[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures of Titanium Dioxide (Rutile and Anatase)[1]

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This paper is the concluding one of a series[3] dealing with low-temperature heat capacities and entropies of titanium containing substances; it presents data for two forms of titanium dioxide, rutile and anatase. The measurements of McDonald and Seltz[4] on rutile, afford the only previous low-temperature heat-capacity data for these substances.

Materials

The samples of rutile and anatase were prepared in this Laboratory by R. J. O'Dea.[5] High-purity titanium metal, prepared at the Boulder City Station of the Bureau of Mines, was dissolved in 6 *N* hydrochloric acid, the titania precipitated with 50% potassium hydroxide solution, washed, redissolved in hydrochloric acid, re-precipitated with ammonium hydroxide, washed repeatedly, and dried at 350°. From this point the two preparations differed. Rutile was prepared by heating a portion of the material to 1000°, grinding to −60 mesh, rewashing with boiling water until free of chlorides, and finally redrying at 1000°. Analysis gave 99.7% titanium dioxide. A 258.75-g. sample was used in the heat-capacity measurements. Anatase was prepared by further heating another portion of the material for one day at 400° *in vacuo*, grinding to −60 mesh, washing free of chlorides, and finally heating *in vacuo* at 550° until the water content, as determined by loss on ignition of a sample at 1100°, was under 0.3%. The anatase analyzed 99.3% titanium dioxide, and a 82.29-g. sample was used in the measurements. The material was very hygroscopic.

X-Ray photographs of both materials were made by A. E. Salo.[6] Each showed only the lines previously reported for that substance.

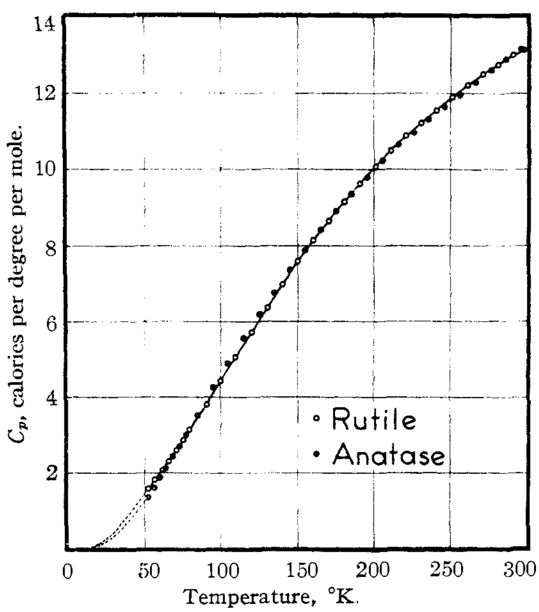

Fig. 1.—Heat capacities of titanium dioxide.

Heat Capacities

The method and apparatus used in the low-temperature heat-capacity measurements have been described in an earlier paper.[7] The experimental results, expressed in defined calories (1 calorie = 4.1833 int. joules),[8] are listed in Table I and shown graphically in Fig. 1. Because of the proximity of the two curves, only the curve for rutile has been drawn. The values of the heat capacities at 298.16°K., read from a smooth curve through the experimental points, are also included in Table I. The molecular weight is in

TABLE I

MOLAL HEAT CAPACITIES OF TITANIUM DIOXIDE

(Mol. wt. = 79.90)

Rutile		Anatase	
T, °K.	C_p, cal./deg.	*T*, °K.	C_p, cal./deg.
52.5	1.572	52.5	1.345
57.0	1.806	56.2	1.598
61.9	2.073	60.1	1.870
66.0	2.307	63.9	2.108
70.8	2.594	68.7	2.416
75.4	2.873	72.9	2.703
79.5	3.127	77.2	2.995
90.5	3.815	84.8	3.517
100.1	4.438	95.2	4.259
109.7	5.066	104.5	4.894
120.2	5.740	115.2	5.587
130.5	6.396	125.3	6.210
140.4	7.004	134.9	6.775
150.7	7.603	145.7	7.374
160.7	8.165	155.5	7.914
170.6	8.681	165.6	8.436
180.7	9.190	175.6	8.942
190.9	9.648	185.6	9.378
201.1	10.09	195.9	9.827
211.2	10.52	205.8	10.25
221.2	10.91	216.3	10.68
231.1	11.23	226.3	11.00
240.9	11.56	235.8	11.35
251.1	11.91	246.2	11.65
261.3	12.22	256.1	11.97
271.1	12.50	266.3	12.30
281.0	12.76	276.5	12.62
290.7	13.00	286.0	12.88
297.7	13.14	295.8	13.17
(298.16)	(13.16)	(298.16)	(13.22)

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

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(3) (a) Shomate, THIS JOURNAL, **68**, 310 (1946); (b) Shomate, *ibid.*, **68**, 964 (1946); (c) Shomate, *ibid.*, **68**, 1634 (1946); (d) Kelley, *Ind. Eng. Chem.*, **36**, 865 (1944).

