THE THERMODYNAMIC PROPERTIES OF THE Pb-Sb SYSTEM

Florentina NICULESCU[1], Ion CONSTANTIN[2], Mihai BUZATU[3], Dragos Florin MARCU[4], Ioana CSAKI[5]

The developing metallurgical processes are characterized by the different parameters describing an equilibrium state at a given moment. The importance of knowing these parameters is underlined within this paper. The aim of this work is to determine, based on the experimental values of the activity coefficients at the temperature of 900K and 923 K,the thermodynamic properties of the Pb-Sb system.

Keywords: the molar partial free energy, the partial excess molar, mixing partial molar enthalpy, excess integral molar thermodynamic measures

1. Introduction

The metallurgical process consisted in the development of aseries of physic-chemical reactions which could take place in homogeneous environments (metallic bath, molten salts, slag), or in heterogeneous environments (metallic-slag bath, molten salts-metallic bath)

For an optimum development of the metallurgical process the necessary conditions for the reaction evolving in the right direction must be known [9-17].The steady state equation must be determined and known, the steady state being characterized by the chemical equilibrium constant and elements activities values or the activity coefficients values, and so the parameters that is influencing the balance as well as parameters influencing steady state.

The importance of knowing the value of the thermodynamic measures (Gibbs free energy, enthalpy, entropy) of a system elements and the variation of those with temperature resulted from an important number of monographs in the scientific literature [1-8]. The thermodynamics data from the recent papers [7]

[1] PhD Eng., Dept. of Engineering and Management of Metallic Materials Production, University POLITEHNICA of Bucharest , Romania, e-mail: flori.pereteanu@yahoo.com
[2] Prof., Dept. of Engineering and Management of Metallic Materials Production, University POLITEHNICA of Bucharest, Romania, e-mail: scremcosrl@yahoo.com
[3] Prof., Dept. of Engineering and Management of Metallic Materials Production, University POLITEHNICA of Bucharest, Romania, e-mail:buzatu.mihai@yahoo.com
[4] Assist. PhD. Eng., Dept. of Engineering and Management of Metallic Materials Production, University POLITEHNICA of Bucharest, Romania, e-mail: dragos.marcu@arasnet.ro
[5] Assoc. prof. PhD Eng., Dept. of Engineering and Management of Metallic Materials Production, University POLITEHNICA of Bucharest, Romania, e-mail: ioana.apostolescu@upb.ro

provide a different presentation and a superior precision over the papers published earlier (1960-1970), the experimental values of the thermodynamic measures are tabled from 100 to 100 degree, without being established the functions $J = f(T)$ ($J = Cp, G, H, S$) as they are found in the old monographs [3,4,5].

The Pb-Sb alloys represent the base of lining production for the electric cable protection of the Pb battery elements, of the antifriction alloys, typographical alloy, for the soft paste. For the letters there are used alloy like Pb-Sn-Sb, sometimes 1,5 % Bi, increasing their fluidity in liquid state and the duration.

2. Materials and method

As a result of the main experimental methods analyses of the thermodynamic activities determination of the metallic melts elements, for getting the thermodynamic activities in the binary system of Pb-Sb alloy, I used the electromotive tension method. This method was chosen due to the high precision and the good reproducibility of the proven by experimental data in other researches regarding the thermodynamic of metallurgical melts. The method is based on the measurement of the electromotive tension in a reversible concentrated galvanic cell with a liquid or solid electrode.

Because in the scientific literature there are no available data for the Pb-Sb system at 923 K, the determined experimental data [18-24] were compared with the ones obtained through the Seltz and DeWitt electromotive measurement force at 900 K [1-2].

Starting from the experimental data of the activity coefficient at the two temperature (900K, 923K) the thermodynamics measurements realized were: the partial molar free energy ($\Delta\overline{G}_i$) and the partial excess ($\Delta\overline{G}_i^E$), mixture partial molar enthalpy ($\Delta\overline{H}_i$), excess molar partial entropy ($\Delta\overline{S}_i^E$) and mixture molar partial ($\Delta\overline{S}_i$), integral molar free energy (ΔG_i) and integral excess molar (ΔG_i^E), integral molar enthalpy (ΔH_i) and integral excess molar (ΔH_i^E),integral molar entropy (ΔS_i) and integral excess molar (ΔS_i^E) of Pb and Sb [25].

