

Low-Temperature Heat Capacities and Thermodynamic Functions of Some Platinum and Palladium Group Chalcogenides. I. Monochalcogenides; PtS, PtTe, and PdTe†

FREDRIK GRØNVOLD AND TORKILD THURMANN-MOE

Chemical Institute A, University of Oslo, Blindern, Norway

AND

EDGAR F. WESTRUM, JR., AND ELFREDA CHANG

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

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Heat capacities of platinum monosulfide, platinum monotelluride, and palladium monotelluride were measured in the range 5–350°K. They show the normal sigmoidal temperature dependence with no evidence of transitions or other anomalies. The derived heat-capacity equations were integrated. Values of heat capacities, entropy and enthalpy increments, and of the free-energy function are tabulated for selected temperatures. At 298.15°K, the third-law entropies are 13.16 cal gfw⁻¹ °K⁻¹ for PtS, 19.41 cal gfw⁻¹ °K⁻¹ for PtTe, and 21.42 cal gfw⁻¹ °K⁻¹ for PdTe. The new data on PtS have been correlated with existing decomposition-pressure data to evaluate ΔH_f , ΔF_f , and ΔS_f at 298.15°K. Entropies for other platinum-metal monochalcogenides were estimated.

INTRODUCTION

THE present paper is concerned with sulfides, selenides, and tellurides of the platinum and palladium. For these chalcogenides, recently surveyed by Haraldsen,¹ no heat-capacity measurements have been reported. Such data are desirable, however, for evaluation of the entropies of the chalcogenides with a better precision than has been possible in the past, and to get an insight into the causes of variations in heat capacity with the nature of the compounding elements and the properties of the compound.

Excluding the oxides, no monochalcogenides are known with certainty for ruthenium, osmium, and iridium; for the remaining metals of the platinum and palladium groups, the following compounds with exact (or approximate) composition MeX have been found: Rh₉S₈ [cu, $a=9.9116$]²; RhTe [hex B8, $a=3.99$, $c=5.66$]³; PdS [tetr B34, $a=6.4287$, $c=6.6082$]⁴; Pd₉Se₈ [cu, $a=10.6060$]²; PdSe [tetr B34, $a=6.73$, $c=6.91$]⁵; PdTe [hex B8, $a=4.1521$, $c=5.6719$]⁴; PtS [tetr B, $a=3.4700$, $c=6.1096$]⁶; Pt₁₀Se₈ [monocl, $a=6.5806$, $b=4.6248$, $c=11.145$, $\beta=78.40^\circ$]⁶; PtTe [orthorh, $a=6.6144$, $b=5.6360$, $c=11.865$]⁶. The structures and lattice dimensions (A) have been included for each substance.

Three of these chalcogenides were chosen for the present investigation, PtS as representative for the tetragonal square-coordinated structures, PtTe for a low-symmetric structure, and PdTe for the NiAs (B8)-type structure. Their heat capacities were determined and the thermodynamic functions obtained. On the basis of these and other data, standard entropies of the remaining chalcogenides are estimated.

EXPERIMENTAL

Preparation of the Samples

The samples were prepared from high-purity elements. The platinum, which came from The Mond Nickel Company, Ltd., contained the following impurities (in ppm): Au (1), Fe (<10), (Pb <10), Pd (7), volatile material (90). The palladium, also from the same company, contained: Ag (30), Au (70), Fe (20), Pb (2), Pt (50), Rh (10), insoluble (principally SiO₂) (60), volatile material (120). Before use, both the palladium and platinum were degassed under high vacuum at 600°C for four hours. Sulfur *cryst. puriss.* from Schering-Kahlbaum A.G. was purified before use by techniques similar to those described by v. Wartenberg⁷ and Skjerven.⁸ The sulfur was first heated by means of a submerged heater with a surface temperature of about 800°C until the carbon deposition ceased; this required about three weeks. Thereafter, it was purified by fractional distillation.

The tellurium was a special product with a stated purity of 99.999% from the American Smelting and Refining Company, in which no impurities had been detected by spectrographic methods.

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¹ H. Haraldsen, Plenary Lecture, XVI. Congress of the IUPAC, Paris, 1957, reprinted in *Experientia Suppl.* VII, 165 (1957), and *Mémoires présentés à la Section de Chimie Minérale, SEDES, Paris*, 1958.

