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Thermodynamic Properties and Homogeneity Regions of Tl_6SCl_4 and Tl_5Se_2Cl

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Abstract—In this activity system $Tl–Tl_2X–X$ (X = S, Se)are studied using emf measurements of concentration chains relative thallic electrode. The solid phase diagrams of these systems are clarified, homogeneity areas of the compounds Tl_6SCl_4 and Tl_5Se_2Cl are determined. On the basis of emf measurement results, relative partial molar functions of thallium in alloys and standard integral thermodynamic functions (ΔG^0(298 K), ΔH^0 (298 K), ΔS^0(298 K)) of the ternary compounds Tl_6SCl_4 and Tl_5Se_2Cl and phases of variable composition based on the latter are calculated.

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INTRODUCTION

Development and optimization of the processes for obtaining and purifying multicomponent inorganic materials is based on data on the phase equilibria and thermodynamic properties of the corresponding systems.

Chalcogenides of metals, in particular, thallium, and phases on their basis are of interest for obtaining new semiconducting and thermoelectric materials.

The ternary system Tl–S–Cl is studied in [1–4]. According to the data of [1], the quasibinary section $TlCl–Tl_2S$ is characterized by formation of the ternary compound Tl_6SCl_4 incongruently melting by a peritectic reaction at 683 K. The compound Tl_6SCl_4 crystallizes in a tetragonal lattice of the type Tl_6HgBr_6 (space group *P*4/*mnc*). In [2–4], the system Tl–S–Cl is studied in the area of compositions Tl–TlCl–S. An elaborated version of the *T*–*x*–diagram of $TlCl–Tl_2S$ system is presented; according to it, the coordinates of the peritectic and eutectic points are 685 K, 55 mol % and 680 K, 60 mol % Tl_2S [4]. These compositions differ significantly from the data of [1] (33 and 35 mol % Tl_2S). In addition, according to [4], in the system $TlCl–Tl_2S$, there is a wide region of immiscibility (13–50 mol % Tl_2S) with a temperature of monotectic equilibrium of 690 K. Polythermal sections of TlCl–TlS and $TlCl–Tl_4S_3$ are nonquasibinary, but they are stable below the solidus; that is, they consist of two-phase mixtures of the initial compounds. In [4], a complete picture of phase equilibria in the system Tl–TlCl–S is obtained; various polythermal sections, an isothermal section at 300 K, and a projection of the liquidus surface are constructed.

The ternary system Tl–Se–Cl is also studied in details in the region of the compositions Tl–TlCl–Se [5–8]. According to [5], the quasibinary system $TlCl–Tl_2Se$ is characterized by formation of one ternary compound, Tl_5Se_2Cl, incongruently melting by a syntectic reaction at 725 K. At the syntectic temperature, the immiscibility region ranges from 15 to 80 mol % Tl_2Se. The compound Tl_5Se_2Cl forms eutectic point with TlCl (5 mol % Tl_2Se, 689 K) and a peritectic point with Tl_2Se (~93 mol % Tl_2Se, 684 K). According to the peritectic reaction $L + Tl_5Se_2Cl \longrightarrow \alpha$, solid solutions based on Tl_2Se with a concentration of TlCl up to 18 mol % are formed [5].

The compound Tl_5Se_2Cl crystallizes into a tetragonal structure of the Cr_5B_3 type with the following lattice parameters: $a = 8.565$, $c = 12.741$ Å, $Z = 4$, space group *P*4/*nnc* [6]. It is interesting that the lower selenide of thallium Tl_5Se_{3-x} ($0.06 < x < 0.5$) has the same structure [9].

It is shown in [7] that the system TlCl–TlSe forms a phase diagram of the simple eutectic type with degenerate eutectics near TlSe.

It is found by a repeated investigations [8] that this section is characterized by eutectic (85 mol % TlSe, 593 K) and monotectic (685 K) equilibrium. At the monotectic temperature, the immiscibility region ranges from 15 to 70 mol % TlSe.

