

## ISOBARIC VAPOR-LIQUID EQUILIBRIA OF TERNARY LEAD–TIN–ANTIMONY ALLOY SYSTEM AT 2 Pa

J. Xu <sup>a,b,c</sup>, J. Gao <sup>a,b,c</sup>, L. Kong <sup>a,b,c,d,\*</sup>, B. Xu <sup>a,b,c,d</sup>, B. Yang <sup>a,b,c,d,\*</sup>, D. Liu <sup>a,b,c</sup>

<sup>a\*</sup> National Engineering Laboratory of Vacuum Metallurgy, Kunming University of Science and Technology, Kunming, PR China

<sup>b\*</sup> Key Laboratory of Vacuum Metallurgy for Non-ferrous Metal of Yunnan Province, Kunming University of Science and Technology, Kunming, PR China

<sup>c\*</sup> Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, PR China

<sup>d\*</sup> State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization in Yunnan Province, Kunming, PR China

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### Abstract

*In this study, the experimental vapor–liquid equilibria data of the ternary Pb–Sn–Sb alloy system are determined using a new experimental method. The experimental VLE data passed the thermodynamic consistency test (Van Ness test), suggesting that the experimental results are reliable. The activities of the components of Pb–Sn–Sb ternary alloy and those of the corresponding three constituent binaries were calculated using the Wilson equation. The predicted values are in good agreement with the data determined from the experiments, and the average relative deviation and average standard deviation were smaller than  $\pm 4.00\%$  and  $\pm 0.03$  for all constituent binaries, respectively, which indicates that the Wilson equation is reliable for calculating the activity of the components of the Pb–Sn–Sb ternary alloy. The VLE data of the Pb–Sn and Sb–Sn binary alloys and Pb–Sn–Sb ternary alloy were calculated based on the VLE theory and the Wilson equation. The calculated VLE data were in good agreement with the data determined from the experiments, indicating that this method is reliable for calculating the VLE of alloy systems. The proposed study offers a valid method for analyzing the composition of products that are dependent on the distillation temperature and system pressure during vacuum distillation, which is of great significance to the experimental design of this process.*

**Keywords:** Pb–Sn–Sb alloy; Activity; VLE; Wilson equation; Thermodynamic consistency test

### 1. Introduction

A significant amount of Pb–Sn–Sb alloys is produced from global smelters annually due to the similar behavior of Pb, Sn, and Sb during the smelting process. This is because of their similar physicochemical properties and association in minerals. Pb, Sn, and Sb are mainly used for the manufacturing of lead-acid batteries, solders, and bearing alloys, which generates large amounts of waste Pb–Sn–Sb alloys. With the increasing demand for Pb, Sn, and Sb in these materials, the amount of waste produced has also increased. Therefore, recycling the Pb–Sn–Sb alloys in an environmentally sound manner is of great realistic significance for saving resources and for protecting the environment, as Pb and Sb are considered as toxic materials worldwide.

Traditional methods for recycling Pb–Sn–Sb alloys can be disadvantageous, as they tend to have a long flowsheet and may cause serious pollution. Vacuum evaporation is recognized as one of the cleanest and most efficient technologies for recycling alloy scraps, and it has been shown to achieve positive results [1–4].

Reliable vapor–liquid equilibrium (VLE) data are crucial for the optimization of the original process and the design of the new process in vacuum distillation. In our previous work [5], VLE data of the binary Pb–Sn and Sb–Sn alloy systems were obtained using the new experimental method proposed in the Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology (KUST), China. Investigating the VLE data of ternary alloy systems has a more practical significance because most of the alloys produced and

\*Corresponding author: kkmust@126.com; kgyb2005@126.com



recovered from smelters and resource recovery industries are ternary or multicomponent alloys. Moreover, there is no reported VLE data for the ternary Pb (1) +Sn (2) +Sb (3) alloy system in the literatures. Therefore, the VLE data for the Pb–Sn–Sb ternary system were determined in this study using the new method.

It is not realistic to determine the VLE data of all alloy systems through experimentation as they require conditions that may be difficult to sustain, such as high temperatures and low pressures. Modeling is a convenient and effective method for obtaining the VLE of alloy systems, especially for multicomponent systems. The well-known Wilson equation was derived from the theory of local concentration of molecules, and it has been shown to present a good prediction [6-9]. In particular, it can predict the activities and other properties of multicomponent alloy systems using only the related parameters of constituent binaries. Therefore, the Wilson equation was employed to calculate the VLE data of Pb–Sn–Sb alloy system based on the VLE theory. The calculated results of the Wilson equation were compared with the experimental VLE data for validation purposes.

This study aims to determine the VLE data of the Pb–Sn–Sb alloy system using the new experimental method and to provide a reliable method for the calculation of the VLE of alloy systems. The proposed study provides reliable VLE data for the Pb–Sn–Sb ternary alloy and demonstrates a reliable and efficient way of predicting the VLE data of alloy systems in the processes of vacuum distillation, especially suitable for the ordinary distillation, batch distillation, and pressure swing distillation processes.

## 2. Experimental

### 2.1. Materials

Metallic Sn (mass fraction = 99.99%), metallic Pb (mass fraction = 99.999%), and Sb lumps (mass fraction = 99.99%) were purchased from Leshan Kai Yada Photoelectric Technology Co., Ltd., China. Prior to the experiments, the chemicals were stored in a container filled with high-purity Ar gas to prevent oxidation. Ar gas (mass fraction purity  $\geq 0.99999$ ) was obtained from Kunming Messer Gas Products Co., Ltd., China. All chemicals were used without further purification. The summary of CAS#, suppliers, and purities of chemicals used in this study are listed in Table 1.

