Low-Temperature Heat Capacities and Thermodynamic Functions of Some Palladium and Platinum Group Chalcogenides. II. Dichalcogenides; PtS₂, PtTe₂, and PdTe₂†

Edgar F. Westrum, Jr., and H. Gary Carlson

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

AND

Fredrik Grønvold and Arne Kjekshus

Chemical Institute A, University of Oslo, Blindern, Norway

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Heat capacities of platinum disulfide, platinum ditelluride, and palladium ditelluride were measured in the range 5° to 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 C_p, $S° - S_0°$, $H° - H_0°$, and $-(F° - H_0°)/T$ are tabulated for selected temperatures. At 298.15°K the entropies are 17.85 cal gfw⁻¹ °K⁻¹ for PtS₂, 28.92 cal gfw⁻¹ °K⁻¹ for PtTe₂ and 30.25 cal gfw⁻¹ °K⁻¹ for PdTe₂. Thermodynamic values have been estimated for other dichalcogenides and related chalcogenides of the platinum group metals.

INTRODUCTION

AS indicated in the first part of this study,[1] no heat-capacity data have been reported on the chalcogenides of the platinum metals, despite the fact that such compounds exist in great number. Dichalcogenides are especially common (except among the oxides), and the majority of them have either pyrite ($C2$)-type structure or cadmium hydroxide ($C6$)-type structure. For a survey of the transition-metal chalcogenides, see Haraldsen.[2] The cubic pyrite-type structure is found for $RuS_2(a=5.6090$ A$)$,[3] $RuSe_2(a=5.933)$,[4] $RuTe_2(a=6.377)$,[5] $OsS_2(a=5.6192)$,[3] $OsSe_2(a=5.945)$,[4] $OsTe_2(a=6.3985)$,[5] and $\sim RhSe_2(a=6.002)$.[6] In addition, there are pyrite-like structures with more metal deficit than $\sim RhSe_2$ (the $\sim$ indicates approximate composition). They are found for $\sim RhS_{2.3}(a=5.58)$,[7] $\sim RhSe_{2.5}(a=5.985)$,[6] $\sim RhTe_{2.4}(a=6.439)$,[7] $IrS_{2.67}(a=5.589)$,[8] $IrSe_{3.0}(a=5.9293)$,[8] and $IrTe_{2.67}(a=6.393)$.[9] The hexagonal cadmium hydroxide-type structure is found for $RhTe_2(a=3.92,\ c=5.41)$,[10] $IrTe_2(a=3.930,\ c=6.414)$,[9] $PdTe_2(a=4.0365,\ c=5.1262)$,[11] $PtS_2(a=3.5432,\ c=5.0388)$,[12] $PtSe_2(a=3.7278,\ c=5.0813)$,[12] and $PtTe_2(a=4.0259, c=5.2209)$.[12] Orthorhombic structures have been found for $PdS_2(a=5.460,\ b=5.541,$ $c=7.531)$ and $PdSe_2(a=5.741,\ b=5.866,\ c=7.691)$ that might be considered to be deformed pyrite-like structures, with $S_2{}^{2-}$ ($Se_2{}^{2-}$) groups, but with square instead of octahedral coordination around the metal atoms.[13] Another orthorhombic structure has been found for $\sim IrSe_2(a=20.94,\ b=5.93,\ c=3.74)$,[14] for which only half of the nonmetal atoms are bonded as pairs. Iridium might accordingly be looked upon as trivalent. There are indications that $\sim IrS_2$[8] and Rh_8S_{15}[7] have related structures.

Among this multitude of dichalcogenides three have been chosen for the present study: PtS₂, PtTe₂, and PdTe₂. These have structures of the cadmium hydroxide-type, and might thus most clearly show the influence of atomic mass on heat-capacity behavior and entropy of the platinum group dichalcogenides. By using the information obtained and other available data, entropy estimates have been made for other dichalcogenides and related chalcogenides of the platinum and palladium groups.

EXPERIMENTAL

Preparation of the Samples

The samples were prepared from the same high-purity elements as the monochalcogenides.[1] Platinum disulfide was synthesized from stoichiometric amounts of the elements in an evacuated and sealed silica tube by heating to 750°C for one day. The sulfide was then in the form of a black powder and was annealed at 500°C for seven days and afterward slowly cooled to room temperature over another seven days.

Platinum ditelluride was prepared by reacting the elements at 1000°C for 5 hr. The grey powder thus obtained was annealed at 500°C for seven days and cooled to room temperature over seven more days.

