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## STUDIES ON THERMODYNAMICS OF As-Sn LIQUID SOLUTION

### BADANIA NAD TERMODYNAMIKĄ CIEKŁEGO ROZTWORU As-Sn

The activity of arsenic in liquid phase in the system As-Sn was studied by means of the isopiestic technique. The all-silica vertical cell sealed under vacuum was used in which two zones of temperature were maintained during the experiment. The arsenic vapour pressure in the system was set by solid arsenic in lower temperature zone, which temperature was varied in the range 585 – 790 K. The liquid As-Sn alloy was kept at the temperature 1173 – 1373 K. The equilibrium arsenic concentration in the alloy was determined from the mass balance. Next, the activities of arsenic in liquid solution referred to the pure liquid as a standard were calculated from the partial pressures of four arsenic species present in gas phase and the free energy change on melting. The experimental results regarding the excess free energy of liquid solution were fitted to the Redlich-Kister formula with three parameters. The activities of both components of liquid solutions determined in the present work are low i.e. the solution shows strong negative deviation from ideal behaviour. These results agree well with these of Kaczmarczyk and Sukiennik, obtained by means of static method. However, two earlier publications suggested much weaker negative deviation from ideal behaviour.

Zbadano aktywność arsenu w ciekłej fazie w układzie As-Sn za pomocą metody izopiesticznej. Zastosowano zamknięte pod próżnią naczynie pomiarowe ze szkła kwarcowego, w którym utrzymywano podczas eksperymentu dwie strefy temperatury. Ciśnienie par arsenu w układzie było zadawane przez stały arsen w strefie niższej temperatury, która była zmieniana w przedziale: 585 – 790 K. Temperatura ciekłego stopu As-Sn wynosiła 1173 – 1373 K. Równowagowe stężenie arsenu w ciekłym stopie określano z bilansu masy. Następnie obliczono aktywności arsenu w ciekłym roztworze względem czystego ciekłego arsenu jako stanu standardowego, posługując się wartościami ciśnień parcjalnych czterech rodzajów cząsteczek arsenu występujących w fazie gazowej oraz zmiany energii swobodnej topnienia. Wyznaczone z wyników pomiarów wartości nadmiarowej energii swobodnej dla ciekłego roztworu zostały opisane wzorem Redlicha-Kistera o trzech parametrach.

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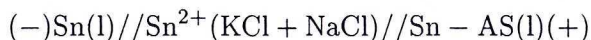
Wartości aktywności obu składników ciekłego roztworu wyznaczone w obecnej pracy są niskie, a zatem roztwór wykazuje silne ujemne odstępstwo od zachowania idealnego. Wyniki te pozostają w dobrej zgodności z wynikami Kaczmarczyka i Sukiennika, którzy zastosowali statyczną metodę pomiaru ciśnienia pary arsenu. Dwie wcześniejsze publikacje sugerują natomiast znacznie słabsze odstępstwo od zachowania idealnego.

## 1. Introduction

The phases containing arsenic, among them multicomponent liquid solutions are present at numerous stages of copper and lead metallurgy. Their thermodynamic characterisation is the starting point in the analysis of these processes, aimed at reduction of harmful environmental interactions and the increase in product purity. However, due to narrow range of temperatures and compositions accessible to experiment and serious difficulties resulting from high vapour pressure of hazardous arsenic, the data on arsenic systems are rather scarce.

The system tin-arsenic is interesting for two reasons: the activity of arsenic in liquid phase can be measured over considerably large temperature range (600–1400 K), and secondly the liquid phase can serve as the reference alloy in the gas-equilibration technique applied to such alloys, like As-Cu or As-Fe.

So far four reports on the experimental data on As-Sn liquid phase have been published. Predel and Emam [1] have used a version of isopiestic technique, in which As-Sn solution was equilibrated through the gas phase with the As-Bi liquid solution of known arsenic activity. Itoh and others [2] made use of concentration cell:



to determine the activity of tin in the solutions containing up to 40 at. pct. As over the temperature range 953–1181 K. Then the arsenic activity was calculated using Gibbs-Duhem integration. Their results suggest small negative deviation from the ideal solution behaviour. Blachnik and Schneider [3] measured the heat content of equimolar liquid phase the temperature range 896–1143 K. Fitzner and Kleppa [4] used the direct synthesis calorimeter to determine the enthalpy of formation of liquid solution at 987 K.

