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

High-Temperature Heat Contents of TiO, Ti_2O_3, Ti_3O_5, and TiO_2[1]

BY B. F. NAYLOR[2]

Continuing the current investigation at the Pacific Experiment Station, Bureau of Mines, of the thermodynamic properties of titanium-containing compounds, high-temperature heat contents of four oxides of titanium (TiO, Ti_2O_3, Ti_3O_5, and TiO_2) were measured. In the case of titanium dioxide, both anatase and rutile were studied. The experimental results together with derived thermodynamic data form the subject of this paper.

No previous reliable high-temperature heat-content data exist for these compounds. However, low-temperature heat capacities have been reported, the dioxide having been investigated by McDonald and Seltz[3] and the tritapentoxide, sesquioxide, and monoxide by Shomate.[4]

Method and Material

The heat-content measurements were made by the "drop" method in an apparatus previously described.[5] The copper-block calorimeter was calibrated with electrical energy, measured in international joules, and the results were converted to the conventional thermochemical calorie by the relation,[6] 1 cal. = 4.1833 int. joules (NBS).

Each sample was enclosed in a platinum–rhodium alloy capsule during the measurements. Except for titanium dioxide, the capsule, after being filled with sample, was evacuated free of air, filled with helium, and sealed with platinum. An open-neck capsule having a tightly fitting cap was employed for the titanium dioxide. The heat contents of the capsules were determined in a separate series of experiments.

All formula weights are in accord with the 1941 International Atomic Weights. Sample weights were corrected to vacuum, using the following densities: TiO, 4.92; Ti_2O_3, 4.56; Ti_3O_5, 4.15; TiO_2 (anatase), 3.88; and TiO_2 (rutile), 4.38 g./cc.[7]

Titanium monoxide was prepared by the reaction of equimolal quantities of titanium dioxide and titanium metal at 1,350° *in vacuo*. Analysis of the product gave 99.2% TiO, 0.1% TiC, and 0.7% Si.

Titanium sesquioxide was prepared by the carbon reduction of the dioxide, according to the reaction

$$2TiO_2 + C \longrightarrow Ti_2O_3 + CO$$

The finely ground reaction mixture was heated at 1,400° *in vacuo* for twenty hours. Analysis showed 99.4% Ti_2O_3, 0.3% TiC, and 0.3% SiO_2. The X-ray diffraction pattern[8] was similar to that of Fe_2O_3, in agreement with previous observations.

Titanium tritapentoxide also was prepared by reduction of titanium dioxide by carbon. The reaction

$$3TiO_2 + C \longrightarrow Ti_3O_5 + CO$$

was carried out *in vacuo* at 1,350° for eight hours. Analysis of the product gave 99.1% Ti_3O_5, 0.2% TiC, and 0.7% SiO_2. The lines in the X-ray diffraction pattern of this substance were weak but they did not correspond with those of any of the other titanium oxides.

The anatase sample was J. T. Baker titanium dioxide. After being dried at 1,050° for four hours, it contained by spectrographic analysis[9] 0.30% SiO_2 and 0.15% CaO. No other impurities were present to the extent of more than 0.07%. From the spectrographic analysis, the sample was computed to be at least 99% pure. X-Ray diffraction measurements, made after the drying treatment, showed the sample to be entirely anatase.

The Australian rutile sample, furnished by the Titanium Alloy Manufacturing Company, contained 0.55% ZrO_2, 0.50% SiO_2, 0.27% V_2O_5, 0.15% CaO, 0.15% Fe_2O_3, and 0.12% Al_2O_3, and was black-colored.[10] No other impurity amounted to more than 0.10%. Chemical analysis gave 97.90% TiO_2, in good agreement with the spectrographic results. X-Ray examination showed it to be rutile.

Results

Experimental heat contents above 298.16°K. are listed in Table I. The columns labeled *T*, °K., give the absolute temperature of the sample before being dropped into the calorimeter, while those marked $H_T - H_{298.16}$ list the heat liberated per mole in cooling from *T* to 298.16°K. The Ti_3O_5 results are arranged to agree with the order

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(2) Formerly chemist, Pacific Experiment Station, Bureau of Mines.

(3) H. J. McDonald and H. Seltz, THIS JOURNAL, **61**, 2405 (1939).

(4) C. H. Shomate, *ibid.*, **68**, 310 (1946).

