cal with that in the crystal. Hence the electronic isomers are present in solution to the same concentration as in the crystal at the same temperature.

Summary

The magnetic susceptibility of $Sm_2(SO_4)_3 \cdot 8H_2O$ was measured from 73.8 to 290.6°K. by a new accurate method.

It was found that Sm^{+++} both in the solid state and in solution consists of a mixture of electronic isomers. These isomers appear to be in thermal equilibrium.

The variation of the susceptibility with the temperature suggests that the isomer stable at the lowest temperature has the electronic configuration

Sm^{+++}	1_1	2_1 to 4_3	4_4	5_1	5_2 electronic shell
	2	full	5	2	6 number of electrons

but such a configuration is not yet completely established.

The conclusion that Sm^{+++} consists of a mixture of electronic isomers varying in concentration with the temperature carried with it the prediction that its absorption spectrum would consist of lines whose relative intensities would vary with the temperature. Such a variation in the intensities of the lines was actually found (in collaboration with Dr. F. H. Spedding)[16] in the absorption spectrum of $SmCl_3 \cdot 6H_2O$ taken from room temperature to that of liquid hydrogen.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COÖPERATION WITH THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITIES AT LOW TEMPERATURES OF ANTIMONY, ANTIMONY TRIOXIDE, ANTIMONY TETROXIDE AND ANTIMONY PENTOXIDE[1]

BY C. TRAVIS ANDERSON[2]

RECEIVED MARCH 26, 1930 PUBLISHED JULY 3, 1930

In a previous paper from the Pacific Experiment Station of the United States Bureau of Mines the author presented low-temperature thermal data for arsenic and its oxides. The present paper deals with the heat capacities of antimony and its oxides. The third and last of this group on bismuth and its oxides will appear later.

The method and apparatus have been described previously.[3]

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Assistant Physical Chemist, Pacific Experiment Station, U. S. Bureau of Mines, Berkeley, California.

[3] Anderson, THIS JOURNAL, 52, 2296 (1930).

Materials

The sample of antimony used was analyzed for arsenic, lead and insoluble matter, and contained less than 0.2% total of these materials. It was therefore of sufficiently high purity. It had a density of 6.74 at 24.1°; 388.5 g. was used for the determinations. The antimony trioxide was material of C. P. grade, which was resublimed, yielding orthorhombic crystals. Each particle was definitely crystalline. The portion used was exceptionally pure, analyzing better than 99.9% Sb_2O_3. Its density was found to be 5.99 at 27.4°. The calorimeter was filled with a 284.0-g. sample.

The antimony tetroxide was made by boiling a mixture of the antimony oxides with concentrated nitric acid for some time. The sample was washed free from nitric acid, dried, and heated in a silica flask, which was continuously evacuated at 850°. The resulting product was analyzed for tri- and pentavalent antimony and had the correct ratio for Sb_2O_4. It had a density of 6.47 at 23.8°. A 236.6-gram sample was studied.

Two samples of antimony pentoxide were used. They were prepared by the hydrolysis of antimony pentachloride. About 1 kg. of antimony pentachloride was twice distilled in an atmosphere of chlorine and once *in vacuo*. The resulting pure antimony pentachloride was then poured, very slowly, into a very large volume of cold water. The hydrolyzed precipitate of antimonic oxychloride was allowed to settle and washed by decantation ten to fifteen times. The precipitate was then dialyzed for several months until chlorides were undetectable, and finally filtered and dried. According to Simon and Thaler[4] it is impossible to prepare pure dry antimony pentoxide in this manner. The air-dried material contains between 4.4 and 4.6 formula weights of water per formula weight of antimony pentoxide. Therefore, the sample of hydrated oxide obtained was divided into two parts. One part was heated in a silica flask and was evacuated continuously for three days at 360°. The analysis of the resulting material was as follows: water, 1.5%; Sb_2O_3, 6.45%; Sb_2O_5, 92.05%. Assuming that the Sb_2O_3 is combined with the Sb_2O_5 to form Sb_2O_4, we have Sb_2O_4, 13.6% and Sb_2O_5 84.9%. This gives a sample of Sb_2O_5 containing 0.317 formula weight of water per formula weight of Sb_2O_5, which corresponds very well with the analysis of Simon and Thaler for their oxide, which had been heated at this temperature. In calculating the specific heats a correction was made for the 13.6% of Sb_2O_4 which was present in this sample. The density of the $Sb_2O_5 \cdot 0.317 H_2O$ was 5.14 at 24.8°; 100.8 g. of the material was used for making the measurements.

