Two Types of Equilibrium.—It is interesting to note the topography of the integral curves about the two equilibrium points. These curves have been drawn in dotted lines also in the negative and mixed quadrants where they have only a geometrical meaning.

Around the point

$$X_1 = \frac{b_2}{a_2} \quad \text{or} \quad x_1 = 0$$

$$X_2 = \frac{a_1}{b_1} \quad \text{or} \quad x_2 = 0$$

the curves form closed contour lines, like those which on a map represent a mountain crest or a trough-shaped valley.

On the other hand near the point

$$X_1 = 0 \quad \text{or} \quad x_1 = -p$$

$$X_2 = 0 \quad \text{or} \quad x_2 = -q$$

the curves follow a course such as the contour lines near a saddle or col in a landscape.

These features are typical of the two kinds of equilibrium. The crest corresponds to a center of oscillation. The saddle point corresponds to a position of unstable equilibrium. For details regarding this feature the reader is referred to a previous publication by the writer.[1]

Rhythmic phenomena are of particular interest in connection with biological systems (*e. g.*, heart-beat). An extension of the method here set forth, in its application to certain biological systems, will appear in a forthcoming issue of the Proceedings of the National Academy of Sciences.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY.]

THE HEATS OF COMBUSTION OF BENZENE, TOLUENE, ALIPHATIC ALCOHOLS, CYCLOHEXANOL, AND OTHER CARBON COMPOUNDS.

BY THEODORE W. RICHARDS AND HAROLD S. DAVIS.

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This paper is a continuation of extended researches concerning the physico-chemical properties of typical compounds of carbon. It enumerates the careful quantitative combustion in an adiabatic calorimeter of the following substances, cane sugar, naphthalene, benzoic acid (these 3 taken as standard substances); benzene, toluene, tertiary butyl benzene, cyclohexanol; together with methyl, ethyl, propyl, butyl and isobutyl alcohols. The main features of the present investigation, which lead to the hope that it may be an improvement over earlier

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[1] Lotka, *Science Progress*, 14, 406 (1920).

work (whether here or elsewhere) are as follows, great care was taken in purifying some of the organic substances; the method of closing the bomb was improved; special study was made of the best method of igniting and burning volatile liquids; particular care was taken to test the completeness of ignition, by analysis of the resulting gases for carbon monoxide or other unoxidized substances; and the thermometer readings were corrected by reference to a very adequately installed platinum thermometer. The calorimetric results were obtained over 6 years ago, but their publication has been postponed by the war, which delayed work needful for the complete removal of a slight uncertainty concerning the thermometric scale.

Apparatus and Method.

The details of the method, together with the necessary apparatus and precautions, have been described already at such length[1] that a very brief recapitulation will suffice. The apparatus consisted of a modification of the Atwater form of the Berthelot bomb,[2] which has been described in the papers just noted; the chief modifications being the doubled ridged closure of the bomb, the continuous gold foil to protect the lead; the firm steel adjustment for the firing connection, and the large phosphor-bronze ring or washer to prevent friction during the screwing into place of the steel cap of the bomb.[3] The Hotchkiss steel[4] cup of the bomb weighed 1609.5 g.; the tool steel[4] collar, cover, and screw valves weighed 1377.4 g.; the platinum parts 190.0 g.; the pure silver calorimeter-can 881.5 g.; the German silver stirrer 61.4 g.; the phosphor-bronze washer 38.8 g. Taking the specific heats of the several substances as 0.1114, 0.1087, 0.032, 0.056, 0.095, 0.087, respectively, these 6 portions would have the heat capacities 179.4, 149.7, 6.1, 49.3, 5.9 and 3.5. Other small items including a brass nut, mica insulation, the lead gasket, the gold lining on the cover, oxygen ($^1/_3$ mol.), thermometer, amounted together to 6.7 cal./°C. 2257.0 g. of water was also present. Hence the heat capacity of the whole adds up to 2657.6—a result not far from that (2660.0) found from the average of the standard materials furnished by the Bureau of Standards, as will be seen. The latter must be taken as the more accurate, since the specific heats of the different kinds of steel in the bomb are perhaps hardly well enough known for the purpose in hand.

