[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Metatitanates of Barium and Strontium

BY S. S. TODD AND R. E. LORENSON

Heat capacity measurements of crystalline barium and strontium metatitanates, and of a crystalline solution containing 54.3 mole % of the former and 45.7 mole % of the latter, were conducted over the temperature range 51 to 300°K. Two heat capacity peaks were found for barium metatitanate, at 201.6 ± 0.2 and 284.9 ± 0.2°K. The entropies at 298.16°K. were obtained as 25.8 ± 0.2, 26.0 ± 0.2 and 27.4 ± 0.2 cal./deg. mole, respectively, for barium metatitanate, strontium metatitanate and the crystalline solution.

Introduction

In a previous paper from this Laboratory, Shomate[1] reported low temperature heat capacity data and entropies at 298.16°K. of the metatitanates of iron, calcium and magnesium. This paper presents similar results for crystalline barium and strontium metatitanates and for a crystalline solution containing 54.3 mole % of the former and 45.7 mole % of the latter. The anomalies found in the heat capacities were examined in detail to determine their magnitudes. No previous heat capacity measurements exist for these substances in the temperature range investigated, 51–300°K.

Recently, much interest has attached to barium metatitanate as a new ferroelectric material. Its unusual dielectric properties were correlated with some other physical properties by von Hippel.[2] Anomalies in properties occur at three reported Curie points, *i.e.*, about 203, 283 and 393°K. The last point was investigated by Sawada and Shirane,[3] whose heat capacity measurements show a maximum at 385 ± 2°K. Similar measurements of a solid solution of barium and strontium metatitanates[4] (9:1 by weight) show the 393°K. Curie point lowered to 357°K.

Materials.—Barium metatitanate was prepared from reagent grade barium hydroxide and titania (purity 99.8%, after ignition) by prolonged heating at 1350°. The material was finely ground, mixed, and screened at intervals during the process, and adjustment to stoichiometrical composition was made upon the basis of chemical analyses for both barium and titanium. The final product contained no free barium oxide and the chemical analysis indicated 99.7% purity. The X-ray diffraction pattern agreed with that for the cubic variety in the A.S.T.M. catalog.

Strontium metatitanate was prepared similarly from reagent grade strontium carbonate and titania by prolonged heating at 1350°. The chemical analysis of the final product indicated 99.5% purity, and its X-ray diffraction pattern also agreed with that of the cubic variety in the A.S.T.M. catalog.

The crystalline solution of barium and strontium metatitanates was prepared by first combining barium hydroxide and titania, and then adding strontium carbonate to complete the reaction. (Durst and co-workers[5] have shown that these metatitanates are miscible in the crystalline state in all proportions.) Prolonged heating at 1400° was required to assure a uniform product. The final product contained 54.3 mole % barium metatitanate and 45.7 mole % strontium metatitanate, the average molecular weight being 210.53. This composition was selected deliberately so as to lower the uppermost Curie point in barium metatitanate to a temperature[6] in the range of our measurements. The X-ray diffraction pattern was entirely similar to those of the individual titanates.

Heat Capacities.—The heat capacities were determined with a precision usually better than 0.1% by previously described[7] methods and apparatus. The results are expressed in defined calories (1 cal. = 4.1833 int. joules), and the molecular weights correspond to the 1949 International Atomic Weights.[8] The masses of the samples employed in the measurements were 398.75, 292.28 and 333.39 g., respectively, of barium metatitanate, strontium metatitanate and the crystalline solution.

The measured results are listed in Table I, and those for barium metatitanate and the crystalline solution are shown in Fig. 1.

