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Metallurgy

Thermodynamics of antimony—selenium alloys formation and evaporation

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ABSTRACT

The thermodynamic functions of alloy formation and evaporation were considered for two particular systems — Sb – Sb_2Se_3 and Sb_2Se_3 – Se in connection with the presence of congruently melting compound Sb_2Se_3 in the antimony—selenium system. The calculations are based on the partial vapor pressure values of the components forming the particular systems. The thermodynamic activity of antimony selenide and selenium as the most volatile components in the systems was calculated based on the saturated vapor pressure values of antimony selenide over the Sb – Sb_2Se_3 and selenium melts over Sb_2Se_3 – Se liquid alloys determined by the boiling point method (isothermal variant). Similar functions of the low volatile components in the above systems: Sb in the first system and Sb_2Se_3 in the latter one was calculated by numerical integration of the Gibbs—Duhem equation using the substitution proposed by Darken. The partial pressures of antimony selenide and antimony over Sb – Sb_2Se_3 and Sb_2Se_3 – Se melts were approximated by temperature—concentration relationships. The system is distinguished with a positive deviation from ideality due to the presence of a delamination region in the first system. The partial and integral entropies and enthalpies of the formation of liquid alloys were calculated based on the values of component activities found as the ratio of the partial vapor pressure of an element or compound above the solution to the saturated vapor pressure of a pure element or compound. The partial and integral functions of alloy formation are presented in the form of graphical dependences on the selenium amount in the melt. The obtained thermodynamic constants will replenish the physical and chemical data base and will be used to calculate the boundaries of the vapor— liquid equilibrium fields on the diagram of state, allowing to determine the possibility and completeness of distillation separation of molten systems.

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

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Introduction

The development of vacuum — the thermal method intended to process polymetallic matte from lead and antimony smelters where this matte is based on copper (Cu_2S) and iron (FeS) sulfides and contains rare elements — cadmium, antimony, arsenic, indium, as well as selenium and tellurium isomorphous substituting sulfur in sulfides, contributed to the emergence of a sufficiently large number of thermodynamic studies devoted to the study of chalcogenides, including those of rare metals. One of them is antimony with the content that varies within 1% in lead production matte, and reaches several percent in antimony production matte.

Polymetallic matte — chalcogenide alloys as an intermediate product are produced during pyrometallurgical processing of sulfide concentrates at copper, lead, and antimony smelters. Copper (Cu_2S) and iron (FeS) sulfides form the basis of polymetallic matte from copper and lead smelters. Rare elements — cadmium, antimony, arsenic, indium, and others in the form of sulfides as well as selenium and tellurium, isomorphically replacing sulfur in sulfides are present in the matte besides the main components. Production and processing technologies for polymetallic matte are well enough studied and developed. However, works on their improvement are still underway due to the involvement in processing of new types of raw materials, including those poor in the main component [[1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11]].

Physical and chemical studies of liquid alloys of the antimony—selenium system were performed by a number of researchers. The authors [12] measured the kinematic viscosity and density of melts in the range of compositions 40 mol. % Sb_2Se_3 + 60 atm. % Se —20 mol. % Sb_2Se_3 + 80 atm. % Sb from melting temperature to 1100 — 1200 °C.

In [13], the crystallization kinetics for glassy alloys of $Se_{100-x}Sb_x$ ($2 \le x \le 10$), was studied by differential scanning calorimetry at different heating rates, the activation energy of the crystallization process, order parameter, rate constant, frequency factor was determined, and it was found that chalcogenide glasses had lower thermal stability while having a higher crystallization rate.

The antimony sesquiselenide behavior during vacuum sublimation was studied by the authors of [14] where the congruent nature of evaporation was noted.

The predominant presence of Sb, Se molecules, half the amount of Sb_2Se_2, three times the amount of Sb_2Se_3 and further, on a downward spiral Sb_3Se, Sb_4Se_4, Sb_4Se_3, Sb_3Se_3, Sb_3Se_2, Se_2, Sb_2Se_4 and very low amount of Sb_2Se_4 were found with mass spectrometric determination of the vapor composition over Sb_2Se_3 [[15], [16]].