The rise of temperature of this calorimetric system (containing the bomb

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[1] T. W. Richards and F. Barry, THIS JOURNAL, **37**, 993 (1915); T. W. Richards and H. S. Davis, *ibid.*, **39**, 341 (1917). Earlier work describing the evolution of the method is referred to in the former of these articles.

[2] W. O. Atwater and J. F. Snell, *ibid.*, **25**, 659 (1903).

[3] These improvements are described on pp. 1004 and 342, respectively of the papers quoted above.

[4] Atwater and Snell, *loc. cit.*, p. 694.

completely immersed under water) was paralleled in an environing bath so that no correction for cooling was needed. The temperature of this bath was automatically controlled to follow as closely as possible that of the calorimeter proper, by a device explained in our earlier paper.[1] Since this device demanded in the case of each new substance a few preliminary experiments in order to discover the precise nature of the curve of temperature change, one or two early trials in each case were usually made merely for the purpose of orientation and are not included in the tables given below. The numbers attached to the several experiments on sugar are the original numbers as recorded in the notebook, the others are serial for convenience. Each series as given below is consecutive, except in the case of sugar, as noted below.

The mercury-in-glass thermometer (No. 11258) used in the calorimeter proper was carefully made for this purpose. It was standardized in 1910 by the Bureau of Standards and also by comparison with the Harvard Baudin instruments so often referred to in communications from this laboratory. Since these standardizations left something to be desired, the instrument has been recently re-standardized by Mr. O. C. Bridgeman with very great care through comparison with a standard calorimetric platinum thermometer. The thermometric resistance box was installed in a thermostat, with every precaution to avoid parasitic effects. It was for this final standardization that the publication of the results had been temporarily withheld. The final estimates agreed usually within 0.001° with the older ones, but gave a somewhat more divergent correction at the 20° point. All the readings were corrected to this final platinum standard and are recorded below in its terms.

Various methods of introducing volatile liquids into the bomb were tried. The old Berthelot method of soaking the volatile liquid into pellets of cellulose, as well as Stohman's later method of enclosing the liquid in glass bulbs, which were broken just before ignition, undoubtedly allowed some of the vapor to evaporate and escape unburned.[2] Later Stohman,[3] suspecting this, used a small flask of platinum having about one cc. capacity to contain the liquid and over it laid a weighed leaf of collodion, or some other material, fastened to the neck by a thick platinum ring. In 1898 Zubow[4] modified this method by placing the liquid in a small platinum cup with a protruding platinum tube covered with a platinum stopper. The top of the cup was sealed with a film of collodion, the substances to be experimented upon being poured in by means of a funnel. This method seems to have given good results, but there is dan-

[1] *Loc. cit.*

[2] T. W. Richards and R. H. Jesse, Jr., THIS JOURNAL, **32**, 282 (1910).

[3] *J. prakt. Chem.*, **44**, 336 (1891).

[4] *J. Russ. Phys.-Chem. Soc.*, **28**, 687 (1896); **30**, 926 (1898); **33**, 708; **35**, 815 (1903).

