Thallous Bromide and Thallous Iodide—Heat Capacities and Thermodynamic Properties from 5° to 350° K.

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The heat capacities of TlBr and TlI have been determined by adiabatic calorimetry from 5° to 350° K. and found to be of normal sigmoid shape without transitions or thermal anomalies. Apparent Debye characteristic temperatures for the low-temperature region show "normal" deviation from the simple Debye theory with minima about 8° K. Values of the heat capacity (C_p), entropy ($S°$), enthalpy function $[(H° - H°_0)/T]$, and Gibbs function $[-(G° - H°_0)/T]$ at 298.15° K. are: 12.55, 29.30, 10.69, and 18.61 for TlBr and 12.74, 30.52, 10.94, and 19.58 for TlI, respectively, in cal. per (g.f.m. ° K.).

AMONG crystalline thallous halides, characterized by massive cations, only TlCl (*1*) has been experimentally investigated with respect to its low temperature thermodynamic properties. High temperature heat contents and thermodynamic functions for TlCl (*4*), TlBr and TlI (*3*) were recently determined by Cubicciotti and Eding. The present investigation provides precise chemical thermodynamic data in the cryogenic range on TlBr and TlI by adiabatic calorimetry, a revised anchor point for the high temperature equilibrium properties, and an insight concerning the characteristic temperatures of these ionic crystals which are closely related to those of the alkali halides.

EXPERIMENTAL

Cryogenic Apparatus. Measurements were made in the Mark II adiabatic cryostat previously described (*12*). The gold-plated, copper calorimeter (laboratory designation W-28, about 92-cc. capacity) was employed for measurements on both samples. Temperatures determined with a capsule-type, platinum resistance thermometer (laboratory designation A-5) are considered to be in accord with the thermodynamic temperature scale within 0.03° K. from 10° to 90° K. and within 0.04° K. from 90° to 350° K. The heat capacity of the empty calorimeter was determined separately with appropriate small corrections for the slight differences in the amount of helium, indium-tin solder, and Apiezon-T grease on the loaded and on the empty calorimeter. The heat capacity of the sample represented about 97% of the total at 15° K., and gradually decreased to 55% above 150° K. for both samples. The calorimetric samples of TlBr and TlI weighed (in vacuo) 210.97 and 194.172 grams, respectively. Buoyancy corrections were made on the basis of densities of 7.45 for TlBr and 7.09 for TlI, in grams per cc. Helium gas (about 150 torr at 300° K.) was used to enhance thermal contact between calorimeter and sample. All determinations of mass, voltage, current, time, and temperatures were referred to calibrations performed by the National Bureau of Standards.

Preparation and Purity of Samples. Thallous bromide and thallous iodide were prepared for this study under the direction of Daniel Cubicciotti at Stanford Research Institute by dissolving 99.95% pure thallium (obtained from American Smelting and Refining Co.) in $5N$ H_2SO_4 solution and adding sufficient amounts of 10% KBr solution to precipitate TlBr and of 10% KI solution to precipitate TlI. The precipitates were washed with deionized water until free of $SO_4^=$, dried, and ground in a glass mortar. Triplicate chemical analyses for thallium content by the chromate method (*5*) yielded thallium (in wt. %): in TlBr–71.91, 71.92, and 71.95 (theoretical value = 71.89); and in TlI–61.73, 61.71, and 61.71 (theoretical value = 61.69). The samples are, therefore, probably at least 99.95% pure.

RESULTS AND DISCUSSION

Heat Capacities and Thermal Properties. The experimental heat capacity values for thallous bromide and thallous iodide are presented in chronological sequence at the mean temperatures of determinations in Table I. Temperature increments employed in the measurements may usually be inferred from the differences in the adjacent mean temperatures. These data have been adjusted for "curvature" occasioned by the finite temperature increments employed in the measurements, and they are considered to have a probable error decreasing from about 3% at 5° to 0.5% at 10° K. and to less than 0.1% above 20° K. These data are based upon a defined thermochemical calorie equal to 4.1840 joules, an ice point of 273.15° K., and gram formula masses of 284.279 for thallous bromide and 331.274 for thallous iodide.