The other portion of hydrated antimony pentoxide was dried in air at 130° for several days. No detectable decomposition of the antimony pentoxide takes place at this temperature. The resulting sample analyzed 11.02% of H_2O and 88.98% of Sb_2O_5, which gives 2.224 formula weights of water per formula weight of antimony pentoxide. These values are also in excellent agreement with those of Simon and Thaler. The

TABLE I

SCREEN SIZES (TYLER) OF SAMPLES

Screen size	Sb, %	Sb_2O_3, %	Sb_2O_4, %
+ 35	..	27.0	..
+ 48	3.5	7.0	..
+ 65	24.0	8.5	..
+100	20.0	9.5	3.0
+150	10.0	5.5	16.0
+200	15.5	10.5	38.0
−200	27.0	32.0	43.0

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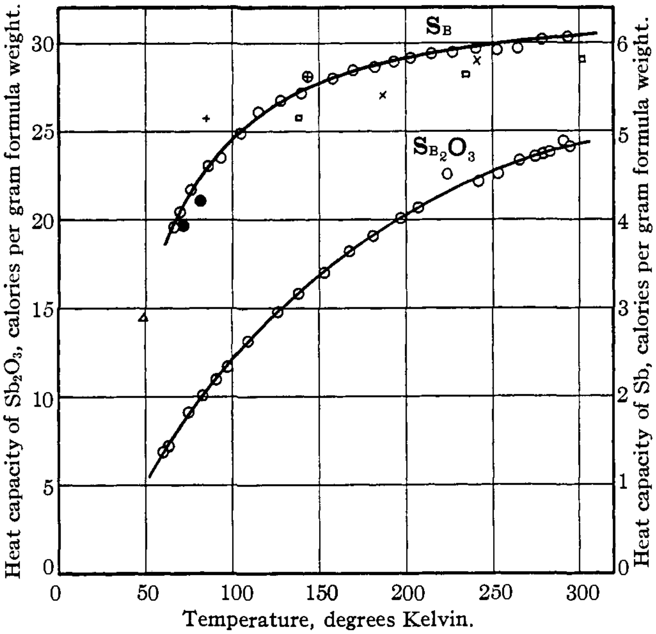
[4] Simon and Thaler, *Z. anorg. allgem. Chem.*, **162**, 113, 253 (1927).

density of this sample of oxide was 4.32 at 26.2°. The calorimeter was filled with 138.7 g. of the material.

Screen tests using Tyler screens were made on these materials, except the antimony pentoxide, which was extremely finely divided. The results are shown in Table I.

The Specific Heats

No previous measurements have been made at low temperatures on any of the oxides of antimony. Several determinations, however, have been made on antimony metal.[5]



○, Anderson; □, Ewald; ●, Simon and Ruhemann; ⊕, Richards and Jackson; ×, Schimpff; +, Günther; △, Dewar.

Fig. 1.—The heat capacity of antimony and antimony trioxide in calories per gram formula weight.

With the exception of those of Günther and of Simon and Ruhemann, the determinations were mean specific heats. Of the true specific heats, Günther and Simon and Ruhemann have several determinations, but over a very small temperature range. While their determinations are within a few degrees of one another, the values they have obtained are far from being in agreement.

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[5] Richards and Jackson, *Z. physik. Chem.*, **70**, 414 (1910); Schimpff, *ibid.*, **71**, 257 (1910); Dewar, *Proc. Roy. Soc.* (London), **A89**, 158 (1913); Ewald, *Ann. Physik*, **44**, 1213 (1914); Günther, *ibid.*, [4] **63**, 476 (1920); Simon and Ruhemann, *Z. physik. Chem.*, **129**, 321 (1927).

The results obtained in this research for the pure substances are shown graphically in Figs. 1 and 2. The various values obtained by other investigators on the heat capacity of antimony are also shown for comparison.

