

## Thermodynamic Characteristics of Triphenylantimony Bis(acetophenoneoximate)

A. V. Markin<sup>a</sup>, I. A. Letyanina<sup>a</sup>, N. N. Smirnova<sup>a</sup>, V. V. Sharutin<sup>b</sup>, and O. V. Molokova<sup>c</sup>

<sup>a</sup> Lobachevskii State University, Nizhni Novgorod, 603005 Russia

<sup>b</sup> Blagoveshchensk State Pedagogical University, Blagoveshchensk, 675015 Russia

<sup>c</sup> Far East Military Institute, Blagoveshchensk, 675021 Russia

e-mail: smirnova@ichem.unn.ru

Received June 10, 2010

**Abstract**—The temperature dependence of heat capacity  $C_p^\circ = f(T)$  of triphenylantimony bis(acetophenoneoximate)  $\text{Ph}_3\text{Sb}(\text{ONCPhMe})_2$  was measured for the first time in an adiabatic vacuum calorimeter in the range of 6.5–370 K and a differential scanning calorimeter in the range of 350–463 K. The temperature, enthalpy, and entropy of fusion were determined. Treatment of low-temperature (20 K  $\leq T \leq 50$  K) heat capacity was performed on the basis of Debye's theory of the heat capacity of solids and its multifractal model and, as a consequence, a conclusion was drawn on the type of structure topology. Standard thermodynamic functions  $C_p^\circ(T)$ ,  $H^\circ(T) - H^\circ(0)$ ,  $S^\circ(T)$ , and  $G^\circ(T) - H^\circ(0)$  were calculated according to the experimental data obtained for the compound mentioned in the crystalline and liquid states for the range of  $T \rightarrow 0$ –460 K. The standard entropy of the formation of crystalline  $\text{Ph}_3\text{Sb}(\text{ONCPhMe})_2$  was determined at  $T = 298.15$  K.

**Keywords:** thermodynamic properties, triphenylantimony bis(acetophenoneoximate), calorimetric methods.

**DOI:** 10.1134/S0036024411080218

### INTRODUCTION

The chemistry of organic complexes of pentavalent antimony has recently attracted considerable interest due to its unusual structural possibilities, which vary from individual monomer structures to supramolecular assemblies. In addition, organic derivatives of antimony exhibit substantial antibacterial properties and antitumor activity [1]. The authors of [2–4] synthesized and identified individual organic compounds of pentavalent antimony, e.g.,  $\text{Ph}_4\text{SbONCPh}_2$ ,  $\text{Ph}_3\text{Sb}(\text{ONCPh}_2)_2$ ,  $\text{Ph}_3\text{SbONCHC}_4\text{H}_3\text{O}$ ,  $\text{Ph}_4\text{SbONCPhMe}$ , and  $\text{Ph}_3\text{Sb}(\text{ONCMe}_2)_2$ . Until recently, there were virtually no physicochemical characteristics for pentavalent antimony compounds mentioned in the literature. Some thermodynamic characteristics for organoantimony compounds were given in [5]. Earlier, we studied the standard thermodynamic properties of pentaphenylantimony  $\text{Ph}_5\text{Sb}$  [6], tetraphenylantimony benzophenoneoximate  $\text{Ph}_4\text{SbONCPh}_2$  [7], and tetraphenylantimony acetophenoneoximate  $\text{Ph}_4\text{SbONCPhMe}$  [8] in the range of 0 to 350–450 K.

This work is a continuation of comprehensive investigations on the standard thermodynamic properties of a number of pentavalent antimony compounds and is devoted to the calorimetric study of the temperature dependence of the heat capacity for

