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Heat Capacity and Thermodynamic Functions of PdS

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Abstract—The temperature-dependent heat capacity of vysotskite, PdS, has been determined for the first time by adiabatic, relaxation, and differential scanning calorimetry in a wide temperature range and standard thermodynamic functions of PdS have been calculated. The 298.15-K values thus obtained are $C_p^\circ = 43.65 \pm 0.09$ J/(mol K), $S^\circ = 51.98 \pm 0.10$ J/(mol K), $H^\circ(298.15\text{ K}) - H^\circ(0) = 8.03 \pm 0.02$ kJ/mol, and $\Phi^\circ = 25.03 \pm 0.05$ J/(mol K). Using the present results and data in the literature, we obtained $\Delta_f H^\circ(\text{PdS, 298.15 K}) = -74.0 \pm 1.0$ kJ/mol and $\Delta_f G^\circ(\text{PdS, 298.15 K}) = -68.7 \pm 1.0$ kJ/mol.

Keywords: heat capacity, palladium sulfide, vysotskite, adiabatic calorimetry, relaxation calorimetry, differential scanning calorimetry, thermodynamic functions

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INTRODUCTION

Synthetic palladium monosulfide is an analog of the natural mineral vysotskite. X-ray diffraction data for PdS indicate that this compound has a tetragonal unit cell (sp. gr. $P4_2\left(C_{4h}^2\right)$) [1–3]. In the phase diagram of the Pd–S system [4], vysotskite is a strictly stoichiometric phase which melts congruently at a temperature 1000°C.

Reliable data on the thermodynamic properties of palladium monosulfide are not available in the literature. In particular, Hummel et al. [5] did not recommend any thermodynamic functions for PdS. Liu-Cheng Chen et al. [6] reported measurements of the electrical, thermal, and structural properties of palladium sulfide with the aim of assessing its thermoelectric performance. In that study, C_p was determined by relaxation calorimetry above 300 K and the data were presented only in graphical form.

Obtaining reliable thermodynamic functions of palladium sulfide is an important issue because such data are necessary, for example, for gaining insight into the mechanisms underlying the formation of hydrothermal palladium deposits in solutions one of whose components is sulfide sulfur.

The purpose of this work was to determine standard thermodynamic functions of PdS using low- and high-temperature measurements of the isobaric heat capacity of palladium sulfide.

EXPERIMENTAL

Synthesis and characterization of the sample. Palladium sulfide powder was prepared by dry synthesis at a temperature of 550°C over a period of ten days in fused quartz ampules pumped down to 10 Pa [7] and placed in horizontal resistance furnaces. The reagents used for PdS synthesis were palladium wire (99.95% purity, 0.3 mm diameter) and crystalline sulfur (LABTEKH) in a stoichiometric ratio. After the first step, the synthesized palladium sulfide was ground and refired for 15–20 days at a temperature of 500°C, followed by cooling of the ampule in air.

The absence of impurities was checked by X-ray powder diffraction (Bruker diffractometer, Cu$K_{\alpha 1}$ radiation, graphite monochromator) and X-ray microanalysis (CAMECA SX100, 15 kV).

Measurement apparatus and technique. The temperature-dependent heat capacity of crystalline palladium monosulfide was determined by relaxation, adiabatic, and differential scanning calorimetry in the range 4.14–954 K.

The low-temperature heat capacity $C_p^\circ(T)$ of the PdS sample was measured using a BKT-3 fully automated adiabatic vacuum calorimeter designed and fabricated at AOZT Termis (Mendeleevo, Moscow oblast, Russia), with helium and nitrogen as cryogenic liquids. The weight of the sample placed in a container was 453.79 mg. After pumping, the calorimetric container was filled with dry helium as a heat-exchange

