Molar volumes, MV_{20}, were calculated for the compounds, also for groups $Si(CH_3)_2$-O-, for $[CH_3 + Si(CH_3)_3]$ and for the contribution from the ring structure.

Graphs for the relation of log η and reciprocal T°K. show a linear relation. Values for $Q\eta$ and A in formula $\log \eta = Q\eta/2.30\,RT + A$ are tabulated.

The ratios of $Q\eta$ to ΔH and $\Delta\epsilon$ of vaporization are given.

The relation between η and n, also between $Q\eta$ and n, are given by graphs.

A curve is given to permit estimation of viscosities of more complex, pure siloxanes than have been prepared.

Values of η, $Q\eta$ and A are nearly the same for two isomers, a straight chain and a branched chain, in spite of the different structure.

Using Batschinski's equation, $\eta = C/(V - \omega)$, values of C and ω were calculated, also a value $\epsilon_{Si} = 22.3$ for Batschinski's additive relation $M\omega = \Sigma n\epsilon$.

There is slight evidence of some association in these liquids.

SCHENECTADY, N. Y. RECEIVED JULY 12, 1945

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

High-Temperature Heat Contents of Titanium Carbide and Titanium Nitride[1]

BY B. F. NAYLOR[2]

Two recent publications[3] of the Pacific Experiment Station of the Bureau of Mines have presented some thermodynamic data for a few metallurgically important compounds of titanium. In continuation of this program of study, the present paper reports high-temperature heat-content measurements for titanium nitride and titanium carbide, two of the products resulting from the addition of titanium to steel and alloys. No previous similar data exist for either of these substances.

Method and Materials

The heat content measurements were made by the "drop" method. The experimental procedure and apparatus have been described previously.[4] The copper calorimeter was calibrated with electrical energy, measured in international joules, and the results were converted to the conventional calorie by the relation,[5] 1 cal. = 4.1833 int. joules (NBS).

During the measurements the samples were enclosed in platinum-rhodium alloy capsules, the heat contents of which were determined separately. The capsules, after being filled with sample, were evacuated of air, filled with helium, and then quickly sealed.

Titanium carbide was prepared by heating powdered metallic titanium with Norblack (99.7% carbon) *in vacuo* at 1,300–1,350°. After grinding to −150 mesh and analyzing, the titanium to carbon ratio was adjusted by adding whichever element was deficient, and then the sample was reheated under similar conditions. Analysis of the final product gave 79.56% titanium and 19.85% carbon and it was calculated to be 99.0% titanium carbide. The principal impurity was about 0.4% unreacted titanium. The analytical results were confirmed by determinations kindly made for us by the Titanium Alloy Manufacturing Co.

Titanium nitride was made by heating powdered titanium in a stream of purified nitrogen and hydrogen, first at 1,000° and finally for ten hours at 1,400°. The product, which was bronze colored, analyzed 77.04% titanium, corresponding to 99.6% titanium nitride content. Silicon nitride probably was the chief impurity.

Results

Fifteen experimental heat content determinations of titanium carbide and fourteen of titanium nitride were made. The results are listed in Table I and also are shown graphically in Fig. 1. In Table I the column labeled T, °K., gives the temperature of the sample immediately before dropping into the calorimeter and $H_T - H_{298.16}$ represents the heat liberated per gram molecular weight in cooling to 298.16°K. The molecular weights accord with the 1941 International Atomic Weights and the sample weights were corrected to vacuum, using the experimentally determined densities, titanium carbide = 4.81 and titanium nitride = 5.24 g./cc.

TABLE I

HEAT CONTENTS ABOVE 298.16°K.

TiC (mol. wt. = 59.910)		TiN (mol. wt. = 61.908)	
T, °K.	$H_T - H_{298.16}$ (cal./mole)	T, °K.	$H_T - H_{298.16}$ (cal./mole)
360.5	576	388.3	875
450.9	1,459	410.6	1,122
587.8	2,943	499.7	2,085
671.5	3,905	615.4	3,407
790.5	5,270	687.3	4,250
891.5	6,470	807.5	5,690
1001.7	7,860	931.7	7,200
1103.0	9,080	1010.0	8,160
1205.1	10,400	1123.3	9,620
1288.2	11,450	1203.5	10,670
1391	12,770	1312	12,080
1454	13,570	1435	13,690
1537	14,600	1559	15,320
1674	16,340	1738	17,760
1735	17,120		

The values for titanium carbide given in Table I include a small correction of less than 0.1% for

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

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

(3) (a) K. K. Kelley, *Ind. Eng. Chem.*, **36**, 865 (1944); (b) B. F. Naylor, THIS JOURNAL, **67**, 2120 (1945).

(4) J. C. Southard, *ibid.*, **63**, 3142 (1941).