The antimony sesquiselenide vapor pressure was determined using radioisotopes within 491—687 K (218— 414 °C) in studies [[17], and [18]]. The temperature dependence of the vapor pressure corresponded to the expression:

lg p [mmHg] = 8,7906 — 6432,3·T^{-1}.

The vapor pressure over liquid antimony selenide within 550—868 °C (823—1201 K) was determined with the static method with the use of a quartz membrane manometer in the study [19]. The results of the determinations are described with the equation:

lg p [mmHg] = (8.4130±0.0328) – (7,220.4 ± 250) T^{-1}.

Later, the authors determined vapor pressures and activities of selenium and antimony at 994 K (721 °C) within 60—100 at. % Selenium and hypothetically propagated it to the whole concentration interval [[20], [21]].

Some researchers performed thermodynamic studies to determine the heat capacity and mixing functions of liquid alloys in the antimony—salenium system [[22], [23], [24]].

The thermodynamics of Sb_2Se_3 was modeled and used in calculations of the antimony—selenium phase diagram together with the thermodynamic properties of the liquid phase obtained based on the associative model [25]. The calculated phase equilibrium lines coincided well with the experimental data.

It should be emphasized in the publications analyzed that the data on evaporation thermodynamics are insufficient, and the results of experimental determinations and calculations are inconsistent despite the presence of a sufficiently large number of works devoted to the study of antimony and selenium melts. So, in [[20], [21], and [25]] thermodynamic activity of selenium was found and calculated for a temperature of 994 K (721 °C) which is higher than the boiling point of solutions of this composition. Thermodynamic constants were not calculated.

Therefore, the authors performed studies aimed to obtain thermodynamic functions for the formation and evaporation of antimony—selenium alloys based on partial pressure values of the components constituting the system.

Experimental part

Antimony and selenium alloys with the contents of 14.82, 26.35, 35.27, 47.51, 60.00, 68.96, 75.37, 83.38, 91.30 at. % (10.14, 18.83, 26.11, 36.99, 49.31, 59.03, 66.49, 76.49, 87.19 %) Se, and the rest — antimony, was taken as the study object. The alloys were prepared by alloying the metals in evacuated quartz ampoules with heating at 100 °C above the liquidus temperature, holding for 12 hours at this temperature with shaking stirring, followed by quenching in water. Selenium with content of 99.99 wt. % and antimony — 99.99 wt. % of the main elements were used for the preparation of alloys.

The activity value defined as the ratio of the partial pressure of the component above the solution to the saturated vapor pressure above the elemental metal was taken as the basis to find the partial thermodynamic mixing functions: $a_i = \overline{p}_i / p_i^o$, where a_i is thermodynamic activity; $\overline{p}_i$ is the partial vapor pressure of *i*— component; p_i^o — saturated vapor pressure of the same component over the elemental metal.

The boiling point method (isothermal variant) detailed earlier was used to determine the saturated vapor pressure value [[26], [27]]. It is based on a significant increase in the evaporation rate at the equality of the external pressure and the saturated vapor pressure of the substance under study when the pressure above the melt decreases at a given temperature. The only congruently melting compound — Sb_2S_3 is present in the antimony—selenium system [28]. In this regard, the Sb — Se system was considered as two particular ones: Sb – Sb_2Se_3 and Sb_2Se_3 — Se. Due to the fact that the vapor pressure of antimony selenide at its melting temperature of 890 K (617 °C) determined with the membrane manometer method according to [29] is 40÷60 times higher than the pressure of elemental antimony [30], and the vapor pressure of elemental selenium [30] at the specified temperature is 200÷300 times higher than the vapor pressure of antimony sesquiselenide, it was considered that the total vapor pressure determined by the boiling point method in the Sb – Sb_2Se_3 system corresponds to the saturated vapor pressure of antimony selenide in the Sb_2Se_3 — Se system. Argon was used as a volume— filler gas in the boiling point method.