(5) (a) J. C. Southard, *ibid.*, **63**, 3142 (1941); (b) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bureau of Mines Technical Paper 686, 34 pp. (1946).

(6) E. F. Mueller and F. D. Rossini, *Am. J. Physics*, **12**, 1 (1944).

(7) Densities were determined by R. J. O'Dea, Pacific Experiment Station, Bureau of Mines.

(8) X-Ray examinations mentioned in this paper were made by Dr. E. V. Potter, physicist, Salt Lake City Station, Bureau of Mines.

(9) Spectrographic analyses of the anatase and rutile samples were kindly carried out by the Titanium Alloy Manufacturing Company, through the courtesy of Dr. J. C. Southard.

(10) This is the usual color of natural rutile and, in fact, synthetic preparations from materials of highest purity often are gray-black. The reason for this is not definitely known. It has been attributed to the presence of minute amounts of trivalent titanium but there appears to be no actual proof of this.

of experimental determination; results for the other compounds are given in order of increasing temperature.

Heat contents read from smooth curves at 100° intervals and corresponding numerically computed entropy increments are given in Table II. Figures 1 and 2 show the smooth curves and experimental points.

The TiO measurements extend from 357 to 1,771°K. and indicate a transition at 1,264°K., with a calculated heat effect of 820 calories per mole. The transition temperature may be in error by as much as 10°, for pretransition effects, perceived as low as 1,224°K., make its exact determination uncertain. Experimental heat content values that appear to involve pretransition effects have been designated "(p)" in Table I. No attempt was made to correct for impurities.

Table I

Heat Contents above 298.16°K. of TiO (Cal. per Mole)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
357.0	608	1170.1	11,060	1323	14,150
419.3	1296	1200.5	11,500	1358	14,790
496.8	2197	1224.0	11,940(p)	1414	15,650
603.4	3450	1235.8	12,150(p)	1506	17,120
669.8	4275	1252.3	12,530(p)	1556	18,050
768.5	5485	1265.4	13,130(p)	1583	18,510
827.8	6285	1273.1	13,440	1684	20,200
967.4	8135	1282.6	13,550	1771	21,580
1127.5	10420				

Heat Contents above 298.16°K. of Ti_2O_3 (Cal. per Mole)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
374.6	1986	549.0	7,510	1181.8	29,080
384.6	2258	660.8	11,140	1292.4	33,060
424.2	3359	780.4	15,090	1356	35,350
453.7	4275	854.4	17,710	1514	41,070
472.4	4905	968.7	21,740	1600	44,180
487.1	5535	1056.4	24,720	1750	49,550
526.5	6825				

Heat Contents of Ti_3O_5 above 298.16°K. (Cal. per Mole)

Run No.	T, °K.	$H_T - H_{298.16}$	Run No.	T, °K.	$H_T - H_{298.16}$
1A	361.7	2,705	1B	360.5	2,640
2A	384.6	3,720	2B	326.0	1,150
3A	417.8	5,270	3B	395.6	4,210
4A	441.3	6,410	4B	432.7	6,000
5A	504.0	12,120	5B	452.0	8,865
6A	464.3	10,120	6B[c]	372.9	3,585
7A	452.1	9,360	7B[d]	375.7	3,637
8A	703.1	21,060	8B[e]	376.9	3,715
9A	397.0	4,500	9B	421.6	5,805
10A	363.8	2,992			
11A	600.2	16,060	1C[f]	409.3	4,895
12A	809.1	25,950	2C	529.8	12,710
13A	904.1	30,500	3C	383.7	3,805
14A	1019.5	36,240	4C	481.7	10,530
15A	1201.9	45,710	5C	387.2	4,125
16A[a]	1340.1	52,810			
17A	361.0	3,013	1D[g]	436.5	6,665
18A[b]	370.0	3,420	2D	396.9	4,690

Heat Contents above 298.16°K. of TiO_2 (Anatase) (Cal. per Mole)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
416.1	1,791	948.3	10,790	1144.7	14,400
545.5	3,810	951.8	10,840	1221.1	15,750
738.7	7,130	1091.4	13,370	1304.8	17,270

Heat Contents above 298.16°K. of TiO_2 (Rutile) (Cal. per Mole)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
393.5	1,443	1133.4	14,010	1597	22,490
762.6	7,520	1328.7	17,520	1746	25,300
1065.9	12,810				

[a] Corrected for slight oxidation due to small leak in capsule. [b] Capsule packed in Dry Ice for fifteen hours previous to making run. [c] Capsule held at 525° for five days previous to making run. [d] Capsule held at 40° for five days previous to making run. [e] Capsule held at room temperature for one month previous to making run. [f] Same sample as series B, but after mild grinding with mortar and pestle and returning to capsule. [g] Capsule heated to 600° for several hours previous to making run.

