TABLE I

HEAT CAPACITY OF TITANIUM

At. wt. = 47.90 g., 2.5481 g. atoms

Mean T, °K.	C_p, cal./deg./g. atom	Mean T, °K.	C_p, cal./deg./g. atom
15.44	0.046	94.76	3.252
17.36	.056	104.49	3.583
18.75	.067	114.76	3.887
20.04	.081	127.07	4.215
21.31	.090	137.65	4.439
22.87	.117	148.70	4.654
24.60	.149	160.37	4.855
26.71	.192	172.74	5.020
29.32	.260	185.70	5.161
32.23	.349	198.46	5.305
35.26	.456	212.40	5.427
38.67	.590	215.29	5.466
43.54	.808	224.52	5.536
49.04	1.085	234.03	5.602
53.89	1.350	248.05	5.682
58.00	1.572	259.30	5.768
59.33	1.653	271.73	5.865
63.95	1.873	283.32	5.913
70.27	2.173	293.57	5.950
77.00	2.489	299.58	5.958
85.62	2.880	305.51	6.005

perature of intersection of the two heat capacity curves being about 180°K., and again the reason

seems to be due to the contaminants in Kelley's titanium.

The heat capacity and derived thermal functions for titanium at integral values of the temperature are presented in Table II. The entropy at 298.16°K. is 7.33 ± 0.02 e.u. of which only 0.13 e.u. was obtained by extrapolation by the Debye T^3 law. This compares with the value 7.24 e.u. obtained by Kelley.[2]

TABLE II

THERMODYNAMIC FUNCTIONS OF TITANIUM

Temp., °K.	C_p^0, cal./deg./g. atom.	S^0, cal./deg./g. atom	$H^0 - H_0^0$, cal./deg./g. atom	$-(F^0 - H_0^0)/T$, cal./deg./g. atom
15	0.040	0.013	0.15	0.003
25	0.157	.054	0.94	.017
50	1.136	.414	15.31	.108
75	2.402	1.123	50.1	.322
100	3.434	1.963	133.7	.626
125	4.155	2.811	229.0	.979
150	4.684	3.652	339.9	1.386
175	5.043	4.403	461.9	1.764
200	5.321	5.095	591.5	2.137
225	5.539	5.735	727.3	2.502
250	5.713	6.328	868.0	2.856
275	5.864	6.879	1012.8	3.196
298.16	5.976	7.334	1149.9	3.478

COLUMBUS, OHIO

The Heat of Formation of Beryllium Oxide[1]

BY LEE A. COSGROVE AND PAUL E. SNYDER

The heat of formation of beryllium oxide has been redetermined by means of the precision oxygen bomb calorimeter. The material burned consisted of high purity foil about two mils thick. Because of the high temperatures involved, the combustion was performed in beryllia crucibles. The results of this investigation yielded a value of −143.1 ± 0.1 kcal./mole for the standard heat of formation of the above compound.

A survey of the literature for values of the heat of formation of BeO showed the usual abundance of values with a range from approximately 131 to 152 kcal./mole of compound. These are listed in Table I. In this table the second, fourth, sixth, eighth and ninth values were obtained by use of the bomb calorimeter. The first, third and fifth values were obtained by solution in HF. Unfortunately, as is usually the case with older work in this field, little attention has been paid to such details as impurities and corrections. Furthermore, metal combustions have been carried out using ignition aids of various kinds. It is felt that, of the values shown, only that of Neuman and co-workers obtained in 1934 and the 1938 value of Roth deserve serious consideration. However, since the other values cannot be completely ignored without further evidence, it was considered proper to make another determination of the standard heat of formation of BeO in order to attempt to clear up the uncertainty.

TABLE I

Investigators	Date	$-\Delta H$, kcal./mole
Copaux and Philips[2]	1920	151.5
Mielenz and Wartenburg[3]	1921	135.9
Copaux and Philipps[4]	1923	131.1
Moose and Parr[5]	1924	134.?
Matignon and Marchal[6]	1926	137.4
Roth and Becker[7]	1929	135
Roth and Bückner[7]	1929	137.6
Newman, Kröger and Kunz[8]	1934	145.3 ± 0.2
Roth and Börger[9]	1937	138
Roth, Börger and Siemonsen[7]	1938	147.3 ± 0.6
This work	1951	143.1 ± 0.1

(1) This work was performed under contract with the Office of Naval Research.

