HEATS OF COMBUSTION OF DIAMOND AND OF GRAPHITE

By Ralph S. Jessup

ABSTRACT

Measurements were made of the heats of combustion of one artificial graphite, two natural graphites, and two samples of diamond. The bomb calorimeter used was calibrated electrically and by means of benzoic acid. The amount of reaction in each combustion experiment was determined from the mass of carbon dioxide formed. This method of determining the amount of reaction automatically eliminates the effect of unburned carbon and of some impurities. It was found, however, that results for different samples did not agree unless the samples were purified. Two methods of purification were used: (a) heating in vacuo to 1,800° C and (b) treatment with hydrochloric and hydrofluoric acids and subsequent heating in vacuo to 200° C to remove traces of the acids. Both methods yielded graphite containing only small amounts of impurities. The mean value obtained for the heat of combustion $(-\Delta H)$ of the purified graphites in oxygen at 25° C and a constant pressure of 1 atmosphere to form gaseous carbon dioxide at the same temperature and pressure was 393.396 international kilojoules per mole (44.010 g of CO_2). The maximum deviation of the mean value for any one of the purified samples from this value was 0.021 percent.

The two samples of diamond, purified by treatment with aqueous hydrochloric and hydrofluoric acids and subsequently heated in vacuo to about 570° C, had average particle sizes of 2.5 μ and 39.5 μ, respectively, and yielded the following respective mean values for the heat of combustion $(-\Delta H)$ at 25° C and 1 atmosphere, in oxygen to form gaseous carbon dioxide: 395.771 and 395.287 international kilojoules per mole. The difference between the two values, which is several times the estimated uncertainty of the measurements, is in proper direction to be accounted for on the basis of particle size, but the first sample appears to be not fine enough to account quantitatively for the difference.

CONTENTS

I. INTRODUCTION

The work described in this paper is part of a joint investigation by the National Bureau of Standards and the Coal Research Laboratory of the Carnegie Institute of Technology in Pittsburgh. When this

work was begun the only published measurements of the heats of combustion of the various forms of carbon which approach modern requirements as to accuracy were those of Roth and his coworkers [10, 11, 12].[1] Since Roth's measurements were made there have been improvements in the experimental technique of heat-of-combustion measurements and in the interpretation of bomb calorimetric data, which made a new investigation of the heat of combustion of carbon desirable.

That part of the work which was done at the Coal Research Laboratory of the Carnegie Institute of Technology is described by Dewey and Harper [2] in the preceding paper in this Journal. It will be seen from their paper that their results on three natural graphites and two samples of an artificial graphite are in excellent agreement, but that their value for Ceylon natural graphite is lower by about 0.2 percent than the mean of their values for the other graphites.

The present work was originally intended to include measurements of the heat of combustion of diamond only. However, at the suggestion of Dr. Lowry, Director of the Coal Research Laboratory, measurements were also made on three of the graphites on which measurements had been made by Dewey and Harper, namely, artificial graphite and Ceylon and Buckingham natural graphites, partly in the hope of finding the cause of their lower value for Ceylon natural graphite and partly for the purpose of obtaining the difference between the heats of combustion of graphite and diamond from measurements made in the same laboratory.

II. APPARATUS AND METHODS

The apparatus, experimental procedure, and methods of calculating results have been described in detail previously [3, 6], so that only a brief description will be given here.

The measurements were made by means of a calorimeter which is essentially the same as that described by Dickinson [3]. The method of measurement consisted in comparing the rise in temperature of the calorimetric system produced by a measured quantity of energy, with the rise in temperature of the same calorimetric system over approximately the same temperature interval produced by the combustion of a sample of carbon in the bomb. The amount of reaction in each experiment was measured by absorbing the resulting carbon dioxide in Ascarite (a sodium hydroxide-asbestos mixture) and weighing [5, 8], using for the atomic weights of carbon and oxygen the values 12.010 and 16.0000, respectively. The glass-stoppered U-tubes containing the Ascarite were filled with hydrogen for weighing, both before and after absorption of the carbon dioxide, in order to minimize the error resulting from uncertainty in the change in volume of the Ascarite upon absorption of carbon dioxide [8].

Usually a small quantity of carbon monoxide was formed in the bomb, amounting on the average to about 0.01 percent of the carbon dioxide formed. The quantity of carbon monoxide formed in each experiment was determined by passing the gas from the bomb, after absorption of the carbon dioxide, through a copper tube heated to redness, absorbing the resulting carbon dioxide in Ascarite and weighing.

---

[1] Numbers in brackets indicate the literature references given at the end of this paper.

Before heating the copper tube for the purpose of oxidizing the carbon monoxide, the absorption train was always flushed with oxygen from the supply tank. However, there is a possibility that some water vapor might be formed by oxidation of hydrogen adsorbed on the copper or copper oxide in the copper tube, or of hydrogen present as a result of incomplete flushing of the absorption train. Consequently, a drying tube was placed between the copper tube and the U-tube containing the Ascarite.

