



Thermodynamics of liquid Sn-Pb alloys determined by vapour pressure measurements

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ABSTRACT

Application of Knudsen method in the studies of liquid Sn-Pb alloys, containing from 4.85 to 95.31 mol% of lead, in temperatures from 851 to 1186 K, and liquid tin and lead, in temperatures 1360 – 1442 and 934 – 1149 K, respectively, provided experimental data which made characterization of thermodynamic properties of liquid phase of Sn-Pb system possible. Parameters of the Redlich-Kister equation, describing excess Gibbs energy of liquid phase of the examined system, were determined. With application of the third law method standard enthalpies of sublimation of tin and lead were calculated.

1. Introduction

An attempt previously made by the author to provide a description of the excess Gibbs energy of the liquid phase of the In-Sn-Pb system using his own experimental data produced by the Knudsen method [1] and a review of current literature thermodynamic data which characterize boundary systems provided an incentive to perform studies of lead activity in liquid alloys of the binary Sn-Pb system [1].

A comprehensive overview of data on phase diagram and thermodynamic properties of the system was presented in the publication by Karakaya and Thompson [2] as well as in the study by Ohtani et al. [3]. Experimental data on molar enthalpy of mixing of liquid Sn-Pb alloys [4–11] show a moderately positive effect of the mixing process. The values of the molar enthalpy of mixing presented in these studies are in good agreement. The situation is radically different with activities of components of liquid Sn-Pb alloys [12–23]. There is an unacceptable discrepancy both in tin activity [15,17,18,20,21,23] and activity of lead [13,14,16,17,19,22].

The experimental part of this study provided data which characterizes vapour pressure over pure tin and lead, as well as lead over liquid Sn-Pb alloys. They were then used to calculate the activity of lead in the liquid phase of the Sn-Pb system.

The values of lead activity, supplemented with literature data which characterize molar enthalpy of mixing of liquid Sn-Pb alloys [4–6,8–10], were used in optimization procedure, aimed at determination of parameters of the Redlich-Kister equation, describing the excess Gibbs energy of liquid Sn-Pb alloys.

2. Experimental

2.1. Sample preparation

The experiments were carried out with samples of liquid tin, lead and Sn-Pb alloys. The samples of liquid alloys were produced by melting of pure components of the system in the Knudsen cell situated in the measuring system of the thermobalance, directly before the measurements. Any losses of mass which occurred during melting of alloys were attributed to vaporization of lead.

Lead of 99.995 mass% purity from The Institute of Electronic Materials Technology, Warsaw, Poland, was used in samples preparation. Tin used in samples preparations was supplied by Alfa Aesar – a Johnson Matthey Company. Tin for the 10SnPb, 25 SnPb and 5 SnPb alloys was of 99.9999 mass% purity. The other alloys were prepared with tin of 99.999 mass% purity.

2.2. Equipment

The measurements of mass loss rate by the Knudsen method (KM) were carried out with “Mettler” TA1 thermobalance. Temperatures were measured with a Pt/Pt-10%Rh thermocouple calibrated at the melting points of tin, lead, silver, copper, and Ag-Sb and Ag-Cu eutectic alloys. All the metals used in the calibration were of purity higher than 99.99 mass%.

Knudsen cells of the same type were used in the experiments. Each cell, made of Ringsdorf's high density graphite and later denoted by G0, G2, G3 and G4, was composed of a crucible of diameter and height of 15E-3 m and a cover with conical effusion orifice.

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Table 1
Characteristics of the measurements and their condition.

Set	m_{Sn} , kg	m_{Pb} , kg	$A_e \pm \sigma$, m^2	Knudsen cell
1	2	3	4	5
Sn	1925.83E-6	–	4.321E-6 ± 0.0977E-6	G4
Pb	–	1925.22E-6	0.1328E-6 ± 0.00270E-6	G2
Pb(a)	–	–	0.760E-6 ± 0.0203E-6	G3
Pb(b)	–	–	0.06926E-6 ± 0.000977E-6	G0
50SnPb	732.70E-6	1299.42E-6	0.760E-6 ± 0.0203E-6	G3
50SnPb(a)	–	–	0.1328E-6 ± 0.00270E-6	G2
50SnPb(b)	–	–	4.321E-6 ± 0.0977E-6	G4
65SnPb	1026.20E-6	978.14E-6	0.760E-6 ± 0.0203E-6	G3
35SnPb	458.12E-6	1511.70E-6	0.760E-6 ± 0.0203E-6	G3
15SnPb	181.33E-6	1835.36E-6	0.760E-6 ± 0.0203E-6	G3
15SnPb(a)	–	–	0.1328E-6 ± 0.00270E-6	G2
15SnPb(b)	–	–	4.321E-6 ± 0.0977E-6	G4
85SnPb	1531.98E-6	486.35E-6	0.760E-6 ± 0.0203E-6	G3
95SnPb	1848.11E-6	202.19E-6	0.760E-6 ± 0.0203E-6	G3
95SnPb(a)	–	–	0.1328E-6 ± 0.00270E-6	G2
95SnPb(b)	–	–	4.321E-6 ± 0.0977E-6	G4
10SnPb	123.72E-6	1909.17E-6	0.1328E-6 ± 0.00270E-6	G2
10SnPb(a)	–	–	0.760E-6 ± 0.0203E-6	G3
10SnPb(b)	–	–	0.06926E-6 ± 0.000977E-6	G0
25SnPb	329.17E-6	1696.11E-6	0.760E-6 ± 0.0203E-6	G3
25SnPb(a)	–	–	0.06926E-6 ± 0.000977E-6	G0
5SnPb	55.09E-6	1956.87E-6	0.760E-6 ± 0.0203E-6	G3
5SnPb(a)	–	–	0.06926E-6 ± 0.000977E-6	G0