ger of throwing some of the liquid out of the side tube without complete combustion. Later Roth and his collaborators[1] developed a method which has much in common with Stohman's and Zubow's latest procedure. A thin glass test-tube was filled nearly to the edge with the liquid to be burned, closed by a tightly fitting gelatine cap, and held in a vertical position in a platinum dish by means of a small glass support. Cotton thread (fastened between the gelatine and the glass in such a way as not to be moistened by the liquid) served for the ignition. It was admitted, however, that with liquids having a high vapor pressure there is danger of blowing off the gelatine cap, incompletely burned. Precisely the same objection applies to the final methods of Stohman and Zubow. According to our experience with methyl alcohol and benzene, if the gelatine cap is fitted over the little test-tube tightly enough to prevent evaporation, it is usually broken inwards when oxygen pressure is applied. Moreover, it prohibits exhausting the air from the bomb before admitting oxygen—an important precaution as regards completeness of combustion, and necessary to diminish the amount of nitric acid formed. Again, the glass tube sometimes seals itself at the high temperature of combustion, and then the sudden explosion drives the vapor out quickly enough to cause incomplete combustion. Nevertheless, with high boiling liquids the method, when carefully executed, will doubtless give good results, as Roth has shown. We have used it with success, *e. g.*, combustion No. 62 below; but the amounts of nitric acid, carbon monoxide and residual carbon were often large, and on the whole we have found it to be less satisfactory than the method of sealing the liquid in perfectly full, very thin, flattened glass bulbs,[2] the method used in almost all the following work. The ignition was effected by the flame from a weighed ring of paraffin encircling the inner rim of the small platinum crucible containing the glass bulbs. The paraffin itself was ignited by a wisp of cotton wool wrapped by a short spiral of exceedingly fine platinum wire (0.02 mm. in diameter) which needed less than an ampere for $^1/_5$ second for the purpose.[3] Fired in this fashion little, if any, of the volatile substance was found to escape combustion. Among the most important features are the size and shape of the small platinum crucible, which should be about 21 mm. diameter and 26 mm. high. The full details

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[1] *Ann.*, **385**, 104 (1911).

[2] This method is an improvement over the somewhat similar one independently devised by Berthelot and Delépine, *Ann. chim. phys.*, [7] **21**, 289 (1900), which we had overlooked until after the present work was completed.

[3] The amount of extra heat thus communicated to the system was computed in various ways to be less than 2 calories. Since it was essentially constant (except perhaps where the rise of temperature was only 2°) even this small correction is eliminated in calculation, occurring both with the standard substance and with the substance to be determined.

may be gathered from the papers already cited, and need not be reiterated.[1]

Attention in these previous papers was called to the fact that different results obtained by different experimenters might well be due to lack of completeness of combustion. This is especially true in the case of volatile substances, such as benzene.[2] Accordingly in many of the present combustions very careful tests for carbon monoxide were made in the residual gases, by passing them slowly through the following train of apparatus: two U-tubes filled with concentrated potassium hydroxide solution and glass pearls; a Liebig absorption tube with saturated barium hydroxide solution in order to make sure that all the carbon dioxide had been absorbed in the preceding potash; a drying tube filled with phosphorus pentoxide; a tube of copper oxide at dull red heat; and finally another tube of phosphorus pentoxide. The carbon dioxide in the gas emerging from this apparatus was estimated at first gravimetrically in a Liebig's potash bulb, but later by absorption in a spiral filled with a known quantity of 0.1 *N* barium hydroxide solution which was titrated at the conclusion of the experiment. When the combustion had been conducted in the older ways, considerable quantities of carbon monoxide were found, but usually very little remained in combustions made by the most approved method.

When carbon monoxide was found, the corresponding correction (2.4 cal. per mg. of the gas, or 0.0009° rise in temperature of our calorimetric system) was added to the observed thermal output of the reaction. Unconsumed carbon in the crucible, if any, was likewise weighed, and its appropriate correction (8.1 cal. per mg.) added. The thermal equivalents of these substances are larger in this relation than is usually appreciated, and the corrections are occasionally important. In the case of sugar, Combustions Nos. 10 and 16 were tested for carbon monoxide, in the case of benzoic acid, No. 21, in the case of naphthalene, No. 23; none was found in any one of these 4 trials. With the other substances (except methyl alcohol) every combustion was tested. Usually the combustion was complete, but in Nos. 21, 32 and 33 (benzene ignited with sugar), 44, 45, 56 and 62[3] the amounts were important; in the last case (conducted by Roth's method) as much as 6 mg. of carbon monoxide were present.

Nos. 9 and 16, showed traces of unburned carbon; all those with benzoic acid (Nos. 20, 21 and 22) left nearly a milligram of carbon a piece. Naphthalene left no carbon in any case, neither did butyl benzene, cyclo-

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[1] T. W. Richards and F. Barry, *loc. cit.*, pp. 1003–1012, also especially the present authors, *loc. cit.*, p. 349.