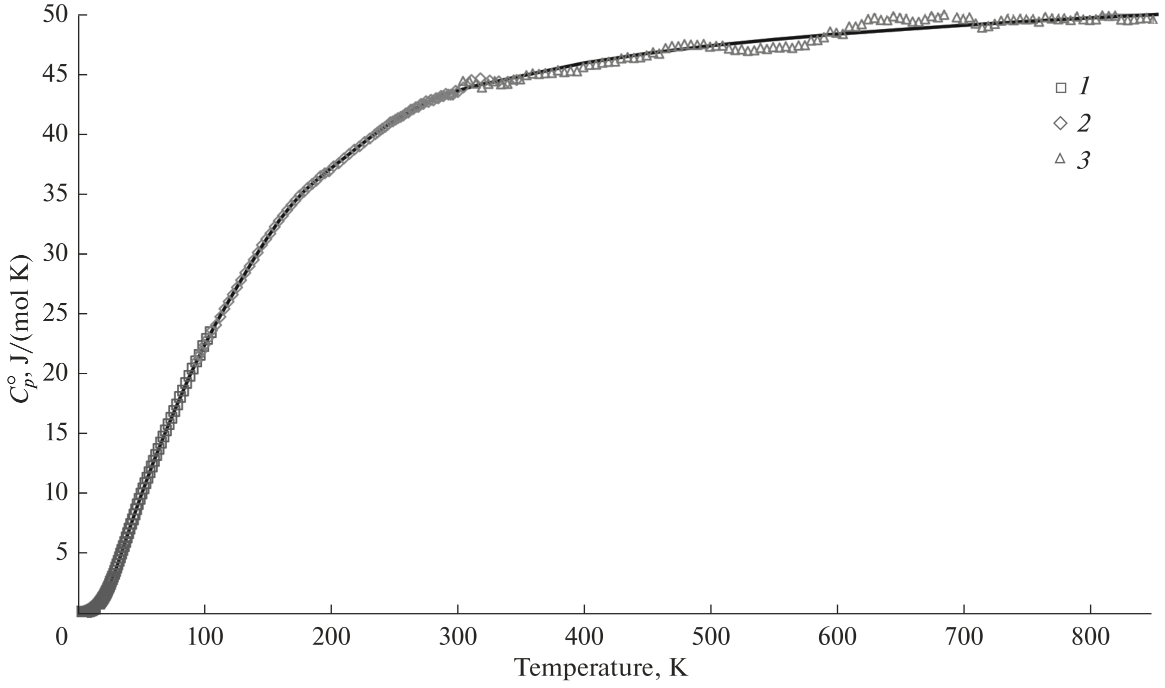

Fig. 1. $C_p^\circ(T)$ data for PdS: (*1*) relaxation calorimetry, 4.14–105.79 K; (*2*) adiabatic calorimetry, 94.45–347.27 K; (*3*) differential scanning calorimetry, 304.9–954.9 K; the solid line represents smoothed heat capacity data.

gas to a pressure of 33 kPa and hermetically sealed. The molar mass of PdS was taken to be 138.485 g/mol [8]. The calorimeter design and measurement procedure were described elsewhere [9]. The estimated limiting relative uncertainty in our heat capacity measurements was 2% below 40 K and decreased to 0.5% in the range 40–350 K.

In addition, the low-temperature heat capacity was measured by the relaxation method using a Quantum Design PPMS-9 automated system, during heating of the sample platform. The design of the system and measurement procedure were described in detail by Lashley et al. [10]. The sample was secured on a measuring cell with Apiezon N grease. The sample weight was 105.98 mg. The measurements took 10–15 min per data point. The temperature was varied in 1-K steps. The relative uncertainty in our measurements was less than 2% and depended on the temperature range of the measurements [10].

The high-temperature heat capacity of PdS was determined by differential scanning calorimetry (DSC) using an STA 449 F1 Jupiter system (Netzsch-Geratebau GmbH, Germany). Experiments were carried out in a 6.0 (99.9999%) helium gas atmosphere. The gas flow rate was 30 (purging) or 20 mL/min (protective). In our measurements, we used lidded platinum crucibles (the diameter of the crucibles was 6.8 mm and their volume was 85 mm^3). As a reference, we used synthetic sapphire, α-Al_2O_3, in the form of a disk 6 mm in diameter and 0.5 mm in thickness, or, directly in experiments, an empty crucible similar in weight to the crucible for the sample, The sample weight was 52.53 mg. After four cycles of pumping and filling the inner volume with helium, we carried out additional thermostating for 20 min. The heating rate was 20 K/min.