In the presented studies, because of the irregular shape of effusion orifices, the values of their effective areas ($A_e = A \cdot W$, where A is the geometrical area of the orifice and W is the transmission probability) were determined experimentally by Knudsen method, as described in an earlier work [24]. Indium of 99.999 mass% purity was used in determination of effective areas of effusion orifices in the current study. The data on indium vapour pressure used in this determination had been experimentally produced in an earlier work [25].

2.3. Data collection and treatment

23 sets of measurements of mass loss rate by the Knudsen method were performed in the experimental part of this study. Table 1 shows description of the conducted tests. The first column contains symbols of the measurement series; the second and third present mass of tin and lead, respectively, in the sample before its preparation. The last two columns show effective areas of the effusion orifices (A_e) together with the cell symbol, respectively. In the case of Pb(a), Pb(b), 50SnPb(a), 50SnPb(b), 15SnPb(a), 15SnPb(b), 95SnPb(a), 95SnPb(b), 10SnPb(a), 10SnPb(b), 25SnPb(a), and 5SnPb(a) series no data on mass are presented because they represent continuation of Pb, 50SnPb, 15SnPb, 95SnPb, 10SnPb, 25SnPb, and 5SnPb series, respectively.

In the description of experimental data produced in this study the Hertz-Knudsen equation was used in a form of:

$$P_{Kn(i)} = \left(\frac{dg}{dt} \right)_i \left(\frac{2 \cdot \pi \cdot R \cdot T}{M_i} \right)^{1/2} \cdot A_e^{-1} \quad (1)$$

where: $P_{Kn(i)}$ is pressure of i -th component of gaseous phase measured by Knudsen method, $\left(\frac{dg}{dt} \right)_i$ is the rate of mass loss due to effusion of the i -th vapour component. R and T denote the universal gas constant and absolute temperature of the sample, respectively. M_i is the molecular mass of the i -th effusing component.

In the Sn-Pb system the following vaporization reactions take place:



After taking under consideration that the rates of mass loss due to effusion have an additive effect, the following relation between mass loss rate, temperature, and vapour pressures is obtained:

$$\left(\frac{dg}{dt} \right)_{total} = \frac{A_e}{(2 \cdot \pi \cdot R \cdot T)^{1/2}} \cdot \sum_i P_{Kn(i)} \cdot M_i^{1/2} \quad (4)$$

The results of experimental studies of pure liquid tin and lead were applied directly for calculation of tin and lead vapour pressure over both mentioned above liquid metals ($P_{Kn(i)}^o = P_{Kn(i)}$), after making an assumption that tin and lead monomers are the only significant components of the gaseous phases [26,27]. It was possible to conduct these calculations separately for every measuring point that produced sets of pairs of data describing tin or lead vapour pressure vs. temperature of the system.

In tin examination potential interferences of equilibrium state resulting from the presence of effusion orifice of a finite value of the effective area were not studied [28], as there were no significant differences between the values of tin pressure obtained in the presented study and the ones available in the literature, despite the fact that Knudsen cell of exceptionally large effective surface area was applied. Based on that behaviour of the examined system it was then assumed that:

$$P_{Eq(Sn)}^o = P_{Kn(Sn)}^o \quad (5)$$

where: $P_{Eq(Sn)}^o$ is equilibrium pressure of tin over liquid tin.

In the case of liquid lead, on the other hand, it was necessary to take under consideration a factor which disturbs state of equilibrium in the investigated system. The reasons for such disturbance had been described in our earlier study [28]. In such a situation the calculation of equilibrium pressure ($P_{Eq(Pb)}^o$) can be performed with application of the equation proposed by Cater [29], which renders it possible to link the pressure measured by the Knudsen method ($P_{Kn(Pb)}^o$) with the equilibrium pressure of lead over liquid lead ($P_{Eq(Pb)}^o$) (Eq. (6)):

$$P_{Eq(Pb)}^o = P_{Kn(Pb)}^o \cdot (1 + A_e / (\alpha \cdot A_s)) \quad (6)$$

where A_s and α are, respectively, surface of the liquid phase and so called vaporization coefficient. The value of the coefficient of vaporization can be calculated by application of measurements with several, at least two, Knudsen cells, of significantly different effective areas of effusion orifices.

Thus obtained values of equilibrium pressures of tin and lead were then used in calculations of standard enthalpies of tin and lead sublimation by the third law method. In this case the following equations (Eq. (7)) and (Eq. (8)) were applied:

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