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Heat Capacities and Thermodynamic Properties of Two Tetramethylammonium Halides*

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Heat capacities of tetramethylammonium chloride and bromide were determined by low-temperature adiabatic calorimetry from 5° to 350°K. Derived thermodynamic properties were then calculated. Two transitions were found in the chloride: a sharp, apparently first-order transition occurs at 75.76°K with an entropy of transition of 0.37 cal $mole^{-1}$ $°K^{-1}$ and a lambda-shaped transition at 184.85°K with an entropy increment of 0.14 cal $mole^{-1}$ $°K^{-1}$. No anomaly has been observed in the bromide. Molal values of heat capacity, entropy, and free energy function at 298.15°K for the chloride and the bromide are: 37.51, 38.64, 45.58, 47.99, and −23.36, −25.36 cal $mole^{-1}$ $°K^{-1}$, respectively.

INTRODUCTION

A CONTRIBUTORY part of the data establishing thermodynamic evidence for the nature of the potential function of the $[Cl—H—Cl]^-$ ion in tetramethyl ammonium hydrogen dichloride[1] involved the determination of the heat capacity of tetramethylammonium chloride from 5° to 350°K. Two transitions were observed in the tetramethylammonium chloride crystal at 75.8° and 184.9°K with small transitional entropy increments. The lower transition appears as a sharp peak and is apparently a first-order transition; however, the anomaly at higher temperature is lambda shaped. It is probable that these transitions are due to the ordering of the cation. Since the tetramethylammonium fluoride is not readily available, and since the iodide has already been studied calorimetrically[2] (but showed no transitions) the bromide was chosen for comparative studies.

EXPERIMENTAL

Preparation and Purification of Halides

Tetramethylammonium chloride made by Eastman Kodak Company was purified by recrystallizing three times from anhydrous methanol. The original (impure) sample was highly hygroscopic, but this property is much less pronounced for the recrystallized calorimetric sample. The latter sample, however, was kept in a vacuum dessicator for about a week and then transferred into a dry box with an anhydrous nitrogen atmosphere in order to avoid possible contamination of the sample by solvent and moisture. Loading and unloading the calorimeter was also done in the dry box. Microchemical analysis indicated the following composition: 43.85% C, 11.19% H, and 12.89% N [calculated for $(CH_3)_4NCl$: 43.83% C, 11.04%H, and 12.78% N].

Tetramethylammonium bromide made by Eastman Kodak Company was purified by three recrystallizations from absolute methanol. Unlike those of the chloride, the bromide crystals appear as hard rectangular prisms, which are slightly hygroscopic in moist air. It was therefore kept in a vacuum dessicator and handling in ambient air was minimized in order to preserve its purity. Analytical data showed the following composition: 31.26% C, 7.74% H, 8.81% N, and 51.78% Br [calculated for $(CH_3)_4NBr$: 31.18% C, 7.85% H, 9.09% N, and 51.84% Br].

Cryogenic Technique

The Mark I adiabatic calorimetric cryostat was employed for the measurement of heat capacities in the range from 5° to 350°K. It is similar to the one described by Westrum, *et al.*[3]

A gold-plated copper calorimeter, laboratory designation W-9, was used for the heat-capacity measurements. It is about 3.8 cm in diameter and 7.7 cm in length with a shell thickness of about 0.4 mm. Four vanes of 0.1-mm copper foil aid the establishment of thermal equilibrium and a cupola of Monel facilitates fusing the solder seal on the removable cover without heating the sample. An axial entrant well is provided in the calorimeter to accommodate the heater-thermometer assembly which consists of a capsule-type platinum-resistance thermometer within a cylindrical, copper, heater sleeve which carries 150 ohm of bifilarly wound, Fiberglas-insulated Advance wire. In determining heat capacities, calorimeter W-9 was loaded with samples of 30.021 and 47.643 g (*in vacuo*) of tetramethylammonium chloride and bromide, respectively. After brief evacuation helium gas at 13.7 and 8.2 cm Hg pressure at 300°K was put into the calorimeter sample space to facilitate heat conduction between the sample and the calorimeter.

