Thermal Properties of Barium Chloride from 300° to 1350° K.

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The heat contents of $BaCl_2$ have been determined from 300° to 1350° K. using an ice calorimeter. The results of this investigation were correlated with low-temperature heat-capacity data on a sample from the same batch of material. A transition at 1198° K. with ΔH_T = 4.05 kcal. per mole and a melting point of 1235° K. with ΔH_f = 3.82 kcal. per mole were found for the sample.

ONE PROJECT of the Bureau of Mines' basic research program has been the determination and correlation of accurate thermodynamic data for various chemical compounds. As a contribution to this program, heat-content measurements were performed on a high-purity sample of barium chloride. Although other investigators (*6, 9*) have measured heat contents of barium chloride over short temperature intervals, this investigation covers a relatively wide range of temperatures, and no comparable study was found in the literature.

EXPERIMENTAL PROCEDURES

Apparatus. The heat-content measurements were made in a Bunsen-type ice calorimeter similar to ones used at the Oak Ridge National Laboratories (*3*) and National Bureau of Standards (*2*). The calorimeter was calibrated using both Al_2O_3 and electrical calibrations (*10*). The resistance-heated furnace contained an Inconel block, the temperature of which was maintained within ±1° C. by a proportional controller, using a Pt-10% Rh control thermocouple. The temperature of the sample was measured by another Pt-10% Rh thermocouple placed in a well at approximately the center of the Inconel block. This thermocouple was close to the sample, which was suspended in the center well of the Inconel block. The measuring thermocouple was checked against an NBS-calibrated platinum resistance thermometer from 50° to 500° C., exhibiting a maximum deviation of 0.2° C. over that range. Above 500° C., the measuring thermocouple was checked against a calibrated thermocouple.

Before measurements were begun on a sample, the enthalpy of the empty Pt-10% Rh capsule was determined over the entire range of temperature measurements. Evaluation of a plot of $(H_T - H_{273})/T$ *vs.* T for the empty capsule showed that individual measurements did not vary more than 0.2% from a curve drawn through the points. The heat content of the barium chloride was determined by subtracting the measured heat contents of the empty capsule from the measured heat contents of the capsule loaded with $BaCl_2$.

Sample. The barium chloride sample was supplied by D. L. Hildenbrand (*5*) and is a portion of the sample used by Goodman and Westrum (*4*) for low-temperature heat-capacity measurements. The sample was prepared by fusing reagent-grade $BaCl_2 \cdot 2H_2O$ in an HCl atmosphere. Gravimetric analysis for barium gave 99.9 ± 0.1% of the theoretical barium content, and a similar chloride analysis gave 99.7 ±0.2% of the theoretical chloride content. X-ray diffraction analysis showed that the sample was orthorhombic (α) $BaCl_2$. No metallic impurities were detected from x-ray fluorescence spectra. The $BaCl_2$ sample was stored and handled in an argon-filled dry box. The $BaCl_2$ sample (22.3716 grams corrected to vacuum, using a density of 3.856 grams per ml. for $BaCl_2$) was sealed in the capsule under 1 atm. of helium. The heat content of the sample was approximately 67% of the total of the loaded capsule at 100° C., increasing to about 75% at 1000° C.

RESULTS AND DISCUSSION

Experimental Measurements and Thermal Properties. The experimental enthalpy measurements are presented in Table I in order of ascending temperature. Check determinations made in the temperature range of the α form, after measurements in the temperature ranges of the β and liquid forms indicated that the high-temperature forms of $BaCl_2$ reverted to the more stable α form upon quenching in the ice calorimeter.

These data were combined with values for $H_T - H_0^\circ$ (220° to 350° K.) obtained from Goodman and Westrum's (*4*) low-temperature heat-capacity measurements on portions of the same sample of $BaCl_2$. An equation of the form recommended by Maier and Kelley (*8*) was fitted to the combined data by the method of least squares, giving

$$H_T - H_0^\circ = -520 + 15.302T + 3.048 \times 10^{-3}T^2 - 9.11 \times 10^4 T^{-1} \qquad (1)$$

(range, 220° to 1198° K.; ±20 cal. per mole)

Table I. Enthalpy of Barium Chloride Above 273.15° K.