Measurements of Ti_2O_3 were carried out at temperatures as high as 1,750°K. The results indicate a small heat of transition, 215 calories per mole, at 473°K. Selection of the transition temperature was difficult and is only considered accurate to about 20°. Again no correction for impurities was made.

Four series of measurements of Ti_3O_5, designated A, B, C, and D in Table I, were made because of the unusual behavior. The results show a transition at about 450°K., but after heating Ti_3O_5 above this temperature it does not return to the original state on cooling. This is illustrated in Fig. 2, in which curve A corresponds to the original material and curve B shows the extreme divergence of results obtained after heating above the transition point.

All attempts to make the material return to the original condition, without removing it from the capsule, failed. Aging at several temperatures was tried as illustrated by runs 18A, 7B, and 8B. The only means found to return the substance to its original condition was to remove from the capsule and grind lightly in a mullite mortar, as shown by run 1C. However, on reheating above the transition point (run 2C), high results again were obtained (runs 3C and 5C). It appears that the alteration in heat content from curve A to curve B is progressive, depending upon both temperature and time of heating above the transition point.

The reason for this unusual behavior was not forthcoming from the present work. It should be mentioned that X-ray examination of the substance in the conditions corresponding to curves A and B showed no perceptible difference.

All evidence favors the selection of curve A as representing the heat content of the stable form of Ti_3O_5 below the transition point. However, because of the difficulty of calculating an un-

TABLE II

HEAT CONTENTS (CAL. PER MOLE) AND ENTROPIES (CAL./DEG. PER MOLE) ABOVE 298.16°K.

T, °K.	TiO		Ti_2O_3		Ti_3O_5		TiO_2 (anatase)		TiO_2 (rutile)	
	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	1,080	3.11	2,610	7.46	4,660	13.43	1,540	4.44	1,540	4.44
450					7,060(α)	19.08				
450					9,300(β)	24.06				
473			4,885(α)	12.67						
473			5,100(β)	13.12						
500	2,220	5.65	5,935	14.84	11,570	28.84	3,100	7.93	3,100	7.93
600	3,410	7.82	9,140	20.68	16,220	37.31	4,735	10.91	4,735	10.91
700	4,640	9.72	12,440	25.77	20,880	44.49	6,440	13.53	6,440	13.53
800	5,910	11.41	15,830	30.29	25,550	50.72	8,170	15.84	8,160	15.83
900	7,230	12.97	19,270	34.34	30,290	56.29	9,930	17.91	9,900	17.88
1000	8,600	14.41	22,740	38.00	35,230	61.54	11,720	19.79	11,650	19.72
1100	10,020	15.76	26,260	41.35	40,370	66.42	13,530	21.52	13,420	21.41
1200	11,490	17.04	29,800	44.43	45,510	70.90	15,350	23.10	15,200	22.96
1264	12,450(α)	17.82								
1264	13,270(β)	18.47								
1300	13,840	18.92	33,360	47.28	50,660	75.03	17,180	24.56	17,000	24.40
1400	15,430	20.09	36,950	49.94	55,810	78.83			18,820	25.75
1500	17,050	21.21	40,560	52.43					20,660	27.02
1600	18,700	22.28	44,180	54.77					22,540	28.23
1700	20,380	23.29	47,830	56.98					24,440	29.38
1800	22,090	24.27	51,490	59.07					26,340	30.47

equivocal heat of transition from either the stable or unstable low-temperature condition to the high-temperature state at 450°K., it was decided to use a mean curve for the heat-content and entropy values at 400° and 450°K. given in Table II. This procedure results in a nominal value of 2,240 calories per mole as the heat of transition.

