Tetrapalladium Sulfide and Tetrapalladium Selenide

Heat Capacities and Thermodynamic Properties from 5° to 350° K.

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The heat capacities of Pd_4S and Pd_4Se were determined by adiabatic calorimetry from 5° to 350° K. and found to be of usual sigmate shape, without transitions or anomalies. Values of the heat capacity (C_p), entropy ($S°$), and Gibbs energy function $[-(G° - H_0^\circ)/T]$ at 298.15° K. (expressed in units of cal. mole^{-1} °K.$^{-1}$) are 27.48, 43.18, and 23.16 for Pd_4S and 32.75, 47.83, and 24.84 for Pd_4Se, respectively. The heat capacity of Pd_4Se exceeds the classical limit near 200° K., probably because of 4d-electron excitations in palladium.

PALLADIUM is apparently the only metal which forms a sulfide and a selenide in the atomic ratio of 4 to 1 (*4, 5*). Therefore, it seemed of interest to study the thermodynamic properties of these rather unusual compounds. The structures of Pd_4S and Pd_4Se are tetragonal (*4, 5*) and characterized by coordination of each palladium atom with two sulfur (selenium) atoms and ten palladium atoms, while each sulfur (selenium) atom is coordinated to eight palladium atoms. Above 150° C. the compounds are almost nonmagnetic ($x_g < 0.2 \times 10^{-6}$), but upon lowering the temperature, field-strength-dependent magnetic susceptibilities develop. This phenomenon apparently needed further consideration; hence, heat capacity measurements were undertaken.

EXPERIMENTAL

Cryogenic Apparatus. Measurements were made in the Mark III vacuum cryostat by heating the sample intermittently under quasi-adiabatic conditions. The gold-plated copper calorimeter (laboratory designation W-29), with a capacity of 41 cc., was surrounded by adiabatic shields provided with three separate channels of recording electronic circuitry with proportional, rate, and reset actions. These kept the temperature differences between calorimeter and shields less than a millidegree. Consequently, the error due to heat exchange was negligible compared with other sources of error. The heat capacity of the calorimeter-heater-thermometer assembly was determined in a separate series of experiments. Small corrections were applied for differences in the amounts of indium-tin solder for sealing the calorimeter, Apiezon-T grease for thermal contact between calorimeter and heater-thermometer assembly, and about 10-torr helium pressure at 300° K. for improving thermal equilibration between calorimeter and sample. Temperatures determined with the strain-free capsule-type platinum resistor (laboratory designation A-3) are considered to be in accord with the thermodynamic temperature scale to within 0.03° K. All measurements of mass, temperature, resistance, voltage, and time are based upon calibrations or standardizations of the National Bureau of Standards.

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Preparation and Purity of Samples. The tetrapalladium sulfide and selenide were synthesized by reaction of palladium metal with elemental sulfur or selenium. High purity palladium, provided by International Nickel, Ltd., contained the following impurities (p.p.m.): Ag(30), Au(70), Fe(20), Pb(2), Pt(50), Rh(10), insoluble material—principally SiO_2—(60), volatile material (120). The metal was degassed in vacuo at 600° C. for 4 hours. The sulfur was a product of the American Smelting and Refining Co., in which no impurities had been detected by spectrographic analysis. The selenium was a gift from Bolidens Gruvaktiebolag which, according to their analyses, contained as impurities (p.p.m.): Cl(2), Fe(0.8), K(0.3), Na(0.4), nonvolatile matter (12). Stoichiometric amounts of palladium and sulfur were heated in an evacuated and sealed quartz tube at 800° C. for 6 days. The resulting regulus was very hard and had to be crushed in a diamond mortar. In the case of Pd_4Se, the heating was carried to 600° C. for 18 hours, and the sample could then be crushed in an agate mortar. Both crushed samples were subsequently heat-treated at 500° C. for 2 weeks and cooled to room temperature in the furnace.

The heat capacity of the Pd_4S sample, weighing 191.599 grams, represented about 90% of the total at 15° K., decreasing to 72% at 350° K. For the Pd_4Se sample, weighing 211.422 grams, the corresponding values are 85 and 67%, respectively.

RESULTS AND DISCUSSION

The experimental heat capacity values for tetrapalladium sulfide and tetrapalladium selenide at the mean temperatures of the measurements are presented in Table I in chronological sequence. The data have been corrected for curvature of the heat capacity and are given in terms of the defined thermochemical calorie (equal to 4.1840 joules), and an ice point of 273.15° K. The probable errors in the measurements are considered to decrease from about 3% at 5° K. to 0.5% at 10° K. and to less than 0.1% above 20° K. The heat capacities of both compounds have the usual sigmate shape, without transitions or anomalies.

