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Thermodynamics of formation and evaporation of lead-tin alloys

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ABSTRACT

Only a few works have been devoted to thermodynamic studies of the lead-tin system by methods including the volatile components evaporation process. When the binary system is separated into metals by distillation, the volatile component is removed from the alloy and the low-volatile component accumulates in the bottom products, that is, there are alloy composition changes over the entire concentration range. It is necessary to know the boundaries position of the melt and vapor coexistence fields on the state diagram, especially for solutions beneficiated with non-volatile metal to assess the quality of the vapor phase by the content of the low-volatile component. In this regard, the study has been completed with the purpose to clarify the values of the thermodynamic functions of the formation and evaporation of lead-tin melts required to calculate the boundaries of the liquid and vapor coexistence fields on the state diagram that enables us to judge the amount of a low-volatile component in the vapor phase under equilibrium conditions. The thermodynamic activity of lead was calculated, as well as the numerical integration of the Gibbs-Duhem equation using the substitution proposed by Darken is the thermodynamic activity and pressure of saturated tin vapor Based on the values of the saturated lead vapor pressure, determined by the boiling point method (isothermal version) for alloys predominantly of the lead edge of the phase diagram. The thermodynamic constants thus obtained will add to the base of physicochemical data and will be used to calculate the boundaries of the vapor-liquid equilibrium fields on the phase diagram, allowing to determine the possibility and completeness of the distillation separation of metals.

Keywords: Lead, tin, alloy, vapor pressure, thermodynamics, formation, mixing, evaporation, partial and integral quantities, entropy, enthalpy.

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Introduction

The development of a vacuum-thermal technology for tin refining from lead impurities with subsequent industrial development [1-3] led to the emergence of a significant number of studies in the field of physical chemistry of lead-tin melts. Most of them are devoted to the study of thermodynamics and physical properties of the condensed phase. The authors [4-11] have determined the thermodynamic functions of formation by various methods, [12-14] - the structure of melts and the associated effects of homogeneity and stratification.

Only a few papers are devoted to thermodynamic studies of the lead-tin system by methods including the process of evaporation of volatiles. The authors of the [4] paper conducted a

study of the thermodynamic properties of the lead-tin system in the entire range of alloy compositions at 730-790 °C based on the lead vapor pressure determined by the modified Knudsen method with the continuous weighing of the effusion cell. At the same time, the values of the lead activity were determined, and based on their thermodynamic functions of the components and solution, a conclusion about the molecular inhomogeneity in liquid alloys was made.

A physicochemical study of the evaporation process of the equimolar lead-tin alloy at 1,100 °C was performed in the [15] paper. The authors studied the dependence of the composition of the condensate on the evaporation time and found that the composition of the vapor above the solution and, therefore, the composition of the condensate is determined by the composition of the surface layer of the melt, which, in turn, depends on the atoms movement speed of the highly volatile component in the liquid alloy.

The thermodynamic study based on the values of the lead vapor pressure determined at 873-1,073 K by the method of evaporation from an open surface, was published in [16] paper. A positive deviation of the system from the law of ideal solutions was found, decreasing to the insignificant one with the temperature rising.

The values of the excess functions of the lead-tin system at 1,050 K, based on which it is possible to calculate the value of the saturated vapor pressure of the melt components under the assumption that the indicated constants are independent of temperature, are given in [17, 18].

Based on the results of all studies, as well as the refined values of the saturated vapor pressure of elemental tin and lead [19], it can be concluded that there are no technological difficulties in the distillation separation of alloys into separate metals.

However, during the development of technology to separate the multicomponent alloys, for example, metal concentrates from waste processing plants, during the distillation excreting of volatile metals (zinc, cadmium, lead) and the concentration of low volatile metals (copper, aluminum tin) in the bottoms, a noticeable amount of tin was found in the lead condensate.

