

Research Article

Thermodynamic Study of Tl_6SBr_4 Compound and Some Regularities in Thermodynamic Properties of Thallium Chalcogenides

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The solid-phase diagram of the Tl-TlBr-S system was clarified and the fundamental thermodynamic properties of Tl_6SBr_4 compound were studied on the basis of electromotive force (EMF) measurements of concentration cells relative to a thallium electrode. The EMF results were used to calculate the relative partial thermodynamic functions of thallium in alloys and the standard integral thermodynamic functions ($-\Delta_f G^0$, $-\Delta_f H^0$, and S^0_{298}) of Tl_6SBr_4 compound. All data regarding thermodynamic properties of thallium chalcogen-halides are generalized and comparatively analyzed. Consequently, certain regularities between thermodynamic functions of thallium chalcogen-halides and their binary constituents as well as degree of ionization (DI) of chemical bonding were revealed.

1. Introduction

Chalcogenides of *p*-elements are of considerable interest as promising functional materials of modern electronic engineering. Multitude of them exhibit semiconductor, thermoelectric, photoelectric, topological insulator, radiation detector, and magnetic properties [1–3]. $Tl_6S(Se)I_4$ ternary compounds are known as effective X-ray and γ -ray detectors, outperforming the current state-of-the-art material for room temperature operation, CdZnTe (CZT) [4, 5]. Given the promising performance of thallium-based chalcogenides and chalcogen-halides, these compounds continue to attract attention despite toxicity of thallium derivatives.

Knowledge of phase equilibria and thermodynamic properties of phases is of key importance in designing techniques and optimizing conditions for the fabrication, crystal growth of multicomponent inorganic materials.

The investigation of phase equilibria in Tl-X-Hal (X-S, Se, Te; Hal-Cl, Br, I) systems was started from the beginning

of the 80th years of the last century. A special attention was paid to quasibinary systems $Tl_2X-TlHal$ because of possibility of formation of ternary compounds [6–11]. Existence of 11 ternary compounds was established in the $Tl_2X-TlHal$ systems: 6 ternary compounds of type Tl_5X_2Hal (all selenium and tellurium systems) and 4 ternary compounds of type Tl_6XHal_4 (all sulphurous systems and Tl-Se-I system). Tl_2TeHal_6 compounds were detected in the systems Tl-Te-Hal [12, 13].

Tl_6SHal_4 (Hal-Cl, Br, I), Tl_6SeI_4 , and Tl_2TeBr_6 compounds crystallize in a tetragonal structure, with space group $P4/mnc$ [6, 7, 14, 15]; $Tl_5Se_2Br(I)$ and Tl_5Te_2Hal compounds have a tetragonal structure, with space group $I4/mcm$ [8, 11, 16–19]. Tl_2TeCl_6 compound crystallizes in a cubic system, Sp.gr. $Fm-3m$ and Tl_2TeCl_6 in a monoclinic system, Sp. gr. $P2_1/c$ [13, 15].

Physicochemical investigation of Tl-X-Hal (X-S, Se, Te; Hal-Cl, Br, I) systems was implemented in detail at a wide or full concentration range. A number of polythermal

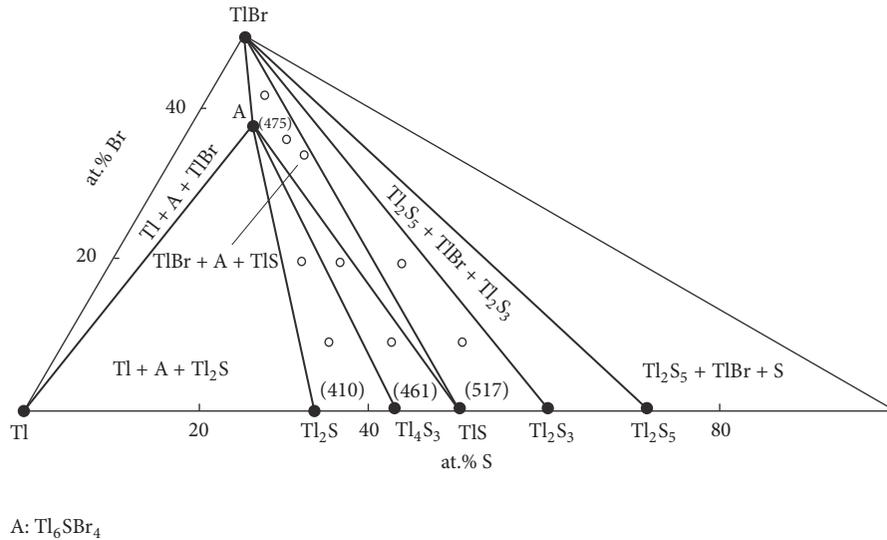


FIGURE 1: Solid-phase equilibrium diagram of the system Tl-TlBr-S at 300 K [24]. The compositions of the studied samples are given by hollow circles in the proper three-phase regions.

and isothermal sections as well as projections of liquidus surfaces were constructed. The primary crystallization and homogeneity areas of phases were fixed and the fundamental thermodynamic functions of ternary compounds and solid solutions were determined [20–23].