(Molecular Weight, 208.246)

T, ° K.	$H_T - H_{273.15}$, Cal./Mole	OBS − CAL,[a] Cal./Mole	T, ° K.	$H_T - H_{273.15}$, Cal./Mole	OBS − CAL,[a] Cal./Mole
340.3	1,207	−17	992.3	13,973	−44
371.2	1,769	−17	1018.3	14,542	−34
371.6	1,779	−15	1018.8	14,550	−37
436.1	2,966	−9	1077.7	15,842	−27
436.1	2,971	−4	1077.9	15,857	−16
478.6	3,766	4	1120.1	16,792	−12
478.6	3,769	7	1153.6	17,572	22
530.2	4,747	18	1153.6	17,576	26
530.6	4,748	12	1190.0	18,393	24
608.5	6,244	24	1196.8	18,578	55
608.6	6,249	27	1196.9	18,692	*[b]
672.8	7,487	19	1197.1	18,767	*
673.2	7,500	24	1198.0	21,201	*
673.4	7,501	21	1201.3	22,749	17
689.7	7,817	17	1206.0	22,880	8
707.1	8,160	16	1215.9	23,143	−22
707.2	8,159	14	1216.8	23,169	−23
739.7	8,806	15	1220.9	23,297	−17
740.0	8,809	12	1222.5	23,371	10
750.5	9,015	8	1223.7	23,401	4
750.6	9,013	4	1228.7	23,546	1
808.8	10,180	−4	1230.9	23,631	21
811.9	10,241	−7	1233.1	23,801	*
834.9	10,714	−4	1238.2	27,648	12
834.9	10,719	1	1244.6	27,796	−6
890.2	11,837	−24	1255.4	28,084	1
897.2	11,985	−21	1284.3	28,821	−13
947.8	13,050	−20	1314.8	29,629	3
949.2	13,078	−21	1347.4	30,477	4

[a] Measured enthalpies (OBS) minus calculated enthalpies (CAL).
[b] *Points showing definite pretransition.

The equations derived in the same way for the β form and the liquid, respectively, are

$$H_T - H^\circ_0 = -9{,}345 + 29.655T \qquad (2)$$

(range, 1198° to 1235° K.; ±20 cal. per mole)

$$H_T - H^\circ_0 = -986 + 25.981T \qquad (3)$$

(range, 1235° to 1350° K.; ±10 cal. per mole)

The derived equations apply within the specified standard deviation over the temperature range given with each equation. Differences in the observed enthalpy values and those calculated from the equation are listed in Table I. Accuracy of the measured values is estimated to be ±0.3%; the average reproducibility is about ±0.05%. Values for the heats of transition and fusion are considered accurate to within ±1.0%.

Table II presents values for smoothed thermodynamic functions of barium chloride, using Goodman and Westrum's data below 300° K. Graphical methods were used to obtain these smoothed functions because Equation 1 does not yield a satisfactory heat capacity curve on differentiation. The equation obtained by differentiating Equation 1 does not join smoothly with the low-temperature data and should not be used below 500° K. This equation has a curvature in the wrong direction and approaches a minimum in the vicinity of 300° K. Heat capacities obtained by the equation differ as much as 1% from the experimental data. Above 300° K., smoothed values for $H_T - H^\circ_0$ were obtained from a large-scale plot of $(H_T - H_{273.15})/(T - 273.15)$ *vs.* T; S° values were obtained by Kelley's method (7) and values for C_p were calculated using the equation

$$C_p = (H_T - H_{273})/(T-273) + (T-273)(d/dT)[(H_T - H_{273})/(T-273)] \qquad (4)$$

with the plot.

