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

RICHARD M. GOODMAN and EDGAR F. WESTRUM, Jr.
Department of Chemistry, University of Michigan, Ann Arbor, Mich.

The temperature dependence of the heat capacity of $BaCl_2$ has been determined by adiabatic calorimetry from 5° to 350° K. and found to be of normal sigmate shape without transitions or thermal anomalies. The values of the heat capacity (C_p), entropy ($S°$), enthalpy function ($[H° - H_0°]/T$), and Gibbs energy function, $-[G° - H_0°]/T$), at 298.15° K. are 17.96, 29.56, 13.39, and 16.16 cal./(g.f.m. °K.), respectively.

AMONG crystalline alkaline earth halides isostructural with $BaCl_2$, only $SrBr_2$ (*11*) has been investigated with respect to low temperature thermal properties. However, work has been reported on the isostructural crystalline halides, $PbCl_2$ (*7*) and $PbBr_2$ (*6*), and a related isostructural chalcogenide compound, ThS_2 (*5*). The present investigation provides chemical thermodynamic data in the cryogenic range for $BaCl_2$ and permits useful correlations of thermodynamic properties of isostructural crystalline salts and their vapors.

EXPERIMENTAL

Cryogenic Apparatus. Measurements were made in the Mark II adiabatic cryostat previously described (*13*). The gold-plated, copper calorimeter (laboratory designation W-28, about 92-cc. capacity) was employed for measurements on the sample. 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 and appropriate small adjustments were made for the slight differences in the amounts of helium, indium-tin solder, and Apiezon-T grease on the loaded and the empty calorimeter. The heat capacity of the sample represented about 93% of the total at 15° K. and gradually decreased to about 80% above 200° K. The calorimetric sample of $BaCl_2$ weighed 230.445 grams in vacuo; buoyancy corrections were made on the basis of a density of 3.856 grams per cc. for $BaCl_2$. Helium gas (about 114 torr at 292° K.) was used to enhance thermal contact between calorimeter and sample. All determinations of mass, voltage, current, time, and temperature were referred to calibrations performed by the National Bureau of Standards.

Preparation and Purity of Sample. The barium chloride was prepared by dehyrating reagent grade $BaCl_2 \cdot 2H_2O$ in an HCl atmosphere, using a platinum container. Final treatment included fusion (m.p. = 962° C.) under HCl and fracturing the sample into fragments with linear dimensions of 1 to 10 mm. A gravimetric analysis of the sample for barium as $BaCl_2$ gave 99.9 ± 0.1% of the theoretical amount of barium, while a less accurate chloride determination gave 99.7 ± 0.2% purity. X-ray diffraction analysis of the sample showed only a small amount—perhaps a few per cent—of monoclinic $BaCl_2$, present with the stable, low-temperature, orthorhombic form. X-ray fluorescence spectra showed no detectable metal impurities. Care was taken to perform all weighings and loading in a water-free, nitrogen atmosphere.

RESULTS AND DICUSSION

Heat Capacities and Thermal Properties. The experimental heat capacity values for barium chloride 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 used and are considered to have a probable error decreasing from about 5% at 5° K. to 1.0% at 10° K. and to less than 0.1% above 20° K. The heat capacities are based upon a defined thermochemical calorie equal to 4.1840 joules, an ice point of 273.15° K., and gram formula mass (g.f.m.) of 208.246 for barium chloride. Since no transitions were detected in the sample, it is reasonable to assume that the presence of the monoclinic modification would introduce, at most, several tenths of 1% increment in the heat capacity at low temperatures and an even smaller contribution to the thermodynamic functions at higher

Table I. Heat Capacities of Barium Chloride

T, ° K.	C_p, Cal./ G.F.M., ° K.	T, ° K.	C_p, Cal./ G.F.M., ° K.	T, ° K.	C_p, Cal./ G.F.M., ° K.
Series I		126.24	15.08	9.44	0.213
		135.97	15.48	10.59	0.306
249.74	17.59	145.80	15.82	12.15	0.454
258.29	17.64	155.76	16.11	13.94	0.676
268.31	17.74	165.86	16.36	15.71	0.924
277.74	17.79	176.12	16.57	17.45	1.189
287.12	17.88	186.23	16.77	19.09	1.458
297.11	17.95	196.21	16.92	20.87	1.768
307.69	18.04	206.08	17.06	23.03	2.159
318.23	18.09	215.85	17.20	25.30	2.590
328.71	18.16	225.64	17.31	27.59	3.040
338.12	18.21	235.46	17.43	30.13	3.552
346.44	18.24	245.20	17.52	33.03	4.151
				36.56	4.885
Series II		Series III		40.44	5.678
				44.36	6.458
75.18	11.309	5.92	0.036	48.54	7.263
81.82	12.062	5.36	0.025	53.29	8.122
88.85	12.754	6.11	0.040	58.61	9.025
96.93	13.393	6.87	0.060	64.90	9.998
106.40	14.034	7.68	0.092	72.12	10.942
116.41	14.603	8.50	0.140	79.66	11.831