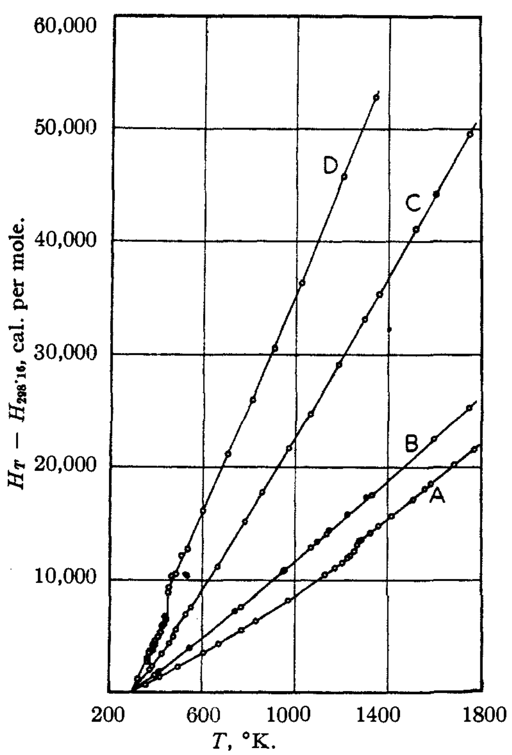

Fig. 1.—High-temperature heat contents of titanium oxides: Curve A, TiO; Curve B, TiO_2 (open circles, rutile; black circles, anatase); Curve C, Ti_2O_3; Curve D, Ti_3O_5.

Heat-content measurements of anatase extended as high as 1,773°K.; however, an X-ray examination of the sample on its removal from the capsule showed that it had become rutile. As stated before, four hours heating at 1,323°K. had effected no measurable conversion to rutile;

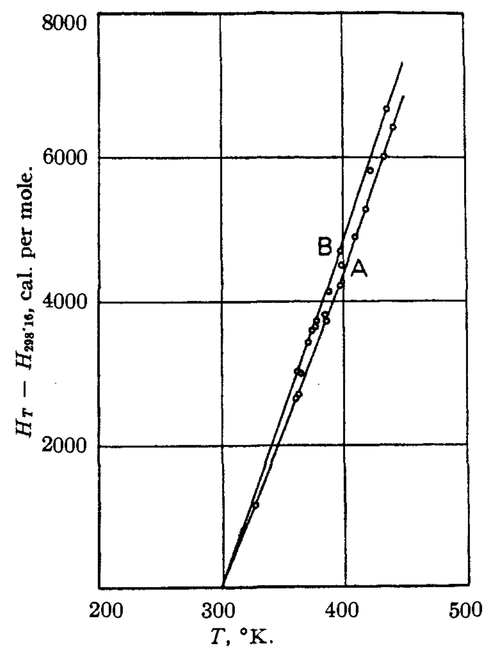

Fig. 2.—High-temperature heat content of Ti_3O_5: Curve A, stable form; Curve B, unstable form.

hence, the conversion to rutile had occurred during measurements at temperatures greater than 1,323°K. Only those results obtained at temperatures less than this figure are given in Table I. All of these measurements had been carried out previous to proceeding to higher temperatures. Correction was made for the SiO_2 and CaO impurities.

Seven determinations of the heat content of rutile were made at temperatures as high as 1,746°K. The heat content of rutile at 1,300°K. is about 1% less than that of anatase. Correction was made for the ZrO_2, SiO_2, CaO, Fe_2O_3, and Al_2O_3 impurities. The experimental results of both anatase and rutile when plotted form smooth curves, and no transition was observed in either substance.

Heat content equations were derived by the method described by Shomate.[11] This method utilizes all the high temperature heat-content data and also the true heat capacity at 298.16°K., if the latter is known and is applicable. The following molal heat capacities[3,4] at 298.16°K. were used in the present derivations: TiO, C_p = 9.55; Ti_2O_3, C_p = 23.27; and TiO_2 (rutile), C_p = 13.49. The heat capacity of anatase at 298.16°K. is not known, and the value for Ti_3O_5 was not applicable because of the unusual behavior between 298.16° and 450°K. The equations follow, the temperature range of validity and the mean percentage deviation from the experimental data being given in parentheses.