² A. Kjekshus, *Acta Chem. Scand.* **14**, 1623 (1960).

³ S. Geller, *J. Am. Chem. Soc.* **77**, 2641 (1955).

⁴ F. Grønvold and E. Røst, *Acta Chem. Scand.* **10**, 1620 (1956).

⁵ K. Schubert, H. Breimer, W. Burkhardt, E. Günzel, R. Hauffer, H. L. Lukas, H. Vetter, J. Wegst, and M. Wilkens, *Naturwissenschaften* **44**, 229 (1957).

⁶ F. Grønvold, H. Haraldsen, and A. Kjekshus, *Acta Chem. Scand.* **14**, 1879 (1960).

⁷ H. v. Wartenberg, *Z. anorg. u. allgem. Chem.* **286**, 243 (1956).

⁸ O. Skjerven, *Z. anorg. u. allgem. Chem.* **291**, 325 (1957).

TABLE I. Heat capacities of platinum and palladium monochalcogenides; in calories/(gram formula weight °K).

T , °K	C_p	T , °K	C_p	T , °K	C_p
PtS; gram formula weight = 227.16 g					
Series I		21.32	0.6224	174.93	8.177
54.00	3.074	23.11	0.7472	183.61	8.388
59.79	3.429	24.99	0.8861	192.20	8.645
65.98	3.783	27.16	1.055	201.20	8.849
73.12	4.152	29.67	1.259	210.37	9.033
80.35	4.511	32.54	1.494	219.30	9.220
87.24	4.843	35.75	1.755	228.33	9.384
94.52	5.175	39.16	2.026	237.28	9.550
Series II		42.88	2.308	246.33	9.712
6.01	0.014	46.97	2.603	255.30	9.836
6.99	0.025	51.33	2.910	263.94	9.961
7.77	0.034	Series III		272.49	10.066
8.80	0.052	94.19	5.158	260.99	9.897
10.11	0.084	101.10	5.465	269.64	10.023
11.47	0.1188	108.84	5.805	278.25	10.136
12.74	0.1610	117.40	6.165	286.91	10.248
13.98	0.2091	125.65	6.499	295.57	10.343
15.32	0.2684	132.91	6.791	304.40	10.442
16.74	0.3408	141.06	7.093	313.45	10.546
18.22	0.4236	149.44	7.391	322.60	10.610
19.70	0.5143	157.89	7.676	331.86	10.675
		166.37	7.939	341.21	10.755
				347.63	10.821
PtTe; gram formula weight = 322.70 g					
Series I		Series II		45.52	4.267
67.93	6.799			50.34	4.875
73.71	7.301	4.92	0.019	55.60	5.503
81.17	7.889	5.83	0.031	61.37	6.141
88.74	8.409	6.78	0.049	67.61	6.758
96.25	8.812	7.76	0.077	Series III	
103.91	9.173	7.67	0.076		
111.67	9.508	8.73	0.1178		
119.76	9.791	9.84	0.1751	261.12	11.725
128.22	10.054	10.83	0.2239	270.18	11.783
136.77	10.287	11.95	0.2857	279.15	11.826
142.66	10.433	13.19	0.3727	Series IV	
151.34	10.599	14.46	0.4735		
160.22	10.774	15.76	0.5841		
169.23	10.905	17.12	0.7091	259.71	11.740
178.35	11.034	18.64	0.8600	268.84	11.781
187.73	11.159	20.32	1.033	277.99	11.827
197.16	11.261	22.16	1.235	287.14	11.876
206.61	11.353	24.14	1.463	296.08	11.927
216.02	11.428	26.30	1.728	304.91	11.971
225.33	11.497	28.40	1.991	313.80	11.985
234.50	11.576	30.92	2.319	322.95	12.009
243.63	11.650	34.06	2.737	332.36	12.053
252.67	11.684	37.40	3.183	340.92	12.098
216.61	11.761	41.20	3.695	347.07	12.118
PdTe; gram formula weight = 234.01 g					
5.21	0.026	41.85	4.847	179.39	11.462
6.17	0.040	45.91	5.452	188.52	11.542
7.06	0.061	50.42	6.074	197.80	11.647
7.97	0.090	55.63	6.713	206.63	11.707
8.89	0.1333	57.71	6.962	215.90	11.778
9.82	0.1923	63.61	7.575	225.32	11.844
10.89	0.2492	70.56	8.162	234.65	11.902
12.14	0.3322	78.54	8.741	243.73	11.974
13.41	0.4429	86.71	9.251	252.83	12.019
14.68	0.5675	95.05	9.641	262.19	12.070
15.99	0.7111	103.27	9.963	258.23	12.027
17.42	0.8839	110.97	10.214	267.35	12.070
19.03	1.095	118.60	10.438	276.52	12.124
20.91	1.361	126.80	10.647	285.76	12.182
23.09	1.694	135.61	10.832	295.02	12.235
25.37	2.065	144.51	10.994	304.21	12.263
28.25	2.556	153.32	11.142	313.44	12.296
31.28	3.085	161.82	11.267	322.78	12.338
34.51	3.645	160.22	11.260	332.13	12.367
38.04	4.249	161.29	11.266	340.56	12.387
		170.34	11.374	347.12	12.414