In [8], a complete *T*–*x*–*y* diagram of the system Tl–TlCl–Se, a number of its polythermal sections, and an isothermal section at 400 K are constructed; fields of primary crystallization of phases and types and coordinates of nonvariant equilibria are determined. According to [8], the compound Tl_5Se_2Cl, in contrast to the data of [5], is a nonstoichiometric phase and has a wide region of homogeneity, which almost completely covers the elementary triangle $Tl_2Se–Tl_5Se_3–Tl_5Se_2Cl$.

The aim of the present paper is to study the solid phase equilibrium in the systems $TlCl–Tl_2X–X$ (X = S, Se) and the thermodynamic properties of thio- and selenochlorides of thallium by the emf method.

EXPERIMENTAL AND RESULTS

For planning of the experiments, we have used the results of [4, 8] that allow us to determine efficient compositions of samples for studies by the emf method and to select conditions for their synthesis and thermal treatment.

We have composed concentration chains of the type

$$(-)\mathrm{Tl(sol.)}|\text{liquid electrolyte, } \mathrm{Tl}^{+}| \\ (\mathrm{TlCl{-}Tl_2X{-}X})(\mathrm{sol.})(+), \tag{1}$$

in which the left electrode is pure metallic thallium and the right electrodes are equilibrium alloys from different phase regions of the systems $TlCl–Tl_2X–X$.

In order to prepare the right electrodes of the chains of type (1), initial compounds TlCl, Tl_2Se, and Tl_2S were synthesized at first. The synthesis of Tl_2Se and Tl_2S was carried out by the ampule method from high-purity primitive components (impurity content of at most 10^{-3} wt %) in vacuum conditions of ~10^{-2} Pa. The alloying temperature was 750 K.

Thallium monochloride was obtained by the technique described in [10]: first, by dissolution of metallic thallium at ~350 K in diluted (~7–10 mol %) sulfuric acid, a solution of Tl_2SO_4 was obtained. Diluted HCl was added to a boiling 2% solution of Tl_2SO_4 until complete sedimentation. After cooling of the mother solution, TlCl was separated, washed with icy distilled water, and dried in a drying oven at 390–400 K for a long period of time.

The synthesized compounds were identified by the methods of differential thermal and x-ray phase analysis.

Via the alloying of initial compounds and elementar sulfur (selenium) in various ratios in evacuated quartz vessels, alloys of the systems $TlCl–Tl_2X–X$ were prepared; they were subjected to a long-term stepped homogenizing annealing under the conditions described in [4, 8]; then, they were additionally held at ~380 K for 300 h.

In order to measure the emf of the chains of type (1), electrodes, electrolyte, and electrochemical cells were prepared. The left electrode was made by attaching metallic thallium (purity of at least 99.99%) 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 [11].

The right electrodes were prepared by pressing of powdered equilibrium alloys of the systems under study into current collectors in the form of cylindrical tablets with a weight of ~0.5 g.

The electrolyte was a glycerin solution of KCl with TlCl added. Taking into account that moisture and oxygen must not be present in the electrolyte, the glycerin (analytically pure) was thoroughly dehydrated and evacuated at a temperature of ~450 K; anhydrous, chemically pure KCl and TlCl were used.

Techniques for assembling the electrochemical cell and for measuring the emf are described in detail in [8, 12]. The emf was measured by the compensation method using V-7-27 digital voltmeter in the range 300–380 K (the system $TlCl–Tl_2S–S$) or 300–430 K (the system $TlCl–Tl_2Se–Se$). Taking into account the recommendations of [12], the first equilibrium values of the emf were measured 60–80 h after the cell holding at 380–400 K; subsequent values were measured every 3–4 h after achievement of the required temperature. The emf values were considered equilibrium if upon repeated measurements at the given temperature they did not differ from each other by more than 0.5 mV, irrespective of the temperature variation direction.