[2] See Richards and Barry, *loc. cit.*, p. 1017; also Roth and Auwers, *loc. cit.*, p. 162.

[3] Unfortunately the other combustions of methyl alcohol were not tested for this gas.

hexanol, or isobutyl alcohol. On the other hand, slight traces of residual carbon or soot were found in Nos. 31, 32, 33, 34, 35, 37, 39 (the other experiments with benzene gave complete combustion), 41, 42, 43, 46, 53, 54, 57, 59, 52, 63, 70 and 71. The necessary corrections in these latter cases could never have amounted to more than 0.001°.

In addition to the additive corrections corresponding to these usually small quantities of unburned material, further corrections had to be applied to the results to take account of the considerable quantity of auxiliary substance used in ignition, the correction for stirring (usually 0.008°), the trace of nitric acid (usually about 0.0003°) and a further correction for the temperature of the protruding thermometer stem. Of these, the quantity corresponding to the heat of combustion of the auxiliary substance was by far the greatest. All are added algebraically together in the figures given under the caption "Total Correction" in the tables which follow. The "Observed Rise in Temperature" in the column preceding gives the difference in thermometric readings corrected for the calibration corrections of the thermometer. The difference between this observed rise and the total correction in each case gives the corrected rise in temperature (given in the next to the last column) corresponding to the weight of substance burned; and in the last column of the table is given the corresponding rise in the temperature of the calorimeter (heat capacity 2,660.0) per gram of substance. For the sake of saving space, the names of the auxiliary substances, cotton, paraffin, beeswax and gelatine are usually abbreviated as "cot.," "par.," "bsw.," and "gel.," respectively.

The possibility of the residual presence of other unburned vapors of compounds of carbon was also considered. Benzene being the most likely substance to have been incompletely burned, the gases remaining from a benzene combustion were tested for reducing vapors by bubbling through a weak solution of potassium permanganate made alkaline with sodium carbonate. Moreover, they were tested for ozone by letting them impinge on filter paper soaked in potassium iodide solution and starch. Both tests gave negative results. In this connection, the question as to the purity of the original oxygen may be raised. It was tested for halogens, and found to contain none. Since it had been prepared by the evaporation of liquid air, its chief impurity was argon. The presence of any combustible substance in it was unlikely; if any were present its effect must have been felt nearly equally with each substance, and, therefore, eliminated in the calculation.

The Source and Preparation of Materials.

The value of an investigation of this sort depends largely on the intelligent purification of the materials burned. Although admixture of some impurities (*e. g.*, toluene in benzene) makes very little difference in the result, the admixture of others (especially, of course, water) makes a very serious difference. Therefore, space must be given to a description of the sources or methods of preparation of the 13 pure substances.

Sucrose.—The first specimen was prepared from a very pure sample of sugar (designated "Diamond A" by the American Sugar Refining Company[1]) through one precipitation from a solution in 50% alcohol by concentrated alcohol. The second preparation was the same material recrystallized twice, and the third, the latter recrystallized yet once more, or 3 times in all. Another sample (our No. 4) was obtained from the United States Bureau of Standards (their No. 17). The first 3 samples were placed over solid potassium hydroxide and calcium chloride in order to remove the water and alcohol and occasionally stirred and pulverized. They lost no important further weight when placed over quicklime or phosphorus pentoxide in a vacuum desiccator. For example, about 5 g. of sugar once recrystallized and dried over calcium chloride and potassium hydroxide was placed in a weighing tube, and after several days over phosphorus pentoxide in a sealed vessel under a pressure of 0.005 mm. mercury (measured on a McLeod gage), the weight was found to be the same to within less than 0.1 mg. Sugar thus carefully dried could be weighed in the dry air of the steam-heated laboratory without important error. Even in half an hour samples weighing 2 g. gained only 0.2 or 0.3 mg. This would doubtless not be the case in an atmosphere of greater humidity.

