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THERMODYNAMIC FUNCTIONS OF TIN SELENIDES

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Abstract. The paper presents the results of a study of the solid-phase equilibria and thermodynamic properties of the Sn-Se system by electromotive forces (EMF) measurements of concentration cells relative to the tin electrode. From the EMF measurements, the relative partial molar functions of tin in the alloys, the standard Gibbs free energy and the enthalpy of formation, and the standard entropies of the $SnSe_2$ and SnSe compounds were calculated. A comparative analysis of the results obtained with literature data is carried out.

Keywords: *$SnSe_2$, SnSe, EMF method, partial molar functions, thermodynamic functions.*

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1. Introduction

Metal chalcogenides are among the promising functional materials (Alonso-Vante, 2018; Ahluwalia, 2016; Liu *et al.*, 2019; Woodrow, 2018). In particular, tin selenides $SnSe_2$ and SnSe, as well as solid solutions and doped phases based on them, have interesting thermoelectric, photoelectric, optical, sensory, and other properties (Liu *et al.*, 2018; Assili *et al.*, 2020; Zhanh *et al.*, 2020; Liu *et al.*, 2020; Shi *et al.*, 2018; Chen *et al.*, 2018).

The development of new materials is based on data on phase equilibria in the corresponding systems and thermodynamic functions of intermediate phases (Matsushita & Mikai, 2018; Voronin & Gerasimov, 1980; Babanly *et al.*, 2019; Imamaliyeva *et al.*, 2018).

The reliability of the phase diagram of the Sn-Se system is not in doubt. This system is characterized by the formation of two compounds $SnSe_2$ and SnSe, melting congruently at 1153 и 930 K (Massalski, 1990; Olamoto, 2010). The thermodynamic properties of these compounds have been studied in many works, the results of which are summarized in modern monographs and reference books (Iorish & Yungman, 2006; Kubaschewski *et al.*, 1993; Barin, 2008, Gerasimov *et al.*, 1974). An analysis of these data shows that the values of the standard integral thermodynamic functions of tin selenides, especially $SnSe_2$, are contradictory and need to be clarified.

This paper presents the results of a thermodynamic study of the Sn-Se system by the electromotive forces (EMF) method. Various modifications of this method, one of

the most accurate equilibrium experimental methods of chemical thermodynamics, are successfully used for the thermodynamic study of inorganic systems (Morachevskii *et al.*, 2003; Babanly & Yusibov, 2011; Babanly *et al.*, 2011; Aspila *et al.*, 2016; Moroz *et al.*, 2018a, 2018b; Voronin *et al.*, 2013; Babanly *et al.*, 2018; Babanly *et al.*, 2019; Aliev *et al.*, 2018; Imamaliyeva *et al.*, 2019). Moreover, to study metal chalcogenides, the EMF method with glycerin electrolyte is more widely used (Morachevskii *et al.*, 2003; Babanly &Yusibov, 2011; Babanly, *et al.*, 2017a, 2017b; Vassliev & Lysenko, 2016; Jafarov *et al.*, 2016; Sidorko *et al.*, 2008).

2. Experimental

For thermodynamic studies of the Sn-Se system, alloys with compositions 51, 60, 68, and 80 at% Se were prepared. The syntheses were carried out by fusion of the initial elements of high purity, purchased from Alfa Aesar (tin, 99.9999+%, selenium, 99.999%) in evacuated (~10^{-2}Pa) quartz ampoules at 1000K. In order to achieve complete homogenization, the alloys were subjected to long-term stepwise annealing: first, the alloys were kept at 800 K (500 h), and then at 400 K (100 h).

For the experiments, concentration chains of the type

$$(-)\ Sn\ (s.)\ |\ liquid\ electrolyte,\ Sn^{2+}\ |\ (Sn\ in\ alloy)\ (s.)\ (+) \qquad (1)$$

In cells of type (1), the KCl glycerol solution with the addition of 0.5 wt% $SnCl_2$ served as the electrolyte. Because the presence of either moisture or oxygen in the electrolyte was inadmissible, glycerol was thoroughly dewatered and degassed by evacuation at ~450 K, anhydrous chemically pure salts were used.

The electrodes were metal tin and pre-synthesized equilibrium alloys of the Sn-Se system with the above compositions. The electrodes were prepared by pressing the piece of metal tin (left electrode) and powdered alloys of the Sn-Se system in the form of pellets (diameter 7 mm and thickness 3-4 mm) in a molybdenum wire.