The smoothed heat capacities and thermodynamic functions at selected temperatures, obtained by integrating these data with a high-speed digital computer, are given in Table II. The heat capacity values of Table II were

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Table I. Heat Capacities of Thallous Bromide and Thallous Iodide[a]

T	C_p	T	C_p
Thallous Bromide (TlBr)			
Series I		Series II	
70.21	10.624	5.10	0.175
76.37	10.822	5.95	0.305
83.35	11.056	6.60	0.410
91.53	11.231	7.36	0.612
100.73	11.346	8.23	0.842
110.54	11.483	9.19	1.120
120.45	11.600	10.31	1.446
130.28	11.718	11.60	1.818
140.05	11.807	13.10	2.277
149.77	11.868	14.81	2.835
159.38	11.942	16.83	3.477
169.33	11.995	19.22	4.210
179.64	12.040	21.92	4.986
189.35	12.090	24.91	5.771
198.81	12.122	28.26	6.542
208.93	12.163	31.97	7.279
219.39	12.221	35.72	7.914
229.78	12.262	39.83	8.480
240.10	12.313	44.38	8.991
250.35	12.359	49.17	9.437
260.56	12.384	54.24	9.808
270.82	12.477	59.63	10.148
281.18	12.491	66.37	10.482
291.50	12.517	74.10	10.745
301.73	12.562		
311.69	12.580		
322.18	12.616		
333.45	12.656		
344.66	12.682		
Thallous Iodide (TlI)			
Series I		Series II	
64.80	10.783	5.46	0.241
70.21	10.949	5.83	0.307
76.12	11.110	6.46	0.442
83.08	11.318	7.00	0.560
90.76	11.464	7.62	0.721
99.48	11.570	8.50	0.976
108.87	11.681	9.46	1.284
118.30	11.793	10.51	1.652
127.95	11.896	11.79	2.111
137.69	11.979	13.33	2.666
146.86	12.054	15.04	3.273
156.45	12.123	17.02	3.956
165.92	12.153	19.49	4.768
175.16	12.196	22.24	5.619
183.92	12.242	25.02	6.360
193.40	12.288	27.77	7.017
203.09	12.330	30.40	7.562
212.88	12.375	33.35	8.102
222.79	12.411	36.58	8.602
232.62	12.457	40.46	9.082
242.38	12.518	45.49	9.588
252.07	12.556	50.87	10.013
261.70	12.587	56.42	10.347
271.35	12.620	62.18	10.652
281.01	12.674	68.07	10.874
290.61	12.707		
300.14	12.753		
309.63	12.796		
318.84	12.824		
327.76	12.876		
336.63	12.894		
345.45	12.949		

[a] Units: cal., g.f.m., ° K.

taken from a smooth curve obtained by a least squares-fitted polynomial function through the experimental points. The thermodynamic functions are considered to have a precision corresponding to a probable error of less than 0.1% above 100° K. An additional digit beyond those significant is given in Table II for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs energies have not been adjusted for nuclear spin and isotopic mixing contributions and hence

Table II. Thermodynamic Functions of Thallous Bromide and Thallous Iodide[a]

T	C_p	$S°$	$H° - H°_0$	$-(G° - H°_0)/T$
Thallous Bromide (TlBr, g.f.m. = 284.279)				
5	0.176	0.060	0.22	0.015
10	1.316	0.478	3.58	0.120
15	2.897	1.304	14.03	0.369
20	4.440	2.352	32.43	0.731
25	5.790	3.492	58.10	1.168
30	6.905	4.650	89.94	1.652
35	7.798	5.784	126.78	2.162
40	8.504	6.873	167.6	2.683
45	9.061	7.908	211.6	3.207
50	9.505	8.887	258.0	3.726
60	10.159	10.682	356.6	4.739
70	10.610	12.284	460.5	5.704
80	10.931	13.722	568.3	6.618
90	11.162	15.024	678.9	7.481
100	11.335	16.209	791.4	8.296
110	11.473	17.296	905.4	9.065
120	11.593	18.300	1020.8	9.793
130	11.703	19.232	1137.3	10.484
140	11.801	20.103	1254.8	11.140
150	11.884	20.920	1373.2	11.765
160	11.950	21.690	1492.4	12.362
170	12.001	22.416	1612.2	12.932
180	12.042	23.103	1732.4	13.478
190	12.081	23.755	1853.0	14.002
200	12.124	24.376	1974.1	14.505
210	12.171	24.968	2095.5	14.990
220	12.221	25.54	2217.5	15.46
230	12.270	26.08	2339.9	15.91
240	12.316	26.60	2462.9	16.34
250	12.357	27.11	2586.2	16.76
260	12.397	27.59	2710.0	17.17
270	12.438	28.06	2834.2	17.56
280	12.481	28.51	2958.8	17.95
290	12.521	28.95	3083.8	18.32
300	12.554	29.38	3209.2	18.68
350	12.695	31.32	3840.5	20.35
273.15	12.45	28.21	2873	17.69
298.15	12.55	29.30	3186	18.61
Thallous Iodide (TlI, g.f.m. = 331.274)				
5	0.196	0.067	0.25	0.017
10	1.473	0.526	3.93	0.133
15	3.259	1.460	15.75	0.410
20	4.934	2.631	36.32	0.816
25	6.353	3.890	64.65	1.304
30	7.487	5.153	99.37	1.841
35	8.363	6.376	139.09	2.402
40	9.034	7.538	182.7	2.972
45	9.549	8.633	229.2	3.541
50	9.951	9.661	278.0	4.102
60	10.536	11.531	380.6	5.188
70	10.938	13.187	488.1	6.214
80	11.222	14.667	599.0	7.180
90	11.425	16.001	712.3	8.087
100	11.575	17.213	827.3	8.940
110	11.699	18.322	943.7	9.744
120	11.810	19.345	1061.2	10.502
130	11.911	20.294	1179.8	11.219
140	12.001	21.181	1299.4	11.899
150	12.075	22.011	1419.8	12.546
160	12.133	22.792	1540.9	13.162
170	12.180	23.530	1662.4	13.750
180	12.223	24.227	1784.5	14.313
190	12.266	24.889	1906.9	14.853
200	12.312	25.52	2029.8	15.37
210	12.360	26.12	2153.1	15.87
220	12.406	26.70	2277.0	16.35
230	12.450	27.25	2401.3	16.81
240	12.493	27.78	2526.0	17.26
250	12.535	28.29	2651.1	17.69
260	12.578	28.78	2776.7	18.10
270	12.623	29.26	2902.7	18.51
280	12.667	29.72	3029.1	18.90
290	12.708	30.16	3156.0	19.28
300	12.749	30.60	3283.3	19.65
350	12.968	32.58	3926.2	21.36
273.15	12.64	29.41	2942	18.63
298.15	12.74	30.52	3260	19.58