(4) McDonald and Seltz, THIS JOURNAL, **61**, 2405 (1939).

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(6) Formerly metallurgist, Pacific Experiment Station.

(7) Kelley, Naylor and Shomate, Bur. Mines Tech. Paper, 686 (1946).

(8) Mueller and Rossini, *Am. J. Phys.*, **12**, 1 (1944).

accordance with the 1941 International Atomic Weights. Corrections were made in the anatase results for an impurity of 0.3% water, using the data of Giauque and Stout[9] for making the corrections. No corrections for impurities were made in the results for rutile.

All weights were corrected to vacuum, using the following densities: rutile, 4.24, and anatase, 3.87 g./cc.

The dioxides exhibited no thermal anomalies in the temperature range studied. The results of McDonald and Seltz[4] for rutile are between 2 and 3% higher than the present results in the temperature range 125–298°K. Below 125°K. their results are more erratic, the disagreement mounting to 8% at 69°K., the temperature of their lowest measurement. This is in marked contrast with the results obtained by this Laboratory for barium nitrate[10] as compared with those of Latimer and Ahlberg,[11] of the Department of Chemistry of the University of California, for this substance. The agreement was within 0.2% on the average; with a maximum deviation of only 0.4% in the duplicated temperature range (52 to 298°K.). This substantiates the policy of this Laboratory of attaching a maximum precision uncertainty of only 0.3% to its low-temperature heat-capacity results. No explanation can be offered for the disagreement with McDonald and Seltz' results on rutile.

Entropies

Evaluation of the entropies at 298.16°K. is obtained from a plot of C_p against log T. This necessitates the extrapolation of the heat-capacity curve from the temperature of the lowest measurement down to the absolute zero of temperature. It was found that the following function sums represent all the measured heat capacities within 2.0 and 0.8%, respectively.

$$\text{Rutile: } D\left(\frac{318}{T}\right) + 2E\left(\frac{685}{T}\right)$$

$$\text{Anatase: } D\left(\frac{343}{T}\right) + E\left(\frac{497}{T}\right) + E\left(\frac{950}{T}\right)$$

The symbols D and E denote, respectively, Debye and Einstein functions. Calculation of Θ in the Debye function, $D(\Theta/T)$, from the six lowest temperature heat-capacity runs of rutile gave 316.2, 319.4, 320.5, 320.0, 316.9 and 312.1. The heat-capacity curve of anatase was steeper than a Debye function at these temperatures, so coincidence with the function, $D(343/T)$, was below 50°K. These functions were used for extrapolating the heat-capacity curves to 0°K. (broken lines in Fig. 1).

Table II summarizes the entropy calculations for rutile and anatase.

TABLE II

ENTROPIES OF TITANIUM DIOXIDE AT 298.16°K. (E. U./MOLE)

	Rutile	Anatase
0–52.00°K. (extrapolated)	0.60	0.50
52.00°K.–298.16°K. (measured)	11.41	11.43
$S^\circ_{298.16}$	12.01 ± 0.05	11.93 ± 0.07

A larger uncertainty has been assigned to the entropy value for anatase, because of the smaller size of the sample used in the heat-capacity determinations and because of the uncertainty in the water impurity. The entropy value of 12.45 E. U./mole for rutile, reported by McDonald and Seltz,[4] is more than 0.4 E. U./mole higher than the present value. Of this amount, 0.3 E. U./mole is the discrepancy in the measured portion.

Summary

The heat capacities of two forms of titanium dioxide, rutile and anatase, were measured in the temperature range 52 to 298°K.

The following molal entropies at 298.16°K. were computed: rutile, 12.01 ± 0.05 and anatase, 11.93 ± 0.07 E. U./mole, respectively.

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(9) Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936).

(10) Shomate and Kelley, *ibid.*, **66**, 1490 (1944).

(11) Latimer and Ahlberg, *Z. physik. Chem.*, **A148**, 466 (1930).