In this contribution, we present the thermodynamic study of Tl_6SBr_4 compound, summarize all data on thermodynamic properties of thallium chalcogenides, and carry out a comparative review between the latter. At the end of the paper, we present some regularities detected in the thermodynamic properties of thallium chalcogenides.

2. Experimental Details

2.1. Synthesis and Analysis. For planning experiments, we have used the solid-phase diagram of the Tl-TlBr-S system [24] which allowed us to determine the relevant compositions of samples for thermodynamic studies and to select conditions for their synthesis and thermal treatment (Figure 1). We have composed electrochemical cell of the type



in which the left electrode was pure metallic thallium and the right electrodes were samples from the mentioned region. A saturated glycerin solution of KBr with the addition of 0.1 mass% TlBr was used as an electrolyte.

Initial compounds Tl_2S and TlBr were synthesized to prepare the right electrodes of the electrochemical cell of the type (1). Tl_2S was synthesized by alloying of stoichiometric amounts of high-purity elemental components (Tl, 99.999 mass%, Alfa Aesar; S, 99.999 mass%, Alfa Aesar) in an evacuated silica ampoules at temperatures 30–50 K above the melting point. Tl_2S , melting congruently at 728 K [17], readily crystallizes while slowly cooling the sample.

TlBr was prepared by an indirect method reported in [18]. At first, metallic thallium was dissolved in the dilute sulphuric acid (7–10 mol%) at 350 K to get the Tl_2SO_4 solution. Then diluted HBr was added to a hot 2% Tl_2SO_4 solution until complete precipitation of TlBr. Yellowish green TlBr was separated from the mother liquor and washed with icy distilled water. The product was dried over KOH in a desiccator at 380–400 K and stored in the dark to prevent its decomposition.

The synthesized compounds were identified by differential thermal analysis DTA (NETZSCH 404 F1 Pegasus system) and X-ray powder diffraction XRD (Bruker D8 ADVANCE diffractometer, $\text{CuK}\alpha_1$ radiation) methods.

Alloys of the subsystem TlBr- Tl_2S - Tl_2S_3 were prepared by blending and interacting TlBr and Tl_2S compounds and elemental sulphur in various ratios in evacuated quartz vessels. They were subjected to a long-term stepped homogenizing annealing under the conditions described in [24]. The total mass of samples was 1 g and, after determining the solidus temperature, samples were additionally held at 20–30 K below the solidus for 500 h.

2.2. EMF Measurements. To measure the EMF of the chains type (1), electrodes, electrolyte, and electrochemical cell were prepared. The left electrode was made by attaching metallic thallium to a molybdenum current collector. Taking into account oxidization of thallium even at room temperature, before assembling electrochemical cell, the left electrodes were kept in glycerin, since metallic thallium does not directly interact with it [19].

The right electrodes (see (1)) were prepared by pressing powdered equilibrium alloys of the system under study into current collectors in the form of cylindrical tablets with a weight of ~0.5 g and placed in a tubular furnace; the temperature was stabilized at 350 K for 40–50 h. The wires were sealed in glass jackets to protect them from contact

TABLE 1: Temperature dependences of EMF of the concentration chains type (1) in some phase regions of the subsystem TlBr-Tl₂S-Tl₂S₃.

Number	Phase region in Figure 1	$E, \text{mV} = a + bT \pm t \cdot S_E(T)$
1	TlBr-TlS-Tl ₂ S ₃	$552,6 - 0,120T \pm 2 \left[\left(\frac{1,8}{24} \right) + 8 \cdot 10^{-5} (T - 342,4)^2 \right]^{1/2}$
2	TlBr-TlS-Tl ₆ SBr ₄	$486,1 - 0,038T \pm 2 \left[\left(\frac{0,9}{24} \right) + 5 \cdot 10^{-5} (T - 342,4)^2 \right]^{1/2}$
3	Tl ₆ SBr ₄ -Tl ₄ S ₃ -TlS	$465,8 - 0,016T \pm 2 \left[\left(\frac{1,5}{24} \right) + 7 \cdot 10^{-5} (T - 342,4)^2 \right]^{1/2}$
4	Tl ₂ S-Tl ₆ SBr ₄ -Tl ₄ S ₃	$383,4 + 0,086T \pm 2 \left[\left(\frac{1,1}{24} \right) + 6 \cdot 10^{-5} (T - 342,4)^2 \right]^{1/2}$

with the electrolyte. EMF was measured by the compensation method in the temperature range of 300–390 K with the accuracy of ± 0.1 mV, using the high-resistance universal B7-34A digital voltmeter. In each experiment the first EMF reading was performed approximately 30 h after the start of the experiment and at least 2-3 h after reaching the desired temperature, which ensures the achievement of equilibrium. The EMF measurements were carried out 2–7 days or more in consideration of homogenization of the electrode alloys, after the cell had been assembled. Equilibrium values were considered the EMF readings that varied by no more than 0.5 mV irrespective of the direction of temperature change at repeated measurements at a given temperature. In order to eliminate the contribution of the thermopower, all contacts and leads were kept at the same temperature.