The used electrochemical cells had the construction of (Babanly & Yusibov, 2011; Imamaliyeva *et al.*, 2019), which allows simultaneously measuring the EMF of 6–7 alloy electrodes relative to one reference electrode. After the evacuation of air, an atmosphere of nitrogen was created in the electrochemical cells (pressure ~300-400 mm Hg).

EMF measurements were carried out using a Keithley 2100 6 1/2 Digit Multimeter in the 300-450 K temperature range. The cell was kept at~400 K within 40–60 h. Further, the first equilibrium EMF values were obtained, and the subsequent values of EMF were obtained 3–4 h after reaching the desired temperature. The system was considered to be in equilibrium if the EMF measurements were constant or their variations were not significant (<0.5 mV) regardless of the direction of the temperature change at repeated measurements at a given temperature.

3. Results and its discussion

The EMF measurements of concentration cell of type (1) confirmed the existence of SnSe+$SnSe_2$ and $SnSe_2$+Se two-phase regions in the SnSe-Se subsystem (Massalski, 1990). As can be seen from the E-x diagram at 400 K (Fig. 1), the EMF has two series of constant values that change drastically at the stoichiometric composition of $SnSe_2$.

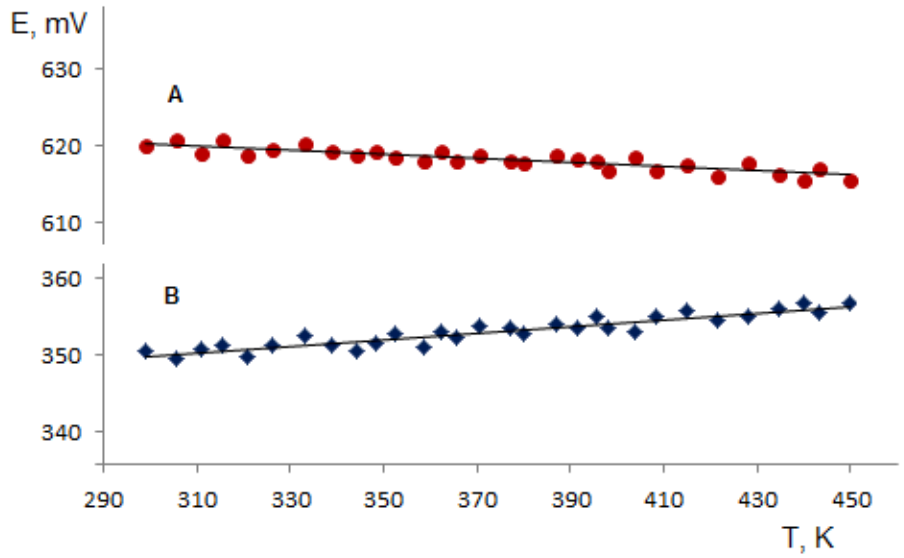

Figure 1. Temperature dependences of EMF of type (1) cells for two-phase alloys $SnSe_2$+Se (A) and SnSe+$SnSe_2$ (B)

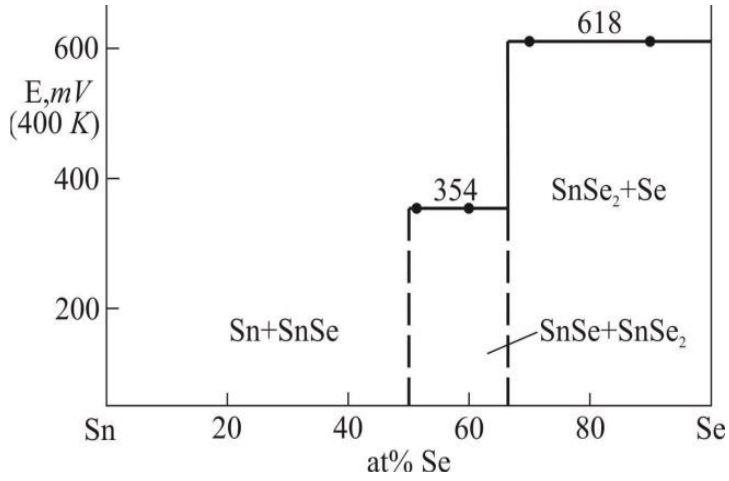

Figure 2. The composition dependence of the EMF of type (1) cells the at 400 K

Experimentally obtained data for temperature (T_i) and EMF (E_i) and data associated with the calculation steps for the $SnSe_2$+Se and SnSe +$SnSe_2$ phase areas are listed in Tables 1 and 2.