Palladium ditelluride was prepared by heating a mixture of the elements to 800°C where it was kept

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

T, °K	C_p	T, °K	C_p	T, °K	C_p	T, °K	C_p	T, °K	C_p	T, °K	C_p
				PtS₂; gram formula weight=259.22 g							
Series I		193.23	13.108	339.37	16.31	12.38	0.209	11.26	0.165	59.20	3.531
		202.13	13.416	347.31	16.40	13.68	0.269	12.37	0.206	64.36	3.962
78.16	5.139	211.12	13.748			15.06	0.328	13.65	0.267	70.93	4.512
84.65	5.758	220.12	14.028	Series II		16.52	0.394	19.12	0.528	78.52	5.187
91.96	6.418	229.28	14.298			18.11	0.475	20.79	0.625	86.06	5.886
99.50	7.089	238.66	14.547	51.46	2.912	19.89	0.572	22.97	0.766	98.86	6.628
107.27	7.750	247.99	14.783	55.22	3.205	21.90	0.693	25.28	0.920		
115.89	8.474	257.14	15.00	58.99	3.479			27.84	1.102	Series V	
124.78	9.200	266.19	15.15	63.28	3.859	Series IV		30.54	1.301		
133.27	9.838	275.17	15.29	68.26	4.275			33.45	1.522	262.55	15.12
142.09	10.446	284.07	15.50	73.24	4.696	5.42	0.009	36.68	1.769	262.07	14.99
151.26	11.026	292.96	15.66			6.33	0.028	40.14	2.043	271.08	15.17
160.30	11.545	301.95	15.81	Series III		7.53	0.045	44.80	2.401	280.06	15.45
165.57	11.816	311.11	15.96			8.61	0.075	49.56	2.772		
174.98	12.297	320.57	16.06	10.17	0.132	9.42	0.106	54.33	3.144		
184.41	12.730	330.17	16.17	11.21	0.164	10.30	0.140	54.28	3.134		
				PtTe₂; gram formula weight=450.31 g							
Series I		143.70	15.82	12.13	0.340	38.92	4.858	167.91	16.49	260.07	17.74
		161.41	16.31	13.50	0.439	42.90	5.701	161.51	16.34	266.80	17.78
64.49	9.744			14.92	0.577	47.14	6.589	170.18	16.52	275.73	17.86
70.99	10.691	Series II		16.36	0.738	51.80	7.512	178.89	16.70	283.06	17.92
77.99	11.569			17.90	0.927	57.10	8.505	187.73	16.86	291.97	18.00
85.00	12.369	5.37	0.024	19.62	1.161	63.45	9.595	196.44	17.00	301.00	18.05
92.84	13.092	6.57	0.047	21.51	1.445	70.39	10.611	205.12	17.11	310.14	18.12
101.23	13.724	7.48	0.071	23.64	1.788			213.88	17.25	319.43	18.17
109.34	14.259	8.22	0.103	26.14	2.228	Series III		222.94	17.36	328.74	18.24
117.58	14.722	9.02	0.137	28.96	2.764			232.31	17.45	337.87	18.28
126.02	15.14	9.89	0.187	32.08	3.396	150.33	16.02	241.69	17.60	346.72	18.32
134.67	15.49	10.89	0.243	35.35	4.079	159.11	16.28	250.92	17.66		
				PdTe₂; gram formula weight=361.62 g							
Series I		182.89	17.03	282.61	18.20	7.13	0.059	21.00	1.648	60.26	9.743
		192.27	17.16	291.69	18.28	8.07	0.093	23.06	2.069	65.95	10.616
106.97	14.452	201.40	17.31	300.74	18.34	9.07	0.1403	25.40	2.570	72.16	11.417
115.44	14.922	210.33	17.44	309.84	18.40	10.14	0.2053	28.00	3.155	79.21	12.237
123.62	15.34	210.19	17.44	391.07	18.42	11.32	0.2769	28.64	3.299	86.75	12.997
131.64	15.66	219.26	17.57	328.32	18.52	12.53	0.3757	31.23	3.897	94.35	13.615
139.67	15.95	228.28	17.67	337.48	18.59	13.73	0.5039	34.08	4.555	102.14	14.144
147.95	16.22	237.29	17.77	346.37	18.64	13.59	0.4878	37.24	5.286		
156.84	16.45	247.17	17.88	Series II		14.81	0.6296	40.93	6.102		
166.07	16.69	255.19	17.96			16.13	0.8116	45.18	7.000		
175.21	16.88	264.33	18.02	5.42	0.023	17.55	1.026	49.96	7.949		
173.55	16.82	273.44	18.07	6.30	0.042	19.15	1.306	54.99	8.869		

molten for about 2 hr. After cooling the sample was fragmented to tin-white metallic, molybdenite-like scales. The sample was sealed into a new silica tube, annealed at 500°C for seven days and cooled to room temperature over a period of two days.

X-ray powder photographs were taken of the samples in cameras with 11.46 cm diam and asymmetric film mounting. The lattice constants corresponded within the limits of experimental error to those reported earlier for these compounds,[11,12] and no lines from foreign phases could be observed.