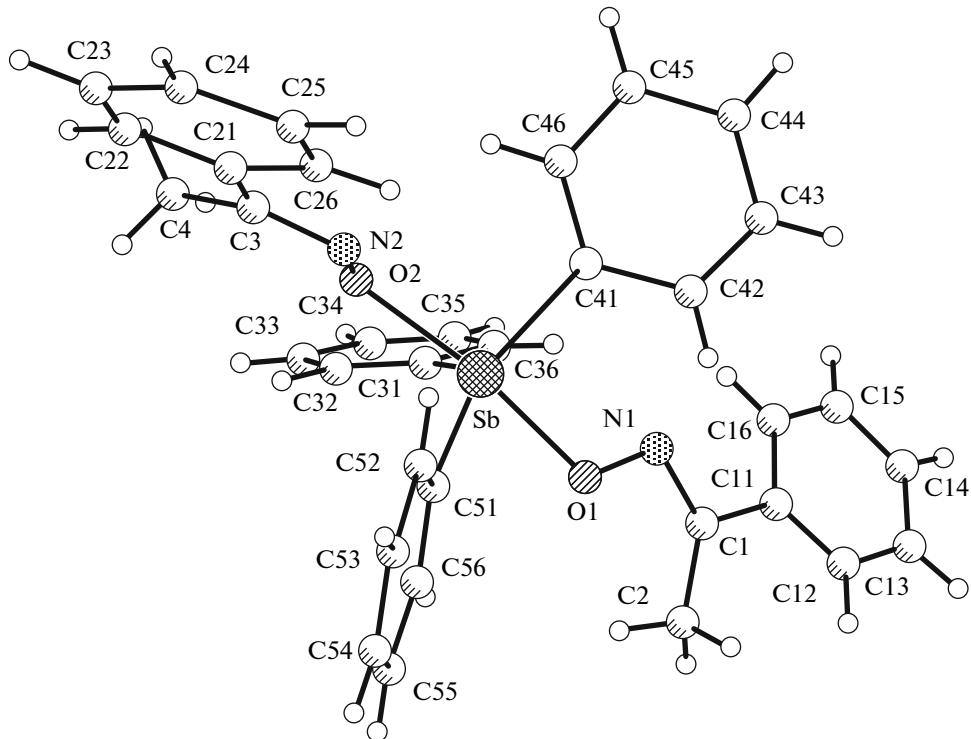
triphenylantimony  $\text{Ph}_3\text{Sb}(\text{ONCPhMe})_2$  (I) in the range of 7–460 K; determining its thermodynamic characteristics of fusion; calculating its standard thermodynamic functions by the obtained experimental data:  $C_p^\circ(T)$ ,  $H^\circ(T) - H^\circ(0)$ ,  $S^\circ(T)$ , and  $G^\circ(T) - H^\circ(0)$  for the sample I in crystalline and liquid states in the range of  $T \rightarrow 0$ –460 K; calculating the standard entropy of formation of crystalline compound I at  $T = 298.15$  K; and determining fractal dimensionality  $D$  and evaluating the type of structure topology.

### EXPERIMENTAL

#### Parameters of the Sample under Study

Sample I was synthesized according to the procedure described in [9]. Aqueous solution of  $\text{H}_2\text{O}_2$  was added to a solution of triphenylantimony and acetophenone oxime in ether. The mixture was kept for 12 h at  $T = 293$  K. Colorless crystals, which were filtered and dried, were formed by the oxidation addition reaction.

The following values were found by elemental analysis (%): C 65.07; H 5.04; N 4.56 (for  $\text{C}_{34}\text{H}_{31}\text{SbO}_2\text{N}_2$ , the calculated values were (%): C 65.73; H 4.99; N 4.51). Values for the IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ) were 1590 ( $\nu_{\text{CN}}$ ), 1310, 1190, 1160, 1070, 1020, 990, and 920 ( $\nu_{\text{NO}}$ ). The structure of compound was deter-



**Fig. 1.** Molecular structure of triphenylantimony bis(acetophenoneoximate).

mined by X-ray analysis. The corresponding data are given in [9]. The molecular structure of compound is shown in Fig. 1. According to the data from our analyses, determined within the experimental error of measurement, the content of the main substance in the sample under study was not less than 99.5 mol %.

The thermal stability of I was studied using TG209F1 thermal microscopes (Netzsch Geratebau, Germany). We determined that a considerable loss in weight related to the destruction of the sample is observed at  $T = 460$  K; further, with an increase in temperature of 10 K, the loss of weight increases from 2% and takes the value of 10% at 500 K. In an inert medium, the sample of triphenylantimony bis(acetophenoneoximate) is thus thermally stable up to 460 K.

#### Apparatus and Measuring Technique

We used a fully automatic BKT-3 adiabatic vacuum calorimeter (AOZT Termis, Russia) to study the temperature dependence of heat capacity  $C_p^\circ = f(T)$  in the range of 6–370 K. Liquid helium and nitrogen were used as refrigerants. An ampoule with the substance was filled to a pressure of 40 kPa at room temperature by dry helium as the thermal exchange gas. Both the design of the calorimeter and the procedure were analogous to those described in [10, 11]. The calorimetric ampoule was a thin-walled cylinder of titanium with a volume of  $1.5 \times 10^{-6}$  m<sup>3</sup>. The temperature was mea-

sured using an iron–rhodium resistance thermometer ( $R \geq 100 \Omega$ ) calibrated according to ITS-90. The temperature difference between the ampoule and adiabatic shell was controlled using a four-soldered copper–iron–chromel thermocouple. The reliability of the calorimeter was verified by measuring  $C_p^\circ$  of standard samples of pure copper, standard corundum, and K-3 brand benzoic acid, and the temperatures and enthalpies of fusion for *n*-heptane. It was determined that the apparatus and measuring technique allowed us to obtain values  $C_p^\circ$  of the substances with an error of  $\pm 2\%$  up to 15 K;  $\pm 0.5\%$  in the range of 15–40 K; and  $\pm 0.2\%$  in the range of 40–370 K; and to measure the temperatures of phase transitions with an error of  $\pm 0.01$  K in accordance with ITS-90.