Temperatures were measured by a platinum resistance thermometer (laboratory designation A-3) which was calibrated by the National Bureau of Stand-

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[1] S. S. Chang and E. F Westrum, Jr., J. Chem. Phys. (to be published).

[2] L. V. Coulter, K. S. Pitzer, and W. M. Latimer, J. Am. Chem. Soc. 62, 2845 (1940).

[3] E. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne, J. Chem. Phys. 21, 419 (1953).

TABLE I. Heat capacities of tetramethylammonium bromide and tetramethylammonium chloride. Units: cal mole^{-1} °K^{-1}.

T, °K	C_p
Tetramethylammonium bromide [$(CH_3)_4NBr$, 1 mole = 154.064 g]	
Series I	
78.21	15.74
84.56	16.59
91.67	17.44
99.41	18.32
107.32	19.27
115.39	20.23
123.78	21.24
132.27	22.20
140.75	23.14
149.39	24.10
158.40	25.12
Series II	
4.99	0.038
5.61	0.066
6.63	0.113
7.64	0.201
8.52	0.306
9.45	0.441
10.51	0.628
11.67	0.872
12.92	1.172
14.28	1.546
15.86	2.030
17.66	2.605
19.61	3.257
21.66	3.969
23.85	4.730
26.27	5.562
28.96	6.448
32.01	7.409
35.41	8.403
39.11	9.371
43.17	10.312
47.63	11.243
Series III	
49.88	11.67
55.49	12.63
61.62	13.58
68.24	14.48
75.40	15.37
Series IV	
161.70	25.44
179.59	27.19
188.32	28.01
197.02	28.82
205.94	29.66
215.07	30.51
224.17	31.36
233.37	32.31
242.63	33.25
Series V	
248.63	33.88
257.46	34.83
266.26	35.38
275.30	36.30
284.39	37.25
293.43	38.19
302.49	39.13
311.61	40.06
Series VI	
318.12	40.72
327.36	41.63
336.57	42.63
345.60	43.51
Series VII	
157.32	24.96
166.60	25.92
175.28	26.75
183.44	27.53
Tetramethylammonium chloride [$(CH_3)_4NCl$, 1 mole = 109.605 g]	
Series I	
5.09	0.021
6.00	0.041
6.94	0.065
7.92	0.102
8.97	0.164
10.04	0.246
11.01	0.334
12.11	0.460
13.29	0.601
14.52	0.792
15.83	1.025
17.21	1.309
Series II	
8.03	0.110
9.00	0.166
12.93	0.559
17.25	1.318
18.94	1.709
20.69	2.161
22.62	2.705
24.92	3.393
27.63	4.233
30.59	5.176
Tetramethylammonium chloride (*continued*)	
33.88	6.206
37.38	7.248
41.18	8.302
45.46	9.390
50.01	10.45
55.00	11.48
60.54	12.57
65.86	13.45
71.88	14.42
ΔH run number 1	
ΔH run number 2	
Series III	
85.97	16.39
93.55	17.39
101.21	18.40
109.64	19.49
118.31	20.59
127.00	21.68
135.92	22.66
144.90	23.89
153.99	24.96
162.90	26.01
171.46	27.14
ΔH run number 3	
ΔH run number 4	
198.47	28.41
Series IV	
200.15	28.49
209.45	29.33
218.72	30.17
228.08	30.89
237.19	31.83
246.30	32.68
255.35	33.54
264.32	34.37
273.13	35.10
281.78	36.00
290.36	36.72
298.94	37.60
Series V	
302.14	37.86
311.87	38.78
321.43	39.68
330.84	40.58
339.21	41.38
346.70	42.14
Series VI	
66.89	13.61
72.47	14.43
76.71	25.09
79.62	14.56
83.43	16.02
Series VII	
71.75	14.37
74.85	14.87
75.37	15.37
75.56	34.65
75.67	75.35
75.76	83.18
75.89	58.61
76.20	26.64
76.65	16.88
77.75	15.31
81.47	15.73
Series VIII	
ΔH run number 5	
Series IX	
72.96	14.56
75.45	32.44
75.75	78.21
75.84	64.59
76.00	39.15
76.26	22.53
76.58	17.08
76.90	15.70
Series X	
175.44	27.49
177.14	27.65
178.29	27.89
179.43	28.07
180.55	28.32
181.66	28.60
182.77	28.89
183.89	29.68
184.99	30.26
186.09	27.58
187.24	27.54
189.01	27.64
191.35	27.79
193.64	27.97
Series XI	
163.64	26.08
172.96	27.23
179.98	28.26
182.70	28.86
183.20	29.13
183.65	29.33
184.00	29.73
184.25	30.18
184.45	30.85
184.64	31.39
184.84	32.91
185.03	30.84
185.23	28.07
185.43	27.71
185.64	27.60
185.90	27.54
186.31	27.53
187.22	27.55