(2) H. Copaux and C. Phillips, Compt. rend., 171, 630 (1920).

(3) W. Mielenz and H. von Wartenburg, Z. anorg. allgem. Chem., 116, 267 (1921).

(4) H. Copaux and C. Phillips, Comp. rend., 176, 579 (1923).

(5) J. Moose and S. Parr, THIS JOURNAL, 46, 2656 (1924).

(6) C. Matignon and G. Marchal, Compt. rend., 183, 927 (1926).

(7) W. Roth, E. Börger and H. Siemonsen, Z. anorg. allgem. Chem., 239, 321 (1938).

(8) B. Newman, C. Kröger and H. Kunz, ibid., 218, 379 (1934).

(9) W. Roth and E. Börger, Ber., 70B, 48 (1937).

Experimental

Apparatus.—In this investigation the precision bomb calorimeter used previously[10] was employed. This instrument was patterned after the one developed by Dickinson[11] at the National Bureau of Standards. The bridge used with the resistance thermometer was a Leeds and Northrup model G2. The thermometer was calibrated according to the recommendations[12] for the International Temperature Scale.

Material.—The material used in this research consisted of high purity foil approximately 4 mils thick. Since the material "as received" had a fairly rough dull surface, this surface was ground or smoothed by means of a power alundum cloth wheel in such a way that the thickness of the foil was reduced to about 2 mils. This treatment gave a bright, clean, metallic appearance to the foil surface. An assay run on this material gave an average value of 99.8% Be. Spectrographic analysis showed 0.4% Al; less than 0.01% each of Ca, Cr, Fe and Mn; less than 0.015% each of Mn and Si. Nitrogen was determined by an appropriate Kjeldahl process and was found to average 0.026%. Vacuum fusion determinations showed an oxygen content of 0.022%. In general all of the impurities can be considered as small in amount with the exception of the aluminum. However, as will be indicated later, corrections were made for the several impurities.

Calibration of the Calorimeter.—In inorganic combustion work the precision obtainable is such that calibration of the calorimeter by means of a standard sample such as benzoic acid is justified. Accordingly, standard sample No. 39f was obtained from the National Bureau of Standards and used for this purpose. The results of the calibration runs, as well as those from the beryllium combustion, were treated by means of Dickinson's[11] graphical method. In view of the fact that conditions in the bomb did not quite correspond to standard, the necessary corrections were made as outlined in the certificate accompanying the benzoic acid sample.

After each combustion, analysis was made for nitric acid and the proper correction made. Actually, this correction usually turned out to be negligible. The reason for this is uncertain. Although it might be argued that the acid reacts with the crucible, the same results are obtained when calibrations are made using a fused silica dish in place of a refractory crucible. In this case it is hardly likely that the acid would react with the smooth fused dish.

One of the requirements of Dickinson's graphical method is that the calibration and combustion runs be of the same shape and duration. Since the metal combustion required a crucible to protect the bomb against the molten oxide formed, it was necessary to make the calibration with a similar crucible in place.

Since it is the practice of this Laboratory to make 12–15 combustions of a given kind, sufficient information is available to obtain a value for the precision of the energy equivalent of the calorimeter. This will, of course, be a random precision only. It was calculated on the basis of the recommendations of Rossini and Deming.[13] The error is defined as $C = 2\sqrt{\Sigma\Delta^2/n(n-1)}$. For this work the value of "C" was 0.03%.

Combustion of Beryllium.—When metal is ignited in high pressure oxygen, the temperature attained is so high that the oxide formed in the combustion melts and forms a solid fused mass upon cooling. To protect the bomb, such combustions must be made within a refractory crucible. In order that no slagging heat effects occur, the crucible should either be made of the oxide in question or be coated on its inside surface with that oxide.