$TiO(\alpha)$: $H_T - H_{298.16} = 10.57T + 0.00180T^2 + 186{,}000/T - 3{,}935$ (298–1264°K.; 1%)

$TiO(\beta)$: $H_T - H_{298.16} = 11.85T + 0.00150T^2 - 4{,}100$ (1264–1800°K.; 0.3%)

$Ti_2O_3(\alpha)$: $H_T - H_{298.16} = 7.31T + 0.02676T^2 - 4{,}559$ (298–473°K.; 1.5%)

$Ti_2O_3(\beta)$: $H_T - H_{298.16} = 34.68T + 0.00065T^2 + 1{,}020{,}000/T - 13{,}605$ (473–1800°K.; 0.2%)

$Ti_3O_5(\alpha)$: $H_T - H_{298.16} = 35.47T + 0.01475T^2 - 11{,}887$ (298–450°K.; 4%)

$Ti_3O_5(\beta)$: $H_T - H_{298.16} = 41.60T + 0.00400T^2 - 10{,}230$ (450–1400°K.; 0.2%)

TiO_2(anatase): $H_T - H_{298.16} = 17.21T + 0.00054T^2 + 359{,}000/T - 6383$ (298–1300°K.; 0.5%)

TiO_2(rutile): $H_T - H_{298.16} = 17.14T + 0.00049T^2 + 350{,}000/T - 6328$ (298–1800°K.; 0.2%)

The corresponding specific heat equations are given

$TiO(\alpha)$: $C_p = 10.57 + 0.00360T - 186{,}000/T^2$
$TiO(\beta)$: $C_p = 11.85 + 0.00300T$
$Ti_2O_3(\alpha)$: $C_p = 7.31 + 0.05352T$
$Ti_2O_3(\beta)$: $C_p = 34.68 + 0.00130T - 1{,}020{,}000/T^2$
$Ti_3O_5(\alpha)$: $C_p = 35.47 + 0.02950T$
$Ti_3O_5(\beta)$: $C_p = 41.60 + 0.00800T$
TiO_2(anatase): $C_p = 17.21 + 0.00108T - 359{,}000/T^2$
TiO_2(rutile): $C_p = 17.14 + 0.00098T - 350{,}000/T^2$

No previous high-temperature heat content data exist for any of the titanium oxides except the dioxide. Nilson and Pettersson[12] have reported the only measurements of titanium dioxide at temperatures above 373°K. The highest of their four determinations was made at 713°K., and their values average about 4% less than the present data.

Summary

High-temperature heat contents above 298.16° K. of TiO, Ti_2O_3, Ti_3O_5, and TiO_2 were measured.

Three oxides, TiO, Ti_2O_3, and Ti_3O_5, exhibited transitions and the transition heats and temperatures were determined.

The results have been summarized by algebraic equations and a table was compiled which gives heat content and entropy increments above 298.16°K. at 100° intervals.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NATIONAL TSING HUA UNIVERSITY, PEIPING, CHINA]

Generalized Beattie-Bridgeman Equation of State for Real Gases[1]

BY GOUQ-JEN SU[2] AND CHIEN-HOU CHANG

In recent years many authors have correlated the compressibility and related thermodynamic properties of real gases on the basis of the law of corresponding states as proposed by van der Waals in 1881. They[3] showed that the compressibility factor μ (= pV/RT) and the fugacity-pressure ratio and some other thermodynamic properties of real gases are approximately functions of the reduced pressure and the reduced temperature. Keyes[4] deduced a simple reduced equation of state for real gases at low pressures. Maron and Turnbull[5] proposed their reduced equations of state, the constants being deduced from the compressibility data of nitrogen.

(1) This paper is in part abstracted from a thesis submitted in July, 1939, to the Faculty of the National Southwestern Associated University, Kunming, China, by Chien-Hou Chang, Shao-Twan King and Chi-Hsun Wang in partial fulfillment of the requirement for the degree of Bachelor of Engineering.

(2) Present address: c/o Dr. Paul Kolachov, Joseph E. Seagram & Sons, Inc., Louisville 1, Kentucky.

(3) J. D. Cope, W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, **23**, 887 (1931); G. G. Brown, M. Souders, Jr., and R. L. Smith, *ibid.*, **24**, 515 (1932); W. K. Lewis and C. D. Luke, *ibid.*, **25**, 725 (1933), *Oil Gas J.*, **32**, No. 40, 114 (1934); W. K. Lewis, *Ind. Eng. Chem.*, **28**, 257 (1936); R. H. Newton, *ibid.*, **27**, 302 (1935); R. H. Newton and B. F. Dodge, *ibid.*, **27**, 577 (1935); K. M. Watson and R. L. Smith, *National Petroleum News*, **28**, No. 27 (1936).

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