A DSC204F1 Phoenix differential scanning calorimeter (Netzsch Geratebau, Germany) was used to measure the heat capacity of sample I in the range of 350–460 K. Both the design of the calorimeter and the procedure were described, e.g., in [12, 13]. The reliability of the calorimeter was verified by standard calibrating experiments on measuring the thermodynamic characteristics of fusion for *n*-heptane, mercury, indium, tin, lead, bismuth, and zinc. It was determined that the apparatus and measuring technique allowed us to measure the temperatures of phase transitions with an error of  $\pm 0.5$  K, and the enthalpies of transitions with an error of  $\pm 1\%$ . The heat capacity was determined by the ratio method, with Corundum

used as a standard reference sample. The technique for determining  $C_p^\circ$  according to the data of DSC measurements is described in detail in [12] and the Netzsch Proteus Software. Individual values  $C_{p,\text{sp}}^\circ$  were determined according to Eq. (1) at different temperatures:

$$C_{p,\text{s}}^\circ = \frac{m_{\text{std}}}{m_s} \frac{\text{DSC}_s(T) - \text{DSC}_{\text{bl}}(T)}{\text{DSC}_{\text{std}}(T) - \text{DSC}_{\text{bl}}(T)} C_{p,\text{std}}^\circ, \quad (1)$$

where  $C_{p,\text{s}}^\circ$  is the specific heat capacity of a sample at temperature  $T$ ;  $C_{p,\text{std}}^\circ$  is the specific heat capacity of the standard (corundum) at temperature  $T$ ;  $m_{\text{std}}$  is the mass of the standard;  $m_s$  is the mass of the sample under study;  $\text{DSC}_s$  is the value of the DSC signal at temperature  $T$  from the curve of sample ( $\mu\text{V}$ );  $\text{DSC}_{\text{std}}$  is the value of the DSC signal at temperature  $T$  from the curve of reference sample ( $\mu\text{V}$ ); and  $\text{DSC}_{\text{bl}}$  is the value of the DSC signal at temperature  $T$  from the baseline ( $\mu\text{V}$ ).

Three different measurements were performed to calculate the heat capacity: one for the baseline, one for the standard (corundum), and one for the sample under study. In these measurements, the following parameters remained identical: the flow of argon, the rate of argon flow, the starting temperature, the heating rate and scanning rate, the mass of the crucible and cap, and the position of the crucible on the sensor. During measurement of the heat capacity, the sample was kept at a constant temperature (293 K) for 30 min in the argon flow; heating was then performed at a constant rate (1 K/min) up to 460 K; and the measurements were terminated with subsequent cooling of the system to room temperature. Measurements for the baseline and standard were performed in the same manner.

Note that the error determining  $C_p^\circ$  by the above method was no worse than  $\pm 2\%$ . Measurements of thermophysical characteristics were performed with an ampoule of substance at an average heating rate of 1 K/min in an atmosphere of argon.

## RESULTS AND DISCUSSION

The heat capacity of I was studied in the temperature range of 6.5–370 K (Table 1) by AVC, and in the range of 350–460 K, by DSC. Subsequent shots of sample were placed in calorimetric ampoules:  $0.5235 \times 10^{-3}$  kg in AVC, and  $0.023 \times 10^{-3}$  kg in DSC. In AVC, 213 experimental values of  $C_p^\circ$  were obtained in two series, reflecting the continuity of the experiment. The heat capacity of the compound under study everywhere assumed value of 45–65% of the total heat capacity of the calorimetric ampoule with the substance. The experimental points of  $C_p^\circ$  were smoothed by means of exponential and semilogarithmic polyn-

oms; corresponding coefficients were calculated by the least squares method with the use of special programs.

The root-mean-square deviation of the experimental points of  $C_p^\circ$  from the corresponding smoothed curve  $C_p^\circ = f(T)$  did not exceed  $\pm 0.5\%$  in the range of 20–90 K;  $\pm 0.2\%$ , in the range of 112–250 K;  $\pm 0.1\%$  in the range of 240–370 K; and  $\pm 0.7\%$ , in the range of 450–463 K. The molar weight of the object under study was calculated from the IUPAC table of atomic weights [14].