The experimental data obtained by DSC were analyzed using Netzsch Proteus software. The estimated limiting relative uncertainty in our heat capacity measurements by DSC was 2.0%.

RESULTS AND DISCUSSION

The heat capacity of crystalline palladium monosulfide was determined by adiabatic calorimetry with the BKT-3 in the temperature range 94.45–347.27 K (83 data points) and by relaxation calorimetry with the PPMS-9 system in the range 4.14–105.79 K (113 data points). The C_p° data thus obtained are presented in Tables 1 and 2 and Fig. 1. The temperature dependence of heat capacity has a small flat anomaly around 310 K (Fig. 1), whose origin is unknown.

The 196 low-temperature heat capacity data points (Tables 1, 2) were smoothed using polynomials of the form [11]

Table 1. Experimental heat capacity (J/(mol K)) data obtained for PdS in the BKT-3 adiabatic calorimeter

T, K	C_p°	T, K	C_p°	T, K	C_p°	T, K	C_p°
Series 1		159.32	32.74	239.29	40.29	257.58	41.54
94.45	21.03	162.63	33.18	243.48	40.61	261.60	41.81
96.51	21.48	165.94	33.64	247.59	40.99	265.60	42.08
98.57	21.88	169.24	34.05	251.63	41.20	269.60	42.26
100.63	22.36	172.55	34.45	255.67	41.44	273.58	42.52
103.30	22.90	175.86	34.88	259.69	41.73	277.55	42.68
106.57	23.60	179.16	35.16	263.70	42.05	281.50	42.81
109.85	24.04	182.47	35.53	267.70	42.25	285.44	42.98
113.14	24.73	185.77	35.83	271.69	42.52	289.36	43.16
116.42	25.39	189.07	36.11	275.66	42.74	293.27	43.30
119.72	25.99	192.38	36.48	279.62	42.87	296.99	43.30
123.01	26.59	195.68	36.72	283.57	43.00	300.86	43.52
126.31	27.19	198.98	36.88	287.50	43.20	305.19	43.89
129.60	27.80	202.69	37.30	291.41	43.36	311.48	44.51
132.90	28.42	206.80	37.57	295.13	43.29	318.77	44.67
136.20	28.96	210.91	37.96	299.01	43.62	325.94	44.48
139.50	29.50	215.01	38.34	Series 2		333.14	44.41
142.80	30.09	219.11	38.70	237.36	40.14	340.19	44.37
146.10	30.73	223.22	38.98	241.42	40.46	347.27	44.51
149.41	31.23	227.14	39.33	245.48	40.77		
152.71	31.69	231.34	39.63	249.52	41.07		
156.02	32.25	235.58	39.99	253.56	41.33		

$$C_p = \sum_0^m A_j U^j, \qquad (1)$$

where A's are the coefficients of the polynomial and

$$U = [1 - \exp(-0.001T)]. \qquad (2)$$

The coefficients of the polynomial used are given in Table 3. The heat capacity values smoothed using polynomial (1) and the low-temperature thermodynamic functions of PdS are presented in Table 4. In smoothing and integrating the experimental heat capacity data, the anomaly at 310 K was left out of consideration because its contribution to the standard entropy and enthalpy was small and because it has not yet been confirmed by other methods in the literature.

At a temperature of 298.15 K, the thermodynamic functions of PdS under standard conditions are as follows: C_p°(298.15 K) = 43.65 ± 0.09 J/(mol K), S°(298.15 K) = 51.98 ± 0.10 J/(mol K), H°(298.15 K) – H°(0) = 8.03 ± 0.02 kJ/mol, and Φ°(298.15 K) = $-[G^\circ(298.15\text{ K}) - H^\circ(0)]/298.15 = 25.03 \pm 0.05$ J/(mol K).