When the binary system is separated into metals by distillation, the volatile component is removed from the alloy and the low-volatile accumulates in the bottom residue, that is, the availability of alloy composition changes over the entire concentration range. In order to assess the quality of the vapor phase by the content of the low-volatile component, it is necessary to know the position of the boundaries of the fields of coexistence of the melt and vapor on the phase diagram, especially for solutions enriched by non-volatile metal.

In [20] paper, based on the results of the study [16] at 873-1,073 K (600-800 °C), a calculation was performed and the phase diagram of the lead-tin system with fields of vapor-liquid equilibrium at atmospheric pressure, 100 and 10 Pa, does not correspond, however, to the cause of the increased tin content in the condensate.

The processes of distillation separation of alloys and refining of metals of the specified system occur at temperatures of 1,000-1,350 °C (1,273-1,623 K) and extrapolation of the vapor pressure values to the indicated temperatures could lead to inaccuracies in the calculations.

In this regard, a study aimed at clarifying the values of the thermodynamic functions of the formation and evaporation of lead-tin melts, which are necessary to calculate the boundaries of the fields of coexistence of liquid and vapor on the phase diagram, which is indicative of the amount of a low-volatile component in the vapor phase under equilibrium conditions.

Study object, research methods, and calculation methods

As an object of research, we used lead-tin alloys of predominantly lead edge of the phase diagram with contents of 93.93, 88.42, 83.08, 70.59, 50.65, and 30.87 at. % (96.43, 93.02, 89.55, 80.73, 64.18 and 43.80 wt. %) Pb, and the rest is tin.

The alloys were prepared by fusing metals in evacuated quartz ampoules with heating at 100 °C above the liquidus temperature, holding at this temperature for 2 hours and stirring with shaking, followed by quenching in water. Alloys were prepared using lead, 99.999 wt. % and tin, 99.99 wt. % of the principal element.

The partial thermodynamic mixing functions was the basis to find the activity value, defined as the ratio of the partial pressure of the component over the solution to the value of the saturated vapor pressure over the elemental metal: $a_i = \overline{p}_i / p_i^o$

where: a_i is thermodynamic activity; $\overline{p}_i$ is the partial pressure of steam; *i* is component; p_i^o is the saturated vapor pressure of the same component over the elemental metal.

The boiling point method (isothermal version) described in detail earlier [21] was used to determine the value of the saturated vapor pressure, the method is based on the significant increase in the evaporation rate when the external pressure and the saturated vapor pressure of the test substance are equal with a decrease in pressure above the melt at a given temperature.

Since the vapor pressure of elemental lead at temperatures of 1,200 – 1,300 °C (1,473 – 1,573 K) according to [19] is (3.5 - 6.5) 10^4 times higher than the tin vapor pressure, it was considered that the total vapor pressure determined by the boiling point method corresponds to the saturated lead vapor pressure. Argon was used as a volume filler gas in the boiling point method.

The partial free energy of alloy formation was calculated as $\Delta\bar{G}_i^{mix} = RT\ln a_i$;

partial entropy of mixing – $\left(\partial\Delta\bar{G}_i^{mix}/\partial T\right)_P = -\Delta\bar{S}_i^{mix}$;

partial enthalpy – $\Delta\bar{H}_i^{mix} = \Delta\bar{G}_i^{mix} + T\cdot\Delta\bar{S}_i^{mix}$.

From now on: $\Delta\bar{G}_i^{mix}$, $\Delta\bar{S}_i^{mix}$ $\Delta\bar{H}_i^{mix}$ - partial free energy, partial entropy, and partial enthalpy of mixing is component, respectively. From now on, T is the temperature, K.

Integral mixing functions are calculated as the sum of the fractions of partial values.