The experimental determinations of heat capacities for antimony, antimony trioxide, antimony tetroxide and the two samples of antimony pentoxide expressed in g. calories (15°) per gram formula weight are given in Table II. The $Sb_2O_5 \cdot 0.317\ H_2O$ has been corrected for the Sb_2O_4 present in the sample. In changing joules to calories the factor[6] 1/4.184 was used. The calculations were made on the basis of Sb = 121.77 and O = 16.

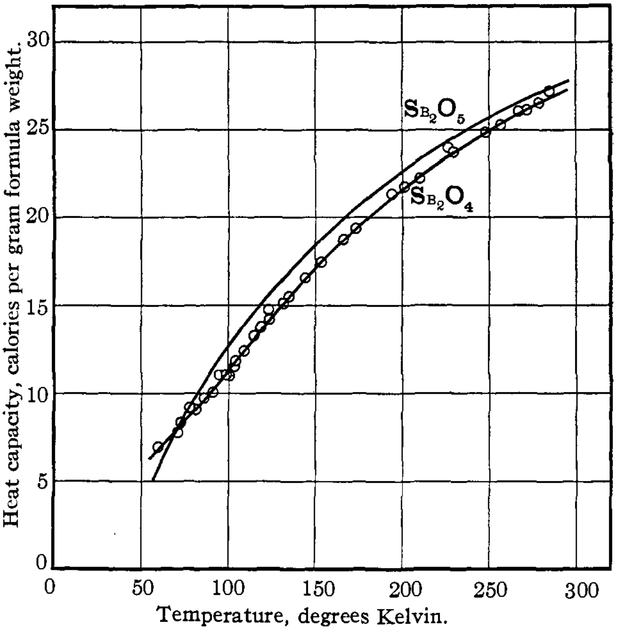

Fig. 2.—The heat capacities of antimony tetroxide and antimony pentoxide per gram formula weight.

The temperature scale is probably accurate within ±0.1°. On the average the heat capacity measurements at 55°K. have an error of about 1%. This is due largely to the diminishing resistance and the decrease of temperature coefficient of the copper resistance thermometer. As the temperature increases above 55° the error decreases to about 0.5% at 100°K. From this temperature the error slowly increases to about 1% at 300°K.

The results for the anhydrous antimony pentoxide were obtained from measurements of two hydrated samples. The uncertainty of composition may be greater than the error of measurement, exclusive of the fact that two series of measurements are involved.

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[6] "International Critical Tables," Vol. I, p. 24. 4.185 abs. joules = 1 cal. = 4.1837 Int. joules.

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT

Sb		Sb_2O_3		Sb_2O_4		$Sb_2O_5 \cdot 0.317\ H_2O$		$Sb_2O_5 \cdot 2.224\ H_2O$	
T, °K.	C_p	T, °K.	C_p	T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
...	...	59.8	6.893	72.8	8.317	63.6	7.283	60.6	10.46
66.0	3.917	63.2	7.189	77.3	9.157	68.0	8.138	64.8	11.60
69.6	4.083	74.7	9.114	80.1	9.061	72.9	9.125	86.7	16.94
75.7	4.337	82.6	10.06	85.6	9.723	77.8	10.01	101.9	20.45
85.8	4.602	90.6	10.97	90.6	10.02	82.1	10.83	125.6	26.16
93.1	4.700	97.2	11.64	94.4	11.02	89.5	11.36	150.3	30.86
104.6	4.982	108.7	13.11	98.5	11.00	101.5	13.31	184.1	36.94
114.8	5.224	125.9	14.79	104.3	11.83	112.7	15.55	209.9	41.41
127.7	5.351	137.4	15.76	115.7	13.64	127.6	17.49	248.1	46.23
139.7	5.431	152.3	16.97	122.6	14.72	133.3	18.19	272.5	49.28
157.9	5.598	167.0	18.18	59.8	6.942	142.9	19.25	280.5	51.07
169.4	5.691	180.4	19.05	70.8	7.756	153.9	20.57	292.1	52.27
181.9	5.726	196.6	20.06	134.5	15.50	162.4	21.57		
193.0	5.789	206.8	20.69	143.8	16.57	171.1	22.69		
202.6	5.834	223.7	22.54	165.6	18.74	181.7	23.42		
214.5	5.878	241.8	22.15	193.7	21.37	197.2	24.70		
227.0	5.893	252.9	22.59	209.7	22.20	201.8	25.05		
240.6	5.943	265.2	23.32	226.1	23.94	210.3	25.21		
252.9	5.923	274.6	23.57	100.1	11.00	221.8	27.05		
264.5	5.940	278.9	23.72	103.7	11.51	233.1	27.89		
278.4	6.043	282.8	23.83	109.0	12.41	241.3	28.02		
293.2	6.073	290.5	24.49	114.8	13.25	256.3	28.96		
		294.4	24.11	118.8	13.75	269.6	29.62		
				123.1	14.17	282.1	28.42		
				131.3	14.11	289.7	31.29		
				153.1	17.44	287.8	30.53		
				172.7	19.37				
				200.9	21.74				
				229.3	23.70				
				247.8	28.84				
				256.4	25.23				
				266.9	26.01				
				271.9	26.10				
				278.8	26.50				
				284.9	27.17				

