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.

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[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]

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

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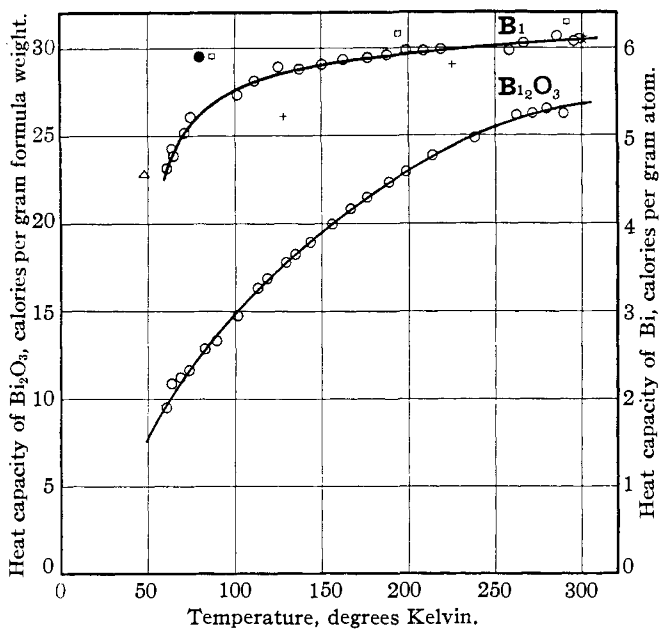
[3] Anderson, THIS JOURNAL, **52**, 2296, 2712 (1930).

The sample of bismuth trioxide was of C. P. grade. On reduction with hydrogen it was found to consist of 99.6% Bi_2O_3 and was of sufficiently high purity. Its density was found to be 9.33 at 23.3°. A 356-g. sample was used for the determinations.

Screen tests, using Tyler screens, were made on the bismuth and bismuth trioxide, and the results are shown in Table I.

The Specific Heats.—No measurements have been made on bismuth trioxide at low temperatures. Several determinations, however, have been made on bismuth metal.[4]



○, Anderson; ×, Jaeger and Diesselhorst; +, Ewald; □, Giebe; △, Dewar; ●, Richards and Jackson.

Fig. 1.—The heat capacities of bismuth and bismuth trioxide in calories per gram formula weight.

All of the determinations are mean specific heats. The various values obtained by these investigators on the heat capacity of bismuth are shown in Fig. 1. The results obtained in this Laboratory on the heat capacity of bismuth and bismuth trioxide, expressed in gram calories (15°) per gram formula weight, are given in Table II and are also shown graphically in

[4] Jaeger and Diesselhorst, *Wiss. abh. Phys.-Tek. Reich*, **3**, 269 (1900); Giebe, *Verhandl. deut. physik. Ges.*, **5**, 60 (1903); 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).

Fig. 1. In changing joules to calories the factor[5] 1/4.184 was used. The calculations were made on the basis of Bi = 209.0 and O = 16.

The accuracy of the measurements has been discussed previously[6] and will apply to both bismuth and bismuth trioxide.

TABLE II

HEAT CAPACITY PER GRAM FORMULA WEIGHT

Bi		Bi		Bi_2O_3		Bi_2O_3	
T, °K.	C_p	T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
60.8	4.631	176.8	5.899	289.3	26.25	118.6	16.86
64.7	4.771	187.7	5.924	262.1	26.17	129.2	17.80
63.4	4.851	198.9	5.976	271.4	26.29	143.1	18.93
71.1	5.040	208.8	5.974	279.7	26.54	155.7	19.96
74.6	5.216	218.8	5.980	60.6	9.50	166.4	20.85
101.3	5.464	258.1	5.874	63.7	10.89	175.8	21.49
111.2	5.674	266.3	6.058	68.7	11.24	188.5	22.35
125.1	5.813	272.8	6.083	73.6	11.64	198.2	22.95
137.2	5.761	285.3	6.139	82.6	12.85	134.7	18.24
150.2	5.817	295.2	6.089	89.3	13.32	213.3	23.87
162.5	5.869	298.2	6.104	101.4	14.72	238.4	24.88
				113.0	16.31		

Calculation of Entropies.—The entropies were determined by the usual graphical method. The experimental heat capacity curves were extrapolated from the lower points so as to coincide with Debye functions having the parameters (Θ) for Bi 147, and for Bi_2O_3, 97. In Table III are given the results of the entropy calculations.

TABLE III

ENTROPIES FROM EXPERIMENTAL DATA

	Bi	Bi_2O_3
Extrap. (0–56.2) °K.	3.13	6.22
Graph (56.2–298.1)	9.31	29.96
$S°_{298}$	12.4 ± 0.3 E. U.	36.2 ± 0.4 E. U.

The following combination of Debye and Einstein functions was found to fit the experimental specific heat curve per gram formula weight of Bi_2O_3 up to 178°K.

$$C_{Bi_2O_3} = D\left(\frac{97}{T}\right) + 2E\left(\frac{225}{T}\right) + 2E\left(\frac{568}{T}\right)$$

Above 178°K. the experimental curve rises above that of the function sum.

The entropy of Bi_2O_3 by use of this function sum was calculated to be 36.4 E. U. It was necessary to add 0.24 unit to the results obtained by the combinations for the rise in C_p above the value given by the function sum.

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

[6] Anderson, THIS JOURNAL, 52, 2712 (1930).

It was not found possible to prepare samples of Bi_2O_4 or Bi_2O_5 of sufficient purity to determine their specific heats. However, by comparison of the entropies of arsenic and antimony it is suggested that until the entropies are actually determined, the value 35.0 ± 2 E. U. may be used for each, with reasonable assurance.

Related Thermal Data.—The heat of formation of Bi_2O_3 has been determined by Mixter[7] and Ditte and Metzner.[8] Mixter gives −136,000 cal., and Ditte and Metzner gives −137,800 cal.

Using Mixter's values of −136,000 cal. with the measured entropies of Bi and Bi_2O_3 and the accepted entropy of O_2, the free energy of Bi_2O_3 is calculated as −118,000 cal.

In conclusion the author wishes to thank K. K. Kelley for his assistance in making the new temperature scale and in checking the calculations in the determinations of the entropies.

Summary

The heat capacities of bismuth and bismuth trioxide from about 60 to 300°K. have been determined and their corresponding entropies calculated. The free energy of Bi_2O_3 has been calculated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

THE SURFACE TENSION OF LIQUID NITROUS OXIDE

BY ELTON L. QUINN AND GRANT WERNIMONT

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Many investigators find carbon dioxide and nitrous oxide an interesting pair of compounds largely because of the similarity of their physical properties. The close agreement between the densities, vapor pressures, critical temperatures, molecular weights, etc., is very remarkable, and it is not uncommon to group them together when considering questions pertaining to their physical make-up. The fact that such an agreement does not extend to the chemical behavior of these two substances, enhances this interest as it indicates that the physical properties are related more to the arrangement of the atoms in the molecules than to the ultimate constitution of the atoms.

Niven[1] gives reasons quite sufficient for concluding that carbon dioxide and nitrous oxide have the same electronic arrangement. Rankine[2] shows from crystal structure data and viscosity data, the similarity in structure of molecules of the two compounds. Many other investigators have dealt

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

[8] Ditte and Metzner, *Compt. rend.*, **115**, 1303 (1892).

[1] Niven, *Phil. Mag.*, [7] **3**, 1314–1334 (1927).

[2] Rankine, *Proc. Roy. Soc.* (London), **A98**, 369–374 (1921).