Techniques of assembling the electrochemical cell and EMF measurements are described in detail in [25, 26].

3. Results and Discussion

3.1. Thermodynamic Study of the Ternary Compound Tl₆SBr₄. The solid-phase equilibrium diagram of the Tl-TlBr-S subsystem that had been constructed in [24] is given in Figure 1. As can be seen from Figure 1, there are 4 three-phase regions in the TlBr-Tl₂S-Tl₂S₃ subsystem: TlBr-TlS-Tl₂S₃ (I), TlBr-TlS-Tl₆SBr₄ (II), Tl₆SBr₄-Tl₄S₃-TlS (III), and Tl₂S-Tl₆SBr₄-Tl₄S₃ (IV). The EMF values measured in heterogeneous phase regions I–IV were processed by the least squares method [25, 26] and presented as the following linear equations:

$$E = a + bT \pm t \left[\frac{S_E^2}{n} + S_b^2 (T - \bar{T})^2 \right]^{1/2}, \quad (2)$$

where n is the number of pairs of E and T values; S_E and S_b are the error variances of the EMF readings and b coefficient, respectively; \bar{T} is the average of the absolute temperature; t is Student's test. At the confidence level of 95% and $n \geq 20$, Student's test is $t \leq 2$ [25, 26]. The composed equation of the mode (2) is presented in Table 1. The experimental data of T_i and E_i and steps of calculation for the phase region II (Table 1), which is of special interest in terms of calculation of thermodynamic functions of the Tl₆SBr₄ compound, are presented in Table 2. The values of \bar{T} , a , b , S_E^2 , and S_b^2 quantities in (2) were calculated based on Table 2.

Our results of measuring the EMF of the cells type (1) in the TlBr-Tl₂S-Tl₂S₃ composition region were fully consistent with the solid-phase equilibrium diagram of the Tl-TlBr-S subsystem [24] (Figure 1). The EMF values at the given temperature, within I–IV three-phase regions, virtually coincide independently of the gross compositions of the right electrodes and vary discontinuously in transition from one of the regions to another. The EMF values at 300 K temperature for the phase areas showing in Table 1 are given in Figure 1.

It should also be noted that numerical values of EMF and equations of their temperature dependence in the phase regions I, III, and IV (Table 1) practically coincide with corresponding data [27] for the binary compounds TlS, Tl₄S₃, and Tl₂S, respectively. This testifies reversibility of the electrochemical cells type (1) and therefore indirectly points to the absence of appreciable regions of solid solutions based on the aforementioned sulfides in the TlBr-Tl₂S-Tl₂S₃ subsystem.

The EMF values measured in the phase region II (Table 1) can be assigned to the compound Tl₆SBr₄ and can be used in thermodynamic calculations. The calculation of the relative partial molar functions of thallium from the equation of the temperature dependence of the EMF in this phase region gave the quantities

$$\begin{aligned} \Delta \bar{G}_{\text{Tl}} &= -45,80 \pm 0,07 \text{ kJ} \cdot \text{mol}^{-1}; \\ \Delta \bar{H}_{\text{Tl}} &= -46,90 \pm 0,48 \text{ kJ} \cdot \text{mol}^{-1}; \\ \Delta \bar{S}_{\text{Tl}} &= -3,71 \pm 1,39 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned} \quad (3)$$

which are thermodynamic functions of the potential-forming reaction



according to Figure 1.

Based on (4), we determined ΔZ^0 , the standard thermodynamic functions of formation (ΔG^0 , ΔH^0) of Tl₆SBr₄:

$$\Delta Z^0 (\text{Tl}_6\text{SBr}_4) = \Delta \bar{Z}_{\text{Tl}} + 4\Delta Z^0 (\text{TlBr}) + \Delta Z^0 (\text{TlS}), \quad (5)$$

where ΔZ^0 is the standard Gibbs free energy $\Delta_f G^0_{298}$ and standard enthalpy of formation $\Delta_f H^0_{298}$ for the corresponding compound. The standard entropy of Tl₆SBr₄ was calculated as

$$S^0 (\text{Tl}_6\text{SBr}_4) = \Delta \bar{S}_{\text{Tl}} + S^0 (\text{Tl}) + 4S^0 (\text{TlBr}) + S^0 (\text{TlS}). \quad (6)$$

TABLE 2: The calculation steps of the EMF measurements for the TlBr-TlS-Tl₆SBr₄ phase region.