The aim of the present work is to determine the activity of arsenic in liquid phase at higher temperatures.

## 2. Experimental technique

The isopiestic method with all-silica cell was employed in the present work. The sample consisted of weighed amounts of high purity tin and arsenic was sealed in the cell under vacuum. The cell was vertically positioned in the furnace with two-zone winding, which resulted in the formation of two regions: higher

temperature where the liquid sample was placed and lower temperature with solid arsenic deposit (Fig. 1). The temperature of the liquid sample and arsenic source was measured by means of PtRh10/Pt thermocouples with  $\pm 1$  K precision. Thermocouple junctions were in a direct contact with silica cell walls. The gas phase in the system contained merely arsenic, its pressure was set by the temperature of upper compartment of the cell ( $T_2$ ), in the range 585 – 790 K. The temperature of liquid alloy ( $T_1$ ) was set in the range 1173 – 1373 K. The equilibration of one sample at given temperature regime took 24 h. Then the cell was removed and quenched in liquid nitrogen within few seconds. The arsenic concentration in the As-Sn alloy was determined from the mass balance.

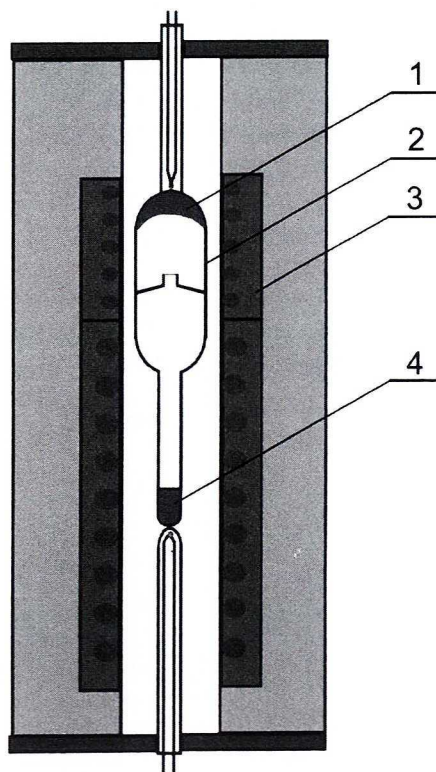


Fig. 1. Equipment for the isopiestic measurements of arsenic activity in liquid solution As-Sn: 1. Solid As condensate; 2. Silica glass cell, 3. Furnace with two-zone winding; 4. Liquid alloy

Next the values of arsenic activities resulting from the given pairs of temperatures  $T_1$  and  $T_2$  were calculated. The calculation employed the equilibrium constants between the arsenic associates in the gas phase ( $\text{As}$ ,  $\text{As}_2$ ,  $\text{As}_3$  and  $\text{As}_4$ ), which were deduced by Wypartowicz [5] on the basis of Gocken's compilation [6], which also reported the free energy of melting for pure arsenic as a function of temperature.

The activity of arsenic in the liquid solution referred to pure liquid arsenic was obtained as:

$$a_{\text{As}} = \frac{P_{\text{As}}(T_1)}{P_{\text{As}}^0(T_1)} = \left[ \frac{P_{\text{As}_2}(T_1)}{P_{\text{As}_2}^0(T_1)} \right]^{1/2} = \left[ \frac{P_{\text{As}_3}(T_1)}{P_{\text{As}_3}^0(T_1)} \right]^{1/3} = \left[ \frac{P_{\text{As}_4}(T_1)}{P_{\text{As}_4}^0(T_1)} \right]^{1/4}, \quad (1)$$

where:  $P_{\text{As}_i}(T_1)$  ( $i = 1, \dots, 4$ ) denotes the pressure of arsenic in equilibrium with the liquid solution, while  $P_{\text{As}_i}^0(T_1)$  — in equilibrium with the pure liquid arsenic.

### 3. Results and discussion

The results of the experiments are presented in Table 1, where the measured values of temperature of arsenic source and the liquid alloy as well as equilibrium arsenic concentrations in the alloys were given together with calculated activities and activity coefficients of arsenic. The whole set of experimental results from isopiestic measurements is presented in Fig. 2.