3. Results and discussions

The molar partial free energy ($\Delta\overline{G}_i$) and the partial excess molar ($\Delta\overline{G}_i^E$)

Using the MATHCAD 12 program, the value of the partial molar free energy and partial excess molar of the Pb and Sb estimated with the relations:

$$\Delta\overline{G}_{Pb} = RT\ln a_{Pb}\,;\Delta\overline{G}_{Sb} = RT\ln a_{Sb}$$

$$\Delta\overline{G}_{Pb}^{E} = RT\ln\gamma_{Pb}\ ;\ \Delta\overline{G}_{Sb}^{E} = RT\ln\gamma_{Sb} \qquad (1)$$

there are presented in the table 1, table 2 and Fig. 1. There are also shown the values of the thermodynamic interactions parameters (ω_i).

Thermodynamics interaction parameters highlight the mutual influence of the concentration of system elements over the activity coefficients of one of the solvents.

In the hypothesis that the Pb-Sb solution is regular, for the binary systems, the interactions thermodynamic parameters are given by the relation:

$$\omega_{Pb} = \frac{\Delta\overline{G}_{Pb}^{E}}{(1-x_{Pb})^2}\ ;\ \omega_{Sb} = \frac{\Delta\overline{G}_{Sb}^{E}}{(1-x_{Sb})^2} \qquad (2)$$

The graphic representation is shown in the fig. 2.

Table 1

The molar partial free energy, excess partial molar and the interaction thermodynamic for Pb, T = 923 K

x_{Pb}	a_{Pb}	γ_{Pb}	$\Delta\overline{G}_{Pb}$ [J/mol]	$\Delta\overline{G}_{Pb}^{E}$ [J/mol]	ω_{Pb} [J/mol]
1.0	1.000	1.000	0	0	0
0.9	0.896	0.995	-847	-38	-3823
0.8	0.787	0.984	-1838	-125	-3133
0.7	0.683	0.976	-2928	-190	-2114
0.6	0.581	0.968	-4170	-250	-1559
0.5	0.481	0.962	-5614	-294	-1177
0.4	0.381	0.953	-7403	-371	-1030
0.3	0.284	0.946	-9668	-428	-874
0.2	0.186	0.928	-12922	-570	-891
0.1	0.091	0.913	-18365	-694	-857
0.0	0.000	0.881	$-\infty$	-972	-972

Table 2

The partial molar free energy, excess molar partial and the interactions thermodynamic parameters for Sb ,T = 923 K

x_{Sb}	a_{Sb}	γ_{Sb}	$\Delta\overline{G}_{Sb}$ [J/mol]	$\Delta\overline{G}_{Sb}^{E}$ [J/mol]	ω_{Sb} [J/mol]
0.0	0.000	0.793	$-\infty$	-1780	-1780
0.1	0.087	0.873	-18713	-1042	-1287
0.2	0.187	0.933	-12884	-532	-832
0.3	0.287	0.958	-9569	-329	-672
0.4	0.389	0.972	-7250	-218	-605
0.5	0.489	0.979	-5482	-163	-652
0.6	0.592	0.987	-4021	-100	-628
0.7	0.694	0.991	-2807	-69	-771
0.8	0.797	0.997	-1736	-23	-576
0.9	0.900	1.000	-809	0	0