It was possible to close the bomb and its valve tightly enough so that there was no perceptible leakage of gas either before or after a combustion experiment. It was found, however, that during the combustion there was always a slight leakage of gas. The amount of gas which leaked out was determined in each experiment by means of the arrangement shown in figure 1. The inverted graduated glass tube T, was initially filled with water, and the gas which leaked out either through the valve or past the gold gasket, G (1 mm wide), was caught in the tube, and its volume observed at the end of the experiment. The bomb threads and the bearing surface, S, were lubricated with vaseline, which also prevented water
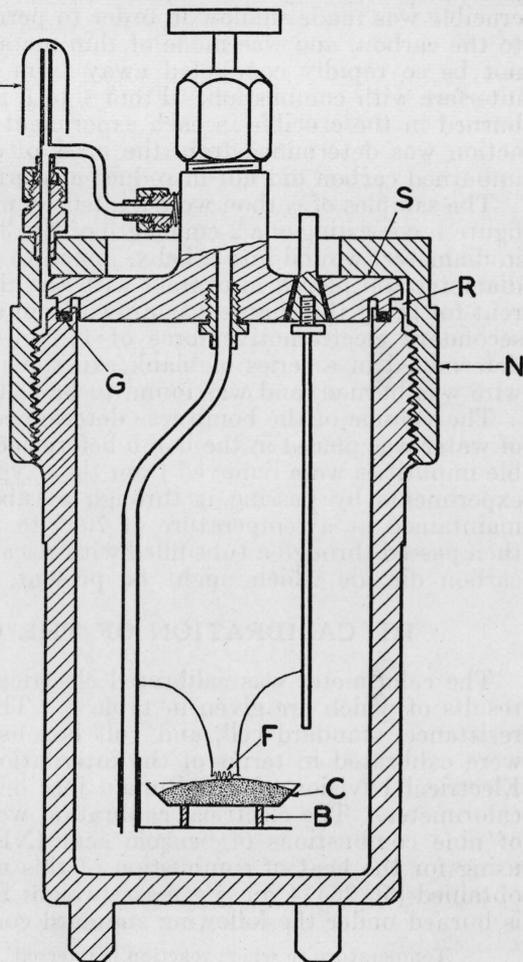
FIGURE 1.—*Schematic drawing of bomb.*

T, graduated glass tube for measuring gas leakage; N, bomb nut; G, gold washer; S, surface between bomb nut and bomb cover; R, annular space between bomb and nut; F, electric fuse of iron wire; C, platinum crucible; B, beryllium oxide ring.

from seeping into the space, R, and displacing the air initially present in this space. The vaseline was carefully removed after each experiment and a weighed amount (0.4 g) was placed on the threads and the surface, S, of the bomb nut, N, before the next experiment. The volume of gas which leaked out during an experiment amounted usually to 0.002 or 0.003 percent of the total quantity of gas in the

bomb. Since the concentration of carbon dioxide in the valve and in the vicinity of the washer, G (fig. 1), was probably very small at the time the leakage occurred, the observed mass of carbon dioxide was not corrected for the leakage.

The samples of about 1 g of carbon were burned in a shallow crucible, C, made of sheet platinum about 0.05 mm thick, which was supported upon a beryllium oxide ring, B, as shown in figure 1. The crucible was made shallow in order to permit ready access of oxygen to the carbon, and was made of thin metal in order that heat might not be so rapidly conducted away from the burning carbon as to interfere with combustion. From 1 to 5 mg of carbon was left unburned in the crucible in each experiment, but as the amount of reaction was determined from the mass of carbon dioxide formed the unburned carbon did not introduce any error into the measurements.

The samples of carbon were ignited by means of an electric fuse, F, figure 1, consisting of a 2-cm length of No. 36 AWG iron wire (0.13 mm in diameter) wound into a helix, joined to platinum leads 0.25 mm in diameter and placed in contact with the charge of carbon. The current for firing the charge was drawn from a toy transformer having a secondary electromotive force of 14 volts. The firing energy was determined in a series of blank experiments in which only the iron wire was burned, and was found to be 23.0 j [6].

The volume of the bomb was determined to be 377 cm³. One cm³ of water was placed in the bomb before each experiment. Combustible impurities were removed from the oxygen used in the combustion experiments by passing it through a tube filled with copper oxide maintained at a temperature of 700° to 800° C. The oxygen was then passed through a tube filled with Ascarite in order to remove any carbon dioxide which might be present.

III. CALIBRATION OF THE CALORIMETER

The calorimeter was calibrated electrically in 14 experiments, the results of which are given in table 1. The potentiometer, standard resistance, standard cell, and volt box used in these measurements were calibrated in terms of the international electrical units by the Electrical Division of this Bureau just before the calibration of the calorimeter. The electrical calibration was supplemented by means of nine combustions of benzoic acid (NBS Standard Sample 39e), using for the heat of combustion of this material the value recently obtained [6], 26414 int. j/g mass (weight in vacuo) when the sample is burned under the following standard conditions:

Temperature to which reaction is referred_____ 30° C.
Initial oxygen pressure in bomb at 30° C_____ 30 atm.
Mass of water placed in bomb per liter of bomb volume____ 3 g.
Mass of benzoic acid burned per liter of bomb volume___ 3 g.

The results of the calibration by means of benzoic acid are given in table 2, and the mean of these results is seen to be in agreement within 0.008 percent with the mean of the results of the electrical calibration given in table 1.

TABLE 1.—*Results of electrical calibration of calorimeter*

Experiment	Energy equivalent at 28.5° C	Deviation from mean	
	Int. j/° C	*Int j/° C*	*Percent*
1	13498. 6	+0. 1	+0. 001
2	13497. 0	−1. 5	−. 011
3	13495. 9	−2. 6	−. 019
4	13496. 0	−2. 5	−. 019
5	13496. 8	−1. 7	−. 013
6	13496. 4	−2. 1	−. 016
7	13503. 4	+4. 9	+. 036
8	13502. 8	+4. 3	+. 032
9	13500. 4	+1. 9	+. 014
10	13500. 6	+2. 1	+. 016
11	13495. 5	−3. 0	−. 022
12	13499. 7	+1. 2	+. 009
13	13499. 7	+1. 2	+. 009
14	13495. 4	−2. 8	−. 021
Mean	13498. 5	±2. 3	±. 017