ards. The temperature scale is considered to correspond 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 precision of the determination of temperature increments is considerably better, and the increments are probably correct to a fraction of a millidegree after making adjustments for the quasi-adiabatic drifts.

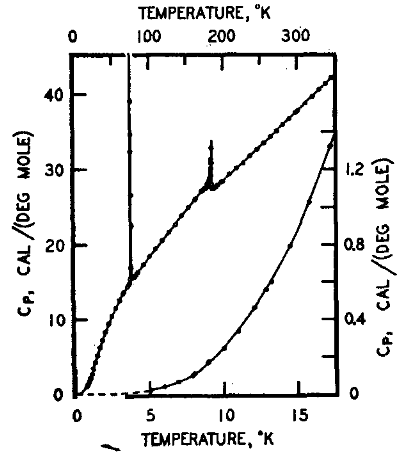

FIG. 1. The heat capacity of tetramethylammonium chloride.

Time durations of the energy inputs were measured with electrical interval timers starting and stopping automatically as the energy was turned on and off by a master switch. The timers, operated by 60-cycle ac from a calibrated tuning fork, dividing circuit, and

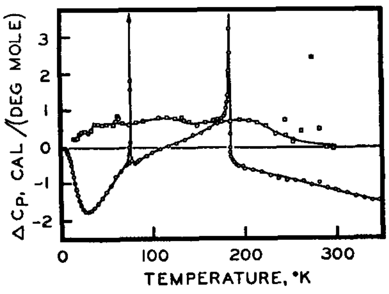

FIG. 2. Differential heat capacities of $(CH_3)_4NCl$ minus $(CH_3)_4NBr$ (○) and $(CH_3)_4NI$ minus $(CH_3)_4NBr$ (□).

TABLE II. Thermodynamic properties of tetramethylammonium bromide and tetramethylammonium chloride. Units: cal, mole, °K.