Tin activity was found from the expression $a_{Sn} = \gamma_{Sn}\cdot x_{Sn}$, tin activity coefficient (γ_{Sn}) by numerical integration of the Gibbs-Duhem equation using the auxiliary function proposed by Darken [22]:

$$\ln\gamma_{Sn} = -\frac{\ln\gamma_{Pb}\cdot x_{Pb}\cdot x_{Sn}}{x_{Sn}^2} + \int_{x_{Pb}=0}^{x_{Pb}}\frac{\ln\gamma_{Pb}}{(1-x_{Pb})^2}dx_{Pb}$$

and then the partial functions of tin mixing during alloy formation.

The partial free energy of evaporation is determined based on the values of the partial pressure of the saturated vapor of the melt components as:

$\Delta\bar{G}_i^{evap} = -RT\ln\bar{p}_i[atm]$, and entropy and enthalpy are similar to those in the formation of an alloy.

The temperature dependences of the activity (a_{Pb}) and the partial pressure of lead vapor ($\bar{p}_{Pb}$) for each of the compositions were described by Arrhenius type equations. Then by approximating the dependence of the coefficients in the equations on the concentration of lead (x_{Pb}) in the alloy, we obtained the temperature-concentration dependence of the activity (a_{Sn}) and the partial pressure of tin vapor ($\bar{p}_{Sn}$).

The error in determining the thermodynamic constants is taken to be equal to the error in determining the values of the saturated lead vapor pressure, as the sum of the errors of independent measurements, %: temperature - 1; weighing - 0.1; pressure 0.5; approximation of experimental data - 6.18, equal to 7.78.

Results and its discussion

The coefficients of the equations of the dependence of the saturated lead vapor pressure on temperature for each of the alloy compositions are given in Table 1, for each of the alloy compositions are given in Table 1, where the vapor pressure of the lead itself was determined by us earlier [23].

Table 1 - Coefficients of the equation of the dependence of the partial lead vapor pressure on temperature

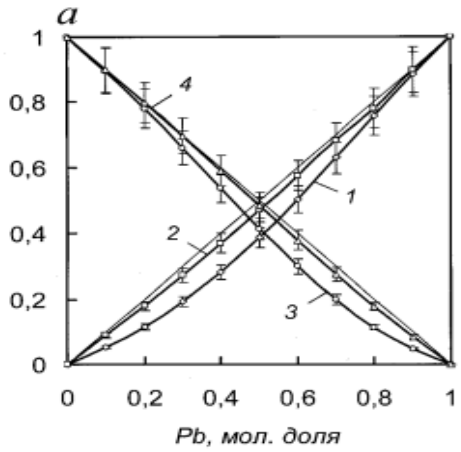
Lead content in the alloy:		$\ln\bar{p}_{Pb}[Па] = \frac{A}{T} + B$	
atom. %	mass. %	A	B
100	100	–22165	22.521
93.93	96.43	–22216	22.490
88.42	93.02	–22291	22.475
83.08	89.55	–22388	22.469
70.59	80.73	–22705	22.493
50.65	64.18	–23458	22.606
30.87	43.80	–24476	22.725

The partial pressure of saturated lead vapor for the entire concentration range of the Pb - Sn system is represented by the expression:

$$\ln\bar{p}_{Pb}[Па] = (-708x_{Pb}^3 - 2368x_{Pb}^2 + 743x_{Pb} - 26525)\cdot T^{-1} + 0{,}197\,x_{Pb}^3 + 1{,}884\,x_{Pb}^2 - 4{,}737\,x_{Pb} + 25{,}177 + \ln x_{Pb},$$

tin corresponds to the dependence:

$$\ln\bar{p}_{Sn}[Па] = (708x_{Sn}^3 - 5554x_{Sn}^2 + 8408x_{Sn} - 39759 + 576\ln x_{Sn})\cdot T^{-1} - 0{,}197\,x_{Sn}^3 + 2{,}77\,x_{Sn}^2 - 4{,}572\,x_{Sn} + 26{,}085 + 0{,}622\ln x_{Sn}$$



1, 3 – 1,273; 2, 4 – 1,573.