### 2.2. Experimental procedure

#### 2.2.1 Alloy preparation

Pb–Sn–Sb alloys were prepared using a quartz tube equipped with a vacuum pump (2XZ-4Z, China),

**Table 1.** CAS#, suppliers, and purities of chemicals used in this study

Chemical name	CAS#	Supplier	Mass fraction purity	Purification method
Lead (Pb)	7439-92-1	Leshan Kai Yada Photoelectric Technology Co., Ltd., China	0.99999	None
Tin (Sn)	7440-31-5	Leshan Kai Yada Photoelectric Technology Co., Ltd., China	0.9999	None
Antimony (Sb)	7440-36-0	Leshan Kai Yada Photoelectric Technology Co., Ltd., China	0.9999	None
Argon gas	7440-37-1	Kunming Messer Gas Products Co., Ltd., China	$\geq 0.99999$	None

Ar gas cylinder, and resistance furnace. Temperatures were measured using a thermocouple (type K) obtained from Jinhong Instrument Co., Ltd., China with an uncertainty of  $\pm 1$  K. Pressures were monitored with a combined pressure and vacuum gauge with an uncertainty of  $\pm 2$  Pa. An OHAUS (Pine Brook, NJ USA) balance, Model AR 1140/C, with an uncertainty of  $\pm 0.0001$  g was used for weighing.

The three high-purity metals were accurately weighed and melted into an alloy with a predetermined composition ( $x_{\text{Pb}} = 0.2000$ ,  $x_{\text{Sn}}/x_{\text{Sb}} = 1/3$ ). Fig. 1 shows the schematic diagram of the experimental device used for the preparation of the Pb–Sn–Sb alloys. For each run, 44.9659 g of Pb particles, 25.7621 g of Sn particles, and 79.2720 g of Sb polycrystalline lumps were put in a high-purity graphite crucible (inner diameter 32 mm  $\times$  Ht 110 mm, purity 99.99%). The graphite crucible was loaded in a quartz tube (inner diameter 82 mm  $\times$  Ht 350 mm), and the quartz tube was sealed with a silicone plug with three holes (inner diameter 6 mm  $\times$  Ht 60 mm), which were used for setting the thermocouple, gas inlet, and gas outlet. Then, the quartz tube was placed in a crucible resistance furnace, as shown in Fig. 1. Thereafter, the system was evacuated to approximately 3 Pa and then filled with high-purity Ar gas to prevent oxidation and heated to and kept at 904 K for 30 min to melt the Pb, Sn, and Sb into a Pb–Sn–Sb alloy under flowing high-purity Ar gas (10 ml·min<sup>-1</sup>). The alloy was remelted three or four times as required to ensure its homogeneity. The resistance furnace was cooled to approximately 30 °C before the alloy was removed from the graphite crucible. The mass losses of the alloy were smaller than 0.01%; therefore, the weighed compositions of the alloys were considered to be correct.



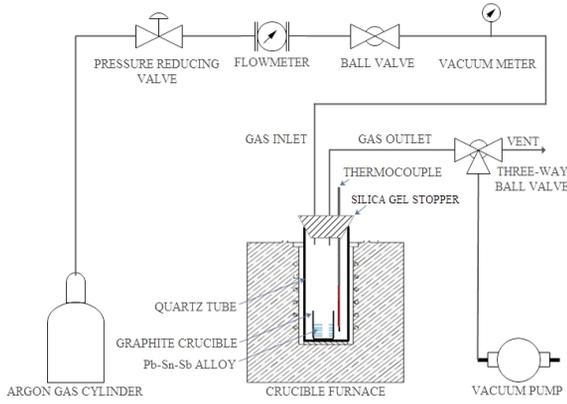


Figure 1. Schematic of the experimental apparatus for the preparation of Pb-Sn-Sb alloys

### 2.2.2 VLE measurements

The VLE data of the Pb-Sn-Sb alloy were determined using a steel chamber, as described in our previous work [5].

In each run, approximately 150 g of the Pb-Sn-Sb alloy ( $x_{Pb} = 0.2000$ ,  $x_{Sn}/x_{Sb} = 1/3$ ) was placed into a stainless steel chamber. The chamber, in which a capillary had been previously inserted, was welded and evacuated to 2 Pa. The chamber was then placed in a resistance furnace [5]. The experiments were conducted at 1023, 1073, 1123, 1173, and 1223 K, respectively, until the system reached equilibrium.

When the composition of the vapor phase and liquid phase no longer changed, the holding time was considered as the equilibrium time. At least four experiments were conducted at each temperature with a time interval of 30 min to obtain the equilibrium time. The composition of the vapor phase and liquid phase began to reach a constant value after over 3 h under the conditions of  $T = 1023$  K and  $P = 2$  Pa. Although the time required for the system to achieve the equilibrium decreases gradually with an increase in the distillation temperature, the final distillation time was 4 h for all the experiments in this study to ensure that the system sufficiently approaches the phase equilibrium.