Platinum monosulfide was synthesized in two steps. First, PtS₂ was prepared by heating appropriate amounts of the elements in an evacuated and sealed silica tube at 750°C for one day. The sintered product was crushed and then heated with stoichiometric amounts of finely divided platinum at 900°C for two days. The resulting dark-grey powder with a bluish cast was annealed at 500°C for two days and finally cooled to room temperature over a period of seven days.

Platinum monotelluride was prepared by allowing the elements to react at 1000°C for six hours, and then raising the temperature to 1200°C in order to melt the sample. After about one hour at this temperature, the furnace was shut off and the sample cooled to room temperature overnight. The melt was broken into flaky fragments with lead-grey metallic luster. These fragments were annealed at 500°C for seven days and slowly cooled to room temperature over another seven days.

Palladium monotelluride was prepared from stoichiometric amounts of palladium and tellurium heated in an evacuated and sealed silica tube to 800°C. It was kept in the molten state for about two hours and, after cooling, was broken into fragments of several millimeters in dimension with splendid pale-yellow metallic luster. After annealing for seven days at 500°C, the sample was cooled to room temperature over a period of two days.

X-ray photographs were taken of the samples in powder cameras of 11.46 cm diam utilizing asymmetric film mounting. The lattice constants corresponded, within the limits of experimental error, to those reported earlier for these compounds,^{4,6} and no lines from foreign phases could be observed.

Cryostat and Calorimeter

The design and operation of the Mark I cryostat for low-temperature adiabatic calorimetry has been described.⁹ A completely gold-plated copper calorimeter, W-7 (similar to W-5 in design except that the volume was only 40.33 cm³ and there were only four vanes) was employed. The same heater, thermometer, amount of indium-tin solder for sealing, and amount of Apiezon-T grease for thermal contact between the heater, thermometer, and calorimeter were used for all measurements. The capsule-type platinum resistance thermometer (laboratory designation A-3) was calibrated by the National Bureau of Standards, and the temperatures are believed to correspond with the thermodynamic scale within 0.03° from 10–90°K, and within 0.04° from 90–350°K. Below 10°K, a provisional scale for temperature was used. Calibrated instruments were used in the determination of all measured quantities.

⁹ E. F. Westrum, Jr., and A. F. Beale, Jr. (to be published).

Procedure

The calorimeter was loaded with sample, evacuated, filled with gaseous helium at 8 cm Hg pressure at 26°C (to provide thermal contact between the calorimeter and sample), and sealed. After adjusting the weights of solder and grease used, it was placed in the cryostat. The weights of samples used were 172.448 g of PtS, 196.792 g of PtTe, and 179.866 g of PdTe.

COMPUTATION AND RESULTS

The experimental heat capacity results for the three chalcogenide samples are presented in Table I in chronological order, so that temperature increments for individual determinations may be inferred from adjacent temperatures. The values are expressed in terms of the defined thermochemical calorie, equal to 4.1840 abs *j*. The ice point is taken as 273.15°K and the gram formula weights of PtS, PtTe, and PdTe as 227.16, 322.70, and 234.01 g, respectively. The densities are found to be 10.09 g cm⁻³ for PtS, 12.01 g cm⁻³ for PtTe (both by pycnometric measurement⁶), and 9.186 g cm⁻³ for PdTe (from x-ray diffraction data).