TABLE 2.—*Results of benzoic acid calibration of calorimeter*

Experiment	Energy equivalent at 28.5° C	Deviation from mean	
	Int. j/° C	*Int. j/° C*	*Percent*
1	13498. 5	−1. 1	−0. 008
2	13490. 2	−9. 4	−. 070
3	13500. 1	+0. 5	+. 004
4	13495. 4	−4. 2	−. 031
5	13499. 8	+0. 2	+. 002
6	13501. 6	+2. 0	+. 015
7	13501. 2	+1. 6	+. 012
8	13510. 3	+10. 7	+. 079
9	13499. 5	−0. 1	−. 001
Mean	13499. 6	±3. 3	±0. 025

The mean value for the energy equivalent obtained from the electrical calibration of the calorimeter was used in calculating the results of experiments 1 to 5, inclusive, on Ceylon graphite (table 7). After experiment 5 on Ceylon graphite, an accident to the calorimeter necessitated repairs involving the addition to the calorimeter vessel of 11.9 g of solder (50 percent of tin, 50 percent of lead), and the removal of 1.3 g of brass. After the repairs, the weight of water used in the calorimeter was decreased by 30.6 g. These changes involved a change in the energy equivalent of the calorimeter, the calculation of which is shown in table 3.

TABLE 3.—*Change in energy equivalent of calorimeter as a result of repairs*

Material added	Mass added	Specific heat at 28.5° C.	Heat capacity of material	Authority for specific-heat value
	g	*Int. j/g °C*	*Int. j/°C*	
Solder	+11.9	0.178	+2.12	ICT 5, 93, 94.
Brass	−1.3	.384	−0.50	ICT 5, 121.
Water	−30.63	4.173	−127.8	ICT 5, 113.

Decrease in energy equivalent	126.2
Original energy equivalent	13498.5
Energy equivalent after repairs	13372.3

The value given in table 3 for the energy equivalent of the calorimeter after repairs was used in the calculation of the results of experiments 6 to 16, inclusive, on Ceylon graphite (table 7), experiments 1 to 8, inclusive, on Buckingham graphite (table 8), experiments 1 to 4, inclusive, on the first sample of artificial graphite (table 9), and experiments 1 to 3, inclusive, on the second sample of artificial graphite (table 9).

For the remaining experiments a new calorimetric resistance thermometer was used. The calorimeter was calibrated with the new thermometer by means of 12 combustions of benzoic acid (Standard Sample 39e), using for the heat of combustion of this material the value given above. The results of this calibration of the calorimeter are shown in table 4.

TABLE 4.—*Results of benzoic acid calibration of calorimeter with new thermometer*

Experiment	Energy equivalent at 28.84 °C	Deviation from mean	
	Int. j/°C	*Int. j/°C*	*Percent*
1	13365.3	−0.3	−0.002
2	13367.3	+1.6	+.012
3	13366.1	+0.2	+.002
4	13364.4	−1.5	−.011
5	13367.4	+1.5	+.011
6	13364.2	−1.7	−.013
7	13365.7	−0.2	−.002
8	13365.3	−0.6	−.005
9	13367.3	+1.4	+.010
10	13366.1	+0.2	+.002
11	13364.4	−1.5	−.011
12	13367.4	+1.5	+.011
Mean	13365.9	±1.0	±0.008

The difference between the mean value of the energy equivalent of the calorimeter given in table 4 and the value given in table 3 was found to be caused by a difference in the temperature intervals defined by the two thermometers under the conditions of the calorimetric experiments. The old thermometer was of an experimental type, and results obtained with it were not quite as precise as those obtained with the new thermometer, which was a calorimetric thermometer of the type which has been used at this Bureau for many years. The difference between the two thermometers did not introduce any systematic error into the measurements of heats of combustion, since

the value of energy equivalent used in calculating the results of heat-of-combustion measurements with either thermometer was the value obtained in the calibration experiments with the same thermometer. In the tabulations of the results of the heat-of-combustion measurements given later in this paper, the values of energy equivalent used for the various experiments are designated by the letters A, B, and C, preceding the experiment number, where these letters have the following meanings: A, mean value of energy equivalent from table 1; B, value of energy equivalent from table 3; and C, mean value of energy equivalent from table 4.

IV. MEASUREMENTS OF HEATS OF COMBUSTION

1. MATERIAL

Measurements were made on the three samples of graphite mentioned previously and on two samples of diamond. The first diamond sample was purchased from a diamond grinding establishment in the Netherlands, with the assistance of Prof. P. E. Verkade of the Commercial University in Rotterdam. This sample was in the form of a very fine powder. The size distribution of the particles was measured microscopically [2] and it was found that the average diameter of the particles was 2.5 μ. Average particle diameter is here defined on the basis that if each particle had the average diameter the surface of the powder per gram of diamond would be the same as that of the actual sample. The ash content [3] of the sample when received was 0.30 percent. Successive treatments of the sample with hydrochloric and hydrofluoric acids [4] reduced the ash content to 0.05 percent. The second sample of diamond was purchased from a dealer in commercial diamonds in this country. It consisted originally of small pieces, of the order of 1 mm in diameter, most of which were clear and "water white." Discolored pieces were rejected; the remainder of the sample was ground in a stainless-steel mortar and treated with hydrochloric and hydrofluoric acids, after which the ash content of the sample was found to be 0.02 percent. The average particle size of the second sample of diamond after grinding was 39.5 μ. About 2 g of the second sample was ground to an average particle size of 22.9 μ.