T_i , K	E_i , mV	$T_i - \bar{T}$	$E_i (T_i - \bar{T})$	$(T_i - \bar{T})^2$	E	$E_i - E$
300,5	476,2	-41,90	-19952,78	1755,61	474,57	1,63
301,2	476,1	-41,20	-19615,32	1697,44	474,54	1,56
305,1	473,5	-37,30	-17661,55	1391,29	474,39	-0,89
311,2	474,9	-31,20	-14816,88	973,44	474,16	0,74
313	473,2	-29,40	-13912,08	864,36	474,09	-0,89
317,7	473,4	-24,70	-11692,98	610,09	473,91	-0,51
319,3	473,2	-23,10	-10930,92	533,61	473,85	-0,65
324,1	472,8	-18,30	-8652,24	334,89	473,66	-0,86
328,7	474,1	-13,70	-6495,17	187,69	473,48	0,62
331,2	472,2	-11,20	-5288,64	125,44	473,39	-1,19
335,4	472,1	-7,00	-3304,70	49,00	473,23	-1,13
341,5	473,9	-0,90	-426,51	0,81	472,99	0,91
345,4	472,1	3,00	1416,30	9,00	472,84	-0,74
349,3	473,1	6,90	3264,39	47,61	472,69	0,41
351,6	472,1	9,20	4343,32	84,64	472,61	-0,51
356,1	472,8	13,70	6477,36	187,69	472,43	0,37
360,4	471,1	18,00	8479,80	324,00	472,27	-1,17
364,2	471,2	21,80	10272,16	475,24	472,12	-0,92
366,3	473,1	23,90	11307,09	571,21	472,04	1,06
369,3	472,9	26,90	12721,01	723,61	471,93	0,97
374,2	473,2	31,80	15047,76	1011,24	471,74	1,46
380,8	472,3	38,40	18136,32	1474,56	471,48	0,82
382,9	470,9	40,50	19071,45	1640,25	471,40	-0,50
388,2	470,6	45,80	21553,48	2097,64	471,20	-0,60

TABLE 3: Standard integral thermodynamic functions of ternary compounds in the Tl-X-Hal (X-S, Se, Te; Hal - I, Br, Cl) systems ($T = 298$ K).

Compound	$-\Delta_f G^0$ (298 K)	$-\Delta_f H^0$ (298 K)	S^0_{298}
	kJ·mol ⁻¹		J·K ⁻¹ ·mol ⁻¹
Tl ₆ SCL ₄	833,5 ± 3,7	928,1 ± 14,0	599 ± 9
Tl ₆ SBr ₄	768,2 ± 2,9	791,3 ± 5,2	644 ± 9
Tl ₆ SI ₄	601,7 ± 2,5	595,1 ± 4,0	672 ± 10
Tl ₆ SeI ₄	613,1 ± 1,5	609,7 ± 2,6	671 ± 5
Tl ₅ Se ₂ Cl	392,8 ± 1,1	421,6 ± 5,1	433,9 ± 7,2
Tl ₅ Se ₂ Br	374,3 ± 1,0	384,3 ± 2,7	447,6 ± 6,4
Tl ₅ Se ₂ I	341,7 ± 0,8	345,3 ± 2,5	449 ± 8
Tl ₅ Te ₂ Cl	355,9 ± 1,1	377,1 ± 5,0	474,1 ± 6,8
Tl ₅ Te ₂ Br	340,6 ± 1,6	344,5 ± 2,7	483,4 ± 6,2
Tl ₅ Te ₂ I	300,4 ± 1,3	301,1 ± 2,3	475,8 ± 6,6

For calculations besides our own $\Delta \bar{Z}_{Tl}$ data, we used the standard integral thermodynamic functions of TlS [27] and TlBr [28] and the standard entropy of thallium [28]:

$$TlS: \Delta_f G^0 = -51,6 \pm 0,42 \text{ kJ}\cdot\text{mol}^{-1}; \Delta_f H^0 = -52,72 \pm 2,01 \text{ kJ}\cdot\text{mol}^{-1}; S^0_{298} = -3,6 \pm 5,8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

$$TlBr: \Delta_f G^0 = -167,4 \pm 0,6 \text{ kJ}\cdot\text{mol}^{-1}; \Delta_f H^0 = -172,7 \pm 0,7 \text{ kJ}\cdot\text{mol}^{-1}; S^0_{298} = 122,6 \pm 0,2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

$$Tl: S^0_{298} = 64,2 \pm 0,2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}.$$

The errors were found by the error accumulation method.

Calculated integral thermodynamic functions of Tl₆SBr₄ compound are given in Table 3. This table also summarizes the thermodynamic functions of other thallium chalcogenides.

