[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 ARSENIC, ARSENIC TRIOXIDE AND ARSENIC PENTOXIDE AT LOW TEMPERATURES[1]

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In continuation of its general program of determination of the heat capacities of the various metals and oxides which are important in metallurgical processes, the Pacific Experiment Station of the U. S. Bureau of Mines has studied the metals and oxides of arsenic, antimony and bismuth at low temperatures. The thermodynamic properties of the metals and oxides of this group are of practical importance because they constitute some of the lead smelters' most difficult problems of reduction and refining, and they also have considerable theoretical interest. The present article deals only with the heat capacities of arsenic and its oxides; later papers will discuss the remaining materials in this group.

Method and Apparatus

With the exception of a few minor details, the methods and apparatus used in this work are identical with those previously described from this laboratory by Millar.[3] The apparatus was provided with a new thermocouple, which was made of wire from the same spool as Thermocouple No. 17 of Giauque, Buffington and Schulze,[4] and which was compared with No. 17 through a secondary standard at the temperature of liquid air, the melting point of toluene crystals and the melting point of ice. The secondary standard was calibrated directly against No. 17 at 28 points by Kelley.[5]

The standard cell was calibrated from time to time against another having a Bureau of Standards certificate.

Using the graphical method of Giauque and Wiebe,[6] a new temperature scale was determined for the resistance thermometer, and it is probably somewhat better than the one previously used in this Laboratory.

The volt-box correction was redetermined by substituting a standard 100-ohm resistance for the calorimeter resistance. The volt-box factor was calculated from accurate measurements of current and voltage when small amounts of electrical energy were passed through the volt-box and standard

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[3] Millar, THIS JOURNAL, **50**, 1876 (1928).

[4] Giauque, Buffington and Schulze, *ibid.*, **49**, 2343 (1927).

[5] Kelley, *ibid.*, **51**, 180 (1929).

[6] Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

resistance. This value is probably more reliable than that previously obtained directly by measuring the high resistance which the volt-box contains.

The heat capacity of the empty calorimeter was redetermined, using the new temperature scale.

By the use of liquid nitrogen instead of liquid oxygen it was possible to cool down to about 55°K. with the present pumping facilities. This temperature is about 5° lower than that previously reached in this Laboratory.

Materials

The sample of arsenic used contained 0.13% antimony, no lead or silica and more than 99.8% arsenic. Its density was found to be 5.48. A 342.9-g. sample was studied.

The arsenic trioxide was of C. P. grade, but was resublimed. Each particle was definitely crystalline and of octahedral structure. It analyzed better than 99.8% arsenic trioxide and had a density of 3.85. The calorimeter was filled with a 267.4-g. sample.

The arsenic pentoxide was a very pure material which was dried at 550° after treatment with concentrated nitric acid. It contained more than 99.7% arsenic pentoxide. The only detectable contamination was 0.2% arsenic trioxide. It contained no antimony. The material did not consist of separate crystals, as did the arsenic trioxide, but of crystalline aggregates; 179.7 g. of the pentoxide was used. It had a density of 4.32.

Screen tests were made on these materials and the results are shown in Table I.

TABLE I

SCREEN SIZES OF SAMPLES MEASURED

Screen size	As, %	As_2O_3	As_2O_5
+ 35	0.25	. . .	80.6
+ 48	. .	4.5	18.0
+ 65	35.0	2.0	. .
+100	30.0	2.5	0.7
+150	13.5	2.5	. .
+200	20.0	8.0	0.7
−200	1.25	80.5	. .

The Specific Heats

The heat capacities of these substances expressed in gram calories (15°) per gram formula weight are given in Table II and are shown graphically in Fig. 1. In changing joules to calories the factor[7] 1/4.184 was used. The calculations were made on the basis of O = 16 and As = 74.96.

Calculation of Entropies.—The entropy calculations were made in the usual manner. The experimental heat capacity curves were extended below the lowest measurements, so as to approach and finally coincide with Debye functions having the following parameters (Θ): for As, 275; As_2O_3,

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[7] "International Critical Tables," Vol. I, p. 24.