The heat capacity of the calorimeter, separately determined, represents a maximum at 350°K of 40%, and 34% of the total heat capacities measured when filled with the PtTe and PdTe samples, respectively. The minimum contribution of the empty calorimeter occurs at 10°K, where it represents 14% of the total heat capacity for both compounds. At 6°K, it represents 20% of the total. The contribution for the PtS sample reaches a maximum of 43% at 90°K and a minimum of 23% at 14°K. At 6°K, the value is 30%; and at 350°K, it is 37% of the total heat capacity.

An analytically generated "curvature" correction for the finite temperature increments of the measurements is added to each of the observed values of $\Delta H/\Delta T$. The derivatives (dH/dT) resulting from this correction are equal to C_p (or to C_{sat}) within the limits of experimental error.

The heat capacity vs temperature curve in Fig. 1 is of the usual sigmoid shape with no anomalous departures. Above 30°K, most of the points in Table I deviate from a smooth curve, discussed below, by less than 0.007 cal mole⁻¹. Below 30°K, the deviations become larger due to the smaller absolute heat capacity, the smaller temperature intervals of measurement, and the decreased sensitivity of the thermometer.

The values of C_p , $S^\circ - S_0^\circ$, $H^\circ - H_0^\circ$, and $-(F^\circ - H_0^\circ)/T$ at selected temperatures are given in Table II. The estimated probable error in these functions is less than 0.1% above 100°K. To make the table internally consistent, an additional figure is given over that justified by experimental accuracy. An IBM 704 digital computer was used to generate a least-squares polynomial in temperature from the curvature-corrected heat-capacity data for the region above 25°K and compared with a large-scale plot of the molal heat-capacity vs temperature for the experimental points.

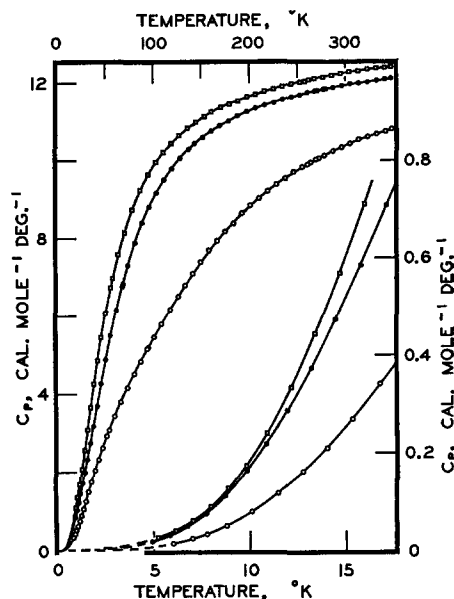


FIG. 1. Heat capacities of the monochalcogenides on a gram formula weight basis: \circ represents PtS, \bullet represents PtTe, and \square represents PdTe.

The values of the heat capacity presented in Table II are read from the plot below 25°K. Above this temperature, values from both the plot and the smooth polynomial curve are identical. Extrapolation is made with a Debye T^3 function below 6°K. Integration of the experimental C_p data was used to derive the entropy and enthalpy values. The free-energy function is computed from these results.

DISCUSSION

The only compound for which some comparison of thermodynamic data can be made is PtS. On the basis of decomposition-pressure measurements by Biltz and Juza¹⁰ in the PtS/Pt range at the temperatures 1060, 1110, and 1186°C, Kelley¹¹ calculated the standard value of the entropy of PtS at 298°K to be $S^\circ = 12.2$ cal gfw⁻¹ °K⁻¹. This was done before heat-capacity data on PtS existed, and the heat-capacity equation assumed by Kelley $C_p = 11.14 + 2.86 \times 10^{-3} T$ cal gfw⁻¹ °K⁻¹ (298–1000°K), resulted in an entropy value in fair accord with that determined in this research: $S^\circ = 13.16$ cal gfw⁻¹ °K⁻¹.