Thus it is seen that sugar may be dried in a satisfactory way without very elaborate precautions—a conclusion which is confirmed through some very careful work by Bates and R. F. Jackson at the United States Bureau of Standards, kindly furnished us, at the time, in manuscript. They state that in their experience the air-dried and pulverized sample lost in weight only about 0.01 to 0.02% at the first drying operation and practically nothing thereafter. Nevertheless, we are inclined to agree with Swientoslawski[2] as to the undesirability of sugar for this purpose, for his reasons numbered (1) and (4).

Benzoic Acid and Naphthalene.—These substances had been prepared with care by the Bureau of Standards to serve as standards (B. of S. Nos. 39 and 38, respectively). Their appearance was entirely satisfactory, and neither left a weighable trace of residue on evaporation.

Benzene.—Three samples of benzene were used in this work. The first and least pure was numbered 4 and was prepared in the following way. A very pure commercial benzene (warranted free from thiophene and once crystallized) after standing several months over sulfuric acid,

[1] This material was obtained through the kindness of F. O. Murphy, a chemist of the company.

[2] W. Swientoslawski, THIS JOURNAL, 39, 2597 (1917).

was thoroughly washed, allowed to remain over sodium for a long time, and then recrystallized twice. The freezing point was constant to within about 0.01° during the complete solidification of the substance. After further standing over sodium, this Sample 4 was crystallized once more and thus yielded Sample 3, which showed no difference as to heat of combustion. Sample 6 had been prepared synthetically from benzoic acid and later recrystallized by J. W. Shipley 5 times.[1] The fourth and fifth recrystallizations gave the same freezing point to within 0.001° and this point was as high as that of any sample which Shipley was able to prepare, thus showing great purity.

Toluene.—One of the specimens of toluene was that very carefully prepared by F. Barry. Another similar specimen was prepared from commercial toluene, shaken with sulfuric acid until it gave no color to the acid, agitated with mercury until it ceased polluting a clean mercury surface, washed and repeatedly distilled. Both these samples boiled at essentially the same point, between 100.3° to 100.4° under normal pressure.

Tertiary Butyl Benzene.—This substance was prepared with great care by an assistant (J. C. Howard) under the direction of G. L. Kelley, to whom we are indebted for his oversight of the work. We redistilled and fractionated a product boiling between 168.6° and 168.7° (barometer, 759 mm.). The substance had a density at 20° of 0.8671.[2]

Decane (Di-iso-amyl).—This substance had been prepared in 1912 by a prominent German firm. It was redistilled several times under normal pressure and collected in the following fractions: Sample 1, 159.2° to 159.5°; Sample 2, 159.5° to 159.7°; Sample 3, 159.7° to 160.1°. No difference could be detected in their heats of combustion.

Methyl Alcohol.—Very pure methyl alcohol made by Shipley[3] for an earlier investigation was used. It had been prepared by the following processes; (1) the preparation of pure methyl oxalate; (2) the saponification of the ester; (3) the fractionation of the liquid product until a product boiling between 68° and 70° was obtained; (4) treatment of this product with a little iodine and sodium hydroxide to eliminate foreign organic matter; (5) drying the alcohol, with potassium carbonate, calcium oxide and pure sodium; (5) fractionation of the alcohol. Density at 20°/4°, 0.7923. Boiling point, 64.51°, bar. 761.5 mm. The combustions with this substance were the least satisfactory, perhaps because of its volatility. Unfortunately only one could be analyzed for carbon monoxide, because of lack of time.

Ethyl Alcohol.—Both the samples of ethyl alcohol described below

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[1] This Journal, **36**, 1830 (1914).

[2] For details see *ibid.*, **37**, 1001 (1915).

[3] Richards and Shipley, *ibid.*, **38**, 996 (1916).

were obtained through the kindness of L. B. Coombs,[1] who prepared them. Sample 1 was prepared from Squibb's 99.8% alcohol. It was refluxed over metallic calcium for a day, then fractionated. B. p. 78.55°–78.60°, bar., 763.9 mm. During distillation, the receiver was carefully protected from aqueous vapor by freshly ignited lime. The alcohol was preserved in a stoppered bottle over sulfuric acid in a desiccator. Sample 2 was prepared in the same way as (1). B. p. 78.50°, bar. 767 mm. This material was doubtless less trustworthy than the methyl alcohol.