1.0	1.000	1.000	0	0	0

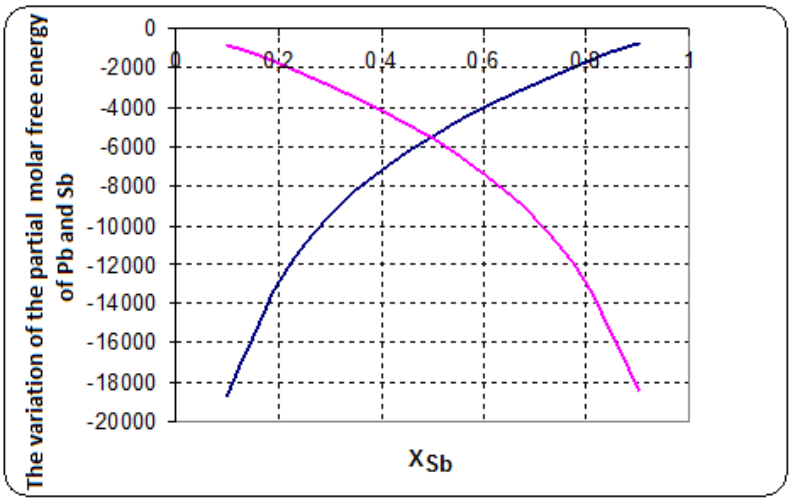

Fig. 1 The variation of the partial molar free energy of Pb and Sb at the temperature of 923K

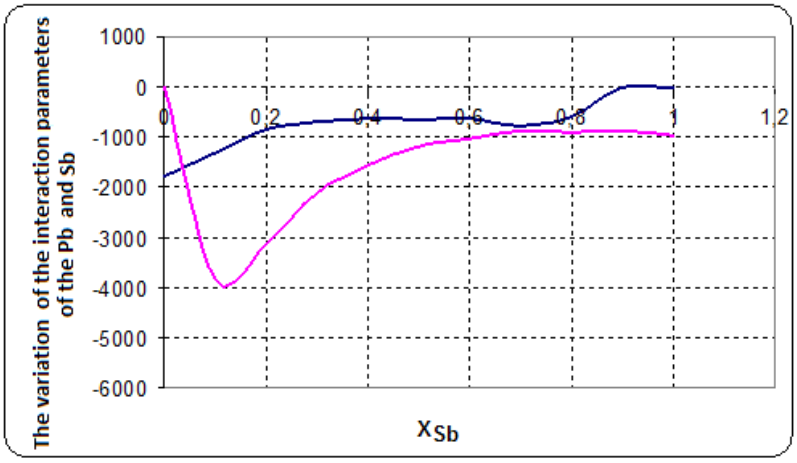

Fig. 2.The variation of the interaction parameters of the Pb and Sb at the temperature of 923K

Mixing partial molar enthalpy ($\Delta\overline{H}_i$)

Mixing partial molar enthalpy ($\Delta\overline{H}_i$) of the Pb and Sb have been calculated with the relation (3) and presented in table no 3:

$$\Delta\overline{H}_i = \Delta\overline{G}_i + T\Delta\overline{S}_i ; \qquad (3)$$

Table .3

Mixing partial molar enthalpy of the Pb and Sb at T = 923 K

x_{Sb}	$\Delta\overline{H}_{Pb}$ [J/mol]	$\Delta\overline{H}_{Sb}$ [J/mol]
0.0	$-1\cdot10^{16}$	$-1\cdot10^{16}$
0.1	-4849	-11950
0.2	-6911	9362
0.3	-6168	11530
0.4	-1392	8945
0.5	-1763	4455
0.6	-5451	1856
0.7	-6893	-725
0.8	-6335	--1052
0.9	-2818	-715
1.0	0	0

Excess partial molar entropy ($\Delta\overline{S}_i^E$)

Excess partial molar entropy ($\Delta\overline{S}_i^E$) and mixture partial molar ($\Delta\overline{S}_i$) of Pb and Sb have been calculated with the relations (4) and (5) and are presented in the table no 4 Figs. 3 and 4.

$$\Delta\overline{S}_i^E = \Delta\overline{S}_i + R\ln x_i \tag{4}$$

$$\Delta\overline{S}_i = \frac{d}{dT}\Delta\overline{G}_i \tag{5}$$

Table.4

The mixture partial molar entropy and excess partial molar of Pb and Sb at T=923 K

x_{Sb}	$\Delta\overline{S}_{Pb}$ [J/mol]	$\Delta\overline{S}_{Sb}$ [J/mol]	$\Delta\overline{S}_{Pb}^E$ [J/mol]	$\Delta\overline{S}_{Sb}^E$ [J/mol]
0.0	0	0	50.456	0.956
0.1	25.15	7.324	44.295	26.469
0.2	21.487	24.101	34.869	37.483
0.3	17.158	22.857	27.168	32.867
0.4	9.529	17.546	17.147	25.165
0.5	4.172	10.766	9.936	16.529
0.6	--1.388	6.367	2.859	10.614
0.7	-4.296	2.255	-1.331	5.221
0.8	-4.873	0.741	-3.018	2.596
0.9	-2.135	0.101	-1.259	0.978
1.0	0	0	0	0