At the end of each experiment, the steel chamber was quickly removed from the furnace and quenched in water. Therefore, the volatiles cooled on the sidewall of the chamber, whereas the residues cooled at the bottom of the chamber.

Finally, the volatiles and residues were collected from the sidewall and the bottom of the chamber, respectively. The Sb and Pb content in the vapor phase (volatiles) and liquid phase (residues) were determined by titration analysis, and the detailed determination procedure is available in Ref. [5]. The Sn content in the volatiles and residues was obtained by solving the equation of mass balance accounting

for the VLE. Using the method in Ref. [5], the combined standard uncertainty at the experimental conditions in this study was estimated to be  $\pm 0.003$  in mole fraction.

## 3. Calculation method

### 3.1 Applied thermodynamic model

The activities or activity coefficients of the alloys in the liquid phase are necessary for calculating the VLE data. Thermodynamic calculation is an effective method for this application, and the Wilson equation is considered as one of the most successful models [10, 11]. The excess free energy  $G^E$  [12] of a multicomponent system can be derived from the Wilson equation and expressed as follows:

$$\frac{G^E}{RT} = -\sum_i x_i \ln \left( 1 - \sum_j x_j A_{ji} \right) \quad (1)$$

where  $R$  is the gas constant ( $8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ );  $x_i$  and  $x_j$  are the molar fraction of component  $i$  and  $j$ , respectively;  $T$  is the absolute temperature; and the adjustable parameters  $A_{ij}$  and  $A_{ji}$  are expressed as:

$$A_{ij} = \frac{V_i}{V_j} \exp \left[ -\left( \frac{g_{ij} - g_{ji}}{RT} \right) \right] \text{ and } A_{ji} = \frac{V_j}{V_i} \exp \left[ -\left( \frac{g_{ji} - g_{ij}}{RT} \right) \right] \quad (2)$$

where  $g_{ii}$ ,  $g_{ij}$ , and  $g_{ji}$  are the  $i$ - $i$ ,  $i$ - $j$ , and  $j$ - $j$  interaction energies, respectively ( $g_{ij} = g_{ji}$ );  $V_i$  and  $V_j$  are the molar volumes of component  $i$  and  $j$ , respectively, as shown in Table 2 [13].

For a binary mixture  $i$ - $j$ , the activities of  $i$  and  $j$  components can be calculated from Eq. (1), respectively, which can be expressed as follows:

$$\ln \gamma_i = -\ln(x_i + x_j A_{ji}) + x_j \left( \frac{A_{ji}}{x_i + x_j A_{ji}} - \frac{A_{ij}}{x_j + x_i A_{ij}} \right) \quad (3)$$

$$\ln \gamma_j = -\ln(x_j + x_i A_{ij}) + x_i \left( \frac{A_{ij}}{x_j + x_i A_{ij}} - \frac{A_{ji}}{x_i + x_j A_{ji}} \right) \quad (4)$$

When  $x_i$  or  $x_j$  infinitely approaching zero, the activity coefficients of  $i$  and  $j$  (i.e.,  $\gamma_i^\infty$  and  $\gamma_j^\infty$ ) can be obtained from Eqs. (3) and (4), respectively, which can be expressed as:

$$\ln \gamma_i^\infty = 1 - \ln A_{ji} - A_{ij} \quad (5)$$

$$\ln \gamma_j^\infty = 1 - \ln A_{ij} - A_{ji} \quad (6)$$

Table 2. The molar volumes of the components of Pb-Sn-Sb ternary alloy [13]

$i$	$V_i/\text{cm}^3\cdot\text{mol}^{-1}$
Pb	19.42 [1 + 1.24 × 10 <sup>-4</sup> (T-600)]
Sn	17.00 [1 + 0.87 × 10 <sup>-4</sup> (T-505)]
Sb	18.80 [1 + 1.30 × 10 <sup>-4</sup> (T-904)]



The initial values of  $A_{ij}$  and  $A_{ji}$  can be obtained from the given data of  $\gamma_i^\infty$  and  $\gamma_j^\infty$  [14] by computing repeatedly (n+1) times until  $|A_{ji(n+1)} - A_{ji(n)}| \leq 10^{-8}$ . The detailed calculation process is available in Ref. [15].

Assuming that  $-(g_{ij} - g_{jj})/R$  and  $-(g_{ji} - g_{ii})/R$  are independent of temperature, and the values of  $A_{ij}$  and  $A_{ji}$  at a certain temperature ( $T_1$ ) are known, the values of  $A_{ij}$  and  $A_{ji}$  at the required temperature ( $T_2$ ) can be calculated from Eq. (2).

The required parameters  $A_{ij}$  and  $A_{ji}$  of the constituent binaries of the Pb-Sn-Sb ternary system are shown in Table 3.

Letting the Pb-Sn-Sb ternary system be a 1-2-3 system, the activity coefficient of component 1 of the system can be expressed as follows:

$$\ln \gamma_1 = 1 - \ln(x_1 + x_2 A_{21} + x_3 A_{31}) - \frac{x_1}{x_1 + x_2 A_{21} + x_3 A_{31}} - \frac{x_2 A_{12}}{x_1 A_{12} + x_2 + x_3 A_{32}} - \frac{x_3 A_{13}}{x_1 A_{13} + x_2 A_{23} + x_3} \quad (7)$$

### 3.2 Saturation vapor pressure

The vapor pressure of pure substances in the saturated state is also indispensable for the calculation of VLE. It can be calculated using the following vapor pressure equation [16]:

$$\lg P^s = AT^{-1} + B \lg T + CT + D \quad (8)$$

where  $P^s$  is the saturation vapor pressure of pure substances in Pa; A, B, C, and D [16] are the component specific coefficients of vapor pressure;  $T$  is the temperature in K. The saturation vapor pressure equations for Sn, Pb, and Sb are listed in Table 4.