(5) E. F. Mueller and F. D. Rossini, *Am. J. Phys.*, **12**, 1–7 (1944).

the 0.4% titanium impurity. The heat content of titanium as reported by Jaeger, Rosenbohm and Fonteyne[6] was used in calculating the correction. No attempt was made to correct for other impurities.

Heat content values read from smooth curves at 100° intervals and corresponding graphically computed entropy increments are given in Table II.

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K.

	TiC		TiN	
T, °K.	$H_T - H_{298.16}$ cal./mole	$S_T - S_{298.16}$ cal./deg./mole	$H_T - H_{298.16}$ cal./mole	$S_T - S_{298.16}$ cal./deg./mole
400	945	2.72	1,000	2.88
500	1,975	5.02	2,090	5.31
600	3,085	7.04	3,230	7.38
700	4,225	8.80	4,400	9.19
800	5,395	10.36	5,590	10.78
900	6,600	11.78	6,810	12.21
1000	7,830	13.07	8,050	13.52
1100	9,080	14.26	9,310	14.72
1200	10,330	15.35	10,600	15.84
1300	11,590	16.36	11,910	16.89
1400	12,860	17.30	13,230	17.87
1500	14,130	18.18	14,550	18.78
1600	15,400	19.00	15,870	19.63
1700	16,670	19.76	17,190	20.43
1800	17,940	20.49	18,510	21.18

Using the method previously outlined by Shomate[7] and the molar heat capacities[3a,8] at 298.16°K. (titanium carbide, $C_{p298.16}$ = 8.04 and titanium nitride, $C_{p298.16}$ = 8.86 cal./deg.) heat content equations fitting the experimental data were derived and are given below, followed by the temperature range of validity and the mean percentage deviation of calculated values from those experimentally determined. The equation for titanium carbide fits with an error of less than 50 calories at all points and deviates by less than 0.5% at temperatures above 500°K. The equation for TiN has a maximum deviation of about 60 calories at 1,010°K. and at temperatures above 500°K. the greatest percentage deviation is 0.7%, which also occurs at the 1,010°K. point.

TiC: $H_T - H_{298.16} = 11.83T + 0.00040T^2 + (358{,}000/T) - 4765$ (298° – 1800°K.; 0.5%)

(6) F. M. Jaeger, E. Rosenbohm and R. Fonteyne, *Proc. Acad. Sci. Amsterdam*, **39**, 442 (1936).

(7) C. H. Shomate, THIS JOURNAL, **66**, 928 (1944).

(8) C. H. Shomate, unpublished data.

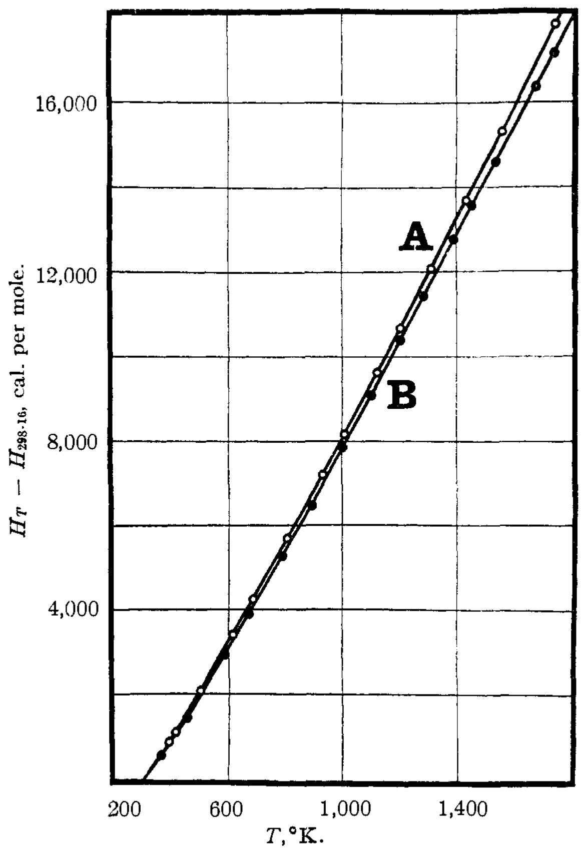

Fig. 1.—High temperature heat contents: curve A TiN; curve B, TiC.

TiN: $H_T - H_{298.16} = 11.91T + 0.00047T^2 + (296{,}000/T) - 4585$ (298° – 1800°K.; 0.5%)

The corresponding molar heat capacity equations (T, °K.), obtained by differentiation, are

TiC: $C_p = 11.83 + 0.00080T - (358{,}000/T^2)$

TiN: $C_p = 11.91 + 0.00094T - (296{,}000/T^2)$

Summary

High-temperature heat contents above 298.16°K. of titanium carbide and titanium nitride were measured from about 373 to 1,735°K. The data have been summarized by heat content and specific heat equations for each substance and also by a table of heat contents and entropies above 298.16°K. at even temperature intervals.

BERKELEY, CALIF. RECEIVED SEPTEMBER 29, 1945