The partial free energy of alloy formation was calculated as $\Delta\overline{G}_i^{mix} = -RT \ln a_i$; partial enthalpy of mixing: $\left(\partial\Delta\overline{G}_i^{mix} / \partial T\right)_P = -\Delta\overline{S}_i^{mix}$; partial enthalpy: $\Delta\overline{H}_i^{mix} = \Delta\overline{G}_i^{mix} + T \cdot \Delta\overline{S}_i^{mix}$. Hereinafter, $\Delta\overline{G}_i^{mix}$, $\Delta\overline{S}_i^{mix}$ $\Delta\overline{H}_i^{mix}$ — partial free energy, partial entropy, and partial enthalpy of mixing of *i*— component, respectively. Hereinafter *T* is temperature, K.

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

The activity of the second component in the melt (on the example of the Sb – Sb_2Se_3 system) was found from the expression $a_{Sb} = \gamma_{Sb} \cdot x_{Sb}$, the tin activity coefficient (γ_{Sb}) — by numerical integration of the Gibbs — Duhem equation with the use of the auxiliary function proposed by Darken [[31], [32]]:

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

The partial free energy of evaporation was determined from the partial pressure values the for saturated vapor of the melt components $\Delta\overline{G}_i^{evp} = -RT \ln \overline{p}_i[atm]$, and entropies and enthalpies were similar to those for alloy formation.

The temperature dependences of activity and partial vapor pressure of volatile components for each of the compositions in each particular system were described by Arrhenius—type equations. Further, the temperature—concentration dependence of activity $\ln a_i = f(x_i, T)$ and vapor pressure $\ln \overline{p}_i = f(x_i, T)$ was obtained approximating the dependence of the coefficients in the equations on the concentration of volatile components in the alloy. Similarly calculated dependences were obtained for the activity and partial vapor pressure of less volatile components of the alloys.

The error in determination of the thermodynamic constants is assumed to be equal to the error in determination of lead saturated vapor pressure values as the number of errors of independent measurements, %: temperature — 1; weighing — 0.1; pressure 0.5; approximation of experimental data for the system Sb – Sb_2Se_3— 3.88, equal to 5.48; in the system — Sb_2Se_3 – Se, the approximation error is 3.12 and overall, 4.72.

Results and their discussion

The coefficients of the equations of dependence of saturated vapor pressure of antimony selenide and selenium on temperature for each of the alloy compositions are specified in Table 1.

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

Content of selenium in the alloy:		$\ln \bar{p}_{Sb_2Se_3}[Pa] = \frac{A}{T} + B$	
atm. %	wt. %	A	B
14.82	10.14	— 14.989	21.887
26.35	18.83	— 15.883	22.926
35.27	26.11	— 16.434	23.490
47.51	36.99	— 16.868	23.972
60.00	49.31	— 17.010	24.264
		$\ln \bar{p}_{Se}[Pa] = \frac{A}{T} + B$	
68.96	59.03	— 11.771	23.051
75.37	66.49	— 11.869	23.578
83.38	76.49	— 12.063	23.949
91.30	87.19	— 12.286	24.341
100	100	— 12.509	24.763

The partial pressure of saturated vapor of antimony selenide in the Sb – Sb₂Se₃ partial system is represented by the expression:

$$\ln \bar{p}_{Sb_2Se_3}[Pa] = (-6358x^4_{Sb_2Se_3} + 16234x^3_{Sb_2Se_3} -$$

$$-10839x^2_{Sb_2Se_3} - 1990_{Sb_2Se_3} - 14057) \cdot T^{-1} +$$

$$+ 4,961x^4_{Sb_2Se_3} - 11,959x^3_{Sb_2Se_3} + 8,019x^2_{Sb_2Se_3} +$$

$$+ 0,379\,x_{Sb_2Se_3} + 22,864 + \ln x_{Sb_2Se_3}$$

where $x_{Sb_2Se_3}$ — mole fraction of antimony selenide in the melt equal to: $0 \le x_{Sb_2Se_3} \le 1$.