Calorimetric Procedure

The Mark I cryostat and its operation for low-temperature calorimetric measurements[15] and calorim-

eter of laboratory designation W-9[16] have been described previously. Only PtTe₂ was determined in calorimeter W-7.[1]

The platinum resistance thermometer (laboratory designation A-3) used in these measurements was calibrated by the National Bureau of Standards from 10° to above 373°K. Below 10°K a provisional scale for temperature was generated. The thermometer is considered to reproduce the thermodynamic scale within 0.1° from 4° to 10°K, 0.03° from 10° to 90°K, and within 0.04° above 90°K. Sample weights of 155.969 g of PtS₂, 197.380 g of PtTe₂, and 253.471 g of PdTe₂ were used. Helium gas at 8 cm Hg pressure and 26°C was added in the sample space for thermal

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TABLE II. Thermodynamic properties of platinum and palladium dichalcogenides.

T, °K	C_p (cal/gfw °K)	$S°-S_0°$ (cal/gfw °K)	$H°-H_0°$ (cal/gfw)	$-(F°-H_0°)/T$ (cal/gfw °K)
		PtS₂; gram formula weight = 259.22 g		
5	0.013	0.004	0.016	0.001
10	0.120	0.038	0.291	0.009
15	0.325	0.124	1.38	0.032
20	0.577	0.250	3.61	0.069
25	0.900	0.413	7.29	0.122
30	1.260	0.608	12.66	0.186
35	1.642	0.831	19.93	0.262
40	2.031	1.076	29.13	0.348
45	2.416	1.338	40.25	0.443
50	2.800	1.612	53.29	0.547
60	3.593	2.192	85.20	0.772
70	4.426	2.808	125.26	1.018
80	5.321	3.457	173.99	1.282
90	6.238	4.136	231.75	1.561
100	7.132	4.840	298.58	1.854
110	7.987	5.561	374.28	2.158
120	8.819	6.292	458.45	2.472
130	9.593	7.029	550.6	2.794
140	10.30	7.766	650.1	3.123
150	10.95	8.499	756.3	3.457
160	11.53	9.224	868.7	3.795
170	12.05	9.940	986.7	4.135
180	12.53	10.642	1109.7	4.477
190	12.97	11.332	1237.2	4.820
200	13.36	12.007	1368.9	5.163
210	13.71	12.668	1504.3	5.504
220	14.03	13.313	1643.0	5.845
230	14.32	13.943	1784.8	6.183
240	14.58	14.558	1929.4	6.519
250	14.82	15.159	2076.4	6.853
260	15.03	15.744	2225.6	7.184
270	15.22	16.315	2376.9	7.511
280	15.42	16.872	2530.2	7.836
290	15.61	17.417	2685.4	8.157
300	15.78	17.949	2842.3	8.474
350	16.43	20.432	3648.2	10.009
273.15	15.29	16.49	2425	7.61
298.15	15.75	17.85	2813	8.42
		PtTe₂; gram formula weight = 450.31 g		
5	(0.019)	(0.006)	(0.024)	(0.001)
10	0.184	0.057	0.439	0.013
15	0.587	0.199	2.25	0.049
20	1.215	0.449	6.67	0.116
25	2.019	0.804	14.70	0.216
30	2.970	1.254	27.11	0.350
35	4.007	1.789	44.54	0.516
40	5.087	2.395	67.29	0.713
45	6.147	3.055	95.39	0.936
50	7.162	3.756	128.69	1.182
60	9.014	5.230	209.79	1.733
70	10.56	6.739	307.88	2.341
80	11.82	8.234	420.00	2.984
90	12.84	9.687	543.4	3.649
100	13.64	11.082	676.0	4.323
110	14.30	12.415	815.8	4.998
120	14.85	13.684	961.7	5.670
130	15.31	14.891	1112.6	6.333
140	15.69	16.040	1267.6	6.986
150	16.01	17.134	1426.2	7.626