An analysis of the temperature dependences of the EMF showed their linearity for both phase regions (Fig. 2). Therefore, they were processed in the approximation of the linear temperature dependence of the EMF by the least-square method using the computer program "Microsoft Office Excel 2003".

The obtained equations of the type (2) are listed in Table 3 in the form

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

recommended in modern thermodynamic literature (Morachevskii *et al.*, 2003). Here n- is the number of pairs of values of E and T; S_E and S_b- are the variances of individual

measurements of EMF and coefficient b, respectively; $\overline{T}$ - average absolute temperature, Student's t-test. At the confidence level of 95% and n=30, the Student's test is t≤2.

Table 1. Experimentally obtained data for temperature (T_i) and EMF (E_i) and data associated with the calculation steps for the $SnSe_2$+Se phase region of the Sn-Se system

T_i, K	E_i, mV	$T_i - \overline{T}$	Ei($T_i - \overline{T}$)	$(T_i - \overline{T})^2$	$\widetilde{E}$	$E_i - \widetilde{E}$	$(E_i - \widetilde{E})^2$
299,3	620,01	-74,93	-46455,28	5614,01	620,40	-0,39	0,15
305,7	620,82	-68,53	-42542,73	4695,90	620,22	0,60	0,36
311,2	619,12	-63,03	-39021,07	3972,36	620,07	-0,95	0,90
315,4	620,81	-58,83	-36520,18	3460,58	619,95	0,86	0,74
320,9	618,81	-53,33	-32999,07	2843,73	619,80	-0,99	0,97
326,3	619,62	-47,93	-29696,32	2296,97	619,64	-0,02	0,00
333,1	620,22	-41,13	-25507,58	1691,40	619,45	0,77	0,59
338,8	619,36	-35,43	-21941,86	1255,05	619,29	0,07	0,00
344,1	618,73	-30,13	-18640,27	907,62	619,14	-0,41	0,17
348,6	619,38	-25,63	-15872,64	656,73	619,02	0,36	0,13
352,5	618,66	-21,73	-13441,42	472,05	618,91	-0,25	0,06
358,7	618,14	-15,53	-9597,65	241,08	618,73	-0,59	0,35
362,3	619,25	-11,93	-7385,59	142,25	618,63	0,62	0,38
365,8	617,92	-8,43	-5207,01	71,01	618,54	-0,62	0,38
370,4	618,87	-3,83	-2368,21	14,64	618,41	0,46	0,21
377,2	618,14	2,97	1837,94	8,84	618,22	-0,08	0,01
380,1	617,91	5,87	3629,19	34,50	618,13	-0,22	0,05
386,9	618,81	12,67	7842,39	160,61	617,94	0,87	0,75
391,4	618,33	17,17	10618,79	294,92	617,82	0,51	0,26
395,6	617,94	21,37	13207,44	456,82	617,70	0,24	0,06
398	616,81	23,77	14663,63	565,17	617,63	-0,82	0,68
403,7	618,52	29,47	18229,85	868,68	617,47	1,05	1,10
408,2	616,85	33,97	20956,45	1154,19	617,35	-0,50	0,25
414,9	617,64	40,67	25121,48	1654,32	617,16	0,48	0,23
421,7	616,16	47,47	29251,17	2253,72	616,97	-0,81	0,65
428,1	617,83	53,87	33284,56	2902,34	616,79	1,04	1,09
434,6	616,26	60,37	37205,67	3644,94	616,61	-0,35	0,12
440,2	615,45	65,97	40603,29	4352,48	616,45	-1,00	1,00
443,3	617,08	69,07	42623,77	4771,13	616,36	0,72	0,52
449,8	615,53	75,57	46517,65	5711,33	616,18	-0,65	0,42
$\overline{T} = 374{,}23$	$\overline{E} = 618{,}30$		Σ=-1603,63	Σ=57169,34			Σ= 12,58

Table 2. Experimentally obtained data for temperature (T_i) and EMF (E_i) and data associated with the calculation steps for the SnSe +$SnSe_2$ phase region of the Sn-Se system