In Table III are shown in Columns (a) and (b) the values for the heat capacities per gram formula weight of $Sb_2O_5 \cdot 2.224\ H_2O$ and $Sb_2O_5 \cdot 0.317\ H_2O$, respectively, which were read at even values of the temperatures from smooth curves representing the experimental data. In (c) the differences between these heat capacities are tabulated, representing 1.907 formula weights of water, corresponding to the difference in the composition of these two oxides. The values in Column (d) represent the heat capacities per formula weight of anhydrous antimony pentoxide, which were calculated as follows.

$$C_p(Sb_2O_5) = C_p(Sb_2O_5 \cdot 0.317\ H_2O) - \frac{0.317}{1.907}\,[C_p(Sb_2O_5 \cdot 2.224\ H_2O) - C_p(Sb_2O_5 \cdot 0.317\ H_2O)]$$

This obviously assumes that the heat capacity per formula weight of the water present in these two samples is independent of the amount, up to 2.224 formula weights of water per formula weight of antimony pentoxide. In (e) are shown the heat capacities per formula weight of this combined water, which are compared graphically in Fig. 3 with the known heat capacity of ice as given by Simon.[7] Values in Columns (a) and (b) are also shown on this graph.

TABLE III

THERMAL DATA ON ANTIMONY PENTOXIDE

T, °K.	(a) $C_pSb_2O_5$·–2.224 H_2O	(b) $C_pSb_2O_5$·–0.317 H_2O	(c) Difference	(d) $C_p(Sb_2O_5)$	(e) $C_p(H_2O)$
60	10.30	6.48	3.82	5.75	2.00
70	12.83	8.54	4.29	7.83	2.25
80	15.33	10.47	4.86	9.66	2.55
90	17.78	12.21	5.57	11.28	2.92
100	20.14	13.73	6.41	12.66	3.36
110	22.42	15.20	7.22	14.00	3.79
120	24.61	16.52	8.09	15.17	4.24
130	26.76	17.78	8.98	16.29	4.71
140	28.85	19.02	9.83	17.39	5.15
150	30.79	20.22	10.57	18.46	5.54
160	32.67	21.32	11.35	19.43	5.95
170	34.50	21.34	12.16	20.32	6.38
180	36.26	23.33	12.93	21.18	6.78
190	38.02	24.24	13.78	21.95	7.23
200	39.71	25.10	14.61	22.67	7.66
210	41.28	25.89	15.39	23.33	8.07
220	42.77	26.67	16.10	23.99	8.44
230	44.13	27.38	16.75	24.59	8.78
240	45.43	27.99	17.44	25.09	9.15
250	46.74	28.58	18.16	25.56	9.52
260	48.05	29.17	18.88	26.03	9.90
270	49.38	29.80	19.58	26.54	10.27
280	50.70	30.44	20.26	27.07	10.62
290	52.03	31.10	20.93	27.62	10.98
300				(28.23)	

Calculation of Entropies

The conventional method was used in calculating the entropies. The experimental heat capacity curves were extended below the lowest measure-

TABLE IV

ENTROPIES FROM EXPERIMENTAL DATA

	Sb	Sb_2O_3	Sb_2O_4	Sb_2O_5
Extrap. (0–56.2) °K.	1.91	4.09	4.31	2.54
Graph (56.2–298.1)	8.59	25.35	26.04	27.32
$S°_{298}$	10.5 ± 0.2 E. U.	29.4 ± 0.4 E. U.	30.3 ± 0.5 E. U.	29.9 ± 1 E. U.