T, °K	C_p (cal/gfw °K)	$S°-S_0°$ (cal/gfw °K)	$H°-H_0°$ (cal/gfw)	$-(F°-H_0°)/T$ (cal/gfw °K)
		PtTe₂; gram formula weight = 450.31 g		
160	16.29	18.176	1587.7	8.253
170	16.52	19.171	1751.8	8.866
180	16.72	20.121	1918.1	9.465
190	16.90	21.030	2086.2	10.050
200	17.05	21.901	2256.0	10.621
210	17.19	22.737	2427.2	11.178
220	17.32	23.539	2599.8	11.722
230	17.44	24.312	2773.6	12.253
240	17.55	25.056	2948.5	12.771
250	17.65	25.775	3124.5	13.277
260	17.74	26.469	3301.5	13.771
270	17.83	27.140	3479.4	14.254
280	17.91	27.790	3658.1	14.726
290	17.98	28.420	3837.5	15.187
300	18.05	29.030	4017.6	15.638
350	18.33	31.835	4927.6	17.76
273.15	17.85	27.35	3536	14.40
298.15	18.03	28.92	3984	15.56
		PdTe₂; gram formula weight = 361.62 g		
5	(0.017)	(0.006)	(0.022)	(0.002)
10	0.185	0.056	0.432	0.013
15	0.653	0.208	2.38	0.049
20	1.459	0.499	7.54	0.122
25	2.482	0.931	17.32	0.238
30	3.612	1.483	32.54	0.398
35	4.768	2.127	53.50	0.598
40	5.895	2.837	80.17	0.833
45	6.961	3.594	112.35	1.098
50	7.955	4.380	149.69	1.386
60	9.713	5.991	238.32	2.019
70	11.16	7.601	342.91	2.702
80	12.32	9.169	460.51	3.413
90	13.27	10.677	588.6	4.137
100	14.01	12.114	725.1	4.863
110	14.63	13.480	868.5	5.585
120	15.16	14.777	1017.5	6.297
130	15.59	16.008	1171.3	6.997
140	15.96	17.177	1329.1	7.683
150	16.28	18.289	1490.4	8.353
160	16.55	19.349	1654.6	9.008
170	16.77	20.359	1821.2	9.646
180	16.97	21.323	1989.9	10.268
190	17.13	22.245	2160.5	10.874
200	17.29	23.128	2332.6	11.465
210	17.43	23.975	2506.2	12.041
220	17.57	24.789	2681.2	12.602
230	17.70	25.573	2857.5	13.149
240	17.81	26.329	3035.1	13.683
250	17.90	27.058	3213.6	14.203
260	17.99	27.762	3393.2	14.711
270	18.07	28.442	3573.5	15.207
280	18.16	29.101	3754.7	15.692
290	18.24	29.740	3936.6	16.165
300	18.32	30.360	4119.5	16.628
350	18.66	33.211	5044.5	18.798
273.15	18.07	28.65	3630	15.36
298.15	18.31	30.25	4086	16.54

conduction. Since the same quantity of helium gas was used for measurements on the empty calorimeter, no correction was necessary.

RESULTS

The actual experimental heat capacity values for the three dichalcogenide samples are presented in Table I in chronological order after the application of the analytically determined curvature correction. The temperature increments of individual determinations may usually be estimated from adjacent mean temperatures in the table. For most of the points the deviation from a smooth curve was less than 0.009 cal gfw^{-1} °K^{-1} above 25°K. Below 25°K the fractional deviations become larger because of the smaller absolute heat capacity, smaller temperature intervals, and decreased sensitivity of the thermometer.

The data are presented in terms of an ice point of 273.15°K and the thermochemical calorie defined as 4.1840 abs j. The gram formula weights of PtS₂, PtTe₂, and PdTe₂ are taken as 259.22, 450.31, and 361.62, respectively. Experimental densities of the dichalcogenides were found to be 7.80 g cm^{-3} for PtS₂, 10.16 g cm^{-3} for PtTe₂ (both by pycnometric measurement), and 8.306 g cm^{-3} for PdTe₂ (from x-ray diffraction data).

The contribution of the empty calorimeter to the total heat capacity when filled with the PtS₂ sample reached a maximum of 59% at 68°K and a minimum of 31% at 10°K. At 6°K the value was 42% and at 350°K the value had dropped to 46%. In contrast the contribution of the calorimeter with the PtTe₂ sample reached a maximum of 38% at 350°K and a minimum of 17% at 10°K. At 6°K the calorimeter accounted for 24% of the heat capacity measured. The behavior of the calorimeter filled with the PdTe₂ sample was similar to this latter case; the maximum of 40% occurred at 350°K and the minimum of 19% at 18°K. At 6°K the value was 27%.

Large-scale plots of heat capacity vs temperature were made over the entire region of investigation. In addition, a least squares polynomial in temperature fit to the data above 25°K with an IBM digital computer gave essentially identical results. The heat capacities at selected temperatures in Table II were taken from the drawn curve below 25°K and calculated by the polynomial representation above 25°K. A Debye T^3 extrapolation was used below 6°K. Values for $H°-H_0°$, $S°-S_0°$, and $(F°-H_0°)/T$ at the selected temperatures listed in Table II were obtained by integration. For internal consistency the values in Tables I and II are given to one more figure than is justified by the estimated experimental precision. In general the thermodynamic functions are believed to have a probable error less than 0.1% above 100°K.