T, °K	C_p	$S°$	$H°-H_0°$	$-(F°-H_0°)T^{-1}$
		Tetramethylammonium bromide [$(CH_3)_4NBr$, 1 mole=154.064 g]		
5	0.042	0.013	0.047	0.003
10	0.534	0.147	1.154	0.032
15	1.757	0.575	6.630	0.133
20	3.397	1.299	19.42	0.328
25	5.128	2.244	40.74	0.614
30	6.788	3.328	70.61	0.975
35	8.272	4.488	108.3	1.393
40	9.576	5.680	153.0	1.854
45	10.71	6.875	203.8	2.346
50	11.70	8.056	259.9	2.858
60	13.34	10.339	385.4	3.916
70	14.72	12.502	525.9	4.990
80	15.97	14.550	679.4	6.058
90	17.19	16.501	845.2	7.111
100	18.40	18.375	1023.1	8.144
110	19.60	20.185	1213.1	9.157
120	20.80	21.942	1415.1	10.149
130	21.96	23.653	1629.0	11.122
140	23.09	25.322	1854.3	12.077
150	24.18	26.953	2090.7	13.015
160	25.23	28.547	2337.8	13.936
170	26.24	30.107	2595.2	14.842
180	27.22	31.635	2862.5	15.732
190	28.17	33.132	3139.4	16.609
200	29.11	34.601	3425.8	17.472
210	30.06	36.044	3721.7	18.322
220	31.01	37.464	4027.0	19.160
230	31.97	38.864	4341.9	19.986
240	32.95	40.245	4666.5	20.802
250	33.93	41.610	5000.9	21.607
260	34.91	42.960	5345.1	22.402
270	35.88	44.296	5699.0	23.188
280	36.85	45.618	6062.6	23.966
290	37.83	46.928	6436.0	24.735
300	38.83	48.227	6819.2	25.496
350	44.02	54.601	8890.1	29.201
273.15	36.18	44.71	5812	23.43
298.15	38.64	47.99	6747	25.36

T, °K	C_p	$S°$	$H°-H_0°$	$-(F°-H_0°)T^{-1}$
		Tetramethylammonium chloride [$(CH_3)_4NCl$, 1 mole=109.605 g]		
5	0.030	0.010	0.036	0.002
10	0.242	0.072	0.546	0.018
15	0.877	0.275	3.152	0.065
20	1.976	0.667	10.103	0.162
25	3.417	1.259	23.49	0.319
30	4.988	2.020	44.48	0.537
35	6.546	2.907	73.35	0.811
40	7.986	3.876	109.74	1.133
45	9.276	4.893	152.95	1.494
50	10.44	5.931	202.28	1.886
60	12.45	8.018	317.05	2.734
70	14.11	10.066	450.11	3.636
80	15.55	12.422	627.0	4.585
90	16.94	14.333	789.3	5.563
100	18.24	16.186	965.3	6.533
110	19.51	17.984	1154.1	7.492
120	20.82	19.738	1355.7	8.440
130	22.08	21.454	1570.3	9.375
140	23.27	23.134	1797.1	10.298
150	24.46	24.780	2035.7	11.209
160	25.69	26.398	2286.5	12.108
170	26.84	27.991	2549.2	13.000
180	28.21	29.560	2823.7	13.872
190	27.72	31.098	3108.2	14.739
200	28.51	32.539	3389.3	15.593
210	29.36	33.951	3678.6	16.434
220	30.25	35.337	3976.6	17.262
230	31.17	36.702	4283.7	18.077
240	32.10	38.048	4600.0	18.881
250	33.03	39.377	4925.6	19.675
260	33.97	40.691	5260.7	20.458
270	34.91	41.991	5605.1	21.231
280	35.84	43.277	5958.8	22.000
290	36.76	44.551	6321.8	22.751
300	37.68	45.813	6694.1	23.499
350	42.48	51.974	8695.7	27.129
273.15	35.20	42.40	5716	21.47
298.15	37.51	45.58	6624	23.36

TABLE III. Enthalpy and entropy increments over the transition regions in tetramethylammonium chloride. Units: cal, mole, °K.