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[7] Simon, "Handbuch der Physik," Verlag Julius Springer, Berlin, 1926, Vol. X, p. 360.

ments to approach and finally coincide with Debye functions having the following parameters (Θ): for Sb, 201; Sb_2O_3, 126; Sb_2O_4, 121 and Sb_2O_5, 183. In Table IV are given the results of the entropy calculations.

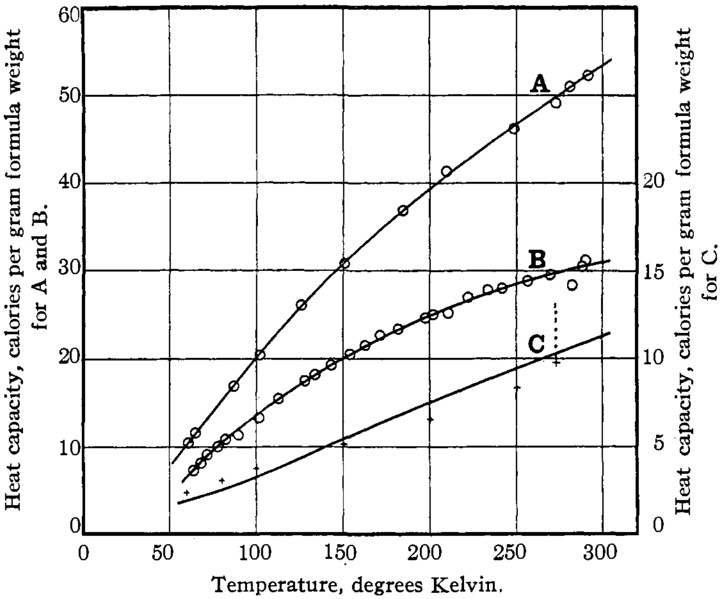

Fig. 3.—Curve A, $Sb_2O_5 \cdot 2.224\ H_2O$; Curve B, $Sb_2O_5 \cdot 0.317\ H_2O$; Curve C, combined H_2O; +, values for H_2O given by Simon in "Handbuch der Physik."

The following combinations of Debye and Einstein functions were found to fit the specific heat curves per formula weights for the three oxides

$$C_{Sb_2O_3} = D\,\frac{(126)}{T} + 2E\,\frac{(557)}{T} + 2D\,\frac{(542)}{T}$$

$$C_{Sb_2O_4} = D\,\frac{(121)}{T} + 2E\,\frac{(314)}{T} + 3E\,\frac{(757)}{T}$$

$$C_{Sb_2O_5} = D\,\frac{(183)}{T} + 2E\,\frac{(303)}{T} + 2E\,\frac{(532)}{T} + 2E\,\frac{(1504)}{T}$$

The Sb_2O_3 combination fits the experimental results up to 298°K., the Sb_2O_4 combination to above 260°K., and that for Sb_2O_5 to about 160°K. Above 260°K. for Sb_2O_4 and 160°K. for Sb_2O_5 the experimental curves rise above those of the function sums, which is due in part to the increase in $C_p - C_v$.

To demonstrate the average agreement between the experimental data and these combinations the entropies of the oxides at 298°K. were calculated by use of these function sums. The results obtained are: for Sb_2O_3, 28.9 E. U.; for Sb_2O_4, 29.6 E. U.; and for Sb_2O_5, 30.4 E. U. It was necessary to add 0.03 unit to the result obtained by the Sb_2O_4 combinations and

0.32 unit to the value obtained by the Sb_2O_5 functions for the rise in C_p above the values given by the function sums. These results agree very well with the experimental values given in Table IV.

A comparison of the general trend of the specific heat curves, the entropies at 298°K., and the theoretical functions which have been used to fit the data empirically indicates (but, of course, does not prove) that the crystalline oxides of antimony have similar structures.