Since it should now be possible to deduce a better high-temperature heat-capacity temperature relationship for PtS, and also because Biltz and Juza appear to have included some questionable values in the low sulfur region (those for PtS_{0.02}, PtS_{0.06}, and PtS_{0.07}) in their average values, a new calculation of the thermodynamic functions was performed.

¹⁰ W. Biltz and R. Juza, *Z. anorg. u. allgem. Chem.* **190**, 161 (1930).

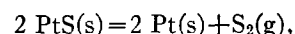
¹¹ K. K. Kelley, "Contributions to the data on theoretical metallurgy. VII," U. S. Bureau of Mines Bulletin 406, Washington, D. C. (1937); cf. K. K. Kelley, "Contributions to the data on theoretical metallurgy. XI," U. S. Bureau of Mines Bulletin 477, Washington, D. C. (1950).

TABLE II. Thermodynamic properties of platinum and palladium monochalcogenides.

$T, ^\circ\text{K}$	C_p cal/gfw $^\circ\text{K}$	$S^\circ - S_0^\circ$ cal/gfw $^\circ\text{K}$	$H^\circ - H_0^\circ$ cal/gfw	$-(F^\circ - H_0^\circ)/T$ cal/gfw $^\circ\text{K}$	$T, ^\circ\text{K}$	C_p cal/gfw $^\circ\text{K}$	$S^\circ - S_0^\circ$ cal/gfw $^\circ\text{K}$	$H^\circ - H_0^\circ$ cal/gfw	$-(F^\circ - H_0^\circ)/T$ cal/gfw $^\circ\text{K}$
PtS; gram formula weight = 227.16 g					PtTe; gram formula weight = 322.70 g				
5	0.008	(0.003)	(0.010)	(0.001)	150	10.58	11.615	949.8	5.283
10	0.077	0.024	0.185	0.006	160	10.77	12.304	1056.6	5.700
15	0.253	0.085	0.968	0.020	170	10.92	12.962	1165.1	6.108
20	0.533	0.194	2.90	0.050	180	11.06	13.590	1275.1	6.507
25	0.888	0.350	6.43	0.093	190	11.19	14.192	1386.3	6.895
30	1.286	0.547	11.85	0.152	200	11.29	14.768	1498.7	7.275
35	1.694	0.776	19.30	0.224	210	11.38	15.321	1612.1	7.645
40	2.091	1.028	28.76	0.309	220	11.46	15.853	1726.3	8.006
45	2.464	1.296	40.15	0.404	230	11.54	16.364	1841.3	8.358
50	2.814	1.574	53.36	0.507	240	11.61	16.856	1957.0	8.702
60	3.444	2.144	84.73	0.732	250	11.67	17.331	2073.4	9.038
70	3.993	2.717	121.97	0.975	260	11.73	17.790	2190.4	9.366
80	4.494	3.284	164.46	1.228	270	11.79	18.234	2308.0	9.686
90	4.969	3.841	211.79	1.487	280	11.85	18.664	2426.2	9.999
100	5.417	4.387	263.72	1.750	290	11.90	19.081	2544.9	10.305
110	5.852	4.924	320.09	2.014	300	11.94	19.485	2664.1	10.604
120	6.272	5.452	380.74	2.279	350	12.14	21.338	3265.5	12.008
130	6.675	5.970	445.51	2.543	273.15	11.81	18.37	2345	9.78