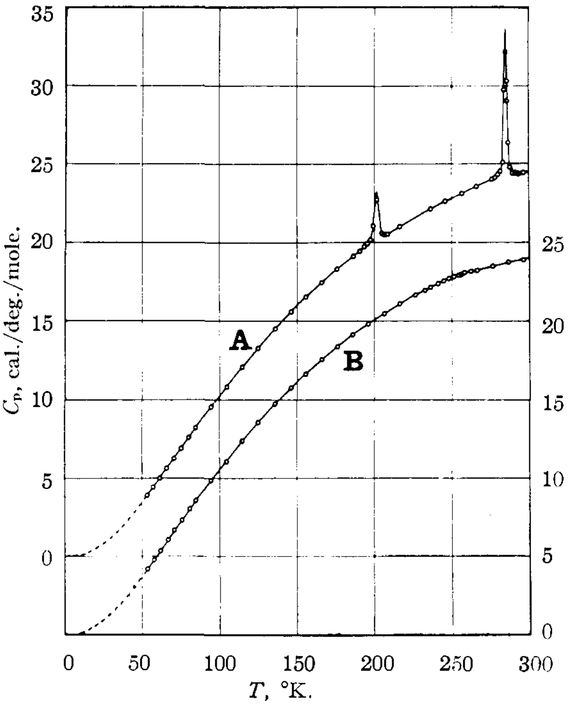

Fig. 1.—Heat capacities: curve A, $BaTiO_3$ (scale at left); Curve B, $0.543\ BaTiO_3 \cdot 0.457\ SrTiO_3$ (scale at right).

The values for strontium metatitanate are normal in all respects and require no discussion or illustration. This is in line with Hulm's[9] work, which

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[1] C. H. Shomate, THIS JOURNAL, **68**, 964 (1946).

[2] A. von Hippel, *Revs. Modern Phys.*, **22**, 221 (1950).

[3] S. Sawada and G. Shirane, *J. Phys. Soc. Japan*, **4**, 52 (1949).

[4] S. Sawada and S. Nomura, *ibid.*, **5**, 231 (1950).

[5] G. Durst, M. Grotenhuis and A. G. Barkow, *J. Am. Ceram. Soc.*, **33**, 133 (1950).

[6] E. N. Bunting, G. R. Shelton and A. S. Creamer, *J. Research Natl. Bur. Standards*, **38**, 337 (1947).

[7] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

[8] E. Wichers, THIS JOURNAL, **72**, 1431 (1950).

[9] J. K. Hulm, *Proc. Phys. Soc.*, **63**, 1184 (1950).

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
		$BaTiO_3$ (mol. wt. = 233.26)			
53.05	3.938	186.89	19.19 (a)	279.99	24.37 (c)
56.86	4.420	190.61	19.48 (a)	281.67	24.55 (b)
61.09	5.009	193.28	19.73 (a)	283.08	25.10 (c)
65.59	5.643	195.32	19.93 (a)	284.02	29.75 (b)
70.23	6.278	195.83	19.94	285.02	32.18 (c)
74.98	6.924	197.31	20.18 (a)	285.67	29.01 (b)
80.02	7.612	199.33	21.07 (a)	285.94	30.33
84.34	8.201	201.70	22.72 (a)	286.92	26.37 (c)
94.66	9.576	204.84	20.57 (a)	287.50	24.80 (b)
104.44	10.84	206.51	20.51	289.29	24.47 (c)
114.54	12.08	208.71	20.53 (a)	290.04	24.42 (b)
124.72	13.29	216.16	21.00	292.77	24.44 (c)
135.99	14.55	236.44	22.15	293.17	24.39 (b)
146.19	15.62	245.77	22.62	296.54	24.49
155.86	16.55	256.26	23.12	296.84	24.46 (b)
165.96	17.47	266.08	23.58	301.23	24.53
175.97	18.31	276.07	24.05	(298.16)	(24.49)
186.23	19.15	278.08	24.12 (b)		
		$SrTiO_3$ (mol. wt. = 183.53)			
54.84	4.843	114.75	12.43	216.32	20.16
58.79	5.409	124.78	13.41	226.26	20.68
63.10	6.058	136.25	14.52	236.39	21.16
67.58	6.700	146.27	15.41	247.32	21.61
71.96	7.294	156.01	16.19	256.49	21.99
76.44	7.887	166.02	16.98	266.22	22.37
80.04	8.368	176.15	17.70	276.19	22.75
84.13	8.897	186.02	18.38	286.38	23.14
94.62	10.19	195.95	19.01	296.47	23.41
104.37	11.31	206.34	19.59	(298.16)	(23.51)
		0.543 $BaTiO_3$:0.457 $SrTiO_3$ (mol. wt. = 210.53)			
53.13	4.190	145.95	15.77	244.74	22.56 (d)
57.28	4.748	155.66	16.66	245.79	22.62
61.63	5.383	165.95	17.58	248.09	22.70 (d)
66.22	6.055	175.97	18.38	251.18	22.80 (d)
70.83	6.705	185.90	19.14	254.41	22.90 (d)
75.55	7.333	195.90	19.84	256.06	22.95
80.52	8.027	206.17	20.46	258.01	23.03 (d)
84.57	8.573	216.23	21.07	262.09	23.14 (d)
94.60	9.891	226.12	21.65	266.21	23.20
104.39	11.10	232.39	21.93 (d)	276.16	23.49
114.52	12.36	236.11	22.18	286.35	23.74
124.88	13.54	237.00	22.18 (d)	296.33	23.90
136.05	14.74	241.03	22.38 (d)	(298.16)	(23.98)