The measurements have shown that the emf values for the chains of type (1) obtained by heating and cooling coincide with an accuracy of ±3 mV; their variations with temperature are nearly linear. Reversibility of the chains of type (1), along with reproducibility of emf values, is also confirmed by an almost complete absence of loss in the electrode weight after the experiments.

The results of the emf measurements, processed in approximation of their linear temperature dependence by the least squares method [13], are presented in the form of equations of the type [14] (Table 1)

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

where S_b^2 and S_E^2 are the dispersions of the constant b and separate measurements of emf, n is the number of pairs of E and T values, and $\bar{T}$ is the mean value of temperature.

On the basis of the data of Table 1, according to known thermodynamic relations, relative partial molar thermodynamic functions of thallium in the alloys at 298 K were calculated (Table 2).

Figure 1 depicts the solid-phase equilibrium diagrams for the systems $TlCl–Tl_2S–S$ and $TlCl–Tl_2Se–Se$ constructed in [4–8], with indicated values of emf (mV) in different phase regions at 300 K. The measurement results have shown that, in the system $TlCl–Tl_2S–S$, the emf values in each three-phase region at the given temperature are constant irrespective of alloy composition and that they vary in steps at the transition from one three-phase region into another (Fig. 1a, Table 1). The stepwise variation in emf from 410 to 426 mV at the stoichiometric composition of the Tl_6SCl_4 compound (Fig. 1a) confirms the data of [1–4] on the absence of an appreciable region of homogeneity of this compound.

Table 1. Temperature dependences of emf of the chains of type (1) in some phase regions of the systems $TlCl–Tl_2X–X$

No.	Phase region in Fig. 1	E, mV = $a + bT \pm 2S_E(T)$
1	$TlCl–TlS–Tl_2S_3$	$550.7 - 0.117T \pm 2[(2.3/25) + 6.2 \times 10^{-5}(T - 345.8)^2]^{1/2}$
2	$TlCl–Tl_4S_3–TlS$	$467.4 - 0.014T \pm 2[(2.2/25) + 6 \times 10^{-5}(T - 345.8)^2]^{1/2}$
3	$TlCl–Tl_6SCl_4–Tl_4S_3$	$452.1 - 0.089T \pm 2[(1.7/25) + 4.6 \times 10^{-5}(T - 345.8)^2]^{1/2}$
4	$Tl_2S–Tl_6SCl_4–Tl_4S_3$	$386.5 + 0.080T \pm 2[(1.3/25) + 3.5 \times 10^{-5}(T - 345.8)^2]^{1/2}$
5	$TlCl–TlSe–Se$	$636.4 - 0.041T \pm 2[(4.2/22) + 8.6 \times 10^{-5}(T - 362.8)^2]^{1/2}$
6	$TlCl–Tl_5Se_2Cl–TlSe$	$473.3 - 0.066T \pm 2[(1.6/22) + 5.1 \times 10^{-5}(T - 362.8)^2]^{1/2}$
7	$Tl_5Se_{2.2}Cl_{0.8}$	$446.4 + 0.012T \pm 2[(1.3/24) + 3.7 \times 10^{-5}(T - 360.6)^2]^{1/2}$
8	$Tl_5Se_{2.4}Cl_{0.6}$	$433.6 + 0.036T \pm 2[(1.8/24) + 5.4 \times 10^{-5}(T - 360.6)^2]^{1/2}$
9	$Tl_5Se_{2.6}Cl_{0.4}$	$413.0 + 0.074T \pm 2[(1.2/24) + 3.2 \times 10^{-5}(T - 360.6)^2]^{1/2}$
10	$Tl_5Se_{2.8}Cl_{0.2}$	$394.7 + 0.091T \pm 2[(1.7/24) + 4.7 \times 10^{-5}(T - 360.6)^2]^{1/2}$
11	Tl_5Se_3	$368.2 + 0.124T \pm 2[(1.5/24) + 5 \times 10^{-5}(T - 360.6)^2]^{1/2}$