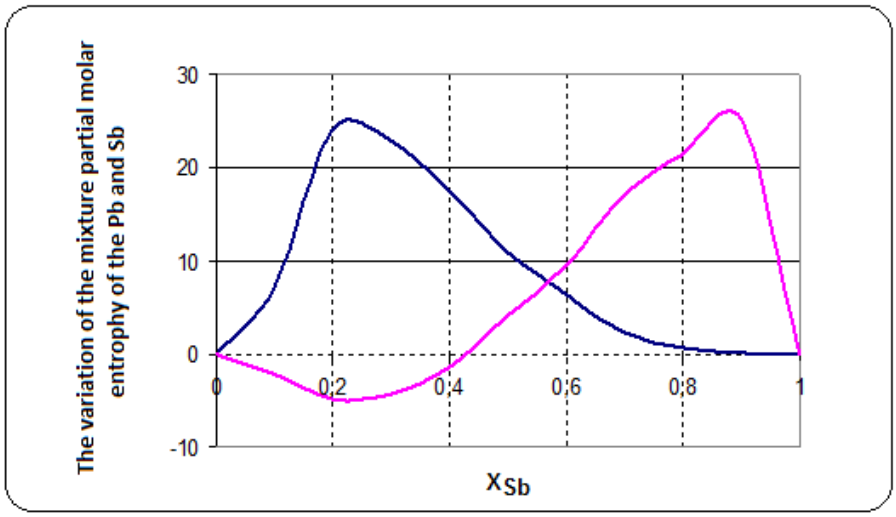

Fig.4. The variation of the mixture partial molar entrophy of the Pb and Sb at the temperature of 923K

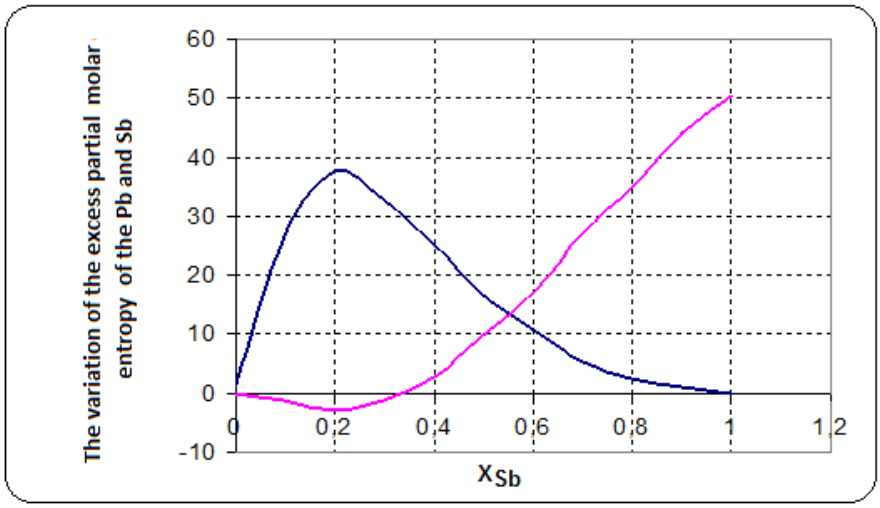

Fig.5.The variation of the excess partial molar entrophy of the Pb and Sb at the tempertaure of 923K

Excess integral molar thermodynamic measures: Integral molar free energy and excess integral molar

The integral molar free energy (ΔG_i) and excess integral molar (ΔG_i^E) have been calculated using the relations (6), (7) and are shown in table no 5.