3.2. Comparative Review of Thermodynamic Properties of Thallium Chalcogenides. Using obtained values of the standard integral thermodynamic functions of formation and standard entropies of thallium chalcogenides, other fundamental characteristics, standard thermodynamic functions of atomization of these compounds, were calculated. As is known, the atomization thermodynamic functions are quantities that characterize the change of relevant thermodynamic functions during decomposition of a compound to monatomic gas mixture. The atomization energy of ternary compounds was calculated using

$$\Delta_{at}H (\text{comp}) = \sum \Delta_{at}H (\text{elem.}) - \Delta_f H (\text{comp}), \quad (7)$$

where $\Delta_f H (\text{comp})$ is the enthalpy of formation of a compound and $\sum \Delta_{at}H (\text{elem.})$ is the sum of atomization

TABLE 4: Standard thermodynamic functions of atomization of thallium chalcogen-halides.

Compound	$\Delta_{\text{at}}G^0$ (298 K)	$\Delta_{\text{at}}H^0$ (298 K)	$\Delta_{\text{at}}S^0$ (298 K)
	kJ·mol ⁻¹		J·K ⁻¹ mol ⁻¹
Tl ₅ Se ₂ Cl	1564	1858	988
Tl ₅ Se ₂ Br	1531	1816	958
Tl ₅ Se ₂ I	1488	1775	962
Tl ₅ Te ₂ Cl	1480	1766	960
Tl ₅ Te ₂ Br	1442	1728	961
Tl ₅ Te ₂ I	1389	1669	939
Tl ₆ SCL ₄	2142	2534	1314
Tl ₆ SBr ₄	1987	2377	1308
Tl ₆ SI ₄	1784	2172	1303
Tl ₆ SeI ₄	1754	2145	1313

TABLE 5: Comparison of thermodynamic functions of atomization, formation from elemental components, and formation from binary compounds of thallium chalcogen-halides.

Compound	$\Delta_{\text{at}}G^0$	$-\Delta_fG^0$	$-\Delta_fG^0$ (b.c)	$\Delta_{\text{at}}H^0$	$-\Delta_fH^0$	$-\Delta_fH^0$ (b.c)
	kJ·mol ⁻¹					
Tl ₅ Se ₂ Cl	1564	392,8	17,0	1858	421,6	28,1
Tl ₅ Se ₂ Br	1531	374,3	16,1	1816	384,3	26,4
Tl ₅ Se ₂ I	1488	334,0	17,9	1775	324,0	15,1
Tl ₅ Te ₂ Cl	1480	355,9	12,5	1766	377,1	7,8
Tl ₅ Te ₂ Br	1442	340,1	14,3	1728	343,9	10,2
Tl ₅ Te ₂ I	1389	296,5	12,8	1669	286,8	12,1
Tl ₆ SCL ₄	2142	833,5	2,8	2534	928,1	3,6
Tl ₆ SBr ₄	1987	787,2	6,6	2377	791,3	8,2
Tl ₆ SI ₄	1784	601,7	9,7	2172	595,1	9,0
Tl ₆ SeI ₄	1754	613,1	16,6	2145	609,7	22,3

enthalpies of elements in a compound. The atomization entropy of ternary compounds was calculated on the following equation:

$$\Delta_{\text{at}}S^0 (\text{comp}) = \sum S^0 (\text{at.gas.}) - S^0 (\text{comp}). \quad (8)$$

Here $S^0 (\text{comp})$ is the absolute standard entropy and $\sum S^0 (\text{at.gas.})$ is the sum of the absolute entropies of elemental constituents of the considered compound in a monoatomic gas state.

The Gibbs free energy of atomization of ternary compounds were calculated from Gibbs-Helmholtz equation using the data obtained from (7) and (8):

$$\Delta_{\text{at}}G (\text{comp}) = \Delta_{\text{at}}H^0 (\text{comp}) - T\Delta_{\text{at}}S^0 (\text{comp}). \quad (9)$$

Results are given in Table 4.

The standard thermodynamic functions of atomization, formation, and formation from appropriate binary compounds (Tl₂X and TlHal) of thallium chalcogen-halides are summarized in Table 5, for comparative analysis.

As can be seen from Table 5, the relationship between the standard thermodynamic functions of atomization, formation, and formation from appropriate binary compounds (Tl₂X and TlHal) for all ternary compounds is as follows:

$$|\Delta_{\text{at}}Z^0| \geq |\Delta_fZ^0| \geq |\Delta_fZ^0 (\text{b.c.})|, \quad (10)$$

where Z is Gibbs free energy (G) or enthalpy (H).

The atomization Gibbs free energies and enthalpies of all ternary compounds are very large positive quantities. The standard thermodynamic functions of formation of ternary compounds are 3–5 times smaller by absolute value than the proper atomization functions. This is associated with the fact that $\Delta_{\text{at}}H^0$ is the minimal energy required to split up the crystal lattice into separate atoms. However, $\Delta_{\text{at}}G^0$ is the driving force of the reverse process, combination of monoatomic gases to form a crystal lattice.