indicates no dielectric constant peaks between 1.3 and 298°K.

The heat capacity of barium metatitanate is lower than that of strontium metatitanate below 132°K. Sharp heat capacity peaks were found at two temperatures near which anomalies occur in other physical properties.[2] The maximum in the lower temperature peak is estimated as 23.3 cal./deg. mole at 201.6 ± 0.2°K., and in the upper as 33.7 cal./deg. mole at 284.9 ± 0.2°K. Three series of measurements (marked (a), (b) and (c) in Table I), with temperature rises much smaller than usual, were made in the transition regions to determine the shape of the peaks. The heat-capacity values in these regions are somewhat less accurate than usual, because the calorimeter required a longer than normal time to reach a steady state after heat input and because of possible lack of complete thermal equilibrium in the substance. This difficulty was not at all serious for evaluating the total heat absorption in the lower temperature peak, which is 211.6 cal./mole between 196.0 and 206.0°K. For the upper temperature peak it was necessary to measure the total heat absorption by separate runs covering the temperature range from 278.0 to 292.0°K. Two measurements gave 366.8 and 366.9 cal./mole. The heat absorptions in the two peaks above so-called "normal" heat capacity curves are about 12 and 26 cal./mole.

The heat capacity curve for the crystalline solution shows no apparent effects corresponding to the two transitions found in pure barium metatitanate. For this composition, the dielectric constant measurements of Bunting and co-workers[6] indicate a possible transition at 248°K. This follows from the progressive shifting of the dielectric constant peak value at 393°K., observed for pure barium metatitanate, to lower temperatures directly as the mole fraction of strontium metatitanate is increased. However, the series of determinations labeled (d) in Table I give no evidence of a heat capacity peak. The only possibly abnormal behavior noted is that the temperature coefficient of the heat capacity of the crystalline solution above 248°K. is lower than was expected. The heat capacity of the crystalline solution deviates from additivity of its components, when anomalies in barium metatitanate are not considered, by −0.07 cal./deg. at 50°K., −0.06 cal./deg. at 298°K., and by more positive amounts at intervening temperatures, reaching a maximum of 0.48 cal./deg. at about 225°K.