		Transition I, T_t=75.76°K		
Energy increments	T_{final}	T_{initial}	$H_{80°K}-H_{70°K}$	$S_{80°K}-S_{70°K}$
2	81.55	68.31	176.70	2.351
1	78.53	74.55	176.83	2.352
8	78.63	75.25	176.81	2.353
4	76.09	75.20	177.11	2.356
Average			176.86±0.12	2.354
		Transition II, T_t=184.85°K		
Energy increments	T_{final}	T_{initial}	$H_{190°K}-H_{180°K}$	$S_{190°K}-S_{180°K}$
5	185.54	184.55	284.31	1.538
1	185.53	184.46	284.47	1.539
3	186.65	183.32	284.51	1.539
8	190.20	179.99	284.58	1.539
Average			284.47±0.10	1.539

amplifier, provided a precision of 0.01 sec for the time interval measurement. Standard resistors used in the potential dividers of the measuring circuits and unsaturated Weston standard cells were calibrated by the National Bureau of Standards. The heat capacity of the empty calorimeter-heater-thermometer assembly represented from 30 to 20% of the total observed heat capacity from 5° to 20°K, increased from 20 to 50% from 20° to 100°K and decreased from 50 to 40% over the range 100° to 350°K.

CALORIMETRIC RESULTS

The experimental heat capacity determinations for the two compounds are listed in Table I in chronological order in terms of the thermochemical calorie defined as 4.1840 absolute joules and the ice point taken as 273.15°K. An analytically determined curvature correction was applied to the observed values of $\Delta H/\Delta T$.

The approximate temperature increments usually can be inferred from the adjacent mean temperature in Table I. The reported values of the heat capacity data are believed to have probable errors less than 0.1% at temperatures above 25°K, about 1% at 10°K, and 5% at 5°K.

Molal values of the heat capacities at constant pressure, the entropies, the enthalpy increments, and the free-energy functions are listed at selected rounded temperatures in Table II. These values were obtained from a smooth curve fit by least squares to the experimental data by means of a digital computer or by appropriate integration based on the curve. The probable errors of the thermodynamic functions are considered to be less than 0.1% above 100°K.

Two transitions have been observed in the heat-capacity behavior of tetramethylammonium chloride (Fig. 1). A sharp, apparently first-order transition occurs at 75.75°K, while a lambda-type anomaly is found at 184.85°K. An approximate resolution of the transitional contributions from those of the lattice vibrations yields transitional enthalpy increments of 27.8 and 25.9 cal mole^{-1}, corresponding to entropy increments of 0.37 and 0.14 cal mole^{-1} °K^{-1} for the lower and higher temperature transitions, respectively. These probably represent minimal values.

Heat capacity-type runs and several enthalpy-type runs in the transitional regions are compared in Table III. These comparisons test the over-all accuracy of the calorimetric measurements and indicate excellent agreement.

The heat capacity vs temperature curve of tetramethylammonium bromide very closely follows that of the iodide and does not show any indication of anomaly in the temperature range studied. Deviation of the molal heat capacity of the iodide[2] from that of the bromide is obtained by subtracting from the actual heat capacity data points of the iodide the corresponding heat capacity value of the bromide as read from a smoothed curve, and is shown in Fig. 2. This figure also shows a similarly derived plot for the deviation of molal heat capacity of the chloride against that of the bromide.

DISCUSSION

It is of interest to note that the crystals of all three halides at room temperatures are isostructural.[4] They belong to the same tetragonal lattice of the space group D_{4h}^{7}-$P4/nmm$ and have two molecules for each unit cell. The cell dimensions *a* and *b* are: 7.78 and 5.53 A for the chloride, 7.76 and 5.53 A for the bromide, and 7.96 and 5.75 A for the iodide. Since the ionic radius for the chloride ion (1.81 A) is less than that of the bromide ion (1.95 A), it is apparent that the tetramethylammonium ion occupies a larger volume in the crystal of the chloride than that in the bromide or the iodide. This may result from the motions of the cation in the chloride lattice in the phase stable at room temperatures. However, the reason for the occurrence of two transitions in the chloride crystal is still not apparent. Further studies on dilatometry, precise x-ray patterns and even nuclear magnetic resonance, piezoelectricity and ferroelectricity are desiderata for the interpretation of the transitions occurring in the tetramethylammonium salts.

ACKNOWLEDGMENT

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[4] R. W. G. Wyckoff, Z. Krist. 67, 91 (1928).