The partial vapor pressure of antimony in this system corresponds to equation:

$$\ln \bar{p}_{Sb} = (-6358\,x^4_{Sb} + 17675\,x^3_{Sb} - 14082\,x^2_{Sb} +$$

$$+ 968\,x_{Sb} - 14958 - 398 \ln x_{Sb}) \cdot T^{-1} +$$

$$+ 4,961^4_{Sb} - 14,5x^3_{Sb} + 13,735\,x^2_{Sb} -$$

$$- 4,2x_{Sb} + 20,312 + 1,384 \ln x_{Sb},$$

Hereinafter x_{Sb} — the mole fraction of antimony.

The activities of antimony selenide and antimony are equal, respectively:

$$\ln a_{Sb_2Se_3}[Pa] = (-6358x^4_{Sb_2Se_3} + 16234x^3_{Sb_2Se_3} -$$

$$-10839x^2_{Sb_2Se_3} - 1990_{Sb_2Se_3} + 2953) \cdot T^{-1} +$$

$$+ 4,961x^4_{Sb_2Se_3} - 11,959x^3_{Sb_2Se_3} + 8,019x^2_{Sb_2Se_3} +$$

$$+ 0,379\,x_{Sb_2Se_3} - 1,4 + \ln x_{Sb_2Se_3}$$

$$\ln a_{Sb} = (-6358\,x^4_{Sb} + 17675\,x^3_{Sb} - 14082\,x^2_{Sb} +$$

$$+ 968\,x_{Sb} + 1797 - 398 \ln x_{Sb}) \cdot T^{-1} +$$

$$+ 4,961^4_{Sb} - 14,5x^3_{Sb} + 0,004 + 13,735\,x^2_{Sb}$$

The partial pressures of selenium and antimony selenide are approximated by the following relationships in the Sb₂Se₃—Se particular system:

$$\ln \bar{p}_{Se} = (1042\,x^3_{Se} - 2226\,x^2_{Se} + 446\,x_{Se} -$$

$$- 11771) \cdot T^{-1} - 0,583\,x^3_{Se} + 2,132\,x^2_{Se} -$$

$$- 1,589\,x_{Se} + 24,803 + \ln x_{Se},$$

where: x_{Se} — mole fraction of selenium in the melt equal to: $0 \le x_{Se_3} \le 1$.

$$\ln \bar{p}_{Sb_2Se_3}[Pa] = (-1042x^3_{Sb_2Se_3} + 2463x^2_{Sb_2Se_3} -$$

$$- 920_{Sb_2Se_3} - 17511 - 880 \ln x_{Sb_2Se_3}) \cdot T^{-1} +$$

$$+ 0,583x^3_{Sb_2Se_3} - 0,491x^2_{Sb_2Se_3} - 1,692x_{Sb_2Se_3} + .$$

$$+ 25,864 + 1,926 \ln x_{Sb_2Se_3}.$$

In the Sb₂Se₃ – Se particular system the activities are equal to, respectively:

$$\ln a_{Se} = (1042\,x^3_{Se} - 2226\,x^2_{Se} + 446\,x_{Se} +$$

$$+ 738) \cdot T^{-1} - 0,583\,x^3_{Se} + 2,132\,x^2_{Se} -$$

$$- 1,589\,x_{Se} + 0,04 + \ln x_{Se},$$

$$\ln a_{Sb_2Se_3}[Pa] = (-1042x^3_{Sb_2Se_3} + 2463x^2_{Sb_2Se_3} -$$

$$- 920_{Sb_2Se_3} - 501 - 880 \ln x_{Sb_2Se_3}) \cdot T^{-1} +$$

$$+ 0,583x^3_{Sb_2Se_3} - 0,491x^2_{Sb_2Se_3} - 1,692x_{Sb_2Se_3} + .$$

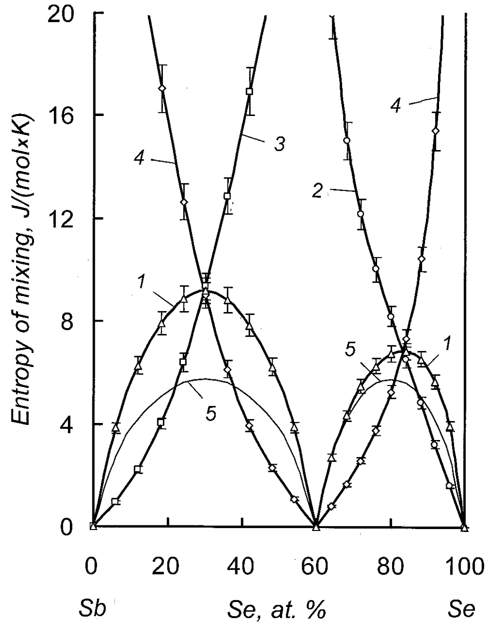
$$+ 1,6 + 1,926 \ln x_{Sb_2Se_3}.$$

The integral entropy of mixing in the antimony—selenium system differs from the ideal system in magnitude in both particular systems. It indicates the positive value of excess functions.

It can be seen from the analysis of the dependencies (Figures 1, 2) that the integral mixing functions of alloys in the antimony — selenide antimony system have a positive maximum — the formation of alloys is accompanied by an increase in disorder in the system and goes with heat absorption.

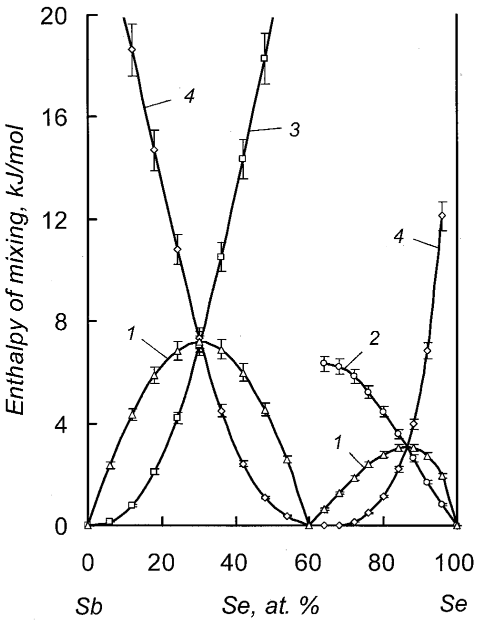
The extremum of the integral entropy of mixing reaches the value of 9.18 ± 0.50 J/ (mol·K), enthalpy of mixing — 7.19 ± 0.39 kJ/mol. The integral enthalpy of mixing of antimony and its selenide has a noticeable positive value (3.03 ± 0.14 J/mol) with a shift of the extremum to the selenium edge of the state diagram, which indicates the absence of interaction of particles in the liquid bath.

The formation of liquid alloys in the Se — Sb system is accompanied with an increase in disorder in the system.



2 - selenium; 3 - selenide of antimony;
4 - antimony; 5 - ideal system.

Figure 1 - Integral (1, 5) and partial (2— 4) entropies of mixing of the components of antimony—selenium melts.



2 — selenium; 3 — aluminum selenide;
4 — aluminum

Figure 2 - Integral (1) and partial (2— 4) enthalpies of mixing of components of antimony— selenium melts

The enthalpy of mixing is positive in the whole range of melt concentrations; hence, the formation of solutions proceeds with heat absorption — the reaction is endothermic.

The values of thermodynamic functions of evaporation of antimony— selenium system melts are summarized in Tables 2 and 3.

The integral function of the vaporization enthalpy in the antimony— selenide system has a slight minimum at 30 at. % selenium and is 133.18 ± 7.30 kJ/mol. The vaporization entropy of Sb_2Se_3 is equal to 105.93 ± 5.12 J/ (mol·K).

Thus, obtained values of saturated vapor pressure and thermodynamic constants are used to construct a complete state diagram including the fields of melt and vapor coexistence at atmospheric pressure and in vacuum.