The plots of the experimental heat capacities vs temperature are presented in Fig. 1. No anomalous deviations from the usual sigmoid form are seen.
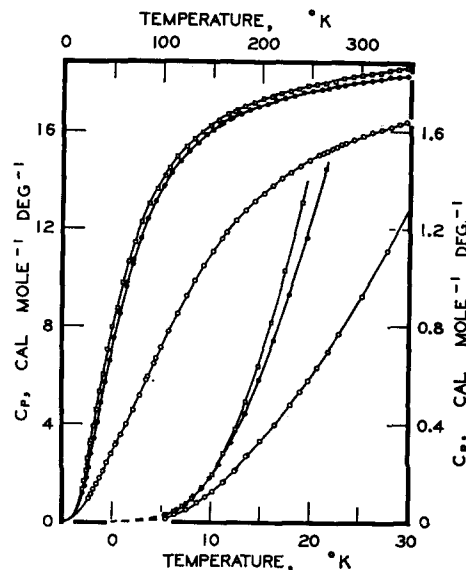

FIG. 1. Heat capacities of the dichalcogenides on a gram formula weight basis: ○ represents PtS₂; ● represents PtTe₂, and □ represents PdTe₂.

DISCUSSION

The entropy value found here for platinum disulfide, 17.85 cal gfw^{-1} °K^{-1}, compares well with that estimated by Kelley,[17] 17.4 cal gfw^{-1} °K^{-1}, on the basis of decomposition pressure measurements on PtS₂ by Biltz and Juza[18] and available data on the entropies of the elements. Just as in the PtS/Pt range,[1] Biltz and Juza apparently have included some low-pressure values in the PtS₂/PtS range also (those for PtS₁.₀₆, PtS₁.₀₁, and PtS₁.₀₅), which probably should have been omitted. Furthermore, the estimation of the partial pressure of the diatomic sulfur molecules in the vapor was based upon the work by Preuner and Schupp[19] which has since been shown to be considerably in error,[20,21] and a re-evaluation of the thermodynamic functions has therefore been made. It appeared possible to obtain consistent data using the available heat-capacity equations for PtS[1] and S₂ gas[22] and assuming the following heat-capacity equation, which satisfies the present data at 300 and 350°K and reaches the value 20 cal gfw^{-1} °K^{-1} at 1000°K, for PtS₂,

$$C_p = 16.39 + 3.77 \times 10^{-3} T - 1.57 \times 10^5 T^{-2}.$$

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

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The heat-capacity change for the reaction

$$2 \, PtS_2(s) = 2 \, PtS(s) + S_2(g)$$
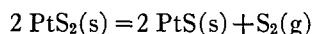
is then

$$\Delta C_p = -4.12 + 0.84 \times 10^{-3}T + 0.78 \times 10^5 T^{-2}.$$

A graphical evaluation of the derived function

$$(\Delta H_0/T) + I = -4.57 \, \log P_{S_2} - 9.49 \, \log T + 0.42$$
$$\times 10^{-3}T + 0.39 \times 10^5 T^{-2}$$

assuming P_{S_2} to be 40, 100, and 250 mm Hg at 889°, 924°, and 964°K, respectively, leads to $\Delta H_0 = 45\,000$ and $I = -72.35$. The constants needed for calculating enthalpy, free energy, and entropy data for the decomposition of PtS_2 are thus available, and the values at 298.15°K are

$$\Delta H° = 44.1 \text{ kcal}, \quad \Delta F° = 30.5 \text{ kcal}, \quad \Delta S° = 44.6 \text{ cal °K}^{-1}.$$

Incorporating the earlier data for PtS,[1] and taking orthorhombic sulfur as the standard state of sulfur instead of the diatomic gas, the following values for the standard heat of formation, free energy of formation, and entropy of PtS_2 are found at 298.15°K;

$$Pt(s) + 2S(rh) = PtS_2(s)$$
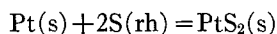
$$\Delta Hf° = -26.3 \text{ kcal}, \quad \Delta Ff° = -24.0 \text{ kcal},$$

$$S° = 18.1 \text{ cal °K}^{-1}.$$

There is good agreement with the enthalpy and free energy values of Kelley[17] ($\Delta Hf° = -26.64$ kcal, $\Delta Ff° = -24.28$ kcal), while another enthalpy estimate[23] ($\Delta Hf° = -27.8$ kcal) seems to be somewhat low.

Although high temperature decomposition data are also available for other palladium and platinum group disulfides, heat-capacity data are not. The thermodynamic functions for RuS_2 have already been estimated by Kelley[17] assuming the heat-capacity change to be $\Delta C_p = -5$ cal gfw^{-1} °K^{-1} for the reaction

$$RuS_2(s) = Ru(s) + S_2(g)$$

studied by Juza and Meyer[24] in the temperature range 1396° to 1481°K. A supposedly better estimate can be made by assuming the heat capacity of RuS_2 to have the same values as FeS_2 (pyrite)[25] at 300 and 350°K (14.90 and 15.66 cal gfw^{-1} °K^{-1}, respectively) and reaching the value 19 cal gfw^{-1} °K^{-1} at 1000°K according to the equation

$$C_p = 16.38 + 2.83 \times 10^{-3}T - 2.10 \times 10^5 T^{-2}.$$

For Ru, the alleged allotropy[26,27] has not been confirmed

[23] Selected Values of Chemical Thermodynamic Properties, U. S. National Bureau of Standards Circ. No. 500 (U. S. Government Printing Office, Washington 25, D. C., 1952).