Note that the heat capacity determined in this study agrees well with C_p°(298.15 K) = 43.39 J/(mol K) [12] and can be compared to the theoretically predicted C_p°(298.15 K) = 48.66 ± 0.09 J/(mol K) [13]. The value C_p°(300 K) = 43.61 J/(mol K) obtained in this study by adiabatic calorimetry is almost 11% lower than the C_p°(300 K) = 48.47 J/(mol K) obtained by Liu-Cheng Chen et al. [6] using a PPMS, which can be accounted for by the increase in relaxation calorimetry uncertainty with increasing temperature and also by the possibility that Liu-Cheng Chen et al. [6] did not follow recommendations as to measurements with that instrument [14]. The entropy S°(298.15 K) = 51.98 ± 0.10 J/(mol K) coincides to within the present experimental uncertainty with the S°(298.15 K) = 56.5 ± 8.4 J/(mol K) [15] evaluated from high-temperature investigation of phase equilibria in heterogeneous PdS–H_2–Pd_4S–H_2S systems [16] and the PdS dissociation reaction [17].

The heat capacity of PdS was also determined by DSC in the temperature range 304.9–954.9 K. The smoothed C_p° data obtained with a step of 10 K are presented in Table 5.

Below the melting point of palladium sulfide, at a temperature of 902.8 K, we observed an heat capacity anomaly in the form of a peak, whose heat effect was

Table 2. Experimental heat capacity (J/(mol K)) data obtained for PdS by relaxation calorimetry using PPMS-9

T, K	C_p°	T, K	C_p°	T, K	C_p°	T, K	C_p°
4.14	0.00912	9.42	0.111	21.92	1.440	51.04	9.941
4.25	0.00915	9.70	0.123	22.55	1.571	52.55	10.37
4.37	0.00975	9.99	0.135	23.23	1.716	54.11	10.82
4.49	0.0104	10.29	0.1466	23.92	1.858	55.70	11.27
4.61	0.0112	10.57	0.1582	24.61	2.028	57.36	11.73
4.74	0.0127	10.88	0.1738	25.36	2.195	59.05	12.21
4.87	0.0137	11.20	0.1892	26.09	2.388	60.79	12.68
5.01	0.0155	11.53	0.2074	26.87	2.583	62.60	13.17
5.15	0.0166	11.87	0.2257	27.67	2.784	64.45	13.68
5.30	0.0179	12.22	0.2461	28.48	3.002	66.36	14.20
5.45	0.0200	12.59	0.2703	29.32	3.236	68.32	14.71
5.61	0.0215	12.96	0.2953	30.19	3.489	70.34	15.23
5.77	0.0242	13.34	0.3232	31.08	3.755	72.42	15.74
5.94	0.0260	13.74	0.3520	32.00	4.032	74.57	16.28
6.11	0.0293	14.14	0.3834	32.95	4.327	76.77	16.83
6.29	0.0314	14.56	0.4186	33.92	4.621	79.04	17.39
6.47	0.0350	14.99	0.4577	34.94	4.914	81.37	18.02
6.66	0.0388	15.44	0.5018	35.96	5.227	83.79	18.55
6.85	0.0429	15.89	0.5484	37.03	5.560	86.26	19.18
7.06	0.0460	16.37	0.5993	38.12	5.905	88.81	19.79
7.26	0.0510	16.85	0.6546	39.25	6.274	91.44	20.39
7.48	0.0560	17.35	0.7148	40.41	6.641	94.15	20.98
7.70	0.0602	17.86	0.7811	41.61	7.016	96.93	21.54
7.92	0.0662	18.39	0.8540	42.84	7.403	99.79	22.28
8.16	0.0726	18.94	0.9346	44.11	7.793	102.75	22.87
8.39	0.0798	19.50	1.021	45.41	8.202	105.79	23.44
8.64	0.0868	20.07	1.114	46.76	8.623		
8.90	0.0956	20.67	1.221	48.15	9.055		
9.16	0.100	21.28	1.328	49.57	9.499		