### 3.3 VLE Calculation

The thermodynamic condition for the VLE is the equality of the fugacities of each component in each phase, which is expressed as follows [17]:

$$\hat{f}_i^V(T, P, y_i) = \hat{f}_i^L(T, P, x_i) \quad (9)$$

When the fugacity coefficient is used in Eq. (9), we obtain:

$$\hat{f}_i^V(T, P, y_i) = \hat{\Phi}_i^V P y_i \quad \text{and} \quad \hat{f}_i^L(T, P, x_i) = \gamma_i x_i P_i^s \Phi_i^s \exp\left(\frac{V_i^L(P - P_i^s)}{RT}\right) \quad (10)$$

**Table 3.** The values of  $A_{ij}$  and  $A_{ji}$ ,  $\gamma_i^\infty$  and  $\gamma_j^\infty$  [14] for the constituent binaries of the Pb-Sn-Sb ternary system

<i>i-j</i>	<i>T</i> /K	$\gamma_i^\infty$	$\gamma_j^\infty$	$A_{ij}$	$A_{ji}$
Pb-Sn	1050	2.195	6.816	0.1352	1.0818
Pb-Sb	905	0.779	0.779	1.1287	1.1287
Sn-Sb	905	0.411	0.411	1.4902	1.4902

Based on Eqs. (9) and (10), the vapor-phase composition  $y_i$  can be expressed as follows [17]:

$$y_i = \frac{\gamma_i x_i P_i^s \Phi_i^s}{\hat{\Phi}_i^V P} \exp\left(\frac{V_i^L(P - P_i^s)}{RT}\right) \quad (11)$$

where  $\Phi_i^s$  and  $\hat{\Phi}_i^V$  are the fugacity coefficient of pure component  $i$  at saturation conditions and the fugacity coefficient of component  $i$  in the vapor phase, respectively;  $x_i$  and  $y_i$  are the mole fractions of component  $i$  in the liquid and vapor phase, respectively;  $P$  and  $P_i^s$  are the system pressure and saturated vapor pressure of pure component  $i$ , respectively;  $\gamma_i$  is the activity coefficient of component  $i$  in the liquid phase;  $V_i^L$  is the molar volume of pure component  $i$  in the liquid phase;  $T$  is the system temperature; and  $R$  is the gas constant.

If the system pressure is considerably low, the vapor phase can behave as an ideal gas; then,  $\hat{\Phi}_i^V = \Phi_i^s = 1$ ; and the Poynting factor  $\exp\left(\frac{V_i^L(P - P_i^s)}{RT}\right)$  is close to 1 at low or moderate pressure. Thus, Eq.

(11) is simplified as the modified Raoult's law [18]:

$$y_i = \frac{\gamma_i P_i^s}{P} x_i = K_i x_i \quad (12)$$

For a multicomponent system:

$$\sum_{i=1}^c x_i = 1 \quad \text{and} \quad \sum_{i=1}^c y_i = 1 \quad (13)$$

Finally, let a function be:

$$f(T) = \sum_{i=1}^c y_i - 1 \quad (14)$$

## 4. Results and Discussion

In this section, we present and discuss the VLE data of the ternary Pb-Sn-Sb system. After presenting the experimental VLE data of the ternary system, the calculated results are shown. The calculated results and experimental data were compared for validation purposes.

**Table 4.** The saturation vapor pressure equation for Sn, Pb and Sb [16]

Substance	Equation for vapor pressure (Pa)	Temperature range (K)
Sn	$\lg p^{\text{sat}} = -15500T^{-1} + 10.355$	505-2875
Pb	$\lg p^{\text{sat}} = -10130T^{-1} - 0.985 \lg T + 13.280$	601-2022
Sb	$\lg p^{\text{sat}} = -6500T^{-1} + 8.495$	904-1860



### 4.1. Experimental results

The experimental VLE data of the Pb–Sn–Sb alloy obtained from the new method are presented in Table 5. Table 5 shows that the Sb content in the residue (liquid phase) decreases with an increase of temperature. At 1123 K, the Sb content in the residue was 0.5726 (mole fraction), and the Pb and Sn content were increased to 0.2211 and 0.2063, respectively. A small quantity of Pb and Sn will evaporate into the volatiles (vapor phase) after the temperature was increased; therefore, the Pb and Sn content in the volatiles, *i.e.*,  $y_{Pb}$  and  $y_{Sn}$ , increased to 0.03945 and 0.0024, respectively. However, the Sb content in the volatiles was much higher than the Sn and Pb content therein, indicating that the vapor phase mainly comprised Sb. This demonstrates that it is effective to separate Sb from a Pb–Sn–Sb alloy by vacuum distillation.