Entropies.—The entropy calculations are summarized in Table II. Entropy increments for ranges of regular behavior above 51.00°K. were obtained from Simpson-rule integrations of plots of C_p against $\log T$. For barium metatitanate, the increments for the peak regions, 196.0 to 206.0°K. and 278.0 to 292.0°K., were calculated from the total heats and average temperatures derived from the continuous series of heat capacity runs. The values for these two intervals are 1.05 cal./deg. mole (211.6/201.0) and 1.29 cal./deg. mole (366.9/285.0), respectively. The entropies in the peaks in excess of "normal" curves are, approximately, 0.06 and 0.09 cal./deg. mole.

Combinations of Debye and Einstein functions, fitted empirically to the measured heat capacities, were used to extrapolate to 0°K. in obtaining $S_{51.00}$. These function sums are given below. They fit the measured data, except in the temperature ranges where anomalies occur and above 250°K. for the crystalline solution, within the maximum deviations indicated in parentheses.

$BaTiO_3$: $D(198/T) + 2E(351/T) + 2E(669/T)$, (1.0%)
$SrTiO_3$: $D(182/T) + 2E(319/T) + 2E(776/T)$, (1.0%)
0.543 $BaTiO_3$:0.457 $SrTiO_3$:
$D(192/T) + 2E(399/T) + 2E(676/T)$, (0.7%)

The result for the crystalline solution contains an entropy of mixing of 1.37 cal./deg. mole, calculated upon the assumption of completely random

TABLE II

ENTROPIES (CAL./DEG. MOLE)

Substance	$S_{51.00}$, (extrap.)	$S_{298.16} - S_{51.00}$, (meas.)	$S_{298.16}$
$BaTiO_3$	1.74	24.08	25.8 ± 0.2
$SrTiO_3$	2.10	23.89	26.0 ± 0.2
0.543 $BaTiO_3$:0.457 $SrTiO_3$	3.22[a]	24.19	27.4 ± 0.2[a]

[a] Includes entropy of mixing, 1.37 units.

occurrence of barium and strontium ions in the crystal lattice.

It is of interest to note that the entropy of barium metatitanate at 298.16°K. is slightly lower than that of the strontium compound, despite its greater molecular weight.

The entropies of formation from the constituent oxides, calculated from the data in Table II and Kelley's[10] values for the oxides, are −3.0, 1.0 and 0.3 cal./deg. mole, respectively. These values are of the magnitude found by Shomate[1] for titanates of iron, calcium and magnesium.

(10) K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat of Solution of Neptunium Metal and the Heats of Formation of Some Neptunium Chlorides. A Microcalorimeter for Heat of Solution Measurements[1]

BY EDGAR F. WESTRUM, JR.,[2a] AND LEROY EYRING[2b]

The heat of reaction of milligram amounts of neptunium metal with 1.5 *M* HCl containing 0.005 *M* Na_2SiF_6 was found to be −165.7 ± 0.2 kcal. per mole at 25°. This value combined with other data yields −132.9 ± 1 and −127.4 ± 1 kcal. per mole for the apparent molal heats of formation of Np(IV) and Np(III) in 1.0 molal HCl. By comparing the heats of solution of other isomorphous actinide chlorides, those of $NpCl_3$ and $NpCl_4$ are estimated and heats of formation of 216 ± 1 kcal. per mole for $NpCl_3$ and 238 ± 1 kcal. per mole for $NpCl_4$ are obtained. A convenient precise calorimeter suitable for the determination of heats of relatively rapid reactions for milligram quantities of materials is described and its performance indicated.

The increasing interest in, and availability of, the synthetically produced transuranium elements occasions a need for precise thermodynamical and thermochemical data on these elements and their compounds for the understanding and correlation of the chemical behavior of these substances. The procurement of thermochemical data on the transuranium elements has involved, and perhaps will continue to involve, quantities of material on the order of a milligram because of the exceedingly small quantities of many of these synthetic elements available and the health hazard of working with large quantities of highly radioactive α-emitters. Furthermore, the generation of energy within the sample by radioactive disintegration and the low thermal conductivities of the metals and compounds make the achievement of a uniform temperature throughout a massive sample difficult. The small quantities of transuranium elements available, the correspondingly small enthalpy change produced, and an anticipated reaction time less than 10 minutes made desirable the construction of a well stirred microcalorimeter of small heat capacity and considerable temperature sensitivity. The thermostat, and circuits of a calorimeter already described[3] were modified; only the most important changes will be indicated here.