Table 2. Partial thermodynamic functions of thallium in some phase regions of the systems $TlCl–Tl_2X–X$ at 298 K

Phase region in Fig. 1	$-\Delta G$(Tl)	$-\Delta H$(Tl)	ΔS(Tl)
	kJ/mol		J/(K mol)
$TlCl–Tl_6SCl_4–Tl_4S_3$	41.06 ± 0.08	43.62 ± 0.45	–8.59 ± 1.31
$TlBr–Tl_6SBr_4–TlS$	44.54 ± 0.08	45.95 ± 0.46	–3.67 ± 1.36
$TlCl–Tl_5Se_2Cl–TlSe$	43.77 ± 0.10	45.67 ± 0.55	–6.37 ± 1.38
$Tl_5Se_{2.2}Cl_{0.8}$	43.42 ± 0.09	43.07 ± 0.22	1.16 ± 1.17
$Tl_5Se_{2.4}Cl_{0.6}$	42.87 ± 0.10	41.84 ± 0.23	3.47 ± 1.42
$Tl_5Se_{2.6}Cl_{0.4}$	41.98 ± 0.08	39.85 ± 0.21	7.14 ± 1.09
$Tl_5Se_{2.8}Cl_{0.2}$	40.70 ± 0.10	38.08 ± 0.23	8.78 ± 1.32
Tl_5Se_3	39.09 ± 0.09	35.53 ± 0.22	11.96 ± 1.36

In the case of the system $TlCl–Tl_2Se–Se$, another picture is observed. The measurements have shown that, through the section $Tl_5Se_2Cl–Tl_5Se_3$, the emf values of the chains of type (1) and the partial thermodynamic functions of thallium are monotonic functions of composition (Tables 1, 2; Fig. 2). This is evidence of formation of a continuous series of solid solutions through this section.

It should also be noted that numerical values of emf and equations of their temperature dependences in phase regions 1, 2, 4, and 5 (Table 1) practically coincide with corresponding data [16, 17] for the binary