### 4.2. Thermodynamic consistency test

The thermodynamic consistency test is a criterion for determining the correctness of the experimental VLE data. In this study, the Van Ness test [19-20] was employed to test the thermodynamic consistency of the VLE data for Pb–Sn–Sb alloy, which can be expressed as follows:

$$y_{(MAD)} = \frac{1}{N} \sum_{i=1}^N 100 |y_i^{exp} - y_i^{cal}| \quad (15)$$

where  $y_{(MAD)}$  is the absolute deviation,  $y_i^{exp}$  is the experimental data,  $y_i^{cal}$  is the calculated results from the Wilson equation, and  $N$  is the number of experimental points.

According to the definition of the Van Ness test, the experimental VLE data are reliable if  $y_{(MAD)}$  is smaller than 1. Table 6 shows that the value of  $y_{(MAD)}$  for Pb, Sn, and Sb is 0.8134, 0.2850, and 0.7300, respectively, indicating that the experimental VLE data obtained by the new method are correct and reliable.

### 4.3 Activity

The activities of the components of the Pb–Sn

binary alloy at 1050 K and Pb–Sb and Sn–Sb binary alloys at 905 K were calculated using Eqs. (3) and (4), respectively, as shown in Fig. 2. The calculated values of activities are in good agreement with the experimental data. To quantify the deviations of the model predictions from the data determined from experiments, the average relative deviation ( $S_i$ ) and average standard deviation were calculated ( $S_i^*$ ) using Eqs. (16) and (17), respectively, as shown in Fig. 2.

$$S_i = \pm \frac{100}{n} \sum_{i=1}^n \left| \frac{a_{i,exp} - a_{i,cal}}{a_{i,exp}} \right| \quad (16)$$

$$S_i^* = \pm \left[ \frac{1}{n} \sum_{i=1}^n [a_{i,exp} - a_{i,cal}]^2 \right]^{1/2} \quad (17)$$

where  $n$  is the number of data points;  $a_{i,exp}$  is the experimental data of activity, and  $a_{i,cal}$  is the calculated value from the Wilson equation.

Figure 2 shows that the average relative deviations of  $a_{Pb}$  and  $a_{Sn}$  were  $\pm 2.870\%$  and  $\pm 3.410\%$ , respectively, and the average standard deviations of  $a_{Pb}$  and  $a_{Sn}$  were  $\pm 0.024$  and  $\pm 0.021$ , respectively. In addition, the average relative deviation and average standard deviation for all constituent binaries was smaller than  $\pm 4.00\%$  and  $\pm 0.03$ , respectively, which demonstrates that the Wilson equation is effective for calculating the activities of the components of the constituent binaries of the Pb–Sn–Sb alloy system.

For the Pb–Sn–Sb ternary alloy, the activity of each component can be calculated from Eq. (7), in which only the simple parameters of the corresponding constituent binary alloys are needed. The activities of the components of the Pb–Sn–Sb ternary alloy were obtained by substituting the Wilson parameters for the Pb–Sn, Sb–Sn, and Pb–Sb binary systems into Eq. (7), as shown in Table 7. As the reliable experimental data of the activity of the Pb–Sn–Sb ternary system were not available, the reliability of calculated activity of the ternary system could not be tested. Nevertheless, according to the

**Table 6.** Thermodynamic consistency test result of Pb-Sn-Sb alloy system at 2.0 Pa

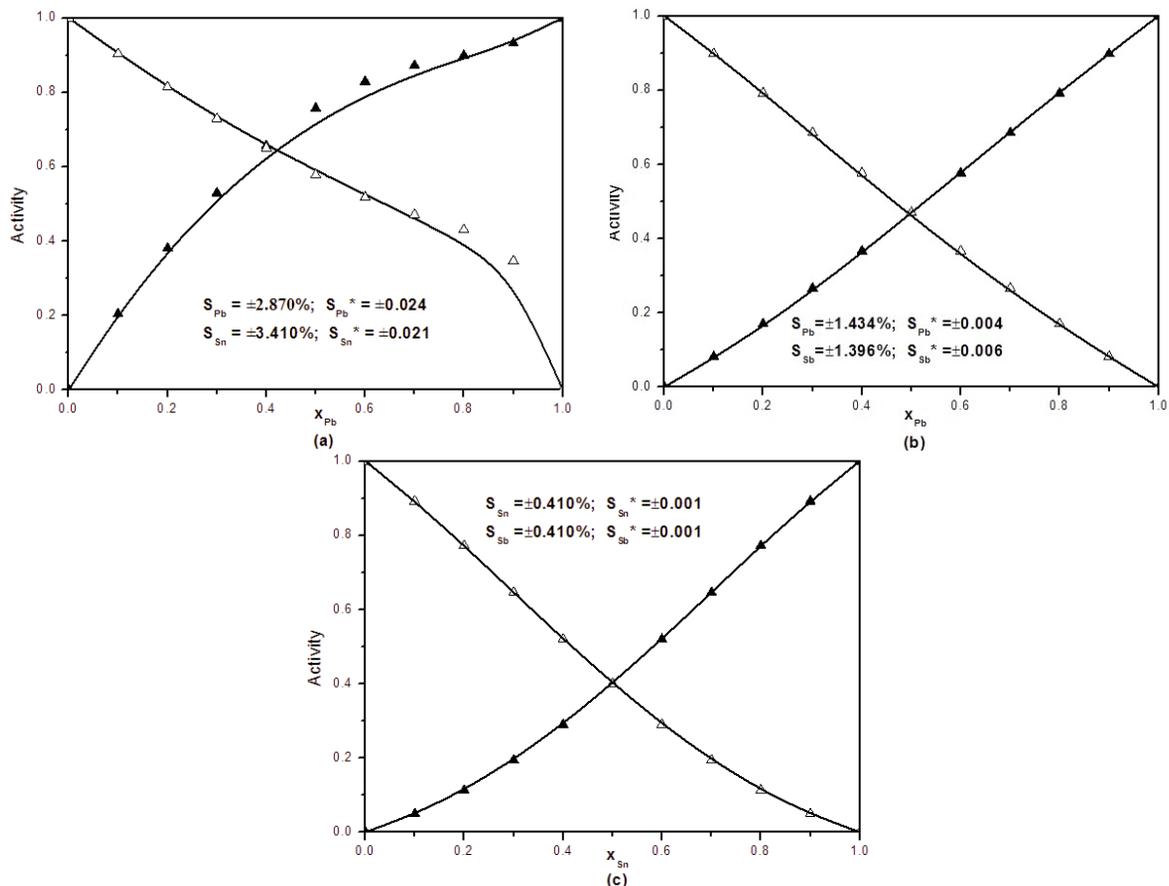
$y_{1(MAD)}$	$y_{2(MAD)}$	$y_{3(MAD)}$
0.8314	0.285	0.73