Table II. Thermodynamic Functions for Barium Chloride

(Molecular Weight, 208.246)

T, ° K.	$H^\circ - H^\circ_0$, Cal./Mole	C_p, Cal./ Mole Deg.	S°, Cal./ Mole Deg.	$(F^\circ - H^\circ_0)/T$, Cal./ Mole Deg.
0	0	0	0	0
50	145.9	7.533	4.373	1.454
100	698.9	13.615	11.794	4.805
150	1,446.1	15.94	17.822	8.181
200	2,272.4	16.98	22.569	11.207
250	3,137.3	17.58	26.426	13.877
273.15	3,547	17.77	27.99	15.01
298.15	3,993	17.96	29.56	16.16
300	4,026	17.97	29.67	16.25
400	5,849	18.49	34.91	20.29
500	7,720	18.88	39.10	23.66
600	9,626	19.24	42.57	26.53
700	11,572	19.64	45.56	29.03
800	13,557	20.11	48.20	31.25
900	15,595	20.69	50.58	33.25
1000	17,699	21.47	52.79	35.09
1100	19,886	22.46	54.88	36.80
1198 (α)	22,132	23.66	56.82	38.35
1198 (β)	26,181	29.66	60.20	38.35
1200	26,249	29.66	60.25	38.38
1210	26,537	29.66	60.50	38.57
1220	26,834	29.66	60.74	38.74
1230	27,130	29.66	60.98	38.92
1235 (β)	27,279	29.66	61.10	39.01
1235 (l)	31,100	25.98	64.19	39.01
1250	31,490	25.98	64.50	39.31
1300	32,789	25.98	65.52	40.30
1350	34,088	25.98	66.50	41.25
1400	35,387	25.98	67.45	42.17

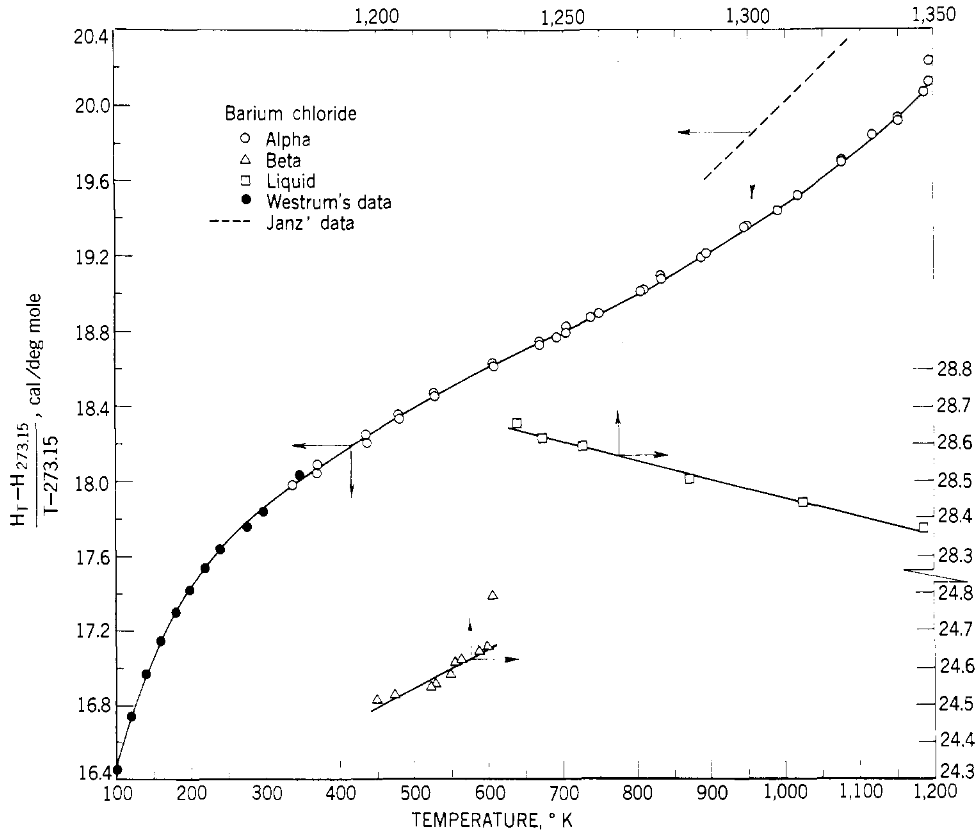

Figure 1. Enthalpy values for $BaCl_2$

Correlation with Other Data. Figure 1 shows relatively good agreement between the present work and the low-temperature heat-capacity measurements of Goodman and Westrum. The ordinate selected for the graph, $(H_T - H_{273.15})/(T - 273.15)$, makes the plot much more sensitive to errors in heat-content measurements than the usual plot of ΔH against T.