Experimental values of the heat capacity of I and the smoothed curve  $C_p^\circ = f(T)$  are given in Fig. 2. In the studied temperature range, triphenylantimony bis(acetophenoneoximate) was in the crystalline (AB section, Fig. 2) and liquid (CD section, Fig. 2) states. The heat capacity of I in the crystalline state smoothly increases with a rise in temperature. The drastic increase in heat capacity and subsequent break in the curve were determined by the fusion of the crystals of substance.

In addition to fusion, a reproducible anomaly is observed on the curve of temperature dependence of the heat capacity of I (FGH section, Fig. 2) in the range of 85–110 K. The temperature corresponding to the maximum value of the apparent heat capacity in the range of transformation was  $99.5 \pm 0.5$  K. According to the McCullough classification [15, 16], this transition could be related to a  $\lambda$  transition in the solid state. Its enthalpy  $\Delta_{\text{tr}}H^\circ = 86.84 \pm 0.17$  J/mol and entropy  $\Delta_{\text{tr}}S^\circ = 0.8827 \pm 0.0018$  J/(mol K) were calculated using the area between the curves  $C_p^\circ = f(T)$  and  $C_p^\circ = f(\ln T)$  with the  $\lambda$  transition and corresponding interpolation curves. The calorimetric data were insufficient for determining the nature of this transition without a number of additional structural investigations.

It was interesting to obtain the value of fractal dimensionality  $D$  for the substance under study [17, 18] by the experimental data on low-temperature heat capacity. Fractal dimensionality  $D$  is an exponent of temperature in the main equation of the fractal model of treatment for low-temperature heat capacity. Values  $D$  allow us to draw some conclusions on the type of the structure topology of solids, and they can be obtained from the graph of  $\ln C_v$  versus  $\ln T$ . This follows from the following equation:

$$C_v = 3D(D+1)kN\gamma(D+1)\xi(D+1)(T/\Theta_{\max})^D, \quad (2)$$

where  $k$  is the Boltzmann constant,  $N$  is the number of atoms in a molecule,  $\gamma(D+1)$  is the gamma function,  $\xi(D+1)$  is the Riman  $\xi$  function, and  $\Theta_{\max}$  is the intrinsic temperature. For a particular solid,  $3D(D+1)kN\gamma(D+1)\xi(D+1)(1/\Theta_{\max})^D = A$  is a constant value. Equation (2) can then be written as follows:

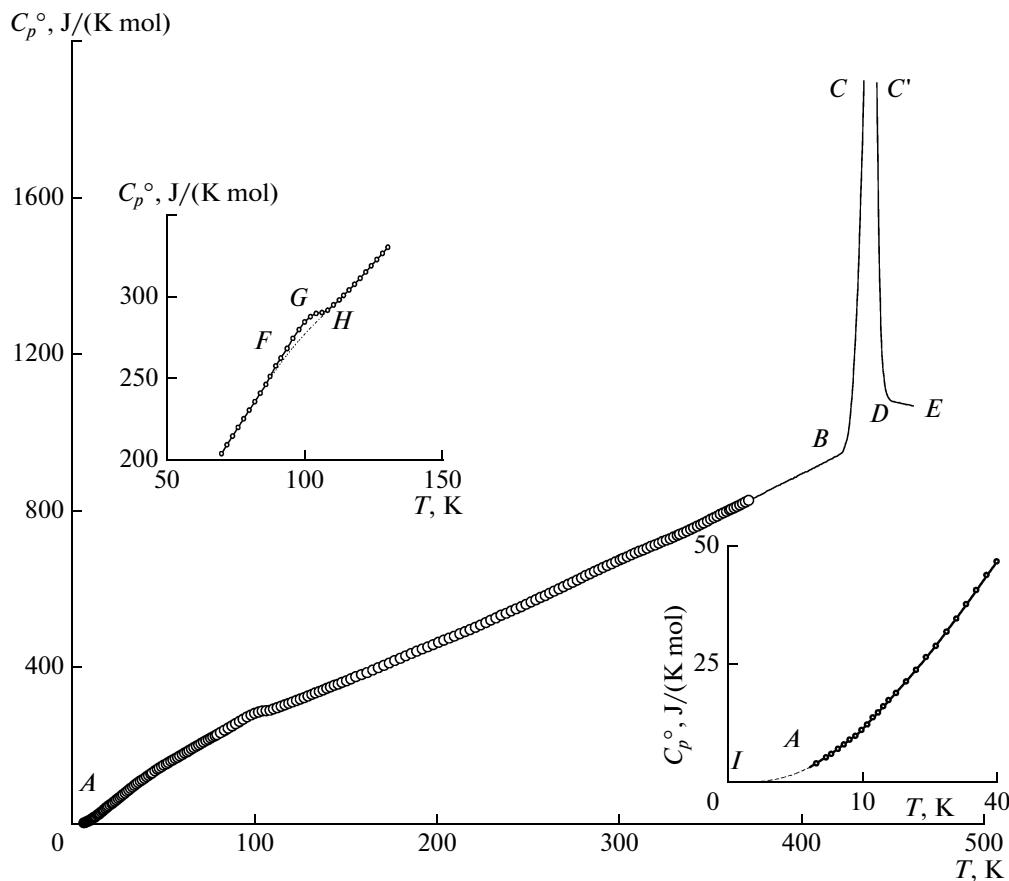
$$\ln C_v = \ln A + D \ln T. \quad (3)$$