**Table 5.** Experimental VLE data for temperature  $T$ , liquid-phase mole fraction  $x_p$  and vapor-phase mole fraction  $y_p$  for the Pb (1) + Sn (2) + Sb (3) ternary system, measured at 2.0 Pa<sup>a</sup>

$T / K$	$P / Pa$	$t / h$	$x_{1,exp}$	$x_{2,exp}$	$x_{3,exp}$	$y_{1,exp}$	$y_{2,exp}$	$y_{3,exp}$	$y_{1,cal}$	$y_{2,cal}$	$y_{3,cal}$
1023	2	4	0.208	0.216	0.5759	0.0009	0.0018	0.9973	0.00029	$1 \times 10^{-5}$	0.9997
1073			0.2139	0.2012	0.5849	0.0009	0.002	0.9971	0.00079	$4 \times 10^{-5}$	0.99917
1123			0.2211	0.2063	0.5726	0.001	0.0019	0.9971	0.00199	0.00018	0.99783
1173			0.2226	0.2092	0.5682	0.0009	0.0023	0.9968	0.00461	0.0007	0.99469
1223			0.2221	0.1795	0.5985	0.0033	0.0094	0.9873	0.03945	0.0024	0.95815

<sup>a</sup>  $u(T) = \pm 2 K$ ,  $u(x) = u(y) = \pm 0.003$ .





**Figure 2.** Comparison of the experimental data (symbols) [14] of activities with the calculated values from the Wilson equation (solid lines): (a) Pb–Sn alloy system at 1050 K; (b) Pb–Sb alloy system at 905 K; and (c) Sn–Sb alloy system at 905 K

results of the binary system, the prediction accuracy of the Wilson equation is high. Furthermore, a good application effect of the Wilson equation has been demonstrated for predicting the thermodynamic properties of ternary Pb-based alloys [15].

#### 4.4. VLE of Pb–Sn–Sb alloy system

The VLE was calculated using an iterative process of estimating a temperature and calculating the partial pressure of the components from the activity coefficients and the vapor pressures of the pure liquids at a given temperature, until the sum of the partial pressures  $P$  equals the total pressure initially set. The steps required to calculate the VLE are as follows:

1. Calculate the saturation temperature  $T_{i,b}$  for component  $i$  from Eq. (8).
2. Set a series of  $x_i$  and calculate the approximate temperature  $T$  from  $T = \sum_{i=1}^c x_i T_{i,b}$  and consider that  $\sum_{i=1}^c x_i = 1$ .
3. Calculate  $P_i^s$  from Eq. (8).

4. Calculate the activity coefficients  $\gamma_i$  from Eqs. (3) and (4) or Eq. (7).

5. Calculate  $K_i$  and  $y_i$  from Eq. (12).

6. Substitute  $y_i$  into Eq. (14). If the absolute difference is less than a tolerance value, then output  $T_b$ ,  $x_p$  and  $y_p$ ; otherwise, estimate a new value for  $T$  and return to step 3 until the sum of the partial pressures  $P$  equals the total pressure initially set (e.g., 2 Pa).

Fig. 3 shows the flowchart for calculating the VLE of the Pb–Sn–Sb alloy system.

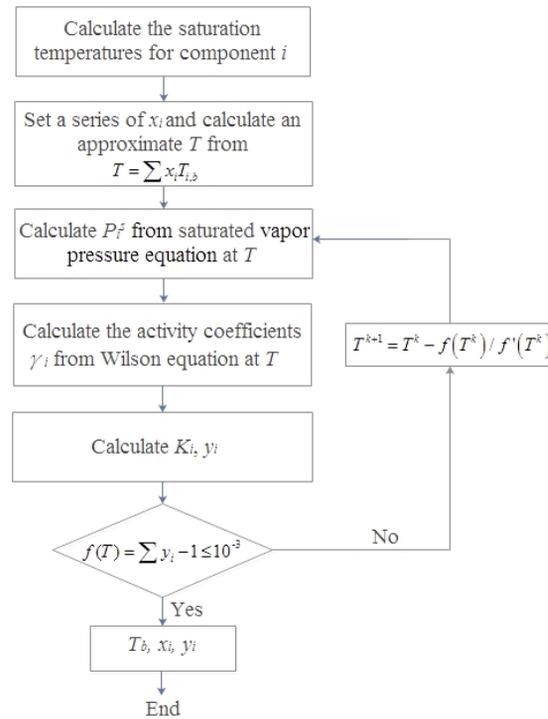
In our previous work, the VLE of Pb–Sn and Sb–Sn alloy systems were experimentally investigated and calculated using the molecular interaction volume model [5]. In this study, the VLE was calculated using the Wilson equation for Pb–Sn and Sb–Sn system at 2 Pa and the experimental data are shown in Fig. 4.