In this work beryllia crucibles were obtained from a commercial supplier. These had been made by sintering fine granulated BeO to temperatures approaching 2000°. Since the thermal shock broke the crucible, each combustion necessitated the use of a new one which had a slightly different weight. For this reason it was necessary to calculate an energy equivalent for each individual combustion. As

was stated previously, a crucible was in place during the calibration. This meant that the calibration energy equivalent was modified for each combustion by an amount determined by the difference in weights of the two crucibles in question. This correction averaged about 0.1%. In general, in this kind of work it is assumed that the calibration crucible is subjected to approximately the same thermal treatment as the combustion crucible thus canceling out small second-order effects. Certainly the crucible as a whole does not reach high temperatures, since the combustion and subsequent cooling is too rapid for this to occur.

In the combustion a suitable quantity of foil was cut into narrow strips which were stacked in the form of an open pyramid in the bottom of the crucible. The iron fuse wire was woven through small pinholes in another strip of foil which was suspended above the open top of the crucible. Closing the firing circuit set fire to the Be fuse strip which then fell on the pyramid below igniting the whole mass. Suitable analysis showed that combustion was complete.

In the combustion runs the necessary corrections were made to the experimental values in order that the value of ΔE obtained could be assigned to the conditions prevailing at the instant of ignition. In line with the requirements of Dickinson's method, an attempt was made to keep the weight of Be the same in each case. These masses, after correction to "*vacuo*," varied between 0.6747 and 0.6764 g. The heat of combustion values varied from 65,490 to 66,207 joules per gram. The mean value of the eleven experiments was 66,083.1 international joules per gram of sample. Using the relation mentioned previously, the combustion error was ±0.06%.

Calculations.—In these calculations the atomic weight of beryllium was assumed to be 9.013. Taking into consideration the several impurities, there is obtained a value of 99.5% for the purity of the sample whose ΔE of combustion was found to be as indicated above. Assuming the several impurity percentages to be correct and making use of available heat of formation data,[14] corrections were made for the seven metals and the two gases. These corrections amounted to 136.8 joules, 90% of which was contributed by the aluminum. These data give ΔE for the reaction

$$Be(c) + \tfrac{1}{2}O_2 \ (g., 300.36°K., 30 \ atm.) = BeO(c)$$
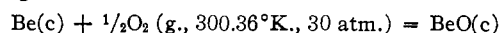
$$\Delta E = -597.312 \text{ international kilojoules}$$

To change the oxygen to unit fugacity, the data of Rossini and Frandsen[15] are used. Under the conditions prevailing, $(\delta E/\delta P)_T = -6.51$ joules per mole per atmosphere. Thus there results
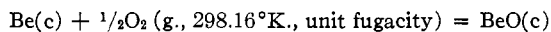
$$Be(c) + \tfrac{1}{2}O_2 \ (g., 300.36°K., unit \ fugacity) = BeO(c)$$
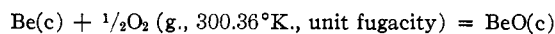
$$\Delta E = -597.410 \text{ international kilojoules}$$

Using the relation $\Delta H = \Delta E + RT\Delta n$ to change the above, yields

$$Be(c) + \tfrac{1}{2}O_2 \ (g., 300.36°, unit \ fugacity) = BeO(c)$$
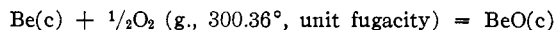
$$\Delta H = -598.658 \text{ international kilojoules}$$

Changing to standard temperature gives

$$Be(c) + \tfrac{1}{2}O_2 \ (g., 298.16°K., unit \ fugacity) = BeO(c)$$

$$\Delta H = -598.6 \pm 0.4 \text{ international kilojoules}$$

or, assuming the "defined" calorie to be 4.1833 international joules

$$\Delta H = -143.1 \pm 0.1 \text{ kcal./mole}$$

PITTSBURGH, PA.

(10) P. E. Snyder and H. Seltz, THIS JOURNAL, **67**, 683 (1945).

(11) H. C. Dickinson, *Bull. Bur. Standards*, **11**, 189 (1915).

(12) H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

(13) F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(14) "Selected values of chemical thermodynamic properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(15) F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).