**Table 1.** Experimental values of the heat capacity (J/(mol K)) of triphenylantimony bis(acetophenoneoximate)  $\text{Ph}_3\text{Sb}(\text{ONCPhMe})_2$  ( $M = 621.38 \text{ g/mol}$ )

$T, \text{K}$	$C_p^\circ$										
Series 1		31.03	88.20	74.53	217.3	122.88	317.0	217.91	497.9	308.29	693.5
6.52	4.05	32.05	92.00	75.86	220.8	124.96	320.7	220.78	503.9	310.50	698.1
7.23	5.32	33.08	96.00	77.11	224.2	127.05	324.3	223.63	509.7	312.64	701.7
7.62	6.07	34.13	99.83	78.42	227.2	129.12	328.3	226.45	516.0	314.81	705.7
8.11	7.15	35.20	103.7	79.72	230.4	131.30	332.3	229.26	522.6	316.97	710.4
8.55	8.09	36.30	107.5	81.03	234.1	133.24	336.4	232.07	528.1	319.10	714.4
8.97	9.09	37.40	110.8	82.26	237.0	135.31	340.0	234.85	534.3	321.21	718.5
9.39	9.93	38.51	114.3	83.65	240.5	137.38	343.6	237.63	539.3	323.30	722.5
9.85	11.2	39.64	118.0	84.82	244.0	139.45	347.5	240.38	545.3	325.33	726.5
10.27	12.3	40.78	121.8	86.26	248.0	141.51	351.5	243.12	551.0	327.38	730.0
10.68	13.8	41.94	125.6	87.58	251.3	143.57	355.5	245.84	556.5	329.31	734.4
11.07	14.9	43.10	129.5	88.89	255.2	145.63	358.9	248.54	562.4	331.32	738.7
11.45	16.2	44.00	132.2	90.20	258.4	147.68	362.8	251.21	568.3	332.65	741.3
11.84	17.5	45.47	137.2	91.52	262.0	150.20	367.4	253.87	574.0	334.64	745.2
12.40	19.1	46.67	141.3	Series 2		152.60	371.9	256.50	580.0	336.59	749.5
13.14	21.5	47.79	144.5	79.29	229.4	155.38	377.5	259.08	585.2	338.53	753.6
13.88	24.0	49.08	148.0	81.31	235.0	158.46	383.1	261.42	590.8	340.38	757.6
14.61	26.7	50.30	152.0	83.37	240.8	161.53	388.6	263.99	596.4	342.28	762.2
15.33	29.10	51.53	154.9	85.44	246.4	164.59	394.4	266.50	602.2	344.15	766.5
16.13	32.13	52.77	158.4	87.50	252.0	167.65	400.4	269.02	607.6	345.70	769.8
16.85	34.90	54.01	161.8	89.56	257.2	170.64	406.4	271.51	613.3	347.75	774.7
17.58	38.00	55.26	165.3	91.63	263.1	173.68	412.6	273.98	618.9	349.55	779.7
18.32	41.00	56.52	168.7	93.69	269.0	176.71	418.9	276.43	624.5	351.34	783.9
19.08	44.20	57.78	172.0	95.76	275.0	179.73	424.5	278.83	630.0	353.09	787.9
19.84	47.10	59.06	175.3	97.96	279.6	182.74	430.6	281.25	635.7	354.83	792.3
20.80	50.60	60.35	178.9	100.00	283.8	185.73	437.0	283.61	640.8	356.54	796.2
21.67	53.60	61.69	182.5	102.06	287.2	188.71	442.9	285.95	646.3	358.23	799.8
22.54	56.70	62.89	185.8	104.14	290.2	191.69	448.3	288.32	651.2	359.81	803.4
23.42	59.67	64.18	189.3	106.21	290.7	194.66	453.9	290.66	656.5	360.71	805.8
24.31	63.00	65.40	193.0	108.29	292.1	197.61	459.6	292.98	661.5	362.35	809.1
25.29	66.62	66.76	196.5	110.38	295.3	200.57	465.3	295.29	666.4	308.29	693.5
26.14	69.85	68.06	200.0	112.46	298.3	203.51	470.8	297.58	671.4	363.95	812.7
27.09	73.45	69.36	203.2	114.54	302.3	206.43	476.2	300.00	676.3	365.54	816.3
28.05	77.06	70.66	206.9	116.63	305.7	209.30	481.1	301.69	679.6	367.11	820.0
29.03	80.90	71.95	210.4	118.72	309.6	212.25	487.4	303.91	683.9	368.64	823.7
30.02	84.31	73.24	214.1	120.60	313.0	215.14	492.5	306.11	688.8	370.35	827.7