140	7.055	6.479	514.2	2.806	298.15	11.93	19.41	2642	10.55
150	7.410	6.978	586.5	3.067	PdTe; gram formula weight = 234.01 g				
160	7.742	7.467	662.3	3.327	5	(0.024)	(0.008)	(0.030)	(0.002)
170	8.045	7.945	741.3	3.585	10	0.184	0.060	0.451	0.015
180	8.324	8.413	823.1	3.840	15	0.602	0.205	2.31	0.051
190	8.585	8.870	907.7	4.093	20	1.230	0.460	6.82	0.119
200	8.820	9.316	994.7	4.343	25	2.004	0.816	14.85	0.221
210	9.034	0.752	1083.9	4.590	30	2.862	1.257	27.01	0.356
220	9.231	10.177	1175.3	4.834	35	3.728	1.763	43.49	0.520
230	9.419	10.592	1268.6	5.076	40	4.559	2.315	64.21	0.710
240	0.597	10.996	1363.7	5.314	45	5.321	2.896	88.93	0.920
250	9.761	11.391	1460.5	5.549	50	6.019	3.494	117.33	1.148
260	9.907	11.777	1558.8	5.781	60	7.209	4.701	183.70	1.639
270	10.04	12.153	1658.5	6.011	70	8.120	5.884	260.56	2.162
280	10.16	12.520	1759.5	6.236	80	8.841	7.018	345.57	2.698
290	10.28	12.879	1861.7	6.459	90	9.410	8.093	436.89	3.239
300	10.39	13.230	1965.1	6.679	100	9.842	9.107	533.2	3.775
350	10.81	14.867	2496.4	7.734	110	10.19	10.062	633.4	4.304
273.15	10.07	12.27	1690	6.08	120	10.48	10.962	736.8	4.822
298.15	10.37	13.16	1946	6.64	130	10.72	11.810	842.8	5.327
PtTe; gram formula weight = 322.70 g					140	10.92	12.612	951.1	5.819
5	(0.020)	(0.007)	(0.025)	(0.002)	150	11.09	13.371	1061.1	6.297
10	0.170	0.055	0.416	0.013	160	11.24	14.092	1172.8	6.762
15	0.518	0.184	2.07	0.046	170	11.37	14.777	1285.8	7.214
20	1.002	0.397	5.82	0.106	180	11.47	15.430	1400.0	7.652
25	1.566	0.679	12.20	0.191	190	11.57	16.053	1515.2	8.078
30	2.198	1.020	21.60	0.300	200	11.66	16.648	1631.4	8.492
35	2.861	1.408	34.24	0.430	210	11.73	17.219	1748.3	8.894
40	3.534	1.835	50.24	0.579	220	11.81	17.767	1866.0	9.285
45	4.197	2.290	69.58	0.743	230	11.87	18.293	1984.5	9.665
50	4.833	2.765	92.17	0.922	240	11.94	18.800	2103.5	10.035
60	5.995	3.751	146.43	1.311	250	12.00	19.288	2223.2	10.396
70	6.983	4.751	211.45	1.731	260	12.06	19.760	2343.5	10.747
80	7.802	5.739	285.52	2.170	270	12.11	20.216	2464.4	11.089
90	8.472	6.698	367.00	2.620	280	12.16	20.658	2585.7	11.423
100	9.009	7.619	454.69	3.075	290	12.20	21.085	2707.5	11.749
110	9.445	8.499	546.8	3.528	300	12.24	21.499	2829.7	12.067
120	9.802	9.337	643.2	3.977	350	12.42	23.401	3446.6	13.553
130	10.11	10.134	742.8	4.421	273.15	12.12	20.36	2502	11.20
140	10.36	10.893	845.1	4.856	298.15	12.23	21.42	2807	12.01