[24] R. Juza and W. Meyer, Z. anorg. u. allgem. Chem. 213, 273 (1933).

[25] F. Grønvold and E. F. Westrum, Jr., (unpublished data).

[26] F. M. Jaeger and E. Rosenl ohm, Proc. Acad. Sci. Amsterdam 34, 808 (1931); Rec. trav. chim. 51, 1 (1932).

[27] F. M. Jaeger and E. Rosenbohm, Proc. Acad. Sci. Amsterdam 44, 144 (1941).

by other investigators, and x-ray photographs up to 1600°K showed only the presence of the hexagonal close-packed form.[28] Therefore, the heat-capacity equation derived by Kelley,[22] $C_p = 5.25 + 1.50 \times 10^{-3}T$ (298–1308°K), has been assumed valid up to 1481°K. The heat-capacity change for the reaction is then

$$\Delta C_p = -2.41 - 1.17 \times 10^{-3}T + 1.20 \times 10^5 T^{-2}.$$

Since the degree of dissociation of the diatomic sulfur gas into sulfur atoms under the experimental conditions of Juza and Meyer does not exceed 2% according to the data giving the highest values,[29] the P_{S_2} values are taken to be 2.8, 5.4, 10.0, and 15.3 mm Hg at 1396°, 1426°, 1457°, and 1481°K, respectively. A graphical evaluation of the derived function

$$(\Delta H_0/T) + I = -4.57 \, \log P_{S_2} - 5.55 \, \log T - 0.59$$
$$\times 10^{-3}T + 0.60 \times 10^5 T^{-2},$$

leads to $\Delta H_0 = 85\,000$ and $I = -68.08$. The enthalpy, free energy, and entropy values for the decomposition of RuS_2 at 298.15°K are accordingly,

$$\Delta H° = 83.8 \text{ kcal}, \quad \Delta F° = 68.4 \text{ kcal}, \quad \Delta S° = 50.9 \text{ cal °K}^{-1}.$$

The related enthalpy and free energy values for the reaction

$$Ru(s) + 2S(rh) = RuS_2(s)$$
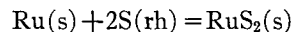
and the entropy of RuS_2 at 298.15°K are

$$\Delta Hf° = -53.0 \text{ kcal}, \quad \Delta Ff° = -49.5 \text{ kcal},$$

$$S° = 10.4 \text{ cal °K}^{-1}.$$

All three values are lower than those of Kelley[17] ($\Delta Hf° = -46.99$ kcal, $\Delta Ff° = -44.11$ kcal, $S° = 12.5$ cal °K^{-1}). Another enthalpy estimate[23] based upon the same data is also higher ($\Delta Hf° = -48.1$ kcal). The uncertainty in the entropy value is rather large, since the equilibrium temperatures were high and no heat-capacity data are available for RuS_2. For ruthenium the value $S_{298}° = 6.82$ cal gfw^{-1} °K^{-1} by Clusius and Piesbergen[30] was chosen.

A corresponding calculation for OsS_2 (using the same heat-capacity equation for the compound as for RuS_2 and the available data[22] for the elements) yields a heat-capacity change of $\Delta C_p = -1.97 - 1.79 \times 10^{-3}T + 1.20 \times 10^5 T^{-2}$ for the reaction

$$OsS_2(s) = Os(s) + S_2(g).$$
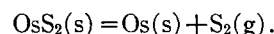
A graphical evaluation of the derived function

$$(\Delta H_0/T) + I = -4.57 \, \log P_{S_2} - 4.54 \, \log T - 0.90$$
$$\times 10^{-3}T + 0.60 \times 10^5 T^{-2}$$

[28] E. O. Hall and J. Crangle, Acta Cryst. 10, 240 (1957).

[29] W. H. Evans and D. D. Wagman, J. Research Natl. Bur. Standards 49, 141 (1952).

[30] K. Clusius and U. Piesbergen, Z. Naturforsch. 14a, 23 (1959).

using the data by Juza,[31] P_{S_2} equal to 27.8, 84.5, 213, and 490 mm Hg at 1217°, 1267°, 1317°, and 1367°K, respectively, leads to $\Delta H_0 = 67\,000$ and $I = -63.61$. The enthalpy, free energy, and entropy values for the decomposition of OsS₂ at 298.15°K are accordingly,

$$\Delta H^\circ = 65.9\,\text{kcal}, \quad \Delta F^\circ = 51.3\,\text{kcal}, \quad \Delta S^\circ = 49.2\,\text{cal }^\circ\text{K}^{-1}.$$
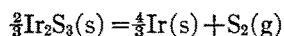
The enthalpy and free energy values for the reaction

$$\text{Os(s)} + 2\text{S(rh)} = \text{OsS}_2(\text{s})$$
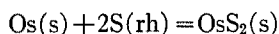
and the entropy of OsS₂ at 298.15°K are then

$$\Delta Hf^\circ = -35.1\,\text{kcal}, \qquad \Delta Ff^\circ = -32.1\,\text{kcal},$$

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

The enthalpy value is about 4 kcal lower than Juza's[31] estimate, but agrees completely with a more recent one[23] also based upon his data ($\Delta Hf^\circ = -35$ kcal).

