10-Alkyl derivatives of 3-methoxy-1,2-benzanthracene were obtained by a similar but simpler process.

CONVERSE MEMORIAL LABORATORY
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[CONTRIBUTION FROM THE METALLURGICAL DIVISION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

The Heat Capacities of Selenium Crystals, Selenium Glass, and Tellurium at Low Temperatures[1]

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The data presented in this report represent a portion of an investigation being carried out at the Pacific Experiment Station of the U. S. Bureau of Mines on the possible specific heat anomalies of manganese selenide, and telluride, similar to those already found in the oxide[3] and the sulfide.[4]

Since it was necessary to prepare pure selenium and tellurium to be used in this investigation, it was considered desirable to make low temperature specific heat measurements on these materials.

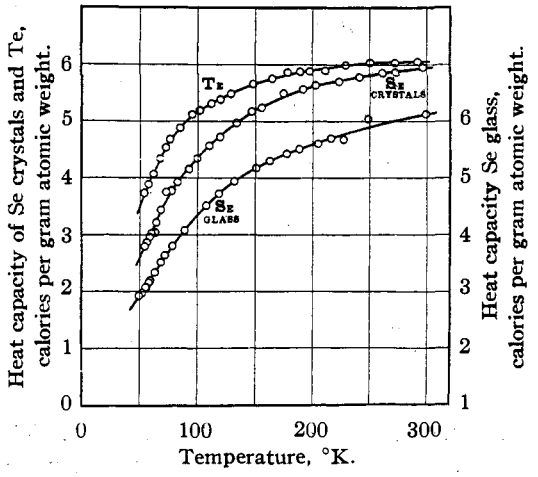

Fig. 1.—The heat capacity of selenium crystals, selenium glass and tellurium, in calories per gram atomic weight.

Materials.—The tellurium used in this investigation was furnished through the courtesy of Mr. J. O. Betterton of the American Smelting and Refining Co. The sample of selenium was of regular C. P. quality.

Both the selenium and tellurium were purified further by vacuum distillation. At temperatures slightly above their melting points, the purification of the selenium was carried out in a glass apparatus while quartz was used for the tellurium. The samples were distilled a number of times, until no residue remained in the distilling flask or condensed material accumulated above the main body of distillate.

In preparing the samples, the glassy form of selenium was usually obtained in the distillation. To convert the glass to the crystals, the selenium was alternately warmed and cooled until the mass crystallized. The only detectable impurities found to be present were approximately 0.2% tellurium in the selenium and a similar amount of selenium in the tellurium. No corrections were made for these small amounts of impurities. Measurements were made on 261.3 g. of the selenium crystals, 237.4 g. of the selenium glass, and 374.2 g. of the tellurium.

The Specific Heats.—The results obtained in this Laboratory on the heat capacities of selenium crystals, selenium glass, and tellurium, expressed in gram calories (15°) per gram atomic weight, are shown graphically in Fig. 1. The experimental values for the heat capacities are given in Tables I, II, and III. The calculations were made on the basis of Se = 78.96 and Te = 127.61.

TABLE I

HEAT CAPACITY PER GRAM ATOMIC WEIGHT OF SELENIUM CRYSTALS

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.4	2.786	77.7	3.772	155.4	5.236
56.1	2.864	82.8	3.920	174.5	5.494
58.7	2.956	92.4	4.149	191.5	5.562
60.1	3.018	99.5	4.342	202.7	5.633
63.4	3.035	110.0	4.566	223.2	5.702
64.6	3.211	119.3	4.724	240.9	5.776
68.3	3.428	133.9	4.974	261.2	5.850
72.9	3.746	147.0	5.166	272.7	5.861
77.6	3.773			296.5	5.952

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(3) Millar, THIS JOURNAL, **50**, 1875 (1928).

(4) Anderson, *ibid.*, **53**, 476 (1931).