T_i, K	E_i, mV	$T_i - \overline{T}$	$Ei(T_i - \overline{T})$	$(T_i - \overline{T})^2$	$\widetilde{E}$	$E_i - \widetilde{E}$	$(E_i - \widetilde{E})^2$
299,3	350,56	-74,93	-26266,29	5614,01	349,87	0,69	0,48
305,7	349,52	-68,53	-23951,44	4695,90	350,14	-0,62	0,39
311,2	350,83	-63,03	-22111,65	3972,36	350,38	0,45	0,20
315,4	351,22	-58,83	-20661,10	3460,58	350,56	0,66	0,43
320,9	349,85	-53,33	-18656,33	2843,73	350,80	-0,95	0,91
326,3	351,24	-47,93	-16833,76	2296,97	351,04	0,20	0,04
333,1	352,56	-41,13	-14499,62	1691,40	351,33	1,23	1,50
338,8	351,41	-35,43	-12449,28	1255,05	351,58	-0,17	0,03
344,1	350,58	-30,13	-10561,81	907,62	351,81	-1,23	1,52
348,6	351,6	-25,63	-9010,34	656,73	352,01	-0,41	0,17
352,5	352,81	-21,73	-7665,39	472,05	352,18	0,63	0,40
358,7	351,16	-15,53	-5452,34	241,08	352,45	-1,29	1,66
362,3	353,08	-11,93	-4211,07	142,25	352,60	0,48	0,23
365,8	352,18	-8,43	-2967,70	71,01	352,76	-0,58	0,33
370,4	353,71	-3,83	-1353,53	14,64	352,96	0,75	0,57
377,2	353,53	2,97	1051,16	8,84	353,25	0,28	0,08
380,1	352,76	5,87	2071,88	34,50	353,38	-0,62	0,38
386,9	354,17	12,67	4488,51	160,61	353,67	0,50	0,25
391,4	353,52	17,17	6071,12	294,92	353,87	-0,35	0,12
395,6	354,94	21,37	7586,25	456,82	354,05	0,89	0,79
398	353,61	23,77	8406,49	565,17	354,15	-0,54	0,30
403,7	353,07	29,47	10406,15	868,68	354,40	-1,33	1,78
408,2	355,06	33,97	12062,57	1154,19	354,60	0,46	0,21
414,9	355,75	40,67	14469,54	1654,32	354,89	0,86	0,74
421,7	354,63	47,47	16835,47	2253,72	355,18	-0,55	0,31
428,1	355,15	53,87	19133,11	2902,34	355,46	-0,31	0,10
434,6	356,08	60,37	21497,74	3644,94	355,75	0,33	0,11
440,2	356,92	65,97	23547,20	4352,48	355,99	0,93	0,87
443,3	355,44	69,07	24551,43	4771,13	356,12	-0,68	0,47
449,8	356,71	75,57	26957,76	5711,33	356,41	0,30	0,09
$\overline{T}$ = 374,23	$\overline{E}$ = 353,12		Σ=2484,73	Σ=57169,34			Σ=15,44

From the obtained equations of the temperature dependences of the EMF (Table 3) according to the relations (Morachevskii *et al*., 2003; Babanly & Yusibov, 2011)

$$\Delta\overline{G}_{Sn} = -zFE \quad (3)$$

$$\Delta\overline{H}_{Sn} = -z[E - T\left(\frac{\partial E}{\partial T}\right)_p] = -zFa \quad (4)$$

$$\Delta\bar{S}_{Sn} = zF\left(\frac{\partial E}{\partial T}\right)_p = zFb \quad (5)$$

the relative partial molar functions of tin in the alloys at 298 K were calculated (Table 4).

Table 3. Relations between the EMF and the temperature for type (1) cells in some phase regions of the Sn-Sb-Se system in the 300–450 K temperature interval

Phase area	E, mV=a+bT±2$\tilde{S}_E$(T)
$SnSe_2$+Se	$628.80 - 0.0281\ T \pm 2\left[\frac{0.42}{30} + 7.3\cdot10^{-6}(T-374.2)^2\right]^{1/2}$
SnSe+$SnSe_2$	$336.86 - 0.0435\ T \pm 2\left[\frac{0.51}{30} + 9.1\cdot10^{-6}(T-374.2)^2\right]^{1/2}$

Table 4. Relative partial functions of tin in the alloys of the Sn-Se system at T = 298.15 K