For ∼IrS₂ the evaluation is dependent upon assumptions regarding the properties of the lower sulfide Ir₂S₃. Decomposition pressures have been measured for both sulfides by Biltz et al.[32] The evaluation is made here on the assumption that the heat capacities of the compounds are equal to those of PtS₂ and PtS + PtS₂, respectively. The heat-capacity change for the reaction

$$\tfrac{2}{3}\text{Ir}_2\text{S}_3(\text{s}) = \tfrac{4}{3}\text{Ir(s)} + \text{S}_2(\text{g})$$

is estimated as

$$\Delta C_p = -1.44 - 3.20 \times 10^{-3}T + 0.63 \times 10^5 T^{-2}.$$

A graphical evaluation of the derived function

$$(\Delta H_0/T) + I = -4.57 \log P_{S_2} - 3.32 \log T - 1.60$$
$$\times 10^{-3}T + 0.32 \times 10^5 T^{-2}$$

leads to $\Delta H_0 = 70\,100$ and $I = -61.35$. The enthalpy, free energy, and entropy values for the decomposition or Ir₂S₃ into the elements according to the above equation at 298.15°K are

$$\Delta H^\circ = 69.3\,\text{kcal}, \quad \Delta F^\circ = 54.3\,\text{kcal}, \quad \Delta S^\circ = 50.4\,\text{cal }^\circ\text{K}^{-1}.$$

The corresponding enthalpy and free energy values for the reaction

$$2\text{Ir(s)} + 3\text{S(rh)} = \text{Ir}_2\text{S}_3(\text{s})$$
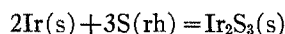
and the entropy of Ir₂S₃ at 298.15°K are

$$\Delta Hf^\circ = -57.7\,\text{kcal}, \qquad \Delta Ff^\circ = -52.7\,\text{kcal},$$
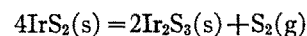
$$S^\circ = 23.2\,\text{cal }^\circ\text{K}^{-1}.$$

Earlier estimates of the enthalpy[23,32] were −51 kcal. In deriving the entropy the value $S_{298}^\circ = 8.50$ cal gfw⁻¹ °K⁻¹ for iridium determined by Clusius and Losa[33] was used.

Assuming the decomposition of ∼IrS₂ to take place according to the simple stoichiometric equation

$$4\text{IrS}_2(\text{s}) = 2\text{Ir}_2\text{S}_3(\text{s}) + \text{S}_2(\text{g})$$

the heat capacity change is

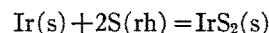$$\Delta C_p = -4.12 + 0.84 \times 10^{-3}T + 0.78 \times 10^5 T^{-2}.$$

A graphical evaluation of the function

$$(\Delta H_0/T) + I = -4.57 \log P_{S_2} - 9.49 \log T + 0.42$$
$$\times 10^{-3}T + 0.39 \times 10^5 T^{-2}$$

gives $\Delta H_0 = 53\,800$ and $I = -69.8$. The corresponding values of the enthalpy, free energy, and entropy of decomposition at 298.15°K are

$$\Delta H^\circ = 52.3\,\text{kcal}, \quad \Delta F^\circ = 39.8\,\text{kcal}, \quad \Delta S^\circ = 42.0\,\text{cal }^\circ\text{K}^{-1},$$

which lead to the following values for the enthalpy, free energy, and entropy of IrS₂ at 298.15°K

$$\text{Ir(s)} + 2\text{S(rh)} = \text{IrS}_2(\text{s})$$

$$\Delta Hf^\circ = -34.2\,\text{kcal}, \qquad \Delta Ff^\circ = -31.5\,\text{kcal},$$

$$S^\circ = 14.7\,\text{cal }^\circ\text{K}^{-1}.$$

An earlier value of the enthalpy of formation[23] is about 4 kcal higher ($\Delta Hf^\circ = -30$ kcal).

For the disulfides of rhodium and palladium only estimates relative to the lower sulfides can be made, but since no heat-capacity data are known for any of the compounds in question, no attempt to evaluate their entropies will be made here.