Table II. Thermodynamic Functions of Barium Chloride

T, °K.	C_p, Cal./ G.F.M., °K.	S°, Cal./ G.F.M., °K.	$H^\circ - H^\circ_0$, Cal./ G.F.M., °K.	$\frac{-(G^\circ - H^\circ_0)}{T, °K.}$
5	(0.020)	(0.007)	(0.02)	(0.002)
10	0.250	0.070	0.54	0.015
15	0.821	0.270	3.10	0.063
20	1.613	0.610	9.12	0.154
25	2.532	1.067	19.45	0.290
30	3.527	1.616	34.57	0.464
35	4.560	2.237	54.78	0.672
40	5.589	2.913	80.16	0.909
45	6.585	3.630	110.61	1.172
50	7.533	4.373	145.94	1.454
60	9.243	5.902	230.0	2.068
70	10.683	7.438	329.9	2.725
80	11.868	8.945	442.8	3.409
90	12.831	10.400	566.5	4.105
100	13.615	11.794	698.9	4.805
110	14.258	13.123	838.3	5.501
120	14.791	14.387	983.7	6.190
130	15.24	15.589	1133.9	6.867
140	15.62	16.733	1288.2	7.531
150	15.94	17.822	1446.1	8.181
160	16.22	18.860	1606.9	8.816
170	16.45	19.850	1770.3	9.436
180	16.65	20.796	1935.9	10.041
190	16.83	21.701	2103.3	10.631
200	16.98	22.569	2272.4	11.207
210	17.12	23.400	2442.9	11.768
220	17.25	24.200	2614.7	12.315
230	17.37	24.970	2787.8	12.848
240	17.48	25.711	2962.0	13.369
250	17.58	26.426	3137.3	13.877
260	17.67	27.117	3313.5	14.373
270	17.75	27.786	3490.6	14.857
280	17.83	28.43	3668.5	15.33
290	17.90	29.06	3847.1	15.79
300	17.97	29.67	4026.4	16.25
350	18.23	32.46	4932.9	18.37
273.15	17.77	27.99	3547	15.01
298.15	17.96	29.56	3993	16.16

temperatures. The adjustment for curvature was everywhere less than 0.05%.

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 in this table were taken from a smooth curve obtained by a least squares-fitted polynomial function through the experimental points. The standard deviation of the polynomial fit of the heat capacity data was 0.02%. The thermodynamic functions are considered to have a precision corresponding to a probable error of less than 0.1% above 100° K. Values of the entropy and enthalpy at 5° K. were obtained by means of a linear extrapolation of the lowest temperatuure data on a C_p/T *vs.* T^2 plot and thus essentially correspond to a Debye T^3 extrapolation. However, an additional digit beyond those significant is often 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 or isotopic mixing contributions and are hence practical values for use in chemical thermodynamic calculations.

Correlation with Other Data. These data accord within 1% with the pioneer data of Schottky (*9*) between 273° and 291° K. Although there is no overlap with the higher temperature enthalpy determinations of Popov and Gal'chenko (*8*) taken from 170° to 700° C., our data accord fairly well with their derived linear relation—i.e.,

$$C_p = 18.17 + 6.889 \times 10^{-3} t \ (\pm 0.7\%, t \text{ in } ° \text{C.})$$

Interesting correlations of the temperature dependence of the apparent Debye characteristic temperatures have been made (*4*) not only with data on the isostructural (or very nearly so) substances previously enumerated ($PbCl_2$, $PbBr_2$, and ThS_2), but also with data on closely related CaF_2-type crystals (*1, 2*) isostructural with monoclinic $BaCl_2$ (*14*): CaF_2 (*3, 12*), $SrCl_2$ (*10*), SrF_2 (*10*). These comparisons reveal that the trends of the family of curves of ($d\ln \theta/d \ln T$) *vs.* T are closely related. The $\theta(T)$'s here are Debye characteristic temperatures per gram atom of substance. Moreover, a heat capacity calculated with Debye functions for the acoustical modes and Einstein functions for the optical modes would provide a simple approximation to the experimental values at low temperatures, since the mass ratio of cation to anion is so great.

ACKNOWLEDGMENT

The authors appreciate the partial financial support of the U. S. Atomic Energy Commission and the assistance of Wen-Kuei Wong and Yoichi Takahashi with the measurements. RMG thanks the National Science Foundation for a research participation award. We thank D. L. Hildenbrand of the Philco Corp. for the preparation and characterization of the calorimetric sample.

LITERATURE CITED

(1) Brackett, E.B., Brackett, T.E., Sass, R.L., *J. Phys. Chem.* **67**, 2132 (1963).

(2) Döll, W., Klemm, W., *Z. Anorg Allgem. Chem.* **241**, 239 (1939).

3) Eucken, A., Werth, H., *Ber. Deut. Physik. Ges.* **15**, 520 (1925).

(4) Goodman, R.M., unpublished honor's thesis, University of Michigan, Ann Arbor, Mich., 1965.

(5) King E.G., Weller, W.W., Bur. Mines Rept. Invest. **5485** (1959).

(6) Latimer, W.M., Hoenshel, H.D., *J. Am. Chem. Soc.* **48**, 19 (1926).

(7) Nernst, W., *Ann. Physik.* Ser. **4**, **36**, 395 (1911).

(8) Popov, M.M., Gal'chenko, G.L., *Zh. Obshch. Khim.* **21**, 2220 (1951).

(9) Schottky, W., *Physik. Z.* **10**, 634 (1909).

(10) Smith, D.F., Gardner, T.E., Letson, B.B., Taylor, A.R., Jr., Bur. Mines Rept. Invest. **6316** (1963).

(11) Taylor, A.R., Jr., Smith, D.F., *Ibid.*, **5967** (1962).

(12) Todd, S.S., *J. Am. Chem. Soc.* **71**, 4115 (1949).

(13) Westrum, E.F., Jr., *J. Chem. Educ.* **39**, 443 (1962).

(14) Wyckoff, R.W.G., "Crystal Structures," Vol. 1, Interscience, New York, 1960.

Received for review May 26, 1965. Accepted March 1, 1966.