The samples of graphite were ground in an agate mortar, and some measurements of heat of combustion were made on each material, without further treatment of the sample. Samples of the two natural graphites were then heated in vacuo in an Acheson graphite crucible by means of an induction furnace to various temperatures, the maximum temperature in each case being about 1,800° C.[5] The mercury-vapor pump used in maintaining the vacuum was capable of reducing the pressure to $<10^{-4}$ mm of mercury when the samples of graphite were cold, but at the higher temperatures the evolution of gas from the thermal insulating material around the graphite crucible was so great that the pressure could not be reduced below about 0.02 mm. The pump was connected to the vessel inclosing the graphite through a trap immersed in liquid air.

---

[2] The microscopic examination of the two samples of diamond was made by C. P. Saylor of this Bureau.
[3] All ash determinations mentioned in this paper were made by C. J. Rodden of this Bureau.
[4] The chemical treatment of both samples of diamond and one sample of graphite and the grinding of the second sample of diamond were done by H. B. Knowles of this Bureau.
[5] W. F. Roeser and A. I. Dahl of this Bureau assisted in heating the samples of graphite and in measurement of the temperatures.

Spectrochemical analyses [6] were made on some of the samples of graphite and diamond, and on the ash from some of the samples. The results of these analyses are given in tables 5 and 6.

TABLE 5.—*Results of spectrochemical analyses of diamond and graphites*

Sample	Major impurities	Traces
Artificial		Si, Mg, Cu.
Buckingham, untreated	Si, Al, Fe, Mg, Ca, Mn, Cu, Na	Hg, Pb.
Buckingham, heated to 1,820° C in vacuo	Si, Mg	Hg, Sn, Fe, Cu.
Ceylon, untreated	Si, Al, Ca, Fe, Mg, Cu, Mn	Na, Pb, Ni, Ag, Hg.
First sample of diamond, untreated	Si, Pb, Mg, Sn, Al, Ca	Fe, B.

TABLE 6.—*Results of spectrochemical analyses of samples of ash*

Carbon sample	Major constituents	Minor constituents	Traces
Buckingham, untreated	Si, Ca, Al, Fe	Mn, V, Mg	Sr, Ba, Ti.
Ceylon, untreated	Si, Ca, Fe	Mn, Al, Mg	Sr, Cr, Ni.
Ceylon, heated to 1,750° C	Fe	Si, Ca, V, Mn, Mg	Al, Ba, Ti, Cr.
Diamond, untreated	Si, Cu, Al	Pb, Ni, Sn, Ti, Fe, Cr, Zr, Ba, Sr, Mg.	V, Mn.

2. CEYLON NATURAL GRAPHITE

The results obtained on this sample are shown in table 7, which is largely self-explanatory. The values used for the energy equivalent of the calorimeter are for the initial calorimetric system, including the oxygen and the charge of carbon, at the mean temperature of the experiment. The values of heat of combustion are therefore referred to the final temperature of the calorimeter, which was sufficiently near to 30° C in all experiments so that the correction to 30.00° C was negligible. The observed values of heat of combustion under the conditions of the bomb process, $-\Delta U_B$, were reduced to the energy change, $-\Delta U_R$, for the reaction at 30° C and a pressure of 1 atmosphere by means of Washburn's complete correction equation [13], modified so as to apply to 30° C instead of 20° C. The Washburn correction for carbon at 30° C is about 9 percent smaller than at 20° C. The first six measurements listed in table 7 were made on a sample of Ceylon graphite which had received no treatment except grinding in an agate mortar. The value of $-\Delta U_R$ from these experiments is seen to be even lower than (although roughly the same as) the value obtained by Dewey and Harper [2] for the Ceylon graphite. Dewey and Harper heated their sample of Ceylon graphite to 225° C in vacuo, and it seemed possible that this heating might be the cause of the difference between their value for Ceylon graphite and that obtained from the first six experiments listed in table 7. To test this hypothesis samples of Ceylon graphite were heated in vacuo in an Acheson graphite crucible by means of an induction furnace to various temperatures ranging from 850° to 1,750° C, and a few measurements were made of the heat of combustion of each sample. It will be seen from table 7 that heating the graphite to 850° C caused an increase in apparent heat of combustion of 0.25 percent, that heating to 900° or 1,200° C caused a further increase of about 0.06 percent, while heating

---
[6] The spectrochemical analyses were made by B. F. Scribner of this Bureau.

to 1,750° C caused a decrease of about 0.07 percent from the value observed after heating to 1,200° C. It was also observed that after heating to 1,750° C the ash content of the sample had decreased from its initial value, 1.50 percent, to 0.06 percent. This suggested that the initial low value for the heat of combustion of the Ceylon graphite, and the changes in heat of combustion upon heating to various temperatures were caused by chemical reactions involving the impurities in the sample. Carbonates, for example, would be decomposed when the graphite was burned in the bomb, resulting in a low value for the observed heat of combustion of the graphite, while carbides, if they burned, would cause the observed heat of combustion to be too high. However, since it has been suggested by Roth [10, 11, 12] that there may be two forms of graphite, there was a possibility that the changes in observed heat of combustion of the Ceylon graphite upon heating might have been at least partly the result of a transformation from one form to the other caused by the heating. In order to determine whether the changes in heat of combustion resulted from reactions involving the impurities, or from a change in the structure of the graphite, a sample of Ceylon graphite which had not been heated was purified by treatment with hydrochloric and hydrofluoric acids, and was then heated in vacuo to about 200° C to remove traces of the acids and of water. After this treatment, the ash content of the sample was found to be 0.02 percent. The results of four measurements of the heat of combustion of the chemically purified material are given in table 7 (experiments 17 to 20, inclusive). A part of the chemically purified sample was then heated in vacuo to 1,820° C, and four measurements were made of the heat of combustion of the material after heating (experiments 21 to 24, table 7). It will be seen from table 7 that the results of the measurements on the sample purified by heating, the sample purified chemically and not heated above 200° C, and the sample purified chemically and subsequently heated to 1,820° C are in agreement within the uncertainty of the measurements. This indicates that the initial low value for the heat of combustion of the Ceylon graphite, and the changes in heat of combustion upon heating to various temperatures were the result of reactions involving the impurities in the sample, rather than the result of a transformation from one form of graphite to another.