Figure 1 - Isoactivities of lead (1, 2) and tin (3, 4) at temperature, K

The isoactivities of lead and tin at the boundary temperatures of processing polymetallic raw materials [1,000 – 1,300 °C (1,273 – 1,573 K)] are shown in Figure 1. The system, in contrast to the research data [16], is characterized by a slight negative deviation from the law of ideal solutions, which indicates some interaction between dissimilar metals in liquid form. The dependence of the activity coefficients of lead and tin depends little on temperature, and at 1,573 K (1,300 °C) the system is close to ideal.

The concentration dependences of the partial and integral entropies and enthalpies of mixing of lead-tin solutions are shown in Figures 2 and 3.

The integral entropy of mixing in the lead-tin system differs significantly from that for an ideal system, both in magnitude and in sign. This indicates a negative value of the excess function. The enthalpy of mixing is negative in the entire range of melt concentrations, therefore, the solutions are formatted exothermic, with the release of heat.

The integral entropy of alloy formation is approximated by the expression:

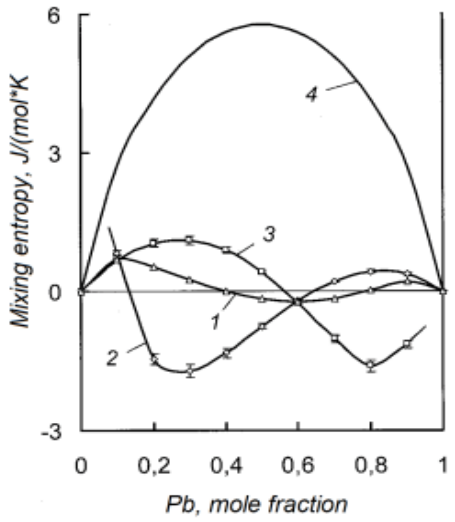
$$\Delta S^{mix}_{Pb-Sn} = -32{,}135x^4_{Pb} + 69{,}807x^3_{Pb} -$$

$$- 47{,}627\,x^2_{Pb} + 9{,}955 \quad \text{J}/(\text{mol}\cdot\text{K}),$$

enthalpy –

$$\Delta H^{mix}_{Pb-Sn} = 9{,}464x^3_{Pb} + 25{,}607x^2_{Pb} - 35{,}071, \quad \text{kJ/mol}$$

The values of the thermodynamic functions of evaporation of lead-tin system alloys are summarized in Table 2.



1 – integral; 2 – lead; 3 – tin;
4 – for an ideal system

Figure 2 – Integral (1, 4) and partial (2, 3) entropies of mixing in the lead-tin system.

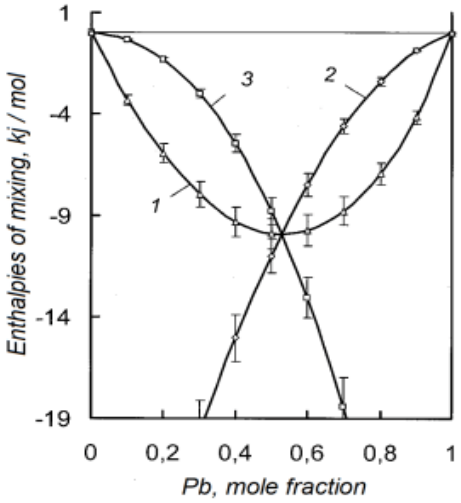


Figure 3 – Integral (1) and partial (2,3) enthalpies of mixing in the lead-tin system

The partial entropies of lead and tin evaporation constant within the experimental error in the entire range of alloy concentrations. The partial enthalpy of metals evaporation is expected to increase as the concentration of each of the constituents in the system decreases. Integral functions are described by concentration equations:

$$\Delta S^{evap}_{Pb-Sn} = -7{,}215x^3_{Pb} + 10{,}499x^2_{Pb} - 16{,}549x_{Pb} + 104{,}43$$

J / (mol K) and

$$\Delta H^{evap}_{Pb-Sn} = -38{,}599x^2_{Pb} - 77{,}535x_{Pb} + 300{,}95 \text{ kJ/mol.}$$