In the absence of any high-temperature enthalpy data on PtS, we will assume the same heat capacity at 1000°K as Kelley did ($C_p = 14 \text{ cal gfw}^{-1} \text{ }^\circ\text{K}^{-1}$) and construct a heat capacity curve which, in addition, goes through our points at 300 and 350°K and obeys the

Maier and Kelley¹² relationship $C_p = A + BT + CT^{-2}$. For the reaction considered,



¹²C. G. Maier and K. K. Kelley, J. Am. Chem. Soc. **54**, 3243 (1932).

the following heat-capacity equations (in cal gfw⁻¹ °K⁻¹) are chosen:

$$\text{PtS(s)}, C_p = 9.97 + 4.11 \times 10^{-3}T - 0.73 \times 10^5 T^{-2},$$

$$\text{Pt(s)},^{13} C_p = 5.81 + 1.26 \times 10^{-3}T + 0.06 \times 10^5 T^{-2},$$

$$\text{S}_2(\text{g}),^{13} C_p = 8.72 + 0.16 \times 10^{-3}T - 0.90 \times 10^5 T^{-2}.$$

Thus,

$$\Delta C_p = 0.40 - 5.54 \times 10^{-3}T + 0.68 \times 10^5 T^{-2},$$

$$\Delta H_T^\circ = \Delta H_0 + 0.40T - 2.77 \times 10^{-3}T^2 - 0.68 \times 10^5 T^{-1},$$

$$\Delta F_T^\circ = -RT \ln K = \Delta H_0 - 0.40T \ln T + 2.77 \\ \times 10^{-3}T^2 - 0.34 \times 10^5 T^{-1} + IT,$$

and

$$(\Delta H_0/T) + I = -4.57 \log p_{\text{S}_2} + 0.92 \log T \\ - 2.77 \times 10^{-3}T + 0.34 \times 10^5 T^{-2}.$$

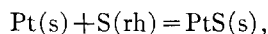
The results of the calculations (and plot of $[\Delta H_0/T] + I$ vs $1/T$) are given in Table III. Using these values, enthalpy, free energy, and entropy data for the decomposition of PtS can be calculated, the latter by the equation

$$\Delta S_T^\circ = (\Delta H_T^\circ - \Delta F_T^\circ)/T = 0.40 + 0.92 \log T \\ - 5.54 \times 10^{-3}T - 0.34 \times 10^5 T^{-2} - I.$$

At 298.15°K, the actual values are

$$\Delta H^\circ = 70.2 \text{ kcal}, \Delta F^\circ = 55.7 \text{ kcal}, \Delta S^\circ = 48.3 \text{ cal } ^\circ\text{K}^{-1}.$$

Taking the orthorhombic crystalline phase instead of the diatomic gas for the standard state of sulfur and incorporating the entropies of the elements,¹⁴ the following values for the standard heat of formation, free energy of formation, and entropy of PtS are found at 298.15°K:



$$\Delta H_f^\circ = -19.7 \text{ kcal}, \Delta F_f^\circ = -18.3 \text{ kcal},$$

$$S^\circ = 13.1 \text{ cal } ^\circ\text{K}^{-1}.$$

The enthalpy and free energy values are in good agreement with those of Kelley¹¹ ($\Delta H_f^\circ = -20.18$ kcal, $\Delta F_f^\circ = -18.55$ kcal). The enthalpy is somewhat higher than another estimate¹⁵ ($\Delta H_f^\circ = -20.8$ kcal). Biltz

TABLE III. Data for the reaction $2 \text{PtS(s)} = 2 \text{Pt(s)} + \text{S}_2(\text{g})$.^a

$T, ^\circ\text{K}$	$p_{\text{S}_2}, \text{atm}$	$(\Delta H_0/T) + I$	$\Delta H_0/T$
1333	0.047	5.27	52.89
1383	0.124	3.23	50.98
1459	0.409	0.67	48.32

^a In col. 3, $\Delta H_0 = 70,500$; $I_{\text{mean}} = 47.67$.

and Juza's own estimate¹⁰ is apparently too high ($\Delta H_f^\circ = -16$ kcal). The entropy is higher than that of Kelley¹¹ but agrees almost exactly with that from the low-temperature heat-capacity data of this work. On the basis of the solubility product of PtS and other data. Zhuk¹⁶ has reported $\Delta F_{298}^\circ = -17.36$ kcal and $S_{298}^\circ = 6.2$ cal gfw⁻¹ °K⁻¹. The free energy of formation of PtS from Pt and S₂ gas at high temperatures has been reevaluated from Biltz and Juza's data¹⁰ by Richardson and Jeffes.¹⁷ The equation reported, $\Delta F_T^\circ = -66.100 + 43.6T$ (1000–1700°K), agrees reasonably well with ours over the common range.

For the other monochalcogenides, no published data exist, and standard entropies are estimated for the compounds mentioned in the introduction. Measured values of the entropies of chalcogenides may be well represented by simple additivity of a chalcogen and a metal contribution. Justification will be presented in a forthcoming paper.¹⁸ The values chosen are [in cal (g atom °K)⁻¹]: 10.5 for the metal (Me²⁺), 3.0 for S²⁻, 7.0 for Se²⁻, and 9.5 for Te²⁻. The estimated values are: 1/9 Rh₉S₈, 13.2; RhTe, 20.0; PdS, 13.5; 1/9 Pd₉Se₈, 16.7; PdSe, 17.5; PdTe, 20.0; PtS, 13.5; 1/10 Pt₁₀Se₈, 16.1; PtTe, 20.0. These values are probably reliable to better than 0.8 cal (g atom °K)⁻¹.

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