Related Thermal Data

The heats of formation of the three oxides have been determined by Mixter[8] by the combination of antimony and its oxides with sodium peroxide. Biltz[9] has calculated the heat of formation from decomposition pressure measurements by the use of Nernst's approximation formula. Simon and Thaler[10] from their decomposition pressure measurements have similarly calculated the heats of formation. The various values, however, are in very poor agreement. Owing to Mixter's method of preparation of antimony pentoxide, there is considerable doubt as to the purity of his material, and consequently no reliance can be placed on his results, as they are all based on thermal measurements on his antimony pentoxide. It is also a well-known fact that the Nernst approximation formula often leads to the calculation of very erroneous thermal data. Consequently no attempt will be made to utilize any of these values in the calculation of free energies.

Schuhmann[11] and Roberts and Fenwick[12] have calculated the free energy of Sb_2O_3 from all measurements. Schuhmann gives ΔF°_{298} for Sb_2O_3 = $-148{,}600$ Cal. While he does not so state, he probably worked with the orthorhombic form or a mixture. Roberts and Fenwick give $-149{,}690$ Cal. for the cubic. For the change Sb_2O_3 (orthorhombic) = Sb_2O_3 (cubic), the latter gives $\Delta F^\circ_{298} = -1800$ Cal., so that the free energy of the orthorhombic form would be $-147{,}900$ Cal. Since the orthorhombic form was used in the present work, the value $-147{,}900$ Cal. may be used in combination with the measured entropies of Sb and Sb_2O_3 and the accepted entropy of O_2 to calculate the heat of formation of Sb_2O_3 as $\Delta H^\circ_{298} = -167{,}300$ Cal. This value is in rather poor agreement with the value of $-165{,}000$ Cal. obtained by Mixter. This value has been corrected for the newer value for the atomic weight of antimony.

In conclusion the author wishes to thank R. W. Millar for making the measurements on antimony trioxide, C. G. Maier for his many helpful suggestions and material assistance, and K. K. Kelley for his assistance in

[8] Mixter, *Am. J. Sci.*, [4] **28**, 103 (1909).

[9] Biltz, *Nach. kgl. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 293 (1908).

[10] Simon and Thaler, *Z. anorg. allgem. Chem.*, **162**, 253 (1927).

[11] Schuhmann, THIS JOURNAL, **46**, 52 (1924).

[12] Roberts and Fenwick, *ibid.*, **50**, 2125 (1928).

calibrating thermocouples, making a new temperature scale, and in checking the numerous calculations necessary in the determination of the entropies.

Summary

The heat capacities of antimony, antimony trioxide, antimony tetroxide and antimony pentoxide, from about 60 to 300°K., have been determined and their corresponding entropies calculated. The heat of formation of antimony trioxide has been calculated.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COÖPERATION WITH THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITIES OF BISMUTH AND BISMUTH TRIOXIDE AT LOW TEMPERATURES[1]

BY C. TRAVIS ANDERSON[2]

RECEIVED MARCH 27, 1930 PUBLISHED JULY 3, 1930

This is the third of a series of papers from the Pacific Experiment Station of the United States Bureau of Mines dealing with thermal data of the metals and oxides of the fifth group of the periodic system. Two previous articles[3] have dealt with the metals arsenic and antimony and their oxides. This paper presents the results for bismuth metal and bismuth trioxide.

Materials

The bismuth metal used was a sample of high purity kindly furnished by the American Smelting and Refining Company. No detectable amounts of lead, arsenic, or antimony were found on analysis. It had a density of 9.86 at 20.6°. The calorimeter was filled with a 552-g. sample of granular metal.

TABLE I

SCREEN SIZES (TYLER) OF BISMUTH AND BISMUTH TRIOXIDE

Screen sizes	Bi, %	Bi_2O_3, %
+ 35	..	1.5
+ 48	..	12.5
+ 65	17.0	12.0
+100	29.5	13.5
+150	14.5	8.5
+200	17.5	16.5
−200	21.5	35.5

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[2] Assistant Physical Chemist, Pacific Experiment Station, U. S. Bureau of Mines, Berkeley, California.

[3] Anderson, THIS JOURNAL, **52**, 2296, 2712 (1930).