TABLE 1  
Results of the measurements of arsenic activity in liquid Sn-As solutions by means of isopiestic technique

No	$T_1$ [K]	$T_2$ [K]	$a_{\text{As}}$	$X_{\text{As}}$	$\gamma_{\text{As}}$	$\ln \gamma_{\text{As}}$
1	1173	585	0.0080	0.161	0.0497	-3.002
2	1173	599	0.0114	0.177	0.0645	-2.741
3	1173	703	0.0816	0.354	0.2305	-1.467
4	1173	772	0.1671	0.426	0.3922	-0.936
5	1173	664	0.0455	0.296	0.1537	-1.873
6	1173	663	0.0447	0.271	0.1649	-1.802
7	1173	770	0.1642	0.426	0.3854	-0.953
8	1173	614	0.0164	0.191	0.0859	-2.455
9	1173	654	0.0380	0.271	0.1402	-1.965
10	1173	725	0.1061	0.359	0.2955	-1.219
11	1173	638	0.0278	0.229	0.1214	-2.109
12	1273	723	0.0779	0.342	0.2278	-1.479
13	1273	791	0.1658	0.432	0.3838	-0.958
14	1373	790	0.1329	0.398	0.3339	-1.097
15	1373	650	0.0143	0.156	0.0917	-2.390
16	1373	692	0.0326	0.242	0.1347	-2.005
17	1373	626	0.0084	0.119	0.0706	-2.651

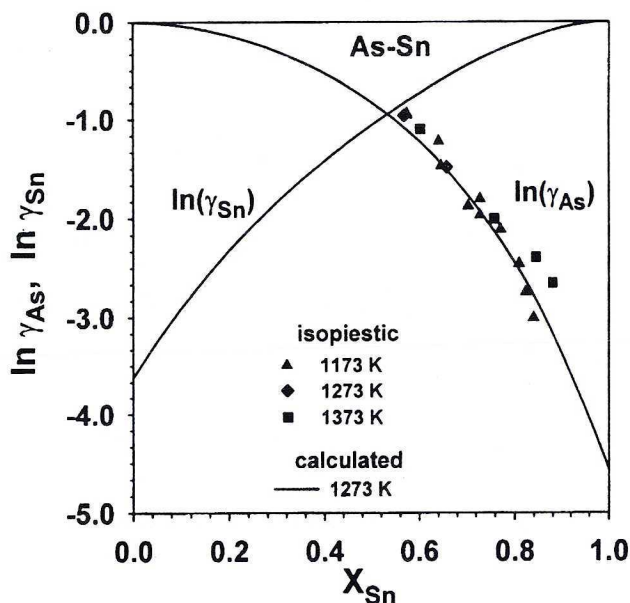


Fig. 2. Experimental results of isopiestic technique and analytical description: Redlich-Kister formula with parameters (3)–(5)

The excess Gibbs energy of liquid As-Sn solution was described with the Redlich-Kister formula (2), taking into account the experimental results from the present work and the values of enthalpy of the liquid phase from the experimental work of Fitzner and Kleppa [3] and from evaluation of Gokcen [7].

$${}^E G_m = X_A \cdot X_B \cdot \sum_{\nu=1}^n {}^{\nu} L_{ij} \cdot (X_A - X_B)^{\nu}. \quad (2)$$

The parameters in Redlich-Kister formula are as follows:

$$L_{As,Sn}^{0,liq.} = +169697.957 - 1480.88221 \cdot T + 184.122817 \cdot T \cdot \ln T, \quad (3)$$

$$L_{As,Sn}^{1,liq.} = +4211.25128 + 0.57733368 \cdot T, \quad (4)$$

$$L_{As,Sn}^{2,liq.} = -3509.50547. \quad (5)$$

The curves representing the activity coefficients of components of liquid solution, presented in Figs. 2 and 3 were calculated from the above equations (2)–(5).