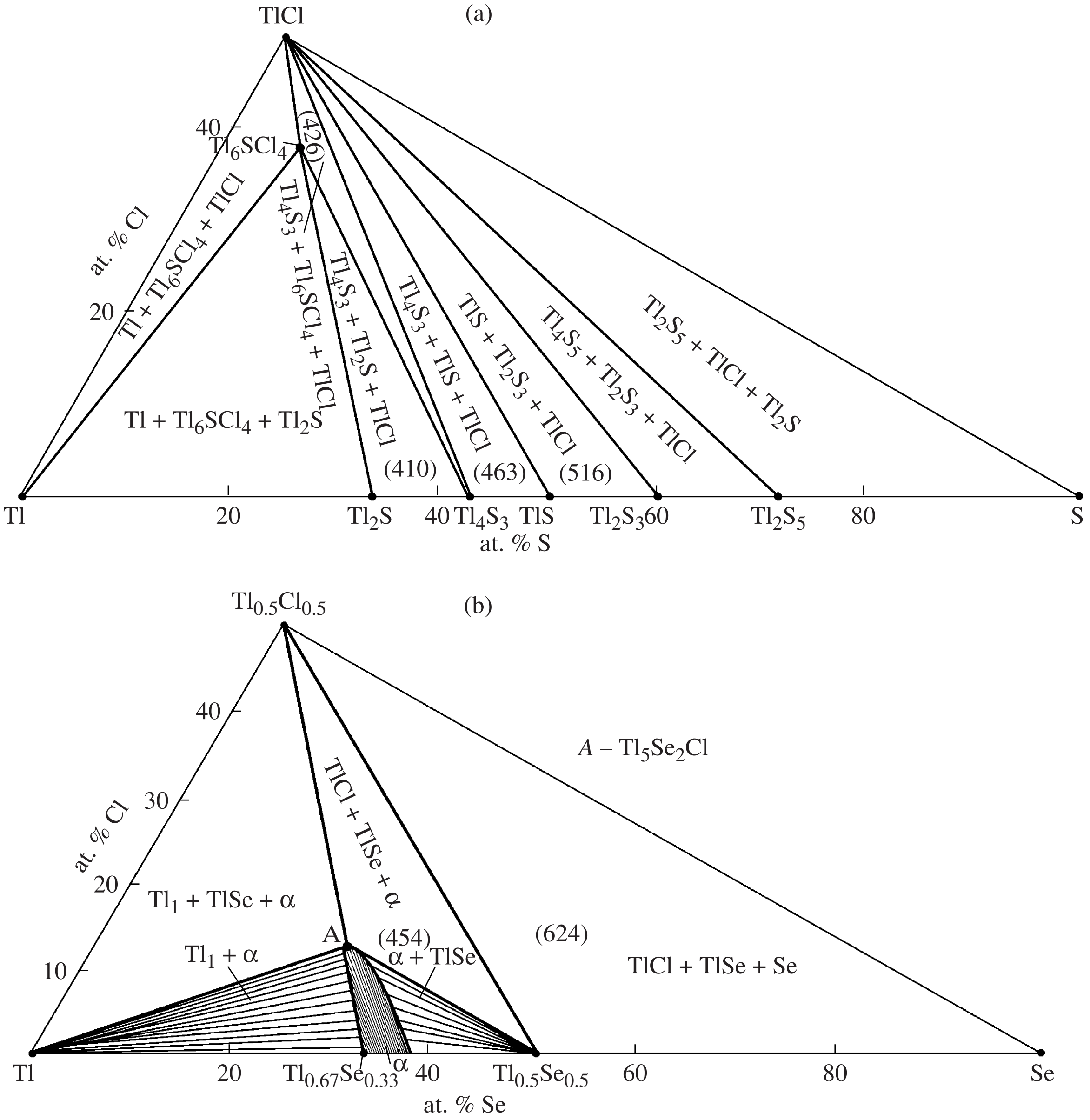

Fig. 1. Isothermal section of the phase diagram of the systems Tl–TlCl–S (a) and Tl–TlCl–Se (b) at 300 K (in brackets, the emf values for the chains of type (1) are given).

compounds TlS, Tl_4S_3, Tl_2S, and TlSe, respectively. On the one hand, this testifies of reversibility of the chains of type (1); on the other hand, this indirectly points to the absence of appreciable regions of solid solutions based on the aforementioned compounds in the systems $TlCl–Tl_2X–X$.

According to [12], the partial thermodynamic functions of thallium in solid-phase regions 3 and 6 (Table 2, Figs. 1a, 1b) are thermodynamic functions of the following potential-forming reactions

$$Tl + 6TlCl + 0.5Tl_4S_3 = 1.5Tl_6SCl_4$$

and

$$Tl + 0.5TlCl + TlSe = 0.5Tl_5Se_2Cl,$$

respectively.

According to the equations of these reactions, we determined ΔZ^0—the standard thermodynamic functions of formation (ΔG^0, ΔH^0):

$$\Delta Z^0(Tl_6SCl_4) = 2/3\Delta \bar{Z}\ (Tl) + 4\Delta Z^0\ (TlCl) + 1/3\Delta Z^0(Tl_4S_3)) \quad (2)$$

and

$$\Delta Z^0(Tl_5S_2C) = 2\Delta Z\ \ (Tl) + \Delta Z^0\ (TlCl) + 2\Delta Z^0\ (TlSe).(3)$$