Fig. 4 shows that Pb and Sb can be concentrated in the vapor phase, and Sn can be concentrated and purified in the liquid phase by vacuum evaporation. The Sn content in the Pb or Sb was low enough for them to be considered as refined Pb and refined Sb. Fig. 4 suggests that the calculated values are more reliable than the experimental data for the liquid phase. This may be due to the following reasons. (1)

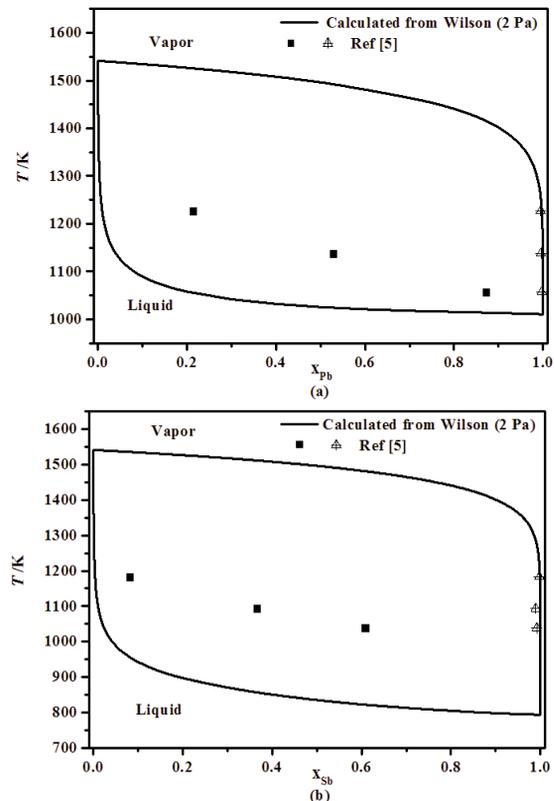
**Table 7.** The calculated activities of components of Pb-Sn-Sb alloy with Wilson equation in the temperature range of 1073-1273 K

$x_{Pb}$	$a_{Pb}$	$a_{Sn}$	$a_{Sb}$
$T = 1073 \text{ K}$			
$x_{Sn}/x_{Sb} = 1/3$			
0.1	0.112	0.164	0.626
0.2	0.222	0.161	0.539
0.3	0.331	0.158	0.456
0.4	0.436	0.153	0.378
0.5	0.538	0.147	0.305
0.6	0.637	0.139	0.236
0.7	0.731	0.129	0.172
0.8	0.822	0.113	0.112
0.9	0.908	0.079	0.058
$T = 1173 \text{ K}$			
$x_{Sn}/x_{Sb} = 1/3$			
0.1	0.112	0.17	0.629
0.2	0.223	0.166	0.543
0.3	0.33	0.162	0.46
0.4	0.436	0.156	0.382
0.5	0.537	0.149	0.309
0.6	0.635	0.141	0.24
0.7	0.729	0.128	0.175
0.8	0.82	0.11	0.115
0.9	0.908	0.079	0.058
$T = 1273 \text{ K}$			
$x_{Sn}/x_{Sb} = 1/3$			
0.1	0.112	0.174	0.632
0.2	0.223	0.17	0.546
0.3	0.33	0.165	0.464
0.4	0.435	0.159	0.386
0.5	0.536	0.151	0.313
0.6	0.634	0.141	0.243
0.7	0.728	0.128	0.179
0.8	0.818	0.108	0.117
0.9	0.907	0.074	0.059

The process did not sufficiently reach the thermodynamic equilibrium, and the determination of the equilibrium state could have had a large error. In other words, the Pb or Sb in the melt was not fully volatilized and remained in the liquid phase, resulting in a higher Pb and Sb content therein. (2) The system pressure was not constant and could have been larger



**Figure 3.** Flowchart for calculating the VLE of the Pb-Sn-Sb ternary alloy



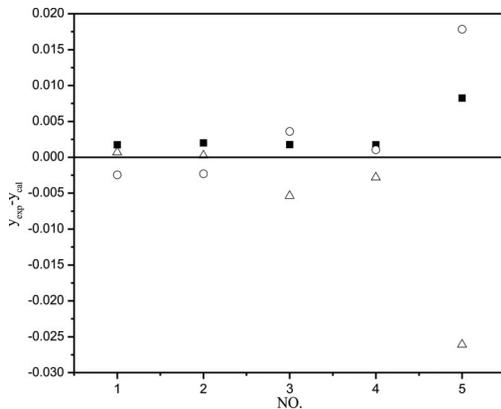
**Figure 4.** VLE phase diagram of alloy systems: experimental data (symbols) [5], calculated data from Wilson equation (solid lines). (a) Pb-Sn, (b) Sb-Sn



than 2 Pa.