Propyl Alcohol already very pure was redistilled with the following outcome: Sample 1, b. p. 96.6°–96.7°; Sample 2, b. p. 96.7°–96.9°; Sample 3, b. p. 96.9°–97.1° (bar. 757 mm. in each case); Sample 4, all the previous fractions were mixed and refluxed with calcium for 2 hours, b. p. 96.8°–97.0°, bar. 766.0 mm.

Butyl Alcohol (Normal).—The butyl alcohol used was that which had been prepared long ago by one of us in collaboration with J. H. Mathews[2] during work on the latent heats of evaporation. It was redistilled, the greater part coming over between 116.0°–116.8°, bar. 766 mm. (Sample 1). This distillate was then refluxed with calcium for 2 hours, the greater part now coming over at 116.3°–117.3°, bar. 765.5 mm. (Sample 2). In spite of the change in the boiling point, the 2 samples differed in their heats of combustion by an amount no greater than possible experimental error.

Isobutyl Alcohol was prepared from the purest obtainable German materials by distillation after refluxing with calcium. B. p. 107.2°–107.3°, bar. 763.4 mm. This appeared to be very pure, all distilling over within the tenth of a degree.

Cyclohexanol.—Cyclohexanol was prepared from a mixture of this substance with cyclohexanone, which had been prepared, with his unfailing courtesy, by G. L. Kelley from phenol by reduction according to the method of Sabatier and Senderens. J. W. Shipley kindly carried out for us the separation of the ketone by means of freshly made sodium hydrogen sulfite, and the cyclohexanol thus obtained was further purified by drying over sodium carbonate, direct distillation and fractional crystallization in a drop-funnel. The samples in the combustion were (A) cyclohexanol recrystallized 8 times, (original m. p. 21.9°), which had, however, remained standing for several months in an ordinary stoppered bottle. This sample had undoubtedly absorbed moisture with its characteristic eagerness, and its results were a full per cent. lower than the others. They are not recorded below, but showed how careful one must be in dealing with

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[1] Richards and Coombs, THIS JOURNAL, **37**, 1669 (1915).

[2] Richards and Mathews, *ibid.*, **33**, 863 (1911).

a substance so hygroscopic. (B) Cyclohexanol freshly distilled from sodium, b. p. 160.8° (bar. 759 mm.). (C) Cyclohexanol obtained from Sample B by crystallization 4 times in a drop-funnel protected by drying tubes from the moisture of the air. (D) Material prepared by Shipley from Sample B by recrystallization. The freezing point of this last sample indicated that the amount of moisture in it must have been less than 0.1%.[1] Zubow's material, purified by fractional distillation, had almost the same boiling point (160.4° under 751 mm.) as ours.

Cotton Wool.—The cotton used was a good, clean-looking sample of absorbent cotton, of the kind used for surgical dressings. Its heat of combustion was found to be 4020 cal. per g.

Gelatine Capsules.—The gelatine capsules (from a prominent American firm) were the kind ordinarily used to enclose disagreeable medicines. The nitric acid formed in the bomb per gram of capsule was about 0.00033 g. The heat of combustion was 4160 cal. per g.

Paraffin.—The samples of hard paraffin used for the combustions were cut from different parts of a uniform-looking cake, so as to obtain a fair average. Its heat of combustion was found to be 11210 cal. per g.

The Beeswax was the hard white commercial material, and yielded on burning 12660 cal. per g.[2]

TABLE I.

Rise of Temperature in Calorimetric System (Heat Capacity 2660.0) Caused by Combustion of 1,0000 g. (Weighed in Air) of Sundry Substances.

Sucrose, Series I, Samples 1 and 2.