The standard thermodynamic functions of formation of ternary compounds are much smaller than the Gibbs free energies and enthalpies of formation from binary constituents. The reason of such a sharp distinction can be explained by the fact that formation of a ternary compound from its binary constituents is not accompanied by a considerable energetic change in the system. Moreover, during

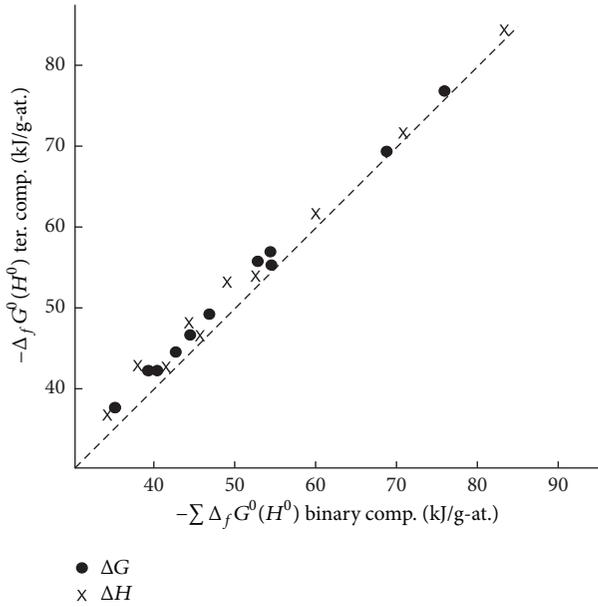


FIGURE 2: The correlation between $\Delta_f G^0$ and $\Delta_f H^0$ functions of thallium chalcogenides and the sum of the proper functions of binary compounds.

the latter process the oxidation state numbers of elements, consequently the type of chemical bonding do not alter significantly. However, during formation of ternary compound from elemental components, quantities change significantly and therefore total energy of the system decreases sharply.

The high numerical values of the atomization entropy of all ternary chalcogen-halides can be explained by the dramatically increase in disorder during the decomposition of their crystal lattice (Table 5).

3.3. Some Regularities in Thermodynamic Properties of Thallium Chalcogen-Halides. The comparative analysis of different thermodynamic functions of thallium chalcogenides with degree of ionization of the chemical bonding in those compounds as well as with the proper thermodynamic functions of binary compounds have shown the availability of some regularities.

The conformity between the standard Gibbs free energies and enthalpies of formation of ternary (Tl_6XHal_4 and Tl_5X_2Hal) compounds and the sum of the proper functions of binary ($TlHal$ and Tl_2X) compounds is demonstrated in Figure 2. As shown in Figure 2, the absolute values of $\Delta_f G^0$ and $\Delta_f H^0$ functions of all ternary compounds are higher (~3–7%) than the sum of the proper functions of binary compounds.

The correlations between $\Delta_f G_{298}^0$ and $\Delta_f H_{298}^0$ functions of ternary and binary $TlHal$ compounds are represented in Figure 3. As can be seen, these dependencies are linear for all compounds of the type Tl_6XHal_4 ; however the linear dependencies for Tl_5Se_2Hal and Tl_5Te_2Hal compounds with the same halogen atoms differ from each other.

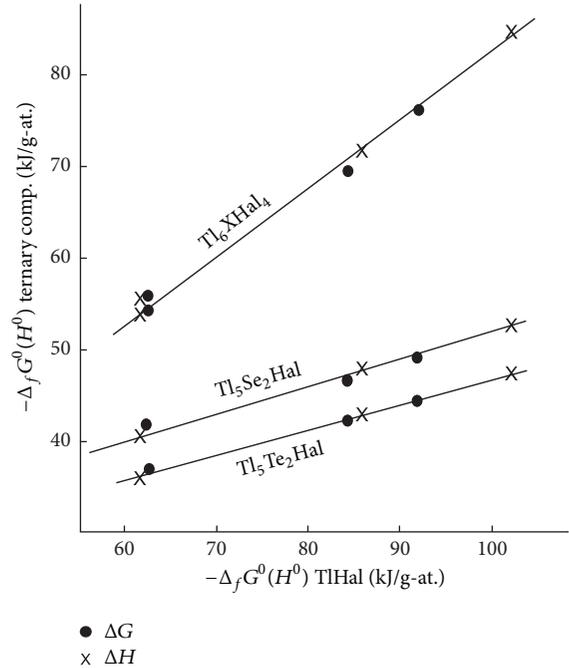


FIGURE 3: The correlation between $\Delta_f G^0$ and $\Delta_f H^0$ functions of ternary and binary $TlHal$ compounds.

This is due to the fact that, $TlHal$ compounds play a decisive role in the thermodynamic functions of the ternary compounds Tl_6XHal_4 . Reversely, the main contribution in the thermodynamic functions of Tl_5X_2Hal compounds belongs to thallium chalcogenides Tl_2X ($X=Se, Te$). Since the thermodynamic functions of formation of Tl_2Se and Tl_2Te compounds are considerably distinctive from each other, the values of relevant functions for Tl_5Se_2Hal and Tl_5Te_2Hal ternary compounds also differ by magnitude (Figure 3).