<center>TABLE 7.—*Results on Ceylon natural graphite*</center>

Experiment [a]	Carbon dioxide formed	Initial oxygen pressure at 30° C	Final temperature of calorimeter	Observed heat of combustion $-\Delta U_B$	Washburn correction	$-\Delta U_R$ at 30° C	Deviation from mean		Remarks
	Moles	*atm*	*°C*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Percent*	
A1	0.082053	34.4	29.38	392.569	−0.392	392.177	−0.275	−0.070	Sample was ground in an agate mortar and burned without further treatment. Ash 1.50 percent.
A2	.082490	34.4	29.62	392.994	−.392	392.602	+.150	+.038	
A3	.082175	34.8	29.86	392.878	−.396	392.482	+.030	+.008	
A4	.081876	33.6	29.97	392.874	−.384	392.490	+.038	+.010	
A5	.088970	33.5	30.02	392.807	−.387	392.420	−.032	−.008	
B6	.081787	34.2	29.83	392.933	−.390	392.543	+.091	+.023	
Mean						392.452	±0.103	±0.026	
B7	0.083484	34.1	30.03	393.992	−0.389	393.603	−0.033	−0.008	Heated in vacuo to about 900° C for 3 hours.
B8	.083470	34.0	29.57	394.058	−.389	393.669	+.033	+.008	
Mean						393.636	±0.033	±0.008	
B9	0.085105	33.6	30.02	393.808	−0.386	393.422	−0.016	−0.004	Heated in vacuo to about 850° C for 18 hours.
B10	.085876	33.9	30.13	393.844	−.390	393.454	+.016	+.004	
Mean						393.438	±0.016	±0.004	
B11	0.083211	34.0	29.94	393.954	−0.389	393.565	−0.111	−0.028	Heated in vacuo to about 1,200° C for 3 hours.
B12	.083523	33.9	29.90	394.172	−.388	393.784	+.110	+.028	
Mean						393.674	±0.110	±0.028	
B13	0.083620	33.5	30.11	393.858	−0.384	393.474	+0.072	+0.018	Heated in vacuo to 1,750° C for 1¼ hours. Ash 0.06 percent.
B14	.083936	34.0	29.90	393.808	−.389	393.419	+.017	+.004	
B15	.084979	34.0	29.89	393.728	−.390	393.338	−.064	−.016	
B16	.083573	33.7	29.81	393.764	−.386	393.378	−.028	−.007	
Mean						393.402	±0.045	±0.011	
C17	0.085399	34.0	30.11	393.769	−0.390	393.379	−0.015	−0.004	Purified by treatment with HCl and HF. Traces of acids and moisture were removed by heating in vacuo to 200° C. Ash 0.02 percent.
C18	.083397	34.1	30.06	393.739	−.390	393.349	−.045	−.012	
C19	.085257	34.0	30.11	393.799	−.390	393.409	+.015	+.004	
C20	.082830	33.9	30.16	393.829	−.388	393.441	+.047	+.012	
Mean						393.394	±0.030	±0.008	
C21	0.082865	34.3	30.04	393.634	−0.392	393.242	−0.082	−0.021	Purified by treatment with HCl and HF, and then heated in vacuo to 1,820° C for 1¼ hours.
C22	.083031	34.3	30.09	393.648	−.392	393.256	−.068	−.017	
C23	.083238	34.0	30.12	393.800	−.389	393.411	+.087	+.022	
C24	.084767	34.1	30.10	393.778	−.391	393.387	+.063	+.016	
Mean						393.324	±0.075	±0.019	

[a] See text, p. 481, for significance of letters preceding experiment numbers.

3. BUCKINGHAM NATURAL GRAPHITE

The results of measurements on this sample of graphite are given in table 8. It will be seen that heating to 1,200° C caused practically no change in heat of combustion. Heating to 1,820° C reduced the ash content of the sample from 0.24 to 0.006 percent, and caused a reduction in heat of combustion of 0.06 percent. The value obtained for the heat of combustion of the purified sample is seen to differ by only 0.015 percent from the mean of the values for the purified samples of Ceylon graphite.

TABLE 8.—*Results on Buckingham natural graphite*

Experiment	Carbon dioxide formed	Initial oxygen pressure at 30° C	Final temperature of calorimeter	Observed heat of combustion $-\Delta U_B$	Washburn correction	$-\Delta U_R$	Deviation from mean		Remarks
	Moles	*atm*	*°C*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Percent*	
B1	0.082913	33.7	29.72	393.814	−0.386	393.428	−0.093	−0.024	Sample was ground in an agate mortar and burned without further treatment. Ash 0.24 percent.
B2	.084410	34.0	29.98	394.003	−.389	393.614	+.093	+.024	
Mean						393.521	±0.093	±0.024	
B3	0.083288	33.9	29.87	393.877	−0.387	393.490	−0.080	−0.020	Heated in vacuo to 1,200° C for 3 hours.
B4	.083700	33.7	29.74	394.080	−.385	393.695	+.125	+.032	
B5	.084024	34.0	29.90	393.914	−.389	393.525	−.045	−.011	
Mean						393.570	±0.083	±0.021	
B6	0.080557	33.3	29.76	393.695	−0.380	393.315	+0.005	+0.001	Heated in vacuo to 1,820° C for 1¼ hours. Ash 0.006 percent.
B7	.082820	33.2	29.83	393.720	−.380	393.340	+.030	+.008	
B8	.081344	33.1	29.94	393.654	−.378	393.276	−.034	−.009	
Mean						393.310	±0.023	±0.006	