Expt. No.	Sample.	Weight of sub. in air. G.	Ignition material in mg.	Final temperature. ° C.	Obs. Rise in temp. ° C.	Total correction. ° C.	Corrected rise in temp. ° C.	Rise per gram. ° C.
3	1	2.2006	Cotton[a]	19.9	3.2727	0.0113	3.2614	1.4820
7	1	2.2038	Cotton	20.0	3.2809	0.0105	3.2704	1.4840
8	1	2.9737	Cotton	20.3	4.4225	0.0145	4.4080	1.4823
14	1	1.3714	Cotton 11.5	18.4	2.0598	0.0242	2.0356	1.4843
15	1	2.1357	Cotton 18.1	19.6	3.2027	0.0341	3.1686	1.4837
16	1	2.2620	Cotton 13.5	19.1	3.3836	0.0283	3.3553	1.4833
17	1	2.0326	Cotton 11.7	19.2	3.0401	0.0266	3.0135	1.4826
6	2	2.2002	Cotton	19.8	3.2761	0.0143	3.2618	1.4825

Average, 1.4831

[a] In the earlier determinations of sugar, the wisp of cotton was weighed with the sugar, and counted as sugar since their heats of combustion per gram are very nearly the same. In such cases the weight of cotton is not recorded above.

Two combustions, Nos. 1 and 13, were rejected; the first because it was merely preliminary, the other because far too much cotton was used. All the remaining work with sugar is given in full.

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[1] Richards and Shipley, THIS JOURNAL, 41, 2008 (1919).

[2] These last 4 heats of combustion are given in our earlier paper, *loc. cit.*, p. 352.

TABLE I (*continued*).

Expt. No.	Sample.	Weight of sub. in air. G.	Ignition material in mg.	Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. sub. ° C.
			Sucrose, Series II, Sample 3.					
2	3	2.1992	Cotton	20.3	3.2770	0.0092	3.2678	1.4842
4	3	2.1987	Cotton	19.8	3.2705	0.0091	3.2614	1.4833
5	3	2.1985	Cotton	20.3	3.2685	0.0094	3.2591	1.4825
9	3	2.7335	Cotton	20.2	4.0675	0.0144	4.0531	1.4828
10	3	2.2316	Cotton	19.4	3.3192	0.0094	3.3098	1.4830
11	3	2.2298	Cotton	18.9	3.3220	0.0116	3.3104	1.4846
12	3	2.1146	Cotton	19.6	3.1466	0.0104	3.1362	1.4831
							Average,	1.4832
			Sucrose, Series III, B. of S. Sample.					
18	4	1.8561	Cotton 6.7	18.5	2.7760	0.0242	2.7518	1.4825
19	4	2.1896	Cotton 3.5	19.3	3.2641	0.0175	3.2466	1.4827
							Average,	1.4826
							Average of 18 Combustions,	1.4831
			Benzoic Acid.					
20	B. of S.	1.3273	Cotton 5.2	19.1	3.1686	0.0133	3.1553	2.3773
21	B. of S.	1.1830	Cotton 4.5	19.4	2.8268	0.0131	2.8137	2.3784
22	B. of S.	0.9810	Cotton 5.4	17.9	2.3483	0.0150	2.3333	2.3784
							Average,	2.3780
							Average corrected for firing heat,[a]	2.3778
			Naphthalene. (Two Series, with Diverse Quantities and Different Final Temperatures.)					
23	B. of S.	1.1226	Cotton 3.5	19.8	4.0779	0.0149	4.0630	3.6193
24	B. of S.	1.1537	Cotton 7.8	20.2	4.1949	0.0220	4.1729	3.6170
25	B. of S.	1.1002	Cotton 9.5	20.0	4.0062	0.0260	3.9802	3.6177
26	B. of S.	1.1023	Cotton 7.3	20.1	4.0100	0.0220	3.9880	3.6180
							Average Series I,	3.6180
27	B. of S.	0.8286	Cotton 8.2	19.4	3.0200	0.0230	2.9970	3.6170
28	B. of S.	0.5415	Cotton 9.2	18.1	1.9843	0.0250	1.9593	3.6182
29	B. of S.	0.5183	Cotton 11.5	17.9	1.9052	0.0291	1.8761	3.6182
30	B. of S.	0.5511	Cotton 10.1	18.0	2.0214	0.0265	1.9949	3.6198
							Average Series II,	3.6186
							Average of Series II corrected for firing heat,	3.6182
							Total average of Series I and II corrected,	3.6181

[a] Whenever the rise of temperature in the calorimeter was about 4°, the heat generated electrically in the platinum wire used for firing was eliminated from the result in latter calculation; but with a rise of temperature of only 2°, half of this firing heat (2 cal.) is not thus eliminated, and must be allowed for as above to secure consistency in the results.