Thermostat.—The toluene–mercury thermoregulator was replaced by one in which the temperature-sensing mechanism was the resistance of about 0.7 kilometer of No. 40 copper wire. This resistance thermometer served as one arm of a bridge, the unbalance of which is fed into a breaker-type amplifier of gain approximately 10^5 and enhanced sufficiently to activate a thyratron circuit including the thermostat heater. This proportional controller yielded maximum fluctuations much smaller than a thousandth of a degree at the calorimeter position over periods longer than the duration of the runs.

Calorimeter.—The general features of the calorimeter[4] may be seen by reference to Fig. 1. It is contained within a stainless steel submarine (D) which is supported on a small cross sectional shaft (E) of the same material. The two external leads to the unit are of No. 12 B. and S. gage copper wire and make contact through massive copper binding posts to fine manganin leads (A) imbedded in paraffin. The calorimeter itself is supported by a machined, thin-walled lucite tube (F) terminating in a screw thread at the lower end. The submarine provides a dead air gap of a centimeter width in accord with the considerations of White.[5] The reaction chamber (G) 2.5 cm. in diameter with 0.2-mm. thick walls is machined from tantalum rod and contains about 8 cc. of solution during operation. A screen closure near the top provides a vapor tight seal against a lapped seat; the threaded connection to the lucite shaft is also vapor tight. The portion of the cylindrical shell in contact with the solution is bifilarly wound with about 16 meters of No. 40 B. and S. gage, annealed, enamelled copper wire which serves both as a resistance thermometer and as a heater coil with very small lags. Two 3-cm. lengths of this wire extend across the air gap and are soldered into lugs and held by a copper set screw in good contact over a considerable area of the corresponding jacks (B) mounted in lucite. The solution is stirred by means of a tetradentive, platinum propeller driven by a slender quartz shaft (C) about a millimeter in diameter. The top end of the quartz shaft is clamped in a plastic collet driven through a flexible shaft by a 75 r.p.m. synchronous motor.

The samples to be dissolved were contained in fragile glass sample bulbs similar to those already described except that the present bulbs were especially thin walled with flat bottoms to facilitate breaking and had a capacity of fifty microliters. These bulbs were sealed onto the stirring shaft just below the propellor and were shattered against a projection by means of a two millimeter depression of the stirring shaft without interference with the rotational motion.

Operation and Performance.—The relative temperature sensitivity of the calorimeter is about 2×10^{-5} degree and the total heat capacity is about nine calories per degree. Consequently, to obtain results accurate to a few tenths of a per cent., a thermal process liberating about 0.2 calorie is

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(1) This research was performed under the auspices of the U. S. Atomic Energy Commission mainly in 1946–1947 and was reported in part by Edgar F. Westrum, Jr., in U. S. Atomic Energy Commission Declassified Document AECD-1903 (April, 1948). Presented at the 118th National Meeting, American Chemical Society, Chicago, Ill., September 6, 1950.

(2) (a) Department of Chemistry, University of Michigan, Ann Arbor, Michigan. (b) Department of Chemistry and Chemical Engineering, The State University of Iowa, Iowa City, Iowa.

(3) Edgar F. Westrum, Jr., and H. P. Robinson, National Nuclear Energy Series, Volume 14B, "The Transuranium Elements," Part 2, Research Paper 6.51, McGraw–Hill Book Co., Inc., New York, N. Y., 1949.

(4) Edgar F. Westrum, Jr., Atomic Energy Commission Declassified Report, AECD-1903. (1948).

(5) W. P. White, "The Modern Calorimeter," Reinhold Publishing Corp., New York, N. Y., 1928.