Janz *et al.* (*6*) have measured the heat content of $BaCl_2$ from 892° to 1339° K. Although the experimental data are not listed in the report, they give linear equations for α, β, and liquid $BaCl_2$ which are 0.45, 0.52, and 0.73 kcal. per mole, respectively, greater than the heat contents determined in this study. Janz' equation for α $BaCl_2$ was used to determine the dashed line shown in Figure 1. Their results for the β and liquid were too high to allow plotting in Figure 1.

Analysis of the data presented here indicates a solid state transition at 1198° K. with a heat effect of 4.05 kcal. per mole. Dworkin and Bredig (*1*) give 1193° K. and 4.10 kcal. per mole for this transition, while Janz *et al.* give 1198° K. and 4.15 kcal. per mole.

The value for the heat of fusion, 3.90 kcal. per mole at 1233° K., as determined by Dworkin and Bredig, is only 2% higher than the value, 3.82 kcal. per mole at 1235° K., determined in this work. The value obtained by Janz *et al.*, 4.13 kcal. per mole at 1235° K., is 8% higher than obtained in this work and would appear to be too high. Popov and Gal'chenko (*9*) report a C_p equation for $BaCl_2$ from 443° to 973° K. Their equation gives values which range from 4% at 450° K. to 8% at 950° K. higher than the results of this investigation.

From the height of the peaks of a DTA curve made on a sample of $BaCl_2$, the ratio ΔH transition/ΔH fusion was calculated to be 1.06. This compares with similar ratios of 1.06 for this investigation, 1.05 for Dworkin's work, and 1.00 for Janz'. The data for the β crystal form (1200° to 1235° K.) appear to show a very small transition (0.05 kcal. per mole) at 1221° K.; however, the measurements were not considered precise enough to establish definitely the existence of this transition.

NOMENCLATURE

α $BaCl_2$ = low-temperature orthorhombic form of barium chloride
β $BaCl_2$ = high-temperature face-centered cubic form of barium chloride
C_p = heat capacity, cal./mole ° K.
1 cal. = 4.1840 absolute joules
H_T = heat content at temperature T
H_0° = heat content at 0° K.
ΔH_T = heat of transition
ΔH_f = heat of fusion
S° = absolute entropy, eu.
T, ° K. = absolute temperature, degrees Kelvin

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Isobaric Vapor-Liquid Equilibrium Data for the Systems 1-Propanol–Methylcyclohexane and Methylcyclohexane–1-Butanol

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Vapor-liquid equilibrium data for the binary systems, 1-propanol–methylcyclohexane and methylcyclohexane–1-butanol, were obtained at 760 mm. of mercury by using a vapor recirculatory equilibrium still. The data are correlated satisfactorily by the Wilson equations.

DISTILLATION operation has been extensively used for the separation of liquid mixtures. Accurate and complete vapor-liquid equilibrium data for the mixtures under consideration are necessary for the rational design of distillation towers. These data are obtainable under two fixed conditions, isothermal and isobaric. Most distillation processes are carried out at constant pressure rather than constant temperature, so that temperature-composition curves are more practical in engineering calculations such as the number of plates, although from theoretical considerations pressure-composition curves are preferable. As part of a continuing equilibrium study of the important alcohol-hydrocarbon systems, hitherto unreported vapor-liquid equilibrium data on 1-propanol–methylcyclohexane and methylcyclohexane–1-butanol systems were determined at 760 mm. of mercury.

EXPERIMENTAL

Purity of Liquids. Analytical reagent grade liquids were used. 1-Butanol (British Drug Houses, India) and 1-propanol (Veb Labor Chemie Apolda, Germany) were further purified by refluxing over fresh quicklime for 6 hours and distilling in a 3 × 100 cm. glass column packed with McMahon packings. Methylcyclohexane (E. Merck, Germany) was distilled in the same column. The predistillate and residual liquids, each approximately one sixth of the original charge, were discarded and the heart cuts were used. Precautions were taken to minimize absorption of atmospheric moisture by the liquids. The physical properties

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