[a] Units: cal., g.f.m., ° K.

are practical values for use in chemical thermodynamic calculations.

High temperature enthalpy determinations on TlBr have been reported by Goodwin and Kalmus (*6*) and recently on TlBr and TlI by Cubicciotti and Eding (*3*). The heat capacity equation derived by the latter investigators is represented by the following equations:

$$\text{TlBr: } C_p = 9.95 + 7.10 \times 10^{-3}T$$

$$\text{TlI: } C_p = 11.56 + 3.32 \times 10^{-3}T$$

These equations yield values of C_{p298} of 12.07 and 12.55 cal. per (g.f.m. ° K.) for TlBr and TlI, respectively. Kelley and King (*8*) estimated the values of entropy at 298.15° K. for TlBr and TlI as 29.5 ± 1.0 and 31.0 ± 1.0 cal. per (g.f.m. ° K.). The present results on TlI are consistent with the value of Cubicciotti (*2*). His sublimation pressure data obtained by the quasi-state method of Rodebush as well as by the transpiration method, combined with the entropy of the gas based on molecular constants gives $S^{\circ}_{298.15} = 30.7$ cal. per (g.f.m. ° K.).

The crystal structure of TlI is reported to be orthorhombic ("TlI-type" structure) below 448° K. (*13*). This structure, characteristic of NaOH, KOH, and RbOH crystals at ordinary temperatures, is a rhombohedrally distorted NaCl-type structure, rather than a CsI-type structure (*11*).

Thermodynamics of Formation. The enthalpy of formation of TlBr and TlI have been reported (*10*) as −41.2 ± 0.7 kcal. per (g.f.m.) and −29.7 ± 0.6 kcal. per (g.f.m.), respectively. Combining these values with the entropies of thallium, bromine, and iodine (*8, 9*), and the data from present work yields entropies of formation ($\Delta Sf°$) and Gibbs energies of formation ($\Delta Gf°$) of −4.3 ± 0.2 cal. per (g.f.m. ° K.) and −39.9 ± 0.8 kcal. per (g.f.m) for TlBr, and of 1.3 ± 0.1 cal. per (g.f.m. ° K.) and −30.1 ± 0.7 kcal. per (g.f.m.) for TlI, respectively, at 298.15° K.

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Osmotic and Activity Coefficients of Tris(hydroxymethyl)aminomethane and Its Hydrochloride in Aqueous Solution at 25° C.

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The isopiestic vapor pressure method has been used to determine the osmotic and activity coefficients of tris(hydroxymethyl)aminomethane and its hydrochloride in aqueous solution at 25° C. The base is an almost ideal solute while the hydrochloride resembles ammonium chloride in behavior.

A BASE of considerable use both as an acidimetric standard and as a biological buffer is 2-amino-2-(hydroxymethyl)-1,3-propanediol or tris(hydroxymethyl)aminomethane, sometimes abbreviated to tris. Its hydrochloride also finds use as a component of buffer solutions.

Bates and Hetzer (*2*) found that tris had an acidic dissociation constant of 8.075 (in pK units) at 25° while Datta, Grzybowski, and Wilson (*4*) found pK = 8.069. The former measurements were made with solutions containing only tris and its hydrochloride, and the results indicated a zero value of the ion-size parameter in the Debye-Hückel equation. This suggests that there is some ion-pair formation in the hydrochloride. The measurements of Datta, Grzybowski, and Wilson, however, were made in potassium chloride and indicated a normal value of the ion-size parameter of about 3 A.