The smoothed heat capacities and the thermodynamic functions derived from them by means of a digital computer using a previously described program (*7*) are given for selected temperatures in Table II. The thermodynamic

Table I. Heat Capacities of Pd_4S and Pd_4Se[a]

T	C_p	T	C_p	T	C_p
Tetrapalladium Sulfide, 1 Mole = 457.67 Grams					
Series I					
5.55	0.037	41.78	8.161	205.24	25.83
6.01	0.058	46.41	9.521	213.99	26.05
6.56	0.072	51.49	10.942	222.66	26.23
7.24	0.105	56.94	12.370	231.26	26.41
8.09	0.149	62.57	13.756	232.28	26.43
9.05	0.217	68.43	15.04	241.06	26.64
10.12	0.312	74.63	16.25	258.73	26.88
11.35	0.424	81.48	17.49	276.24	27.16
12.68	0.580	88.77	18.64	285.01	27.29
14.06	0.780	96.20	19.58	293.45	27.41
15.52	1.021	103.97	20.44	301.78	27.54
17.14	1.321	111.99	21.24	310.02	27.62
18.99	1.704	120.37	21.98	318.43	27.74
18.75	1.653	128.67	22.63	326.86	27.87
20.87	2.135	137.48	23.20	335.43	27.94
23.20	2.717	146.26	23.70	345.10	28.05
25.75	3.399	152.15	24.01	Series II	
28.63	4.210	154.50	24.12		
30.51	4.768	163.37	24.49	237.57	26.52
34.02	5.823	170.20	24.77	246.50	26.66
37.71	6.950	178.82	25.06	255.48	26.81
		187.54	25.35	264.46	26.96
		196.41	25.60	273.43	27.10
Tetrapalladium Selenide, 1 Mole = 504.56 Grams					
Series I		17.93	1.065	151.64	27.55
		19.78	1.432	160.75	28.16
66.02	15.54	21.82	1.901	168.29	28.61
70.74	16.65	24.11	2.490	177.03	29.09
76.16	17.88	26.70	3.229	184.81	29.47
82.70	19.27	29.68	4.150	193.93	29.86
90.10	20.65	33.15	5.299	203.05	30.22
97.86	21.86	36.93	6.592	212.11	30.55
105.98	23.00	41.19	8.040	221.06	30.86
114.33	24.06	45.79	9.577	230.00	31.12
Series II		45.77	9.573	238.94	31.39
		50.78	11.189	247.80	31.63
5.43	0.028	55.67	12.667	256.62	31.84
5.90	0.033	61.24	14.268	265.39	32.04
6.51	0.048	66.77	15.71	274.17	32.23
7.46	0.064	73.11	17.20	282.96	32.44
8.47	0.093	80.03	18.71	291.74	32.61
9.41	0.143	87.51	20.19	300.56	32.81
10.43	0.186	95.26	21.47	309.47	32.95
11.73	0.265	109.01	23.43	318.41	33.12
13.14	0.387	117.03	24.41	327.44	33.27
14.65	0.557	125.20	25.31	336.61	33.44
16.22	0.777	133.58	26.11	345.81	33.56
		142.52	26.86		

[a] Units. Cal., mole, ° K.

Table II. Thermodynamic

T	C_p	$S°$	$H° - H_0$	$-(G° - H_0)/T$
Tetrapalladium Sulfide, 1 Mole = 457.67 Grams				
5	0.025	0.006	0.022	0.001
10	0.292	0.086	0.677	0.019
15	0.929	0.312	3.562	0.074
20	1.934	0.709	10.588	0.179
25	3.192	1.272	23.32	0.339
30	4.615	1.978	42.78	0.552
35	6.124	2.802	69.61	0.813
40	7.633	3.719	104.02	1.118
45	9.113	4.704	145.90	1.461
50	10.535	5.738	195.1	1.837
60	13.137	7.894	313.7	2.666
70	15.371	10.092	456.6	3.569
80	17.24	12.270	619.9	4.521
90	18.78	14.392	800.2	5.501
100	20.04	16.44	994.5	6.493
110	21.09	18.399	1200.4	7.487
120	21.96	20.273	1415.7	8.475
130	22.70	22.060	1639.2	9.452
140	23.33	23.767	1869.4	10.414
150	23.88	25.396	2105.5	11.358
160	24.35	26.952	2346.8	12.285
170	24.77	28.441	2592.4	13.192
180	25.13	29.867	2841.9	14.079
190	25.44	31.234	3094.8	14.946
200	25.71	32.55	3350.6	15.79
210	25.95	33.81	3608.9	16.62
220	26.17	35.02	3869.5	17.43
230	26.37	36.19	4132.2	18.22
240	26.56	37.31	4396.9	18.99
250	26.74	38.40	4663.4	19.75
260	26.91	39.45	4931.6	20.49
270	27.07	40.47	5201.5	21.21
280	27.22	41.46	5472.9	21.91
290	27.37	42.42	5745.9	22.60
300	27.50	43.35	6020.2	23.28
310	27.63	44.25	6295.9	23.94
320	27.76	45.13	6572.9	24.59
330	27.89	45.99	6851.1	25.22
340	28.00	46.82	7130.6	25.85
350	28.06	47.63	7411.0	26.46
273.15	27.12	40.79	5286.8	21.43
298.15	27.48	43.18	5969.4	23.16

[a] Units. Cal., mole, ° K.

functions may be considered reliable to better than 0.1% at temperatures above 100° K., even taking possible departures from the assumed compositions into account. No adjustments have been made for nuclear spin or isotopic mixing contributions to the entropy and Gibbs energy function, and hence they are practical values for use in chemical thermodynamic calculations.