Table II

Heat Capacity per Gram Formula Weight

As		As_2O_3		As_2O_5	
T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
57.2	2.400	60.2	5.839	63.5	4.511
61.1	2.458	63.9	6.200	67.1	4.947
70.2	2.889	76.9	7.646	80.8	7.101
80.9	3.584	89.0	8.647	91.6	8.266
85.2	3.536	100.0	9.702	101.9	9.713
91.0	3.703	108.1	10.55	114.0	11.57
98.6	3.883	121.1	11.98	127.8	13.31
115.5	4.481	132.0	12.95	143.5	15.10
128.2	4.626	143.0	13.80	160.9	17.01
140.6	4.800	154.9	14.90	173.2	18.41
155.5	4.990	168.9	16.14	184.1	19.29
174.4	5.137	181.0	16.92	168.5	17.91
202.7	5.448	194.7	17.93	181.5	19.28
212.7	5.536	210.4	19.00	196.9	20.70
227.1	5.592	223.0	19.58	209.8	21.89
242.4	5.743	241.9	20.48	222.0	22.87
258.9	5.767	253.7	21.23	239.1	24.10
267.2	5.734	272.2	21.83	251.1	25.08
272.8	5.754	288.7	22.46	270.3	26.50
285.7	5.848	291.6	22.61	287.1	27.45
291.0	5.990	296.6	22.78	291.7	27.69
				296.2	27.68

141; As_2O_5, 240. In Table III are given the results of the entropy calculations.

Table III

Entropies from Experimental Data

	As		As_2O_3	
Extrap.	(0–56.2)°K.	1.20	(0–56.2)°K.	3.54
Graph.	(56.2–298.1)	7.16	(56.2–298.1)	22.04
S_{298}		8.4 ± 0.2 E. U.		25.6 ± 0.4 E. U.

	As_2O_5	
Extrap	(0–63.1)°K.	1.94
Graph.	(63.1–298.1)	23.30
S_{298}		25.2 ± 0.4 E. U.

It was found possible to fit the molal specific heat curves of the two oxides by the following combinations of Debye and Einstein functions

$$C_{As_2O_3} = D\left(\frac{141}{T}\right) + 2D\left(\frac{567}{T}\right) + 2D\left(\frac{1054}{T}\right)$$

$$C_{As_2O_5} = D\left(\frac{240}{T}\right) + 2E\left(\frac{368}{T}\right) + 2E\left(\frac{727}{T}\right) + 2D\left(\frac{1600}{T}\right)$$

The arsenic trioxide combination fits the experimental results up to 298°K., and that for arsenic pentoxide up to 125°K. Above 125°K. the experimental curve for arsenic pentoxide begins to rise above that of the function sum, probably due to $C_p - C_v$ becoming appreciable. Similarly, it may be that C_p and C_v for arsenic trioxide are very nearly equal up to 298°K.

As a means of demonstrating the average agreement between the experimental results and these combinations, the entropies at 298°K. were calculated, using these function sums. The results obtained are for arsenic trioxide 25.6 E. U., and for arsenic pentoxide 25.2 E. U., which are identical with the values previously given. In calculating the entropy of arsenic pentoxide by use of the functions, it was necessary to add an entropy difference of 0.17 unit, representing the difference between the experimental curve and the theoretical curve, in order to obtain the above values.