Table 2 - Variation of partial and integral entropies of vaporization of Sb— Se system

Alloy composition, atm. %		$\Delta\overline{S}^{evp}_{Se}$, J/(mol·K)	$\Delta\overline{S}^{evp}_{Sb_2Se_3}$, J/(mol·K)	$\Delta\overline{S}^{evp}_{Sb}$, J/(mol·K)	ΔS^{evp}_{Sb-Se}, J/(mol·K)
Se	**Sb**				
0	100	—	—	73.02 ± 4.00	73.02 ± 4.00
10	90	—	81.32 ± 4.46	71.28 ± 3.91	72.95 ± 4.00
20	80	—	90.42 ± 4.95	68.28 ± 3.74	75.66 ± 4.15
30	70	—	96.90 ± 5.31	63.67 ± 3.49	80.28 ± 4.40
40	60	—	101.32 ± 5.55	57.50 ± 3.15	86.71 ± 4.75
50	50	—	104.03 ± 5.70	49.25 ± 2.70	94.90 ± 5.20
60	40	—	105.93 ± 5.12	—	105.93 ± 5.12
70	30	96.59 ± 4.56	113.02 ± 5.33	—	108.92 ± 5.14
80	20	101.85 ± 4.81	122.86 ± 5.80	—	112.36 ± 5.30
90	10	106.02 ± 5.00	137.71 ± 6.50	—	113.94 ± 5.38
100	0	110.06 ± 5.19	—	—	110.06 ± 5.19

Table 3 - Variation of partial and integral enthalpies of vaporization of Sb— Se system

Alloy composition, atm. %		$\Delta\overline{H}^{evp}_{Se}$, kJ/mol	$\Delta\overline{H}^{evp}_{Sb_2Se_3}$, kJ/mol	$\Delta\overline{H}^{evp}_{Sb}$, kJ/mol	ΔH^{evp}_{Sb-Se}, kJ/mol
Se	**Sb**				
0	100	—	—	139.31 ± 7.63	139.31 ± 7.63
10	90	—	121.52 ± 6.66	138.81 ± 7.61	135.93 ± 7.45
20	80	—	128.06 ± 7.62	136.59 ± 7.49	133.75 ± 7.33
30	70	—	134.11 ± 7.35	132.25 ± 7.23	133.18 ± 7.30
40	60	—	138.41 ± 7.58	126.26 ± 6.92	134.36 ± 7.36
50	50	—	140.63 ± 7.71	119.71 ± 6.56	137.15 ± 7.52
60	40	—	141.43 ± 6.68	—	141.42 ± 6.68
70	30	97.96 ± 4.62	141.36 ± 6.67	—	130.51 ± 6.16
80	20	99.56 ± 4.70	140.31 ± 6.62	—	119.93 ± 5.66
90	10	101.84 ± 4.81	136.22 ± 6.43	—	110.44 ± 5.21
100	0	104.00 ± 4.91	—	—	104.00 ± 4.91

Conclusions

When the studies were conducted by the boiling point method, the values of saturated vapor pressure of antimony selenide and selenium in the

$Sb – Sb_2Se_3$ and $Sb_2Se_3 – Se$ partial systems were determined, and the partial pressures of antimony and antimony sulfide were found by numerical integration of the Gibbs—Duhem equation, respectively. Thermodynamic functions of formation and evaporation of alloys were calculated based on experimental values of thermodynamic activity for components and partial values of vapor pressure. It enabled to add these data to the base of physical and chemical properties of antimony—selenium system.

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Conflict of interest. The corresponding author declare that there is no conflict of interest.

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Сурьма және селен қорытпаларының түзілу және булану термодинамикасы