The values of saturated vapor pressure and thermodynamic constants obtained in this way are used to construct a complete phase diagram,

Table 2 – Partial and integral entropies and enthalpies of formation and evaporation of lead-tin alloys

Alloy composition, mol. share.		$\Delta\bar{S}_{Pb}^{evap}$, J/(mol K)	$\Delta\bar{S}_{Sn}^{evap}$, J/(mol K)	ΔS_{Pb-Sn}^{evap}, J/(mol K)	$\Delta\bar{H}_{Pb}^{evap}$, kJ/mol	$\Delta\bar{H}_{Sn}^{evap}$, kJ/mol	ΔH_{Pb-Sn}^{evap}, kJ/mol
Pb	**Sn**						
1.0	0	91.42±7.11	-	91.42±7.11	184.29±14.34	-	184.29±14.34
0.9	0.1	91.06±7.08	105.57±8.21	92.51±7.20	185.13±14.40	335.06±26.07	200.12±15.57
0.8	0.2	91.00±7.08	106.03±8.25	94.00±7.31	186.69±14.52	326.09±25.37	214.57±16.69
0.7	0.3	91.20±7.10	105.45±8.20	95.48±7.42	188.93±14.70	319.36±24.85	228.06±17.74
0.6	0.4	91.61±7.13	104.69±8.14	96.84±7.53	191.80±14.92	314.00±24.43	240.68±18.72
0.5	0.5	92.16±7.17	104.01±8.09	98.09±7.63	195.28±15.19	309.74±24.10	252.51±19.64
0.4	0.6	92.74±7.22	103.54±8.06	99.22±7.72	199.33±15.51	306.42±23.84	263.58±20.51
0.3	0.7	93.13±7.25	103.32±8.04	100.26±7.80	203.92±15.86	303.95±23.65	273.94±21.31
0.2	0.8	92.88±7.23	103.39±8.04	101.29±7.88	209.00±16.26	302.25±23.52	283.60±22.06
0.1	0.9	90.58±7.05	103.75±8.07	102.43±7.97	214.56±16.69	301.27±23.44	292.60±22.76
0	1.0	-	104.43±8.12	104.43±8.12	-	300.95±23.44	300.95±23.44

including the fields of coexistence of melt and vapor at atmospheric pressure and in a vacuum.

The partial entropies of evaporation of lead and tin are constant within the experimental error in the entire range of alloy concentrations.

The partial enthalpy of vaporization of metals is expected to increase as the concentration of each of the components in the system decreases.

Integral functions are described by concentration equations:

$$\Delta S_{Pb-Sn}^{evap} = -7,215x_{Pb}^3 + 10,499x_{Pb}^2 - 16,549x_{Pb} + 104,43 \quad \text{J / (mol K) and}$$

$$\Delta H_{Pb-Sn}^{evap} = -38,599x_{Pb}^2 - 77,535x_{Pb} + 300,95 \quad \text{kJ/mol.}$$

Conclusions. As a result of the study conducted by the boiling point method at processing temperatures of metal concentrates from garbage processing, the values of the saturated vapor pressure of lead and its thermodynamic activity were determined, based on which the partial and integral entropies and enthalpies of formation of evaporation of liquid lead-tin alloys were calculated using known methods.

The values of saturated vapor pressure and thermodynamic constants produced in this way are used to construct a complete phase diagram, including the fields of coexistence of melt and vapor at atmospheric pressure and in a vacuum.

Similar works [24-28], performed at the Institute earlier, showed the practical significance and technological relevance.