Phase area	$-\Delta\bar{G}_{Sn}$	$-\Delta\bar{H}_{Sn}$	$\Delta\bar{S}_{Sn}$,
	κJ·mol^{-1}		J·K^{-1}·mol^{-1}
$SnSe_2$+Se	119.73±0.09	121.34±0.39	-5.41±1.05
SnSe+$SnSe_2$	67.51±0.10	65.00±0.44	8.39±1.16

Given the insignificance of the homogeneity regions of tin selenides (Massalski, 1990), these partial molar quantities are thermodynamic functions of the following potential-forming reactions (all substances are crystalline) (Morachevskii *et al.*, 2003; Babanly & Yusibov, 2011):

$$Sn+2Se=SnSe_2$$
$$Sn+SnSe_2=2SnSe$$

Therefore, the standard thermodynamic functions of the formation of tin selenides are calculated by the relations

$$\Delta_f Z°(SnSe_2) = \Delta\bar{Z}_{Sn}$$
$$\Delta_f Z^0_{SnSe} = 0.5\overline{\Delta Z_{Sn}} + 0.5\Delta_f Z^0(SnSe_2)$$

here ΔZ= ΔG or ΔH, while standard entropy

$$S°(SnSe_2) = \Delta\bar{S}_{Sn} + S°(Sn) + 2S°(Se)$$
$$S°(SnSe) = 0.5\Delta\bar{S}_{Sn} + 0.5S°(Sn) + 0.5S°(SnSe_2)$$

In the calculations, in addition to our experimental data, we used the values of standard entropies of tin (51.55±0.21 J·K^{-1}· mol^{-1}) and selenium (42.13±0.21 J·K^{-1}·mol^{-1}) given in (Iorish & Yungman, 2006). In all cases, the estimated standard uncertainties were calculated by accumulating the errors.

The calculation results are presented in Table 5. The relevant literature data for SnSe and $SnSe_2$ are also provided here. From Table 5 it is seen that the SnSe data available in the literature are consistent with each other with an accuracy of 10%. Our data are better consistent with the results of calorimetric (Gadzhiev & Sharifov, 1960) and electrochemical (Melekh, *et al.*, 1971) studies, as well as with the values recommended in the references (Barin, 2008; Gerasimov *et al.*, 1974; Iorish & Yungman, 2006; Kubaschevski, 1993).

Table 5. Standard integrated thermodynamic functions of tin selenides

Com-pound	$-\Delta_f G^0(298K)$	$-\Delta_f H^0(298K)$	$S_f^0(298K)$	Ref.
	κJ·mol^{-1}		J·K^{-1}·mol^{-1}	
$SnSe_2$	119.7±0.1	121.3±0.4	130.4±1.7	this work
	119.7±0.2	124.7±1.2		Melekh *et al*., 1971
		119.0±4.2		Novoselova & Pashinkin, 1977
	110.0	117.2	111.7	Barin, 2008
		124.7±8.4	118.0	Kubaschevski, 1993
		82.4		Iorish & Yungman, 2006
	91.4	82.4	119.0±4.2	Gerasimov *et al.*, 1974
SnSe	93.6±0.1	93.2±0.4	95.0±1.6	this work
	96.2±0.2	94.6±1.2		Melekh *et al*., 1971
		90.8±0.5		Gadzhiev & Sharifov, 1960
	87.5	88.7	89.5	Barin, 2008
		94.1±3.8	98.1	Kubaschevski, 1993
		90.8±3.3		Iorish & Yungman, 2006
	90.0±7.0	90.0±7.0	90.0	Gerasimov *et al*., 1974

For $SnSe_2$, the published thermodynamic data differ from each other by up to 40%. The complex of standard thermodynamic functions we obtained is in good agreement with the data of original studies (Melekh, *et al.*, 1971; Novoselova, Pashinkin, 1977) and the values recommended in the (Barin, 2008; Kubaschevski, 1993). The data given in the handbooks (Gerasimov *et al.*, 1974; Iorish & Yungman, 2006) are underestimated. They are even lower than for the SnSe, which is impossible.

4. Conclusion

In this paper, we presented new sets of mutually consistent data on the partial molar functions of the tin selenide in alloys of the Sn-Se system and standard integrated thermodynamic functions of tin selenides obtained by using the EMF method. These results supplement and clarify the thermodynamic data available in the literature for these compounds, which are of great practical interest as functional materials.

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