^2$$

$$\ln\gamma_2 = \omega_1x_1^2 + 2\omega_2x_1^2x_2 + 3\omega_3x_1^2x_2^2 + \ln\frac{1-\lambda x_2-\lambda' x_2^2}{1-(\lambda+\lambda')x_1-\lambda x_2^2-\lambda' x_2^3} - \lambda x_2(2-x_2)\ln\left(\frac{x_1}{x_2^2}+1\right) -$$
$$-\lambda' x_2^2(3-2x_2)\ln\left(\frac{x_1}{x_2^3}+1\right) + [\lambda x_2(2-x_2)+\lambda' x_2^2(3-2x_2)]\ln\frac{1-(\lambda+\lambda')x_1-\lambda x_2^2-\lambda' x_2^3}{x_2-\lambda x_2^2-\lambda' x_2^3} \quad (20)$$

where: $\omega_1 = Q_1/RT;\quad \omega_2 = Q_2/RT;\quad \omega_3 = Q_3/RT;$

Sizes $\omega_1, \omega_2, \omega_3, \lambda, \lambda'$ were determined using the method of least squares relationship (18). This is written:

$$\Phi = \sum_{i=1}^{11}\left(\tilde{y}_{Pb,i} - y_{Pb,i}\right)^2, \quad (21)$$

where: $y_{Pb,i} = \ln \gamma_{Pb,i}$ ($\gamma_{Pb,i}$ - experimental value of the coefficient of activity at the point ,i"), $\tilde{y}_{Pb,i} = \ln \tilde{\gamma}_{Pb,i}$ - value calculated with relation (18) in section i.

The cancellation of partial derivatives of function (21) against the unknown quantities to obtain a system of five equations with five unknown whose solution is difficult. To simplify the calculations which are lengthy and cumbersome, it was necessary to find another method of solving the problem.

Different values have been given to λ and λ' $\{\lambda, \lambda' \in [0,1]\}$ parameters and value for $\omega_1, \omega_2, \omega_3$ have been determined for each pair of values, by using the least square method. The Gauss compliance criterion (Ω) values for Pb and Sb have olso been calculate.

The values of $\omega_1, \omega_2, \omega_3, \lambda, \lambda'$ obtained for the minimum of the sum $\Omega_{Pb} + \Omega_{Sb}$ have been considered solutions of the problem. The obtained values are the following:

$$\lambda = 0,\ \lambda' = 0{,}0173,\ \omega_1 = -0{,}2335,\ \omega_2 = 0{,}30046,\ \omega_3 = -0{,}19373 \tag{22}$$

$$Q_1 = -1791{,}9\ J/mol,\ Q_2 = 2305{,}8\ J/mol,\ Q_3 = -1486{,}7\ J/mol, \tag{23}$$

Under these conditions, the mathematical model given by relations (18) and (20) becomes:

$$\ln\gamma_{Pb} = x_{Sb}^2\left(-0{,}53396 + 0{,}98838x_{Sb} - 0{,}58118x_{Sb}^2\right) + 0{,}9827\ln\frac{0{,}9827}{0{,}9827 + 0{,}0173x_{Sb}\left(1 - x_{Sb}^2\right)} + \\ + 0{,}0346x_{Sb}^3\ln\frac{x_{Sb} - 0{,}0173x_{Sb}^3}{0{,}9827 + 0{,}0173x_{Sb}\left(1 - x_{Sb}^2\right)} - 0{,}0173\left(1 - 2x_{Sb}^2\right)\ln\left(1 - x_{Sb} + x_{Sb}^3\right) - 0{,}1038x_{Sb}^3\ln x_{Sb} \tag{24}$$

$$\ln\gamma_{Sb} = \left(1 - x_{Sb}\right)^2\left(-0{,}2335 + 0{,}60092x_{Sb} - 0{,}58118x_{Sb}^2\right) + \ln\frac{1 - 0{,}0173x_{Sb}^2}{0{,}9827 + 0{,}0173x_{Sb}\left(1 - x_{Sb}^2\right)} - \\ - 0{,}0173x_{Sb}^2\left(3 - 2x_{Sb}\right)\ln\frac{\left(1 - 0{,}0173x_{Sb}^2\right)\left(1 - x_{Sb} + x_{Sb}^3\right)}{0{,}9827x_{Sb}^2 + 0{,}0173x_{Sb}^3\left(1 - x_{Sb}^2\right)} \tag{25}$$

and the values of activity coefficients of lead and antimony, calculated using relations (24) and (25), are presented in table 1.

Table 1

Experimental and calculated values of the activity coefficients at 923K using POSS model

x_{Sb}	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Experimental values											
γ_{Sb}	0.793	0.873	0.933	0.958	0.972	0.979	0.987	0.991	0.997	1.000	1.000
γ_{Pb}	1.000	0.995	0.984	0.976	0.968	0.962	0.953	0.946	0.928	0.913	0.881
Calculated values											
γ_{Pb}	1.000	0.996	0.987	0.977	0.968	0.960	0.953	0.944	0.932	0.912	0.881
γ_{Sb}	0.806	0.877	0.924	0.953	0.970	0.979	0.985	0.990	0.995	0.998	1.000

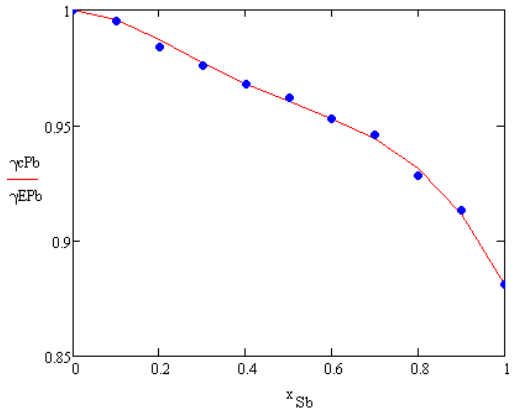

Fig.1. Graphical comparison between the activity coefficients of Pb: experimental-(E) and calculated by the POSS model (C) at 923K

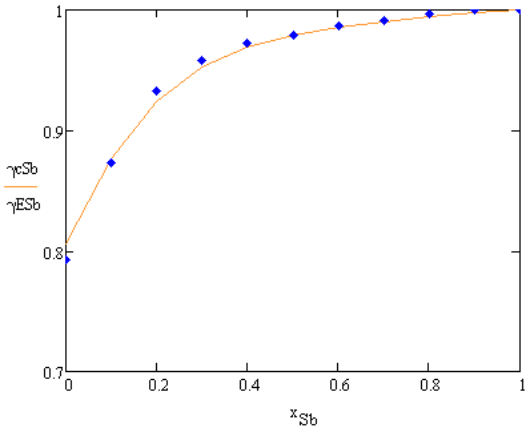

Fig.2. Graphical comparison between the activity coefficients of Sb: experimental-(E) and calculated by the POSS model (C) at 923K

5. Disscussion and conclusions

From a thermodynamic point of view the two elements Pb and Sb in the Pb-Sb system behave similarly.

The model makes a very good description of the thermodynamic properties of lead.

The experimental and calculated activity coefficients of lead and antimony are subunitary (negative deviations from Raoult's law). but close to unity throughout the investigated range of concentrations, indicating a near ideal solution.

The good agreement between the experiment and theoretical data calculated by the POSS model suggest that the liquid Pb-Sb alloy behave as a partially ordered subsubregular solution.

R E F E R E N C E S

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