The experimental values  $C_p^\circ$  can be considered as  $C_v$  without considerable error for  $T < 50 \text{ K}$ . Using the corresponding experimental data on heat capacity for the range of 20–50 K and Eq. (3), the  $D$  value can then be obtained. It was discovered that for I, the fractal dimensionality was 1.6 and intrinsic temperature

$\Theta_{\max} = 194.8 \text{ K}$ . These values were determined with an error of  $\pm 0.9\%$ . According to the Tarasov theory of the heat capacity of solids [19, 20],  $D = 1$  corresponds to the chain structure;  $D = 2$ , to the layer structure; and  $D = 3$ , to the spatial structure. Our obtained  $D$  value indicates a layer-chain topology for the structure of I. In Table 2, the corresponding values are given for I and



**Fig. 2.** Temperature dependence of the heat capacity of triphenylantimony bis(acetophenoneoximate):  $AB$  is crystal,  $BCC'D$  is the apparent heat capacity in the fusion range,  $DE$  is liquid,  $FGH$  is the apparent heat capacity in the range of the  $\lambda$  transition, and  $IA$  represents the extrapolation values of  $C_p^\circ$  according to Eq. (7).

the compounds we studied earlier: pentaphenylantimony  $\text{Ph}_5\text{Sb}$  [6], tetraphenylantimony benzophenoneoximate  $\text{Ph}_4\text{SbONCPh}_2$  [7], and tetraphenylantimony acetophenoneoximate  $\text{Ph}_4\text{SbONCPhMe}$  [8]. The values of the intrinsic Debye temperatures  $\Theta_{\max}$  calculated for the same degrees of freedom and temperature range allow us to draw some conclusions on the relative rigidity of the structures of solids. According to our results,  $\Theta_{\max}(\text{Ph}_4\text{SbONCPh}_2) \approx \Theta_{\max}(\text{Ph}_3\text{Sb}(\text{ONCPhMe})_2) < \Theta_{\max}(\text{Ph}_4\text{SbONCPhMe}) < \Theta_{\max}(\text{Ph}_5\text{Sb})$ . The rigidity of the crystalline structures of the compared compounds increases in the same order. This tendency should apparently hold at higher temperatures.

#### *Thermodynamic Characteristics of Fusion*

Temperature range of fusion from 423 to 453 K was determined graphically according to the DSC curves. The temperature corresponding to the onset of transition was, in accordance with the Netzsch Proteus Software, considered the fusion temperature:  $T_{\text{fus}}^\circ =$

$434.5 \pm 0.5$  K. Fusion enthalpy  $\Delta_{\text{fus}}H^\circ = 42.0 \pm 0.6$  kJ/mol was determined as the average from three experiments, also in accordance with the software's standard procedure. Fusion entropy  $\Delta_{\text{fus}}S^\circ = 96.7 \pm 1.4$  J/(K mol) was determined using the following equation:

$$\Delta_{\text{fus}}S^\circ = \Delta_{\text{fus}}H^\circ / T_{\text{fus}}^\circ. \quad (4)$$

**Table 2.** Fractal dimensionalities  $D$  and intrinsic temperatures  $\Theta_{\max}$

Substance	$T$ , K	$D$	$\Theta_{\max}$ , K	$\delta$ , %
$\text{Ph}_3\text{Sb}(\text{ONCPhMe})_2$	7–11	3.0	63.7	1.4
	20–50	1.6	194.8	0.9
$\text{Ph}_5\text{Sb}$ [6]	6–11	3.0	60.6	1.7
	20–50	1.3	246.7	1.0
$\text{Ph}_4\text{SbONCPh}_2$ [7]	6–11	3.0	76.1	0.4
	20–50	1.6	195.3	1.0
$\text{Ph}_4\text{SbONCPhMe}$ [8]	6–11	3.0	64.5	1.6
	20–50	1.6	210.1	0.7

**Table 3.** Standard thermodynamic functions of triphenylantimony bis(acetophenoneoximate)  $\text{Ph}_3\text{Sb}(\text{ONCPhMe})_2$  ( $M = 621.38 \text{ g/mol}$ )