As it may be seen from Fig. 3, the results regarding the activities of components obtained in the present work strongly differ from these obtained in the previous publications, which suggest rather small deviations from ideal solution behaviour. This difference may be partly attributed to the specific features of different experimental techniques used. If both As-Bi and As-Sn liquid solutions studied by Predel and Emam [1] show small negative deviations from ideal

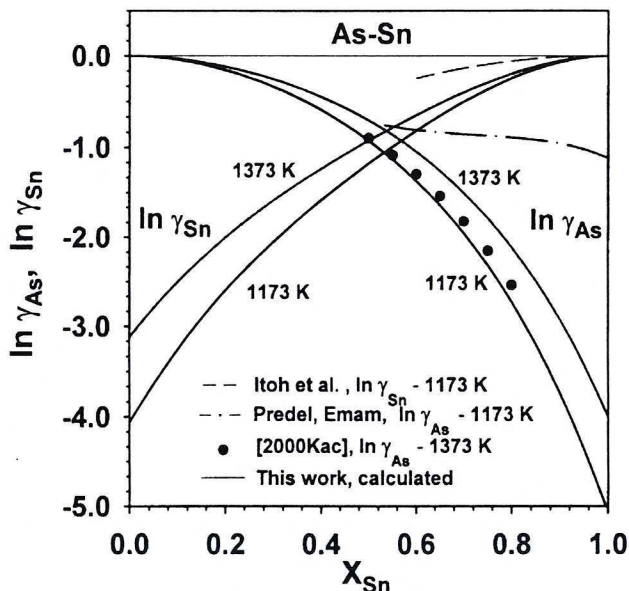


Fig. 3. Activity coefficients of tin and arsenic in liquid Sn-As solutions. Comparison of the results of the present work with the data of [1], [2] and [15]

behaviour, then the precision of isopiestic method is low. Besides, they calculated the arsenic activities in Bi-As system from Hultgren's [8] data on the equilibrium constants regarding various arsenic particles in gas phase. These considerably differ from the data reported by Gokcen [6], and the difference in values of the activity coefficient of arsenic higher than one order of magnitude may be expected [5].

The accuracy of the data regarding the composition of vapour phase of arsenic as well as the free energy change on melting appears to be the crucial point in the studies of numerous liquid phases containing arsenic, where the vapour pressure methods are mainly applied. The partial pressures of arsenic species were established by Gokcen [6] on the ground of spectrometric experiments and direct pressure measurements [9]–[12], but they still need experimental verification. The authors of the database regarding thermodynamics of III–V group compounds [13] accepted the set of data, which yield partial pressures similar to these of Gokcen.

In the isopiestic as well as static techniques the liquid alloy is equilibrated with solid arsenic. Thus, the temperature dependence of the free energy of melting for arsenic is necessary to consider pure liquid arsenic as a standard for activity. However, the relation commonly used does not come from the experiment, but it is obtained from the simple correlation of  $\Delta C_p$  with a group number in periodic system ( $\Delta C_p$  of arsenic is taken as an average between these for germanium and selenium) [14].

In the case of electrochemical cell [2] one can hardly avoid oxidation of tin, the valence of which should be kept at the lowest possible level 2+. Otherwise, the emf values obtained are too low, which results in weaker negative deviation from the ideal behaviour. Moreover, the activities of arsenic were calculated from the activities of tin, what might introduce additional error.

Recently Kaczmarczyk and Sukiennik [15] applied the static method to measure the equilibrium vapour pressures of pure arsenic over the temperature range 700–872 K and arsenic pressure in equilibrium with arsenic-tin solutions containing 22–45 at pct of arsenic.

Their results, presented in Fig. 3, are in general agreement in comparison to ours, and they show only slightly higher negative deviation of ideal behaviour in As-Sn solution.

#### 4. Conclusions

1. The isopiestic method with silica vertical cell was applied to measure the composition of liquid Sn-As alloy in equilibrium with arsenic vapour, which was generated by solid arsenic at chosen temperature.

2. The activity coefficients of arsenic referred to pure liquid As as a standard state were deduced from the partial pressures of gaseous arsenic species and the free energy of melting of arsenic.

3. The activities of both components of liquid solutions determined in the present work are low i.e. the solution shows strong negative deviation from ideal behaviour. These results and the results of the study carried out by means of static method are in good agreement. However, two earlier publications reported much weaker negative deviation from ideal behaviour.

4. The choice of thermochemical data for pure arsenic strongly affects the interpretation of experimental data and may create the difference in the results from different methods.

These data require stronger experimental background. Further studies on thermodynamic properties of As-Sn system are also needed, including assessment of the phase diagram.

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