

# The Heat of Formation of Titanium Diboride

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Oxygen bomb calorimetry has been carried out on an analyzed sample of titanium diboride. The calculated heat of formation of this material,  $\text{TiB}_{2.02} \pm 0.01$ , was  $-77.4 \pm 0.9$  kcal. per mole.

THERE ARE several values in the literature, both estimated (1, 10) and derived, for the heat of formation of titanium diboride. The latter have been determined from vapor pressure measurements (11), mass spectrometric measurements (12, 13), high temperature calorimetric measurements (7), and heat of combustion measurements (2). These values range from  $-32$  to  $-73$  kcal. per mole.

This paper describes the determination of the amount of heat evolved from the combustion of an analyzed sample of titanium diboride in an oxygen bomb at a known initial pressure of oxygen. The method has been described (4).

The energy equivalent of the calorimeter as determined by the combustion of standard benzoic acid was  $2384.3 \pm 0.6$  cal. per degree.

## MATERIAL

The titanium diboride, a product of U. S. Borax Research Corp., was obtained through the courtesy of L. Kaufman, Manlabs, Inc. In addition to analyses made by Jarrell Ash Co., Newtonville, Mass., and LeDoux and Co., Teaneck, N. J., on this material, a complete analysis was made at this laboratory. Listed in Table I are average weight % values for each of the elements detected by the three independent analyses.

Table I. Analysis of  $\text{TiB}_2$

	Wt. %		Wt. %
Ti	68.48	Si	0.010
B	30.75	Cr	0.001
N	0.065	Mn	0.001
C	0.100	Fe	0.100
O	0.454	Ca	0.010
H	0.0072	Zr	0.010
Mg	0.002	V	0.010
Al	0.005		

The material was calculated to be (weight %): 98.12  $\text{TiB}_{2.022 \pm 0.006}$ , 0.29 TiN, 0.49 TiC, 0.79  $\text{TiO}_2$ , 0.07  $\text{H}_2\text{O}$ , 0.03  $\text{SiO}_2$ , 0.14  $\text{Fe}_2\text{O}_3$ , 0.02 CaO, and 0.05 other metallic oxides. An x-ray pattern revealed a small proportion of an unidentified constituent. The unit cell dimensions of the  $\text{TiB}_2$  were  $a = 3.029$  and  $c = 3.228$  Å, leading to a calculated density of 4.50 grams per cc.

## METHOD AND RESULTS

The sample was burned in oxygen at 25-atm. pressure on sintered disks of  $\text{TiO}_2$  (rutile). Ignition was made by passing an electrical current through a 10-mil diameter titanium fuse wire. The average initial temperature was  $24.90^\circ\text{C}$ . with an average temperature rise of  $1.15^\circ$ .

The completeness of combustion was determined by the molten KOH method (3). Combustion varied from 99.53 to 99.76% of completion. Only lines of  $\text{TiO}_2$  (rutile structure) were found on the x-ray pattern of the combustion products. A micro-examination of a combustion product showed only a single detectable crystalline phase, the rutile form of  $\text{TiO}_2$ .

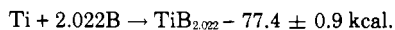
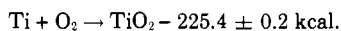
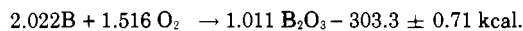
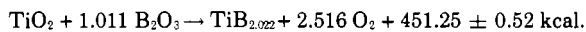
The specific heats of  $\text{TiO}_2$  and  $\text{B}_2\text{O}_3$  were taken as 0.165 and 0.216 cal. per gram per degree, respectively. The eight runs are listed in Table II.

Upon making corrections for impurities the average combustion value of  $-6352.6 \pm 6.2$  cal. per gram was increased by 1.45% to  $-6445.0$  cal. per gram. These corrections were made in a manner described previously (3) using  $-43.9$  kcal. per mole for the heat of formation of TiC (6) and  $-80.4$  kcal. per mole for the heat of formation of TiN (6, 8). The correction for impurities introduced an additional uncertainty of 0.05%, which increased the over-all uncertainty to 0.12% and yielded a value of  $-449.6 \pm 0.6$  kcal. per mole for the heat of combustion of  $\text{TiB}_{2.022}$  under bomb conditions (mol. wt.  $\text{TiB}_{2.022} = 69.76$ ). After reduction to unit fugacity of oxygen and conversion to a constant process, the result-