As the experimental VLE data of the Pb–Sb alloy system determined using new method were not available in the literatures until now, only the activities of the components were predicted using the Wilson equation (Fig. 2). It can be seen from the calculations that the predicted value of the Wilson equation is very consistent with the data determined from experiments.

Following steps 1–6 as described previously, the VLE data of the Pb–Sn–Sb ternary system were obtained. The experimental VLE data and calculated vapor-phase compositions from the Wilson equation at 2 Pa are listed in Table 5. The calculated results from the Wilson equation agree well with the data determined from experiments. Meanwhile, under the condition of 2 Pa, the deviations between the calculated values from the Wilson equation and the experimental data in the vapor phase are shown in Fig. 5. The VLE data of the Pb–Sn–Sb ternary alloy calculated by this method are also in agreement with the data determined from experiments, although some deviations are observed especially at high temperatures.



**Figure 5.** Deviation in the calculations from the Wilson equation and experimental data in the vapor phase for the Pb (1) + Sn (2) + Sb (3) ternary system at 2 Pa. (Δ):  $y_{1exp} - y_{1cal}$ ; (■):  $y_{2exp} - y_{2cal}$ ; and (○):  $y_{3exp} - y_{3cal}$ .

The deviations mainly come from the following aspects: (1) the activity coefficient predictions of the constituent binary systems have an impact on the multicomponent systems, especially for asymmetric systems. (2) for multicomponent systems, only binary interactions between atoms are considered, and when Wilson equation is extended to multicomponent alloy systems, atomic interactions between the constituents are usually ignored. (3) the assumptions that were adopted in the process of VLE calculation resulted in certain errors. (4) there was large error in the calculated saturated vapor pressure of the pure components of the alloy. (5) the new experimental

conditions are still different from the ideal equilibrium state. So far, the above-mentioned factors are still inevitable.

## 5. Conclusions

Reliable VLE data of the Pb–Sn–Sb ternary alloy system were determined at 2 Pa using a new experimental method. The experimental results indicate that Sb can be satisfactorily removed from Pb–Sn–Sb alloy melt. The VLE data of the Pb–Sn, Sb–Sn, and Pb–Sn–Sb alloy systems were predicted based on the Wilson equation and the VLE theory. The good agreement between the experimental data and calculated values of VLE demonstrates that this calculation method is reliable for alloy systems, and it can serve as a convenient and effective method for calculating their VLE. Based on the VLE data, the separation conditions can be conveniently chosen and the product compositions can be quantitatively predicted.

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## IZOBARSKA RAVNOTEŽA PARA-TEČNOST U TROJNOM OLOVO-KALAJ-ANTIMON SISTEMU PRI 2 Pa

J. Xu <sup>a,b,c</sup>, J. Gao <sup>a,b,c</sup>, L. Kong <sup>a,b,c,d,\*</sup>, B. Xu <sup>a,b,c,d</sup>, B. Yang <sup>a,b,c,d,\*</sup>, D. Liu <sup>a,b,c</sup>

<sup>a\*</sup> Nacionalna inženjerska laboratorija vakuumske metalurgije, Univerzitet nauke i tehnologije u Kunmingu, Kunming, Kina

<sup>b\*</sup> Glavna laboratorija vakuumske metalurgije za obojene metale provincije Junan, Univerzitet nauke i tehnologije u Kunmingu, Kunming, Kina

<sup>c\*</sup> Fakultet za metalurško i energetska inženjerstvo, Univerzitet nauke i tehnologije u Kunmingu, Kunming, Kina

<sup>d\*</sup> Glavna državna laboratorija za iskorišćenje resursa kompleksnih obojenih metala korišćenjem čiste tehnologije provincije Junan, Kunming, Kina

### Apstrakt

U ovoj studiji eksperimentalni podaci ravnoteže para-tečnost u trojnom Pb-Sn-Sb sistemu legure određeni su korišćenjem nove eksperimentalne metode. Eksperimentalni VLE podaci prošli su test termodinamičke konzistentnosti (Van Ness test). Aktivnosti komponenti Pb-Sn-Sb trojne legure izračunate su pomoću Vilsonove jednačine kao i aktivnosti komponenti dvojnih legura ova tri konstituenta. Predviđene vrednosti su u skladu sa podacima utvrđenim iz eksperimenata, i prosečna relativna devijacija i prosečna standardna devijacija su bile manje od  $\pm 4.00\%$  i  $\pm 0.03$  za sve dvojne sastavne legure, pojedinačno, što pokazuje da je Vilsonova jednačina pouzdana za izračunavanje aktivnosti komponenti Pb-Sn-Sb trojne legure. VLE podaci dvojnih legura Pb-Sn i Sb-Sn, kao i Pb-Sn-Sb trojne legure izračunati su na osnovu VLE teorije i Vilsonove jednačine. Izračunati VLE podaci bili su u skladu sa podacima utvrđenim iz eksperimenata, što ukazuje da je ovaj metod pouzdan za izračunavanje VLE sistema legura. Predložena studija nudi validan metod za analizu sastava proizvoda koji zavise od temperature destilacije i pritiska sistema tokom vakuumske destilacije, što ima izuzetan značaj za eksperimentalni dizajn ovog procesa.

**Ključne reči:** Pb-Sn-Sblegura; Aktivnost; VLE; Vilsonova jednačina; Test termodinamičke konzistentnosti