In estimating entropies for chalcogenides for which no data exist, the additivity principle of a chalcogen and a metal contribution can be used. Justification for this is seen in the data presented here and will be discussed more thoroughly in a forthcoming paper.[25] The values chosen are 10.5 cal g atom⁻¹ °K⁻¹ for the metal (Me^{2+}, Me^{3+}, Me^{4+}), 3.0 both for S^{2-} and S_2^{2-}, 7.0 for Se^{2-}, 10.0 for Se_2^{2-}, and 9.5 for Te^{2-} and 13.5 for Te_2^{2-}. Estimates in cal gfw⁻¹ °K⁻¹ are then as follows: RuSe₂, OsSe₂, 19.5; RuTe₂, OsTe₂, 24.0; RhTe₂, IrTe₂, 29.5; PtSe₂, 24.5; ∼IrSe₂, 22.5; ⅛Rh₈S₁₅, 15.0. These values are probably reliable to about 0.8 cal g atom⁻¹ °K⁻¹. For the deformed pyrite-like structures of PdS₂ and PdSe₂, and those of the rhodium and iridium chalcogenides, corresponding estimates would probably give entropy values that would be too low, because the compounds are hyperelectronic with regard to forming pyrite-type structures, just as CoS₂, NiS₂, and NiSe₂. An increase in entropy of about 3.0 cal gfw⁻¹ °K⁻¹ for the rhodium and iridium chalcogenides and about 5 cal gfw⁻¹ °K⁻¹ for the palladium chalcogenides would seem necessary. For platinum only tetravalent dichalcogenides are known, and the entropy of PtSe₂, for example, is thus expected to be lower than that of PdSe₂ by 5 cal gfw⁻¹ °K⁻¹.

[31] R. Juza, Z. anorg. u. allgem. Chem. 219, 129 (1934).
[32] W. Biltz, J. Laar, P. Ehrlich, and K. Meisel, Z. anorg. u. allgem. Chem. 233, 257 (1937).
[33] K. Clusius and C. G. Losa, Z. Naturforsch. 10a, 545 (1955).

Transport Properties of Polar Gases*

L. MONCHICK

Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland

AND

E. A. MASON

Institute for Molecular Physics, University of Maryland, College Park, Maryland

(Received February 13, 1961)

A model is proposed for the calculation of viscosity, diffusion, thermal diffusion, and the translational part of the heat conductivity of dilute polar gases. It is assumed that the molecular-collision trajectories are negligibly distorted by transfer of internal rotational energy, and that the relative orientation of two colliding dipoles remains fixed throughout the significant portion of the collision trajectory around the distance of closest approach. For this model, the Chapman-Enskog theory retains its usual form, but the collision integrals which appear must be averaged over all possible relative orientations occurring in collisions. Collision integrals have been calculated for the Stockmayer (12-6-3) potential,

$$\varphi(r) = 4\epsilon_0[(\sigma_0/r)^{12} - (\sigma_0/r)^6 + \delta(\sigma_0/r)^3],$$

for kT/ϵ_0 from zero to 100 and for δ from -2.5 to $+2.5$, and averaged over all orientations (assumed equally probable). Sufficient collision integrals are tabulated that the convergence error of the Chapman-Enskog theoretical expressions is not a problem.

Experimental viscosities and dipole moments of a number of polar gases have been used to determine the potential parameters ϵ_0, σ_0, and δ, which were then used to calculate other properties for comparison with experiment. The over-all agreement between experiment and this model for polar gases is comparable to that of the Lennard-Jones (12-6) model for nonpolar gases.

I. INTRODUCTION

GAS kinetic theory has been most completely worked out for particles interacting with central forces,[1,2] and has proved rather successful for those molecules which can be considered to have spherical symmetry and no internal degrees of freedom.[2] In the important case of polar gases, however, the facts that the molecules have an angle-dependent potential and that rotational-energy transfers are possible on every collision must be taken into account. Although several treatments have been developed for particles with internal degrees of freedom (Taxman[3] for the classical case and Wang Chang and Uhlenbeck[4] for the quantum case), they would tax even the present generation of computing machines if carried out rigorously. In light of this, we are limited to approximate treatments.

The interaction potential which has been used almost exclusively for polar gases (and which will be used here) is the Stockmayer potential,

$$\varphi(r) = 4\epsilon_0[(\sigma_0/r)^{12} - (\sigma_0/r)^6] - (\mu_1\mu_2/r^3)\zeta, \quad (1)$$

where

$$\zeta = 2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi, \quad (2)$$

and μ_1 and μ_2 are the dipole moments of the two interacting molecules, θ_1 and θ_2 the angles of inclination of the axes of the two dipoles to the line joining the centers of the molecules, and ϕ is the azimuthal angle between them. In the limit as μ_1 or $\mu_2 \to 0$, $\varphi(r)$ is just the Lennard-Jones (12-6) potential with a potential-

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[1] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1952), 2nd ed.

[2] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954). Hereafter referred to as MTGL.

[3] N. Taxman, Phys. Rev. **110**, 1235 (1958).

[4] C. S. Wang Chang and G. E. Uhlenbeck, University of Michigan Engineering Research Report No. CM-681 (July, 1951). See also MTGL pp. 501–506.