Table II. Heat of Combustion of Titanium Diboride

Mass Burned, G.	Wt. Fuse Wire, Mg.	Wt. $\text{TiO}_2$ , G.	Energy Equiv., Cal./Degree, Total	$\Delta T, ^\circ\text{C}$ .	Energy from		Dev. from Mean, Cal./G.
					Firing, cal.	$\text{TiB}_2$ , cal./g.	
0.4476	16.70	17.3	2390.6	1.2252	4.2	-6359.2	6.6
0.4163	16.38	16.9	2390.6	1.1390	3.9	-6346.6	6.0
0.4103	16.21	17.3	2390.6	1.1247	4.1	-6357.5	4.9
0.3853	15.87	17.0	2390.6	1.0591	4.3	-6366.7	14.1
0.4209	15.42	17.3	2390.6	1.1507	3.7	-6355.2	2.6
0.4131	15.36	17.7	2390.7	1.1286	3.5	-6348.3	4.3
0.4282	16.01	17.3	2390.6	1.1702	3.7	-6349.1	3.5
0.4391	14.32	16.6	2390.5	1.1934	2.4	-6338.4	14.2
					Av.	-6352.6	7.0
					Std. dev.		3.1

ant value,  $-451.25 \pm 0.52$  kcal. per mole, was combined with the values for the heat of formation of amorphous  $B_2O_3$ ,  $-300.0 \pm 0.7$  kcal. per mole (3), and with the heat of formation of  $TiO_2$  (rutile) (5, 9)  $-225.4 \pm 0.2$  to give  $-77.4 \pm 0.9$  kcal. per mole for the heat of formation of  $TiB_{2.022} \pm 0.006$ , as shown in the following equations:



This value is somewhat more negative than those reported earlier. If it is assumed that most of the oxygen was present as  $B_2O_3$  instead of  $TiO_2$ , both the original formula of the material and the heat of formation lie well within the stated uncertainties.

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#### LITERATURE CITED

- (1) Brewer, L., Haraldsen, H., *J. Electrochem. Soc.* **102**, 399 (1955).
- (2) Epel'baum, V.A., Starostina, M.I., *Bor. Tr. Konf. po Khim. Bora i Ego Soedin.* **1955**, 97 (1958).
- (3) Huber, E.J., Jr., Head, E.L., Holley, C.E., Jr., *J. Phys. Chem.* **68**, 3040 (1964).
- (4) Huber, E.J., Jr., Matthews, C.O., Holley, C.E., Jr., *J. Am. Chem. Soc.* **77**, 6493 (1955).
- (5) Humphrey, G.L., *Ibid.*, **73**, 1587 (1951).
- (6) *Ibid.*, p. 2261.
- (7) Lowell, C.E., Williams, W.S., *Rev. Sci. Instr.* **32**, 1120 (1961).
- (8) Neumann, B., Kroger, C., Haebler, H., *Z. anorg. Chem.* **196**, 65 (1931).
- (9) Neumann, B., Kroger, C., Kunz, H., *Z. anorg u. allgem. Chem.* **218**, 379 (1934).

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## Solubility of Cyclopropane in Some Lower Alcohols

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The solubility of cyclopropane was determined at 1-atm. partial pressure and 0° to 40° C. in methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol.

THE solubility of cyclopropane has been determined at 1-atm. partial pressure and temperatures ranging from 0° to 40° C. in five lower alcohols: methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol. A literature survey has shown that the solubilities of many of the common nonpolar gases have not been measured in several of the lower alcohols.

#### EXPERIMENTAL

**Materials.** The cyclopropane was obtained from the Matheson Co. and had a reported minimum purity of

99.5%, which was confirmed by mass spectrometry. No further purification was performed. The alcohols were dried with Linde Type 4A molecular sieves using a Soxhlet extraction unit (6). They were then distilled in a laboratory fractionation column of about 30 theoretical plates packed with ¼-inch i.d., single-turn helices. Central cuts were collected and used. The sources and physical properties of the alcohols are summarized in Table I. In each case, the alcohols had a purity of greater than 99.7% and a water content of 0.1% or less as indicated by chromatographic analysis.

**Apparatus and Procedures.** The apparatus and method have been described (7).

<sup>1</sup> Present address: Celanese Chemical Co., Corpus Christi, Tex.

Table I. Sources and Physical Properties of the Alcohols

Alcohol	Vendor's Specifications			Refractive Index, 25° C.	
	Source	Grade	B.P., ° C.	Exptl.	Lit.
Methanol	J. T. Baker Chemical Co.	Baker analyzed reagent	64.6	1.3266	1.32663(6) 1.32657(1)
Ethanol	U. S. Industrial Chemicals Co.	U.S.P. reagent quality	...	1.35946	1.35941(1, 6)
2-Propanol	J. T. Baker Chemical Co.	Baker analyzed reagent	82.3	1.37508	1.3747 (6) 1.37527(1)
1-Propanol			97.2	1.38323	1.38314(6) 1.38355(1)
1-Butanol			117.5	1.39726	1.3970 (5) 1.3974 (5) 1.3973 (1)