4. ARTIFICIAL GRAPHITE

The results of measurements on two samples of this material are listed separately in table 9, although there was no reason for believing that there was any difference between the two samples. In experiments 3, 4, 5, and 6 on the first sample about 5 mg of benzoic acid was used to start the combustion, the electric fuse being placed in contact with the benzoic acid and not in contact with the graphite. The purpose of these experiments was to determine whether any error resulted from conduction of electricity through the powdered graphite in the usual method of igniting the sample. The results for experiments 3, 4, 5, and 6 are in agreement within the limits of experimental error with the other results on the artificial graphite.

TABLE 9.—*Results on artificial graphite*

Experiment	Carbon dioxide formed	Initial oxygen pressure at 30° C	Final temperature of calorimeter	Observed heat of combustion $-\Delta U_B$	Washburn correction	$-\Delta U_R$ at 30° C	Deviation from mean		Remarks
	Moles	*atm*	*°C*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Percent*	
B1	0.085838	33.5	29.94	393.784	−0.385	393.399	−0.050	−0.013	First sample. In experiments 3, 4, 5, and 6 about 5 mg of benzoic acid was used to start the combustion. Ash <0.002 percent.
B2	.084434	33.4	29.86	393.734	−.383	393.351	−.098	−.025	
B3	.083970	34.0	30.03	393.894	−.389	393.505	+.056	+.014	
B4	.083067	33.6	29.94	393.814	−.385	393.429	−.020	−.005	
C5	.085125	34.5	30.18	393.900	−.396	393.504	+.055	+.014	
C6	.084061	34.6	30.08	393.900	−.396	393.504	+.055	+.014	
Mean						393.449	±0.056	±0.014	
B1	0.083637	33.3	29.89	393.756	−0.382	393.374	−0.064	−0.016	Second sample. Ash not determined.
B2	.085022	33.2	29.92	393.906	−.382	393.524	+.086	+.022	
B3	.085836	33.2	29.98	393.798	−.382	393.416	−.022	−.006	
Mean						393.438	±0.057	±0.015	

5. RÉSUMÉ OF RESULTS ON PURIFIED GRAPHITE

The results of all the measurements on purified samples of graphite are assembled in table 10.

TABLE 10.—*Résumé of results on purified graphite*

Sample and method of purification	Experiment	$-\Delta U_R$ at 30° C	Deviation from mean of all observations		Mean for sample	Uncertainty of mean for sample	Deviation from mean of all observations	
		Int. kj/mole	*Int. kj/mole*	*Percent*	*Int. kj/mole*	*Percent*	*Int. kj/mole*	*Percent*
Ceylon natural graphite heated in vacuo to 1,750° C. Ash 0.06 percent_____	B13 B14 B15 B16	393. 474 393. 419 393. 338 393. 378	+0. 081 +. 026 −. 055 −. 015	+0. 021 +. 007 −. 014 −. 004	393. 402	±0. 019	+0. 009	+0. 002
Ceylon graphite purified by treatment with HCl and HF. Ash 0.02 percent_____	C17 C18 C19 C20	393. 379 393. 349 393. 409 393. 441	−. 014 −. 044 +. 016 +. 048	−. 004 −. 011 +. 004 +. 012	393. 394	±. 026	+. 002	. 001
Ceylon graphite purified by treatment with HCl and HF. Sample then heated in vacuo to 1,820° C_____	C21 C22 C23 C24	393. 242 393. 256 393. 411 393. 387	−. 151 −. 137 +. 018 −. 006	−. 038 −. 035 +. 005 +. 002	393. 324	±. 032	−. 068	−. 017
Buckingham graphite heated in vacuo to 1,820° C. Ash 0.006 percent_____	B6 B7 B8	393. 315 393. 340 393. 276	−. 078 −. 053 −. 117	−. 020 −. 013 −. 030	393. 310	±. 015	−. 083	−. 021
Artificial graphite. First sample. Ash <0.002 percent_____	B1 B2 B3 B4 C5 C6	393. 399 393. 351 393. 505 393. 429 393. 504 393. 504	+. 006 −. 042 +. 112 +. 036 +. 111 +. 111	+. 002 −. 011 +. 028 +. 009 +. 028 +. 028	393. 449	±. 020	+. 055	+. 014
Artificial graphite. Second sample. Ash not determined_____	B1 B2 B3	393. 374 393. 524 393. 418	−. 019 +. 131 +. 025	−. 005 +. 033 +. 006	393. 438	±. 025	+. 045	+. 011
Mean of individual observations_____		393. 393	±. 060	±. 015			±. 043	±. 011

The uncertainties of the mean values for the various samples given in the last column of this table were calculated as follows [9]: For those experiments based on the electrical calibration of the calorimeter the uncertainty was calculated by means of the relation

$$e=\sqrt{e_1^2+e_2^2},$$

where

$$e_1=2\sqrt{\frac{\Sigma\Delta_1^2}{n_1(n_1-1)}} \text{ and } e_2=2\sqrt{\frac{\Sigma\Delta_2^2}{n_2(n_2-1)}}$$