$$\Delta G_i = \sum x_i \Delta \overline{G}_i = x_{Pb}\Delta \overline{G}_{Pb} + x_{Sb}\Delta \overline{G}_{Sb} \quad (6)$$

$$\Delta G^E = \Delta G - \Delta G^{id} = RT(x_{Pb} \ln \gamma_{Pb} + x_{Sb} \ln \gamma_{Sb}) \quad (7)$$

Table.5

The integral molar free energy and the excess integral molar at T = 923K

x_{Sb}	ΔG [J/mol]	ΔG^E [J/mol]
0.0	0	0
0.1	-2633	-139
0.2	-4047	-207
0.3	-4920	-232
0.4	-5402	-237
0.5	-5548	-229
0.6	-5373	-209
0.7	-4865	-177
0.8	-3973	-132
0.9	-2564	-69
1.0	0	0

Integral molar enthalpy (ΔH_i) and excess integral molar (ΔH_i^E)

Integral molar enthalpy **(**ΔH_i) and excess integral molar (ΔH_i^E) of the Pb –Sb alloy at the 923K temperature have been calculated with the relations (8), (9) and shown in table 6:

$$\Delta H_i = \sum x_i \Delta \overline{H}_i = x_{Pb} \Delta \overline{H}_{Pb} + x_{Sb} \Delta \overline{H}_{Sb} \quad (8)$$

$$\Delta H^E = \Delta H^M - \Delta H^{id} = \Delta H^M \quad (9)$$

Table.6

Integral molar enthalpy and excess integral molar of Pb and Sb at T = 923K

x_{Sb}	ΔH [*J/mol*]	ΔH^E [*J/mol*]
0.0	0	0
0.1	-3731	1258
0.2	-3196	4484
0.3	-1367	8009
0.4	308	10640
0.5	1346	11980
0.6	1671	12000
0.7	1343	10720
0.8	541	8221
0.9	-159	4831
1.0	0	0

Integral molar entropy (ΔS_i) and excess integral molar (ΔS_i^E)

Integral molar entropy (ΔS_i) and excess integral molar (ΔS_i^E) of the Pb – Sb alloy at 923K temperature have been calculated with the relations (10), (11) and shown in table. 7:

$$\Delta S_i = \sum x_i \Delta \bar{S}_i = x_{Pb}\Delta \bar{S}_{Pb} + x_{Sb}\Delta \bar{S}_{Sb} \tag{10}$$

$$\Delta S^E = \Delta S - \Delta S^{id} = \frac{\Delta H \ - \Delta G}{T} + R(x_{Pb}\ln x_{Pb} + x_{Sb}\ln x_{Sb}) = \frac{\Delta H \ - \Delta G^E}{T} \tag{11}$$

Table 7

Integral molar entropy and excess integral molar at *T = 923K*

x_{Sb}	ΔS [*J/mol*]	ΔS^E [*J/mol*]
0.0	0	0
0.1	-1.189	1.514
0.2	0.922	5.082
0.3	3.85	8.929
0.4	6.186	11.781
0.5	7.469	13.232
0.6	7.632	13.228
0.7	6.726	11.805
0.8	4.89	9.051
0.9	2.606	5.309
1.0	0	0

4. Conclusions

Based on the experimental values of the activity coefficients at the temperature of $900K$ and $923K$ there have been determined the thermodynamic measures:

- ✓ Partial molar free energy ($\Delta \bar{G}_i$) and excess partial molar ($\Delta \bar{G}_i^E$),
- ✓ Mixture partial molar enthalpy ($\Delta \bar{H}_i$),
- ✓ Excess partial molar entropy ($\Delta \bar{S}_i^E$) and mixture partial molar ($\Delta \bar{S}_i$),
- ✓ Integral molar free energy (ΔG_i) and excess integral molar (ΔG_i^E),
- ✓ Integral molar enthalpy (ΔH_i) and excess integral molar (ΔH_i^E),
- ✓ Integral molar entropy (ΔS_i) and excess integral molar (ΔS_i^E).

The thermodynamic measures for the Pb- Sb binary alloy systems, allow through calculation, to be over all the temperature –concentration main points,

with a high precision. The obtained values are experimentally verified and could be used in thermodynamic calculation.

R E F E R E N C E S

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