Table 3. Coefficients of Eq. (1)

j	A_j, J/(mol K)
0	-0.28×10^{-1}
1	-0.6476×10^{1}
2	0.602386×10^{4}
3	-0.9764712×10^{6}
4	$0.903836815 \times 10^{8}$
5	$-0.3809806654 \times 10^{10}$
6	$0.93353352185 \times 10^{11}$
7	$-0.148752178262 \times 10^{13}$
8	$0.162930651279 \times 10^{14}$
9	$-0.126101317791 \times 10^{15}$
10	$0.696383225903 \times 10^{15}$
11	$-0.272908984116 \times 10^{16}$
12	$0.741670765311 \times 10^{16}$
13	$-0.132929578809 \times 10^{17}$
14	$0.141329803374 \times 10^{17}$
15	$-0.67518824707 \times 10^{16}$

determined to be $\Delta_{tr}H$ = 1713 J/mol, with $\Delta_{tr}S = \Delta_{tr}H/T$ = 1.897 J/(mol K). Starting at 983 K, the weight of the sample was observed to gradually decrease, which was accompanied by an endothermic peak. According to the phase diagram of the S–Pd system [4], it is reasonable to assume that, at a temperature above 983 K, the substance began to decompose to form Pd_4S and $S_2(g)$.

Using the high-temperature measurement results in the range 330–845 K, we determined the coefficients of the Maier–Kelley equation (J/(mol K)):

$$\begin{gathered} C_p^\circ = a + bT + cT^{-2} = (47.3 \pm 0.1) \\ + (3.9 \pm 0.8) \times 10^{-3} T - (4.7 \pm 0.5) \times 10^{5} T^{-2}. \end{gathered} \tag{3}$$

Figure 1 shows the $C_p^\circ(T)$ curve obtained using Eqs. (1) and (3).

Using the coefficients of Eq. (3) and the entropy S°(298.15 K) obtained in this study, we calculated high-temperature thermodynamic functions:

Table 4. Thermodynamic functions of PdS derived from relaxation and adiabatic calorimetry data

T, K	$C_p^\circ(T)$, J/(mol K)	$S^\circ(T)$, J/(mol K)	$H^\circ(T) - H^\circ(0)$, J/mol	$\Phi^\circ(T)$, J/(mol K)
5	0.0143	0.00475	0.0178	0.00119
10	0.1344	0.04524	0.3447	0.01077
15	0.4533	0.1507	1.701	0.03730
20	1.106	0.3618	5.452	0.08920
25	2.121	0.7113	13.38	0.1761
30	3.433	1.210	27.17	0.3043
35	4.931	1.850	48.03	0.4777
40	6.509	2.611	76.62	0.6955
45	8.085	3.469	113.1	0.9557
50	9.612	4.400	157.4	1.252
60	12.47	6.409	268.0	1.942
70	15.13	8.534	406.2	2.731
80	17.66	10.72	570.2	3.593
90	20.03	12.94	758.8	4.509
100	22.22	15.16	970.2	5.458
110	24.22	17.38	1203	6.444
120	26.08	19.57	1454	7.453
130	27.86	21.72	1724	8.458
140	29.61	23.85	2011	9.486
150	31.28	25.95	2316	10.51
160	32.82	28.02	2637	11.54
170	34.16	30.05	2972	12.57
180	35.28	32.04	3319	13.60
190	36.23	33.97	3677	14.62
200	37.08	35.85	4043	15.64
210	37.91	37.68	4418	16.64
220	38.75	39.46	4801	17.64
230	39.59	41.20	5193	18.62
240	40.38	42.91	5593	19.61
250	41.08	44.57	6000	20.57
260	41.72	46.19	6414	21.52
270	42.30	47.78	6834	22.47
280	42.85	49.33	7260	23.40
290	43.30	50.84	7691	24.32
298.15	43.65	51.98	8034	25.03
300	43.69	52.31	8126	25.22
310	43.95	53.75	8563	26.13
320	44.17	55.14	9003	27.01

$$C_p^\circ(T),\ S^\circ(T),\ H^\circ(T) - H^\circ(298.15K),$$
$$\Phi^\circ(T)' = -[G^\circ(T) - H^\circ(298.15K)]/T.$$

The calculation results are presented in Table 6.