$T, \text{ K}$	$C_p^\circ(T), \text{ J/(K mol)}$	$H^\circ(T) - H^\circ(0), \text{ kJ/mol}$	$S^\circ(T), \text{ J/(K mol)}$	$-(G^\circ(T) - H^\circ(0)), \text{ kJ/mol}$
Crystalline state				
5	1.87	0.00230	0.625	0.000781
10	11.6	0.0332	4.50	0.0118
15	27.9	0.131	12.2	0.0521
20	47.55	0.3174	22.80	0.1385
25	65.55	0.5994	35.31	0.2834
30	84.51	0.9747	48.94	0.4935
35	102.5	1.443	63.33	0.7739
40	119.6	1.998	78.15	1.128
45	135.7	2.637	93.18	1.556
50	150.6	3.353	108.3	2.060
60	178.2	4.998	138.2	3.292
70	205.1	6.915	167.7	4.822
80	231.5	9.098	196.8	6.644
90	258.4	11.55	225.6	8.756
100	283.8	14.27	254.2	11.16
110	294.6	17.16	281.8	13.84
120	311.5	20.19	308.2	16.79
130	330.3	23.40	333.8	20.00
140	348.5	26.80	359.0	23.46
150	366.8	30.37	383.7	27.18
160	385.9	34.14	407.9	31.13
170	405.6	38.09	431.9	35.33
180	425.4	42.25	455.7	39.77
190	444.8	46.60	479.2	44.45
200	463.9	51.14	502.5	49.35
210	483.0	55.88	525.6	54.49
220	502.6	60.80	548.5	59.87
230	523.3	65.93	571.3	65.46
240	544.8	71.27	594.0	71.29
250	565.7	76.83	616.7	77.34
260	587.4	82.59	639.3	83.62
270	609.9	88.58	661.9	90.13
280	632.7	94.79	684.5	96.86
290	655.1	101.2	707.1	103.8
298.15	672.5	106.6	725.5	109.7
300	676.3	107.9	729.6	111.0
310	696.5	114.8	752.1	118.4
320	716.0	121.8	774.6	126.0
330	735.9	129.1	796.9	133.9
340	757.1	136.5	819.2	142.0
350	780.1	144.2	841.5	150.3
360	804.1	152.1	863.8	158.8
370	828	160	886	168
380	851	169	908	177
390	874	177	931	186
400	898	186	953	195
410	921	195	976	205
420	944	205	998	215
430	968	214	1021	225
434.5	978	219	1031	229
Liquid state				
434.5	1094	261	1128	229
440	1088	267	1141	236
450	1078	277	1166	247
460	1068	288	1189	259

The increase in heat capacity  $\Delta C_p^\circ(T_{\text{fus}}^\circ) = 116 \text{ J/(K mol)}$  of the substance under study upon fusion was found graphically by extrapolating the normal path of  $C_p^\circ$  versus  $T$  to the temperature of phase transition  $T_{\text{fus}}^\circ$ . Using the thermodynamic characteristics of fusion for I, we calculated the first  $A (\text{K}^{-1})$  and the second  $B (\text{K}^{-1})$  cryoscopic constants according to the following equations:

$$A = \Delta_{\text{fus}} H^\circ / [R(T_{\text{fus}}^\circ)^2] = 0.0268 \pm 0.0003, \quad (5)$$

$$B = (T_{\text{fus}}^\circ)^{-1} - \frac{1}{2} \frac{\Delta C_p^\circ(T_{\text{fus}}^\circ)}{\Delta_{\text{fus}} H^\circ} = 0.00092 \pm 0.00003, \quad (6)$$

where  $R$  is a universal gas constant.

### Standard Thermodynamic Functions

To calculate the standard thermodynamic functions (Table 3), the temperature dependence of the heat capacity of I was extrapolated from 6.5 to 0 K by the Debye function of the heat capacity of solids:

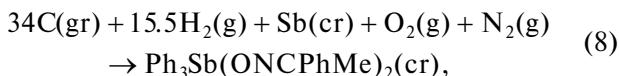
$$C_p^\circ = nD(\Theta_D/T), \quad (7)$$

where  $D$  is the Debye function of heat capacity,  $n = 6$  is the number of degrees of freedom, and  $\Theta_D = 63.7 \text{ K}$  is the Debye intrinsic temperature. Equation (7) describes the experimental values of heat capacity  $C_p^\circ$  with these parameters in the range of 6.5–12 K with an error of  $\pm 1.4\%$ . We accepted that in the range of 0–6.5 K, Eq. (7) reproduces the heat capacity values with the same degree of error.

### CONCLUSIONS

The procedure for calculating enthalpy  $H^\circ(T) - H^\circ(0)$ , entropy  $S^\circ(T)$ , and Gibbs function  $G^\circ(T) - H^\circ(0)$  was described in detail, e.g., in [21, 22]. The error of the calculated function values assumed a value of  $\pm 2\%$  at  $T < 15 \text{ K}$ ,  $\pm 0.6\%$  in the range of 15 to 40 K, and  $\pm 2.5\%$  in the range of 370 to 463 K.