Conflicts of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Қорғасын-қалайы қорытпаларының түзілуі мен булануының термодинамикасы

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ТҮЙІНДЕМЕ

Құрамындағы ұшатын құраушыларының (компоненттерінің) булану процесінен тұратын әдістермен қорғасын-қалайы жүйесін термодинамикалық зерттеулерге бірнеше жұмыстар ғана арналған. Қос жүйені дистилляция әдісімен металдарға бөлгенде, ұшатын компонент қорытпадан шығарылады және аз ұшатын компонент төменгі қалдықта жиналады, яғни қорытпа құрамы бүкіл концентрация ауқымында өзгереді. Бу фазасының сапасын аз ұшқыш компоненттің мөлшері бойынша бағалау үшін балқыманың және будың қатар жүретін өрістерінің күй диаграммасындағы шекаралық орнын, әсіресе ұшпайтын металдармен байытылмаған ерітінділер үшін орналасуын, білу қажет. Осыған байланысты қорғасын-қалайы балқымаларының пайда болуы мен булануының термодинамикалық функцияларының мәндерін нақтылау мақсатында зерттеу жүргізілді, олар күй диаграммасындағы сұйықтық пен будың бірге болатын жағдайдағы өрістерінің шекараларын есептеу үшін қажет тепе-теңдік жағдайында бу фазасындағы аз ұшқыш компоненттің мөлшерін анықтауға мүмкіндік береді. Күй диаграммасының негізінен қорғасын орналасқан жағындағы қорытпалар үшін қайнау температурасы әдісімен (изотермиялық нұсқа) анықталған қорғасынның қаныққан бу қысымының мәндеріне сүйене отырып, қорғасынның термодинамикалық белсенділігі есептелді және Даркен ұсынған алмастыруды қолданатын Гиббс-Дюхем теңдеуін сандық интегралдау арқылы қалайының термодинамикалық белсенділігі мен қаныққан бу қысымы есептелді. Осылайша алынған термодинамикалық тұрақтылар физикалық-химиялық мәліметтерді толықтырады және фазалық диаграмма бойынша бу-сұйықтық тепе-теңдік өрістерінің шекараларын есептеу үшін пайдаланылатын болады, бұл металдарды дистилляциялық бөлудің мүмкіндіктері мен толықтығын анықтауға мүмкіндік береді.

Түйінді сөздер: Қорғасын, қалайы, қорытпа, бу қысымы, термодинамика, пайда болу, араласу, булану, парциальді және интегралды шамалары, энтропия, энтальпия.

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Термодинамика образования и испарения свинцово-оловянных сплавов

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АННОТАЦИЯ

Термодинамическим исследованиям системы свинец – олово методами, включающими процесс испарения летучих составляющих, посвящено лишь несколько работ. При разделении двойной системы на металлы дистилляцией происходит удаление летучего компонента из сплава и накопление мало летучего в кубовом остатке, то есть имеет место изменение состава сплава во всем интервале концентраций. Для оценки качества паровой фазы по содержанию мало летучего компонента необходимо знание положения границ полей сосуществования расплава и пара на диаграмме состояния, особенно для растворов, обогащенных не летучим металлом. В этой связи, выполнено исследование, имеющее целью уточнение величин термодинамических функций образования и испарения свинцово-оловянных расплавов, необходимых для расчета границ полей сосуществования жидкости и пара на диаграмме состояния, позволяющих судить о количестве мало летучего компонента в паровой фазе в равновесных условиях. На основании величин давления насыщенного пара свинца, определенного методом точек кипения

	(изотермический вариант) для сплавов преимущественно свинцового края диаграммы состояния, рассчитана термодинамическая активность свинца, а также численным интегрированием уравнения Гиббса-Дюгема с использованием подстановки, предложенной Даркеном, - термодинамическая активность и давление насыщенного пара олова. Полученные, таким образом, термодинамические константы пополнят базу физико-химических данных и будут использованы для расчета границ полей парожидкостного равновесия на диаграмме состояния, позволяющих определить возможность и полноту дистилляционного разделения металлов.
	Ключевые слова: Свинец, олово, сплав, давление пара, термодинамика, образование, смешение, испарение, парциальные и интегральные величины, энтропия, энтальпия.
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