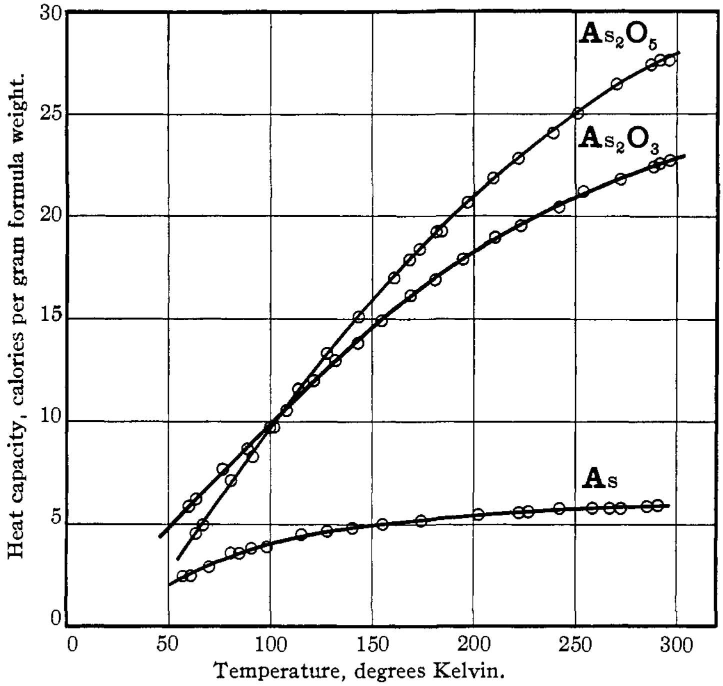

Fig. 1.—The heat capacities per gram formula weight of arsenic trioxide and arsenic pentoxide.

Related Thermal Data

The heats of formation of the oxides have been determined by Thomsen.[8] For arsenic trioxide he gives −154,700 Cal., and for arsenic pentoxide −219,400 Cal. Berthelot[9] gives −156,400 for the heat of formation of

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[8] Thomsen, "Thermochemistry," Longmans, Greene and Co., London, 1908, p. 227.

[9] Berthelot, "Thermochemie," Vol. II, 1897, p. 117.

arsenic trioxide. Schuhmann[10] determined the free energy of formation of arsenic trioxide from cell measurements. Correcting Schuhmann's result by the use of Eastman's[11] value for the free energy of formation of liquid water, ΔF°_{298} for arsenic trioxide was calculated to be $-137{,}000$ Cal. Using the integrated Gibbs–Helmholtz equation, Schuhmann calculated from the temperature coefficient of his cells, over a 20° temperature range, that the heat of formation of arsenic trioxide was $\Delta H_{298} = -153{,}800$. Previous experience at this Laboratory with oxide cells[12] has shown that free energies may be obtained from oxide cells with high precision, but because of the usually low magnitude of the cell coefficient, and the inherent fluctuations and polarizability of such cells, thermal values from this source are often not entirely satisfactory. It is justifiable, therefore, to calculate heats of formation from free energies and entropies, when these latter quantities have a high probable accuracy. In this way, using the free energy from Schuhmann's cell value, and the entropies of arsenic and arsenic trioxide, the heat of formation of arsenic trioxide was calculated as $-156{,}500$ Cal. This value agrees very well with the value of $-156{,}400$ given by Berthelot.

In the case of the pentoxide, direct free energy data are unavailable, and the free energy of formation of arsenic pentoxide was calculated from Thomsen's value of $-219{,}400$ Cal. for the heat of formation, and the entropies of arsenic and arsenic pentoxide, to be $\Delta F^\circ_{298} = -185{,}400$ Cal. All of the data are summarized in Table IV.

TABLE IV

SUMMARY OF ENTROPIES, FREE ENERGIES AND HEATS OF FORMATION

	S_{298}	ΔF°_{298}	ΔH°_{298}
As	8.4	....	....
As_2O_3	25.6	$-137{,}100$	$-156{,}000$
As_2O_5	25.2	$-185{,}400$	$-219{,}400$

In conclusion the author wishes to thank R. W. Millar for making the measurements on arsenic trioxide and arsenic pentoxide, and K. K. Kelley for his assistance in calibrating thermocouples, making the new temperature scale, and in fitting the Debye and Einstein curves to the experimental values.

Summary

The heat capacities of arsenic, arsenic trioxide and arsenic pentoxide from about 57 to 300° Kelvin have been determined, and the corresponding entropies calculated. The heat of formation of arsenic trioxide and the free energy of formation of arsenic pentoxide have been calculated.

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[10] Schuhmann, THIS JOURNAL, **46**, 1445 (1924).

[11] Eastman, Information Circular, Bureau of Mines, No. 6125, p. 13, May, 1929.

[12] Maier, THIS JOURNAL, **51**, 194 (1929).