In these expressions the subscripts 1 and 2 refer to the calibration and combustion experiments, respectively, Δ represents the percentage deviation from the mean, and n the number of experiments. For those experiments based on the calibration with benzoic acid the uncertainty was calculated by means of the relation

$$e=\sqrt{e_1^2+e_2^2+e_3^2},$$

where e_1 and e_2 have the same meanings as above, and e_3 is the estimated uncertainty (0.023 percent) in the value used for the heat of

combustion of benzoic acid. It will be seen from table 10 that, with the exception of the value for Buckingham natural graphite, the mean value for each sample is in agreement within the calculated uncertainty of that value, with the mean of all the individual results on the purified samples. The average deviation of the individual results from this mean value is 0.015 percent, and the maximum deviation is 0.038 percent. The average deviation of the means for the various samples from the mean of all the results is 0.011 percent, while the maximum deviation of the mean for any one sample is 0.021 percent. The results therefore indicate that the three varieties of graphite are identical, at least so far as their energy content is concerned.

Using the values 8.78, 20.82, and 28.08 j/mole [4] for the specific heats at constant volume of graphite, oxygen, and carbon dioxide, respectively, the value calculated for the temperature coefficient $(d(-\Delta U_R)/dT)$ of the heat of combustion of graphite is 1.5 j/mole °C. Using this value for the temperature coefficient of $-\Delta U_R$ and the mean value of $-\Delta U_R$ at 30° C from table 10, the value calculated for $-\Delta U_R$ at 25° C for the reaction

$$C \text{ (graphite)} + O_2(\text{gas}) = CO_2(\text{gas})$$
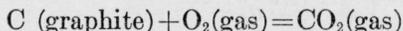
is 393.385 int. kj/mole. The value of $-\Delta$ (pv) for the above reaction calculated by means of the Beattie-Bridgeman equation of state [1] is 0.011 kj, so that the value derived from the results of the present work for $-\Delta H = -\Delta U_R - \Delta(pv)$ for the above reaction at 25° C and a constant pressure of 1 atmosphere is 393.396 int. kj/mole (44.010 g of carbon dioxide).

6. DIAMOND

As the first sample of diamond was very finely powdered, it was thought that there might be an appreciable thermal effect due to adsorption of oxygen. About 5.6 g of the sample was therefore put in a Pyrex glass tube and evacuated by means of a mercury-vapor pump connected to the tube containing the diamond through a trap immersed in liquid air. The tube containing the diamond was heated to temperatures ranging from 550° to 575° C, and the evacuation was continued for several days. Most of the adsorbed gas was removed in this way, as may be seen from the fact that at the end of the first day, with the diamond at a temperature of 570° C and with the pump operating, the minimum pressure reached was 0.0035 mm, and when the pump was shut off the pressure rose to 0.13 mm in 10 minutes, while on the last day of the pumping with the diamond at a temperature of 575° C, a pressure of <0.0001 mm was attained with the pump operating, and when the pump was shut off the pressure rose to only 0.003 mm in 10 minutes.

After evacuation, the tube containing the diamond was sealed off, immersed in the water of a calorimeter, and after sufficient time had elapsed for the attainment of thermal equilibrium, dry oxygen was admitted to a pressure of 1 atmosphere, and the temperature change of the calorimeter was observed. The evacuation of the diamond was then repeated and a second measurement was made of the thermal effect of adsorption of oxygen. The observed thermal effect in the two experiments was 2.5 and 2.8 j/g of diamond, or 0.032 kj/mole. The internal surface of the glass tube which contained

the diamond in these experiments was only about 0.2 percent of the surface of the diamond itself, so that the effect of adsorption on the surface of the tube was probably negligible and a blank experiment was considered unnecessary. In similar experiments covering the pressure range 1 to 30 atmospheres, no thermal effect due to adsorption of oxygen was observed. As the specific surface of the second sample of diamond was much smaller than that of the first, it was assumed that the thermal effect of adsorption of oxygen on this sample was negligible, and no measurement of the effect was made. The sample was, however, heated in vacuo to about 550° C to remove traces of acids used in purifying it.

The results of the heat of combustion measurements on the two samples of diamond are given in tables 11 and 12.

TABLE 11.—*Results on first sample of diamond*

Experiment	Carbon dioxide formed	Initial oxygen pressure at 30° C	Observed heat of combustion at 30° C $-\Delta U_B$	Washburn correction	$-\Delta U_R$ at 30° C	Deviation from mean		Remarks
	Moles	*atm*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Percent*	
C1	0.082878	33.5	395.907	−0.384	395.523	−0.203	−0.051	Average particle diameter 2.5 μ. Ash 0.05 percent.
C2	.083895	33.8	396.115	−.387	395.728	+.004	+.001	
C3	.083182	33.4	396.232	−.383	395.849	+.125	+.032	
C4	.083308	33.9	396.227	−.388	395.839	+.115	+.029	
C5	.083724	33.8	396.327	−.387	395.940	+.216	+.055	
C6	.083677	33.8	395.965	−.387	395.578	−.146	−.037	
C7	.083556	33.9	395.999	−.388	395.611	−.113	−.029	
Mean					395.724	±0.132	±0.033	
Correction for heat of adsorption of O₂					+0.032			
Corrected value of −ΔU_R					395.756			