Thermodynamic properties of PdS(*cr*). Niwa et al. [16] investigated phase equilibria in the PdS–H_2–Pd_4S–H_2S and Pd_4S–H_2–Pd–H_2S heterogeneous systems at temperatures from 612 to 795 K. Using the equilibrium constants obtained and results on PdS and

Table 5. Smoothed heat capacity data (J/(mol K)) obtained for PdS by DSC with a step of 10 K

T, K	C_p°	T, K	C_p°	T, K	C_p°	T, K	C_p°
304.9	43.43	474.9	47.08	644.9	48.70	804.9	49.74
314.9	43.79	484.9	47.20	654.9	48.78	814.9	49.79
324.9	44.11	494.9	47.32	664.9	48.85	824.9	49.85
334.9	44.42	504.9	47.44	674.9	48.92	834.9	49.91
344.9	44.70	514.9	47.55	684.9	48.99	844.9	49.96
354.9	44.96	524.9	47.65	694.9	49.06	854.9	50.02
364.9	45.20	534.9	47.76	704.9	49.12	864.9	50.07
374.9	45.42	544.9	47.86	714.9	49.19	874.9	50.12
384.9	45.63	554.9	47.95	724.9	49.25	884.9	50.18
394.9	45.83	564.9	48.04	734.9	49.32	894.9	50.23
404.9	46.02	574.9	48.13	744.9	49.38	904.9	50.28
414.9	46.19	584.9	48.22	754.9	49.44	914.9	50.33
424.9	46.36	594.9	48.31	764.9	49.50	924.9	50.38
434.9	46.52	604.9	48.39	774.9	49.56	934.9	50.44
444.9	46.67	614.9	48.47	784.9	49.62	944.9	50.49
454.9	46.81	624.9	48.55	794.9	49.68	954.9	50.54
464.9	46.95	634.9	48.63				

Table 6. High-temperature thermodynamic functions of PdS

T, K	$C_p^\circ(T)$, J/(mol K)	$S^\circ(T)$, J/(mol K)	$H^\circ(T) - H^\circ(298.15\text{ K})$, J/mol	$\Phi^\circ(T)'$, J/(mol K)
350	44.84	59.04	2.28	52.51
400	45.93	65.10	4.56	53.72
450	46.75	70.56	6.87	55.29
500	47.38	75.52	9.23	57.07
550	47.91	80.06	11.61	58.96
600	48.35	84.25	14.02	60.89
650	48.74	88.14	16.44	62.84
700	49.09	91.76	18.89	64.78
750	49.41	95.16	21.35	66.69
800	49.71	98.36	23.83	68.57
850	49.99	101.38	26.32	70.41

PdS_2 dissociation reactions [17], Niwa et al. [16] obtained the temperature dependence of the standard Gibbs energy (J)

$$\Delta_r G^\circ = -137235 + 97.5T \tag{4}$$

for the reaction

$$Pd + 0.5S_2(g) = PdS. \tag{5}$$

The $C_p^\circ(T)$ data obtained in this study for PdS (Eq. (3)), equations for temperature-dependent heat capacity, and the absolute entropy of Pd [18] and $S_2(g)$ [19] at 298.15 K, as well as fixation of S°(PdS, 298.15 K), allow us to calculate the enthalpy of reaction (1) using data reported by Niwa et al. [16] and the second ($\Delta_r H^\circ = -138.2$ kJ/mol) and third ($\Delta_r H^\circ = -138.4$ kJ/mol) laws of thermodynamics. From the $\Delta_r H^\circ$ calculated using the third law of thermodynamics and $\Delta_f H^\circ(S_2(g)$, 298.15 K) [20], we can evaluate the enthalpy of formation of PdS: $\Delta_f H^\circ$(PdS, 298.15 K) = –74.0 ± 1.0 kJ/mol.

To the S°(PdS, 298.15 K) and $\Delta_f H^\circ$(PdS, 298.15 K) recommended in this work corresponds $\Delta_f G^\circ$(PdS, 298.15 K) = –68.7 ± 1.0 kJ/mol.

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