Using the value of absolute entropy of I (Table 3) and simple substances (carbon [23], hydrogen [24], oxygen [25], nitrogen [25], and antimony [25]), we calculated the standard entropy of formation of crystal I  $\Delta_f S^\circ = -1935.5 \pm 1.9 \text{ J/(K mol)}$  at  $T = 298.15 \text{ K}$ . The obtained value corresponds to the following equation:



where the physical states of reagents are indicated in parentheses: gr is graphite, g is gas, and cr is crystalline.

### REFERENCES

1. A. Gupta, R. K. Sharma, R. Bohra, et al., *Polyhedron* **21**, 2387 (2002).
2. V. V. Sharutin, O. K. Sharutina, O. V. Molokova, et al., *Zh. Obshch. Khim.* **71**, 1317 (2001) [Russ. J. Gen. Chem. **71**, 1243 (2001)].
3. V. V. Sharutin, O. K. Sharutina, O. V. Molokova, et al., *Zh. Obshch. Khim.* **70**, 1990 (2000) [Russ. J. Gen. Chem. **70**, 1872 (2000)].
4. V. A. Dodonov, A. V. Gushchin, D. A. Gor'kaev, et al., *Izv. Akad. Nauk, Ser. Khim.*, No. 6, 965 (2002).
5. I. B. Rabinovich, V. P. Nistratov, V. I. Tel'noi, et al., *Thermodynamics of Metal-Organic Compounds* (Nizhegor. Gos. Univ., Nizh. Novgorod, 1996) [in Russian].
6. N. N. Smirnova, I. A. Letyanina, V. N. Larina, et al., *J. Chem. Thermodyn.* **41**, 46 (2009).
7. N. N. Smirnova, I. A. Letyanina, A. V. Markin, et al., *Zh. Obshch. Khim.* **79**, 553 (2009) [Russ. J. Gen. Chem. **79**, 717 (2009)].
8. I. A. Letyanina, N. N. Smirnova, A. V. Markin, et al., *J. Therm. Anal. Cal.* **103**, 355 (2011).
9. V. V. Sharutin, O. K. Sharutina, O. V. Molokova, et al., *Koord. Khim.* **28**, 497 (2002) [Russ. J. Coord. Chem. **28**, 464 (2002)].
10. R. M. Varushchenko, A. I. Druzhinina, and E. L. Sorkin, *J. Chem. Thermodyn.* **29**, 623 (1997).
11. V. M. Malyshev, G. A. Mil'ner, E. L. Sorkin, et al., *Prib. Tekh. Eksp.* **6**, 195 (1985).
12. G. W. H. Hohne, W. F. Hemminger, and H. F. Flammersheim, *Differential Scanning Calorimetry* (Springer, Berlin; Heidelberg, 2003).
13. V. A. Drebushchak, *J. Therm. Anal. Cal.* **79**, 213 (2005).
14. *Atomic Weights of the Elements 1993, IUPAC Commission on Atomic Weights and Isotopic Abundance's, J. Phys. Chem. Ref. Data* **24**, 1561 (1995).
15. *Physics and Chemistry of The Organic Solid State*, Ed. by D. Fox, M. Labes, and A. Weissberger (Interscience, New York London, 1965; Mir, Moscow, 1968).
16. D. Stull, E. Westrum, and G. Sinke, *Chemical Thermodynamics of Organic Compounds* (Wiley, New York, 1969; Mir, Moscow, 1971).
17. T. S. Yakubov, *Dokl. Akad. Nauk SSSR* **310**, 145 (1990).
18. V. B. Lazarev, A. D. Izotov, K. S. Gavrichov, et al., *Thermochim. Acta* **269–270**, 109 (1995).
19. V. V. Tarasov, *Zh. Fiz. Khim.* **24**, 111 (1950).
20. V. V. Tarasov and G. A. Yunitskii, *Zh. Fiz. Khim.* **39**, 2077 (1965).
21. B. V. Lebedev, *Thermochim. Acta* **297**, 143 (1997).
22. J. P. McCullough and D. W. Scott, *Calorimetry of Non-Reacting Systems* (Butterworth, London, 1968).
23. *Codata Key Values for Thermodynamics*, Ed. by J. D. Cox, D. D. Wagman, and V. A. Medvedev (New York, 1984).
24. M. W. Chase, Jr., *J. Phys. Chem. Ref. Data, Monograph* **9**, 1951 (1998).
25. *Thermal Constants of Materials. Handbook*, Ed. by V. P. Glushko (VINITI, Moscow, 1965–1981), Nos. 1–10 [in Russian].