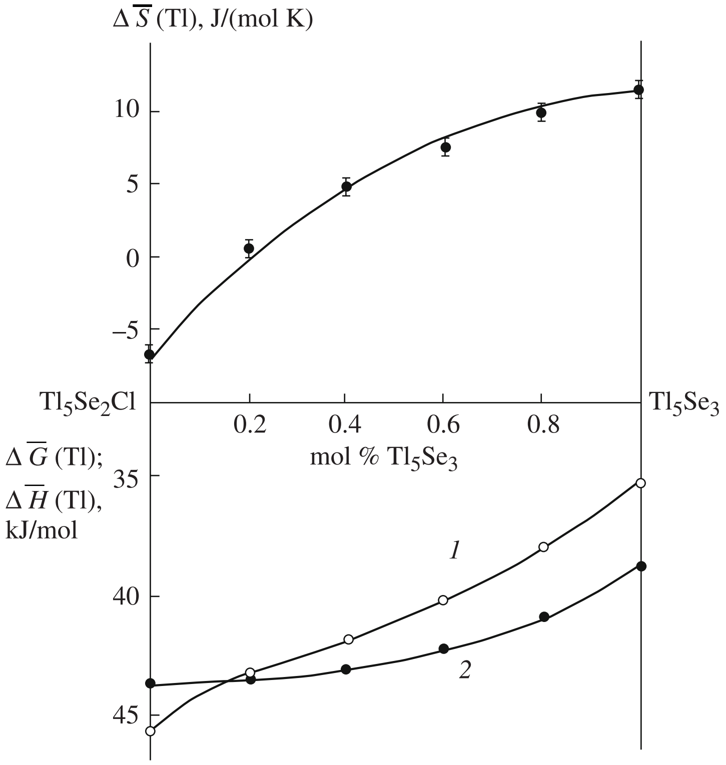

Fig. 2. Dependences of the partial thermodynamic functions in the system Tl_5Se_2Cl–Tl_5Se_3 at 298 K: (*1*) $\Delta\overline{H}$ (Tl, (*2*) $\Delta\overline{G}$ (Tl).

Here, $\Delta\overline{Z}$(Tl) is the respective partial molar values of thallium.

The standard entropies of the ternary compounds were also calculated on the basis of the potential-forming reactions by the relations

$$S^0(Tl_6Cl_4) = 2/3[\Delta\bar{S}(Tl) + S^0(Tl)] + 4S^0(TlCl) + 1/3\Delta S^0(Tl_4S_3) \quad (4)$$

$$S^0(Tl_5S_2C) = 2[(\Delta\bar{S}(Tl) + S^0(Tl)] + S^0(TlCl) + 2S^0(TlSe).(5)$$

In the calculations by relations (2)–(5), in addition to our own data on $\Delta\overline{Z}$(Tl), we used more reliable thermodynamic data for TlCl [15], Tl_4S_3 [16], TlSe [17], and Tl [15].

The integral thermodynamic functions of the solid solutions $Tl_5Se_{2-x}Cl_x$ were calculated by integrating the Gibbs–Duhem equation by the technique of [12, 18].

Table 3. Standard integral thermodynamic functions of the ternary phases of the systems Tl–TlCl(Br)–S and Tl–TlCl–Se

Phase	$-\Delta G^0$(298 K)	$-\Delta H^0$(298 K)	S^0(298 K)
	kJ/mol		J/(K mol)
Tl_6SCl_4	833.5 ± 3.7	928.1 ± 14.0	599 ± 9
Tl_5Se_2Cl	392.8 ± 1.1	421.6 ± 5.1	434 ± 7
$Tl_5Se_{2.2}Cl_{0.8}$	378.5 ± 1.2	395.1 ± 5.3	437 ± 8
$Tl_5Se_{2.4}Cl_{0.6}$	351.4 ± 1.4	367.1 ± 5.6	439 ± 9
$Tl_5Se_{2.6}Cl_{0.4}$	327.5 ± 1.4	330.6 ± 5.6	444 ± 10
$Tl_5Se_{2.8}Cl_{0.2}$	293.6 ± 1.5	290.7 ± 5.7	448 ± 11

The calculation results are presented in Table 3. The errors were found by the error accumulation method.

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