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ТҮЙІНДЕМЕ

Екі нақты жүйе үшін – $Sb\text{-}Sb_2Se_3$ және $Sb_2Se\text{-}Se$, Сурьма-селен жүйесінде Sb_2Se_3 конгруентті балқыту қосылысының болуына байланысты қорытпаның түзілуі мен булануының термодинамикалық функциялары қарастырылды. Есептеулер нақты жүйелерді құрайтын компоненттердің ішінара бу қысымының мәндеріне негізделген. Жүйелердегі ең ұшқыш компоненттер ретінде сурьма селениді мен селеннің термодинамикалық белсенділігі қайнау температурасы әдісімен (изотермиялық нұсқа) анықталатын $Sb\text{-}Sb_2Se_3$ және Sb_2Se_3 - Se сұйық қорытпалары бойынша селен балқымалары үстіндегі сурьма селенидінің қаныққан бу қысымының мәндері негізінде есептелді. Жоғарыда аталған жүйелердегі аз ұшқыш компоненттердің ұқсас функциялары: бірінші жүйеде Sb және соңғысында Sb_2Se_3 Даркен ұсынған алмастыруды пайдаланып Гиббс-Дюхем теңдеуін сандық интегралдау арқылы есептелді. $Sb\text{-}Sb_2Se_3$ және $Sb_2Se_3\text{-}Se$ балқымаларындағы сурьма селениді мен сурьманың парциалды қысымдары температура-концентрация қатынасы арқылы жуықталды. Бірінші жүйе деламинация аймағының болуына байланысты идеалдылықтан оң ауытқуымен ерекшеленеді. Сұйық қорытпалардың түзілуінің парциалды және интегралдық энтропиялары мен энтальпиялары элементтің немесе қосылыстың ерітінді үстіндегі парциалды бу қысымының таза элементтің немесе қосылыстың қаныққан бу қысымына қатынасы ретінде табылған құрамдас белсенділік мәндері негізінде есептелді. Қорытпа түзілуінің парциалды және интегралдық функциялары балқымадағы селен мөлшеріне графикалық тәуелділіктер түрінде берілген. Алынған термодинамикалық константалар физика-химиялық деректердің базасын толықтырады және балқытылған жүйелердің ректификациялық бөліну мүмкіндігін және толықтығын анықтауға мүмкіндік беретін фазалық диаграммадағы бу-сұйықтық тепе-теңдік өрістерінің шекараларын есептеу үшін пайдаланылады.

Түйін сөздер: Қорғасын, қалайы, қорытпа, бу қысымы, термодинамика, түзілу, араласу, булану, парциалды және интегралдық шамалар, энтропия, энтальпия.

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Термодинамика образования и испарения сплавов сурьмы и селена

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АННОТАЦИЯ

Рассмотрены термодинамические функции образования и испарения сплава для двух частных систем — $Sb—Sb_2Se_3$ и $Sb_2Se_3—Se$ в связи с наличием конгруэнтно плавящегося соединения Sb_2Se_3 в системе сурьма—селен. Расчеты основаны на значениях парциального давления паров компонентов, образующих конкретные системы. Термодинамическую активность селенида сурьмы и селена как наиболее летучих компонентов в системах рассчитывали по значениям давления насыщенных паров селенида сурьмы над жидкими сплавами $Sb–Sb_2Se_3$ и селена над жидкими сплавами $Sb_2Se_3–Se$, определенными методом температуры кипения (изотермическая вариант). Аналогичные функции малолетучих компонентов в указанных выше системах: Sb в первой системе и Sb_2Se_3 во второй были рассчитаны численным интегрированием уравнения Гиббса—Дюгема с использованием замены, предложенной Даркеном. Парциальные давления селенида сурьмы и сурьмы над расплавами $Sb—Sb_2Se_3$ и $Sb_2Se_3—Se$ аппроксимированы зависимостью температура—концентрация. Система отличается положительным отклонением от идеальности из-за наличия в первой системе области расслоения. Парциальные и интегральные энтропии и энтальпии образования жидких сплавов рассчитывали на основе значений активностей компонентов, найденных как отношение парциального давления пара элемента или соединения над раствором к давлению насыщенного пара чистого элемента или соединения. Частные и интегральные функции сплавообразования представлены в виде графических зависимостей от количества селена в расплаве. Полученные термодинамические константы пополнят базу физико-химических данных и будут использованы для расчета границ полей парожидкостного равновесия на диаграмме состояния, позволяющих определить возможность и полноту ректификационного разделения расплавленных систем.

Ключевые слова: Свинец, олово, сплав, давление паров, термодинамика, образование, смешение, испарение, парциальные и интегральные величины, энтропия, энтальпия.

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