Electrical conductivity measurements (*3*) on Pd_4S have shown it can be a conductor, $\rho = 3.20 \times 10^{-4}$ ohm cm. and $(\partial\rho/\partial T) = 1.05 \times 10^{-6}$ ohm cm. ° K.$^{-1}$. Pd_4S is not superconducting above 0.32° K., while Pd_4Se becomes superconducting at 0.42° K. (*10*). Therefore, the heat capacity behavior at low temperatures was examined by plotting C_p/T *vs.* T^2 for both compounds (see Figure 1). Corresponding data for palladium metal (4 moles) taken from the literature (*6, 8, 9, 11*) are also shown in the figure. Apparently, the conduction electron contributions in Pd_4S and Pd_4Se are negligible compared to that of palladium. According to recent theoretical prediction (*1, 2*), the interactions between low energy spin fluctuations and conduction electrons in a nearly ferromagnetic metal result in a large renormalization of the *d*-electron mass, which gives rise to a corresponding increase in the linear term of the heat capacity. Because of the difficulties in resolving the lattice heat capacities in these compounds, the electronic contributions are not easily discernible. However, the heat capacity for Pd_4Se exceeds the classical limit near 200° K. This is taken as an indication of 4*d*-electron excitations in palladium.

Properties of Pd_4S and Pd_4Se[a]

T	C_p	$S°$	$H° - H_0°$	$-(G° - H_0°)/T$
	Tetrapalladium Selenide, 1 Mole = 504.56 Grams			
5	0.024	0.008	0.029	0.002
10	0.155	0.053	0.393	0.014
15	0.604	0.188	2.121	0.046
20	1.478	0.471	7.153	0.113
25	2.734	0.930	17.54	0.228
30	4.259	1.560	34.94	0.395
35	5.928	2.340	60.37	0.616
40	7.641	3.244	94.29	0.886
45	9.323	4.241	136.73	1.203
50	10.936	5.308	187.4	1.560
60	13.908	7.570	311.9	2.371
70	16.50	9.914	464.3	3.281
80	18.72	12.266	640.7	4.257
90	20.61	14.583	837.6	5.276
100	22.21	16.839	1051.9	6.320
110	23.57	19.022	1281.0	7.376
120	24.74	21.124	1522.7	8.435
130	25.76	23.145	1775.3	9.489
140	26.65	25.087	2037.4	10.534
150	27.42	26.953	2307.8	11.567
160	28.11	28.745	2585.6	12.585
170	28.71	30.468	2869.8	13.587
180	29.24	32.124	3159.6	14.571
190	29.71	33.72	3454.4	15.54
200	30.12	35.25	3753.6	16.48
210	30.49	36.73	4056.6	17.41
220	30.82	38.16	4363.2	18.32
230	31.12	39.53	4672.9	19.22
240	31.40	40.86	4985.5	20.09
250	31.67	42.15	5300.8	20.95
260	31.92	43.40	5618.8	21.79
270	32.16	44.61	5939.2	22.61
280	32.38	45.78	6261.9	23.42
290	32.59	46.92	6586.7	24.21
300	32.78	48.03	6913.5	24.98
310	32.96	49.11	7242.3	25.74
320	33.14	50.16	7572.8	26.49
330	33.31	51.18	7905.1	27.22
340	33.48	52.18	8239.0	27.94
350	33.63	53.15	8574.6	28.65
273.15	32.23	44.98	6041	22.87
298.15	32.75	47.83	6853	24.84

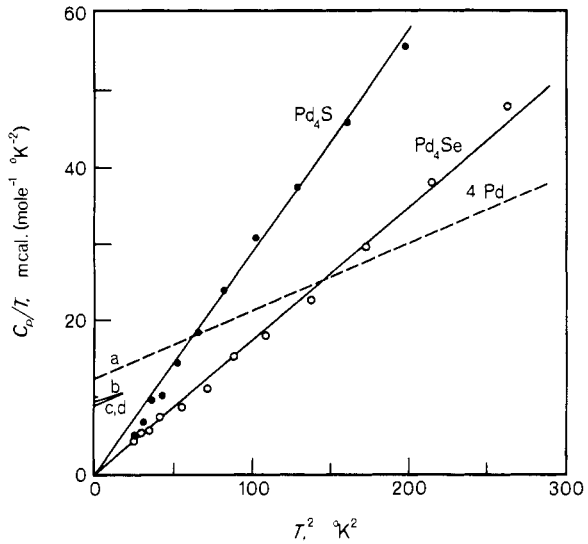

Figure 1. Heat capacities of Pd_4S, Pd_4Se, and 4Pd plotted as C_p/T vs. T^2

a. Pickard (9) c. Hoare and Yates (6)
b. Rayne (11) d. Mackliet and Schindler (8)

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