The dependence graphs of the standard thermodynamic functions (Gibbs free energy and enthalpy) of formation and atomization of the ternary compounds Tl_6XHal_4 and Tl_5X_2Hal upon the ionization degree (ID) of chemical bonding are demonstrated in Figure 4.

The ID of a chemical bond in thallium chalcogenides was calculated by classical method [29]. For this aim, the chemical bond in CsF compound with the highest value of ID was considered pure ionic type and the difference of the relative electronegativities of elements (Δ_{REN}) in this compound was found to be $\Delta_{REN} = 3,2$. Taking into account the equalities $\Delta_{REN} = 0$ and $ID = 0\%$ for nonpolar covalent bonds, the following equation was obtained.

$$ID (\%) = 31,25 \cdot \Delta_{REN}. \quad (11)$$

Calculation of the Δ_{REN} for thallium chalcogenides is demonstrated by an example of Tl_6SBr_4 compound.

All thallium atoms in Tl_6SBr_4 compound are in Tl^{1+} state. The values of relative electronegativities (REN) of Tl , S , and Br that were used in calculations are, respectively, 1,4; 2,6; and 2,9 [29].

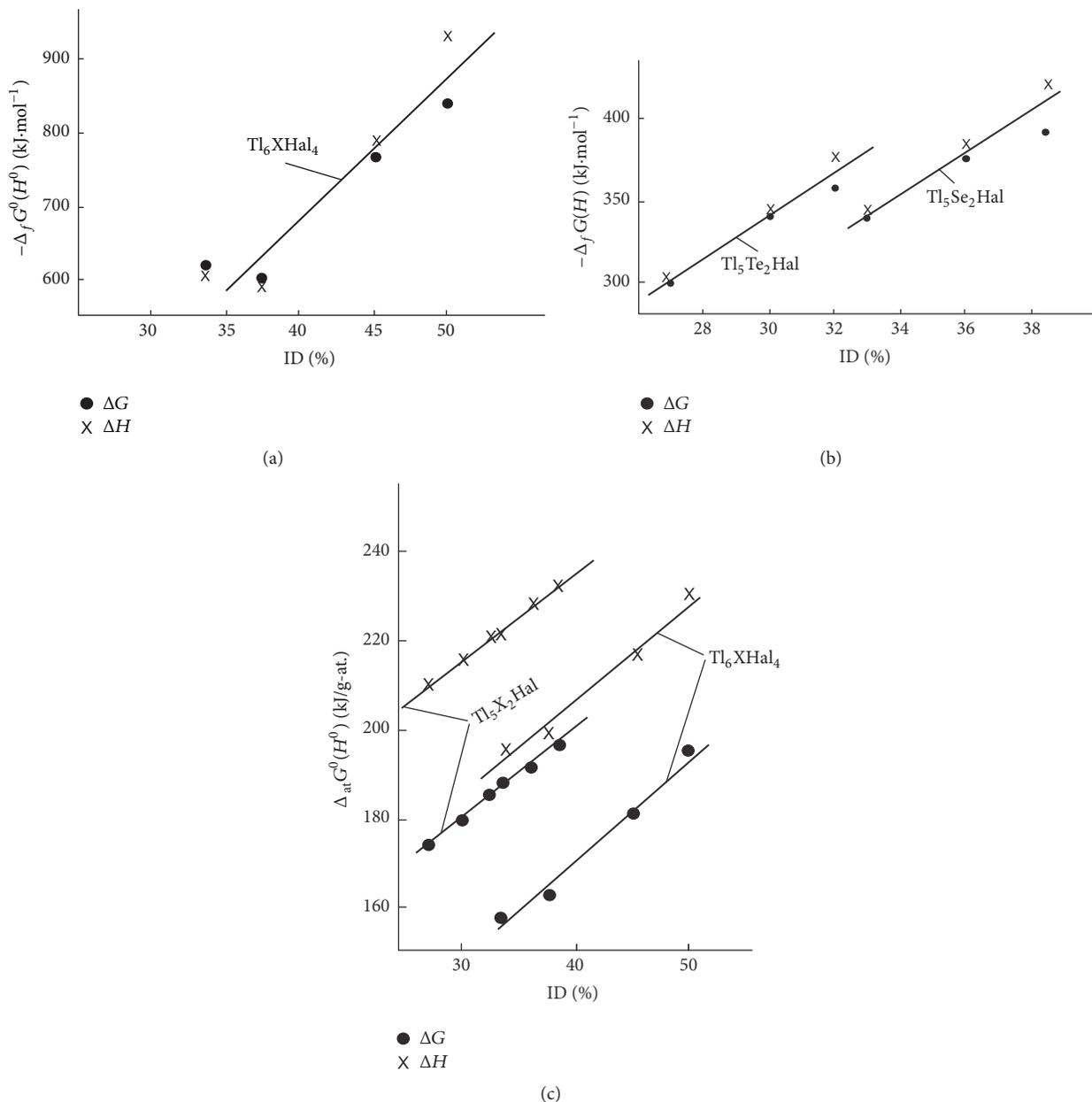


FIGURE 4: The dependence of the standard thermodynamic Gibbs free energy and enthalpies of formation (a, b) and atomization (c) of the ternary compounds on the degree of ionization (ID) of chemical bonding.