TABLE II

HEAT CAPACITY PER GRAM ATOMIC WEIGHT OF SELENIUM GLASS

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
49.9	2.916	71.9	3.634	162.7	5.302
52.5	2.974	78.3	3.798	177.4	5.428
55.5	3.066	88.9	4.070	188.4	5.515
56.2	3.071	107.7	4.509	205.0	5.606
58.1	3.155	118.6	4.720	216.2	5.704
59.5	3.188	132.0	4.942	227.3	5.684
63.3	3.327	150.7	5.175	249.0	6.040
68.2	3.513			299.1	6.127

TABLE III

HEAT CAPACITY PER GRAM ATOMIC WEIGHT OF TELLURIUM

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
54.0	3.729	95.1	5.121	189.4	5.866
57.6	3.884	101.8	5.185	198.0	5.876
61.8	4.063	111.6	5.310	211.8	5.892
67.4	4.337	119.5	5.383	229.5	5.994
72.3	4.536	128.5	5.479	250.3	6.034
76.0	4.677	147.9	5.654	272.6	6.027
84.9	4.878	164.4	5.747	292.0	6.054
		178.4	5.859		

Calculation of Entropies

In fitting the experimental data with Debye and Einstein functions it was found desirable to plot three times the specific heat against the logarithm of the temperature. This method can best be demonstrated by use of the recent data given by Eastman and McGavock[5] for sulfur, which is a member of the same periodic group. Their measurements were extended to lower temperatures than those reported in this paper, and the heat capacity of sulfur was lower than that of either selenium or tellurium at corresponding temperatures. By plotting 3 C_p *vs.* log T, their points fall on a Debye curve up to about 30°K., while on the usual C_p *vs.* log T plot the points fall below the Debye curve above 17°K. Combinations of Debye and Einstein functions can be used to fit their experimental data accurately to above 100°K. Unless this method of extrapolating were used it would be very difficult to obtain good values for the entropies of selenium and tellurium. The extended curves coincided with Debye functions having the following parameters (Θ): selenium crystals, 74; selenium glass, 65; and tellurium, 45.

The following combinations of Debye and Einstein functions were found to fit the specific heat curves.

$$C_{\text{Se cryst.}} = \frac{1}{3}\,\mathrm{D}\left(\frac{74}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{180}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{321}{T}\right)$$

$$C_{\text{Se glass}} = \frac{1}{3}\,\mathrm{D}\left(\frac{65}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{152}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{361}{T}\right)$$

$$C_{\text{Te}} = \frac{1}{3}\,\mathrm{D}\left(\frac{45}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{142}{T}\right) + \frac{1}{3}\,\mathrm{E}\left(\frac{206}{T}\right)$$

The results of the entropy calculations from the experimental heat capacity data as well as from the function sums are given in Table IV. The reader should note that the entropies given are the summations from 0 to 298.1°K., which are identical with $S°_{298.1}$ for the crystalline materials, but not for the selenium glass, which presumably has zero-point entropy. Existing high temperature specific heat measurements on selenium from 298.1° to the melting point are inadequate to calculate the actual entropy of the glass at 298.1°.

TABLE IV

ENTROPY DATA

	Selenium crystals	Selenium glass	Tellurium
Extrap. (0–50.1)°K.	2.26	2.61	3.54
Graph. (50.1–298.1)	8.23	8.54	9.31
$S_{0-298.1}$ graphical	10.49 ± 0.4	11.15 ± 0.4	12.85 ± 0.5
$S_{0-298.1}$ calcd. from functions	10.4	10.8	12.8

Summary

The heat capacities of selenium crystals and tellurium from about 50 to 300°K. have been determined and their corresponding entropies calculated as 10.49, and 12.85, respectively. Measurements for selenium glass over the same range indicate the difference in entropy from 0 to 298.1° for this material to be 11.15.

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(5) Eastman and McGavock, THIS JOURNAL, **59**, 145 (1937).