TABLE 12.—*Results on second sample of diamond*

| Experiment	Carbon dioxide formed	Initial oxygen pressure at 30° C	Observed heat of combustion at 30° C $-\Delta U_B$	Washburn correction	$-\Delta U_R$ at 30° C	Deviation from mean		Remarks
	Moles	*atm*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Percent*	
C1	0.083133	34.0	395.720	−0.389	395.331	+0.075	+0.019	Average particle diameter 39.5 μ. Ash 0.02 percent.
C2	.083424	34.0	395.566	−.389	395.177	−.079	−.020	
C3	.083206	34.0	395.550	−.389	395.161	−.095	−.024	
C4	.083376	34.3	395.696	−.392	395.304	+.048	+.012	
C5	.083230	34.3	395.588	−.392	395.196	−.060	−.015	
C6	.084311	34.0	395.754	−.389	395.365	+.109	+.028	
Mean					395.256	±0.078	±0.020	
C7	0.074524	34.5	395.788	−0.387	395.401	+0.079	+0.020	Average particle diameter 22.9 μ.
C8	.074897	34.2	395.627	−.385	395.242	−.080	−.020	
Mean					395.322	±0.080	±0.020	
Mean of all results on second sample					395.272			

It will be seen from these tables that the mean value of $-\Delta U_R$ for the first sample, when corrected for the thermal effect of adsorption of oxygen, is higher by 0.500 kj/mole, or 0.13 percent, than the value

for the coarser fraction of the second sample; and that the value for the finer fraction of the second sample is higher by 0.066 kj/mole, or 0.017 percent, than that for the coarser fraction. This last difference is within the uncertainty of the measurements.

The difference between the observed heats of combustion of the two samples is in the direction to be expected from the relative sizes of the particles, but is greater than the difference obtained by a rough calculation of the effect of particle size. This calculation was based on the assumption that the energy content of the finer sample of diamond was greater than that of macrocrystalline diamond as a result of unsaturated bonds at the surface. In making the calculation it was assumed that the carbon-carbon bond energy in diamond is 70 kcal/mole, so that the corresponding surface energy is 35 kcal per N unsaturated bonds, or 70 kcal per N surface atoms, where N is Avogadro's number. The surface energy of the finer sample calculated in this manner is about 25 percent of the difference between the observed heats of combustion of the two samples of diamond.

It has been reported by Robertson, Fox, and Martin [7] that there are two types of diamond which differ in a number of physical properties, and it is conceivable that one of the samples in the present work consisted largely of one of these types, while the other sample consisted largely of the other type of diamond. This is extremely unlikely, however, because of the comparative rarity of one of the types. Robertson, Fox, and Martin found one specimen of the rarer type by accident, and then examined between 200 and 300 other diamonds before finding a second specimen of the rarer type. Also, it seems unlikely that the difference between the heats of combustion of the two types of diamond could be as great as 25 percent of the difference between the heats of combustion of graphite and diamond. In this connection it may be noted that Robertson, Fox, and Martin found that the two types of diamond did not differ appreciably in a number of properties including density, specific heat, refractive index, dielectric constant, and the arrangement of the atoms in the crystal lattice.

Since the difference between the two sets of data in tables 11 and 12 has not been explained there is considerable uncertainty as to the value of the heat of combustion of diamond. Because of the possibility of surface effects other than the one considered above, it is believed that the mean value of $-\Delta U_R$ from the eight experiments on the second sample of diamond, namely 395.272 int. kj/mole, is as good a value for $-\Delta U_R$ at 30° C for the combustion of macrocrystalline diamond as can be derived from the results of the present investigation. The change in this value by reduction to 25° C is +0.004 kj/mole. The corresponding value of $-\Delta H$ for the reaction

$$C \text{ (diamond)} + O_2 \text{ (gas)} = CO_2 \text{ (gas)}$$
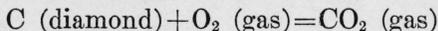
is 395.287 int. kj/mole (44.010 g of carbon dioxide) at 25° C and a constant pressure of 1 atmosphere. The uncertainty in this value, calculated as described previously, is 0.029 percent, while the calculated uncertainty of the mean result for the first sample of diamond is 0.038 percent.

In conclusion, the author gratefully acknowledges his indebtedness to numerous members of the bureau staff who have cooperated in this work. Especial credit is due F. D. Rossini who has been much interested in this investigation, and who has given much valuable advice throughout the course of the work. The author is also grateful to H. H. Lowry for the samples of graphite, and to P. E. Verkade for his assistance in obtaining one of the samples of diamond.

V. REFERENCES

[1] James A. Beattie and Oscar C. Bridgeman, Proc. Am. Acad. Arts and Sci. **63**, 229 (1928).
[2] Phillip H. Dewey and D. Roberts Harper, 3d, J. Research NBS **21**, 457 (1938) RP1139.
[3] Hobert C. Dickinson, Bul. BS **11**, 189 (1914) S230.
[4] Int. Crit. Tables **5**, 94 (1928).
[5] Ralph S. Jessup, J. Research NBS **18**, 115 (1937) RP966.
[6] Ralph S. Jessup and Carleton B. Green, J. Research NBS **13**, 469 (1934) RP721.
[7] Robert Robertson, J. J. Fox, and A. E. Martin, Phil. Trans. Roy. Soc. (London) [A] **232**, 463 (1934); Proc. Roy. Soc. (London) [A] **157**, 579 (1936).
[8] Frederick D. Rossini, BS J. Research **6**, 37 (1931) RP260.
[9] Frederick D. Rossini. Chem. Rev. **18**, 233 (1936).
[10] W. A. Roth and H. Wallasch, Ber. deut. chem. Ges. **46**, 896 (1913).
[11] W. A. Roth and H. Wallasch, Z. Elektrochem. **21**, 1 (1915).
[12] W. A. Roth and W. Naeser, Z. Elektrochem. **31**, 461 (1925).
[13] Edward W. Washburn, BS J. Research **10**, 525 (1933) RP546.

WASHINGTON, July 15, 1938.