Since there are different anions (chalcogen and halogen) in the compound, firstly the average REN for the $[SBr_4]$ anion group and later Δ_{REN} for Tl_6SBr_4 compound were calculated:

$$REN [SBr_4] = (2,6 + 2,9 \cdot 4) / 5 = 2,84;$$

$$\Delta_{REN} Tl_6SBr_4 = 2,84 - 1,4 = 1,44.$$

The averaged ID of the chemical bonds in thallium chalcogen-halides were calculated using (11): $ID (\%) = 31,25 \cdot \Delta_{REN} = 31,25 \cdot 1,44 = 45\%$. The calculated Δ_{REN} and ID values for all thallium chalcogen-halides are summarized in Table 6.

Both thermodynamic properties of ternary compounds have a positive linear tendency with ID of bonding. Since

the lattice energy of substance rises with an increase in the ID of chemical bond, the extension of the above-mentioned thermodynamic functions is natural (Figure 4).

Unlike the energetical by nature thermodynamic functions (ΔG^0 , ΔH^0) the atomization entropy of the ternary compounds Tl_6XHal_4 and Tl_5X_2Hal has virtually the same values within a certain error: $S^{at} = 120 \pm 3 K \cdot mol^{-1} \cdot K^{-1}$ (Figure 5).

It can be explained by the fact that the entropy of atomization is an indicator of the rise of irregularity during decomposition of crystal lattice into monatomic gas mixture. The same numerical value of atomization entropies of all

TABLE 6: Δ_{REN} and ID values for thallium chalcogenides.

Compound	Δ_{REN}	ID, %
Tl_6SCl_4	1,6	50
Tl_6SBr_4	1,44	45
Tl_6SI_4	1,2	37,5
Tl_6SeI_4	1,04	33,5
Tl_5Se_2Cl	1,23	38,5
Tl_5Se_2Br	1,17	36
Tl_5Se_2I	1,07	33
Tl_5Te_2Cl	1,03	32
Tl_5Te_2Br	0,97	30
Tl_5Te_2I	0,87	27

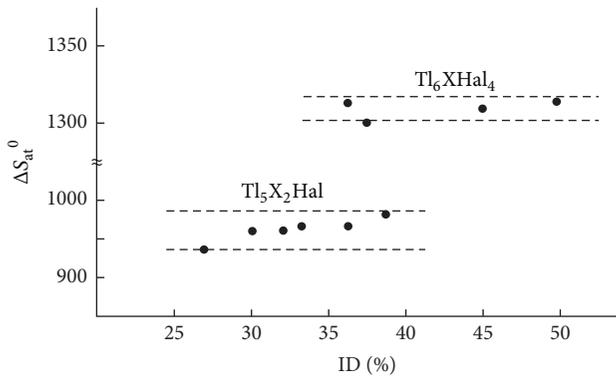


FIGURE 5: The correlation between the atomization entropy of ternary compounds and the ionization degree (ID) of chemical bonding.

considered ternary compounds is the result of the transformation of the system from regular crystalline state with the lowest value of entropy into the irregular atomic gas mixture during the atomization process. The difference between the entropy of a substance (with the same formula) in a crystal state and the entropy of a monoatomic gas mixture is nearly two orders smaller than the value of the atomization entropy and therefore does not affect the magnitude of the latter.

4. Conclusion

By using electromotive force (EMF) measurements a regulated complex of thermodynamic properties for the Tl_6SBr_4 compound was obtained. The data regarding the thermodynamic properties of thallium chalcogen-halides were systematized and comparatively analyzed. Some correlations between thermodynamic functions of thallium chalcogen-halides and their binary constituents as well as ionization degree of chemical bonding were revealed.

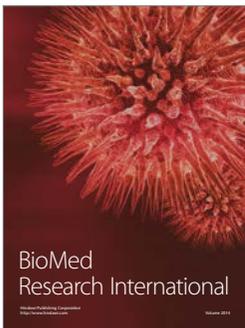
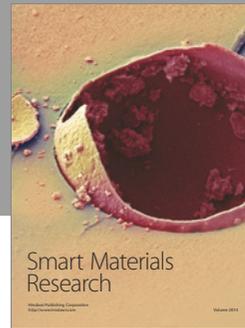
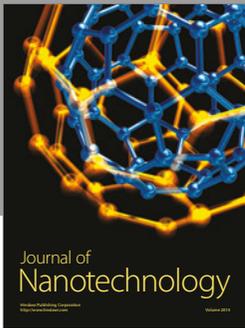
Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publishing of this paper.

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