TABLE I (*continued*).

Expt. No.	Sample.	Weight. G.	Ignition material in mg.		Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. ° C.
			Benzene.						
31	3	0.6743	Sug.	143.0	19.1	2.7627	0.2165	2.546	3.775
32	3	0.7166	Sug.	185.0	19.5	2.9835	0.2805	2.703	3.772
33	4	0.7435	Sug.	212.1	19.3	3.1340	0.3300	2.804	3.771
34	3	0.6284	Par.	27.2	19.0	2.5090	0.1423	2.367	3.767
			Cot.	13.2					
35	4	0.7738	Bsw.	25.6	19.7	3.0538	0.1400	2.914	3.766
			Cot.	23.0					
36	4	0.7988	Bsw.	27.0	19.6	3.1532	0.1412	3.012	3.771
			Cot.	20.3					
37	4	0.6752	Bsw.	34.8	19.2	2.7283	0.1830	2.545	3.769
			Cot.	24.9					
38	6	0.8438	Par.	139.3	20.3	3.7842	0.6128	3.172	3.759
			Cot.	10.3					
39	6	0.8106	Par.	103.4	20.1	3.5083	0.4545	3.054	3.768
			Cot.	5.0					
								Average,	3.769
			Toluene.[a]						
40	2	0.7982	Bsw.	27.3	19.8	3.1781	0.1236	3.0545	3.827
			Cot.	4.8					
41	2	0.8374	Bsw.	35.2	19.5	3.3488	0.1488	3.2000	3.821
			Cot.	2.6					
42	2	1.1059	Par.	48.0	20.0	4.0960	0.2170	3.8790	3.818
			Cot.	3.1					
43	1	0.9154	Par.	98.2	19.9	3.9230	0.4258	3.4972	3.820
			Cot.	3.6					
44	2	0.9986	Par.	95.3	19.8	4.2326	0.4144	3.8172	3.823
			Cot.	3.0					
45	3	1.0566	Par.	79.7	20.4	4.3725	0.3348	4.0377	3.821
			Cot.	7.9					
								Average,	3.822

[a] Determinations 43, 44 and 45 are those given in THIS JOURNAL, **39**, 353 (1917). The slightly different figures now recorded are due to the recalibration of the thermometer. The average of the 3 remained unchanged. Nos. 44 and 45 were among the worst of those which left unburned CO, as detailed in the place just cited.

Expt. No.	Sample.	Weight. G.	Ignition material in mg.		Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. ° C.
			Tertiary Butyl Benzene.						
46	1	1.0024	Par.	119.8	20.46	4.4589	0.5220	3.937	3.927
			Cot.	5.1					
47	1	0.8420	Par.	106.8	19.9	3.7806	0.4720	3.929	3.929
			Cot.	6.5					
48	1	0.9070	Par.	122.3	20.1	4.0884	0.5276	3.926	3.926
			Cot.	4.3					
								Average,	3.927

Table I (*continued*).

Expt. No.	Sample.	Weight. G.	Ignition material in mg.		Final Temp. ° C.	Obs. Rise in Temp. ° C.	Total Correction. ° C.	Corr. Rise in Temp. ° C.	Rise per gram. ° C.
			Cyclohexanol.						
49	B	1.0610	Sug.	153.3	20.2	3.7849	0.2380	3.5469	3.343
50	B	0.7824	Sug.	124.4	18.7	2.8026	0.1924	2.6102	3.336
51	C	1.0233	Bsw.	24.6	20.3	3.5846	0.1650	3.4196	3.342
			Cot.	20.9					
52	D	0.8545	Bsw.	47.7	18.9	3.0814	0.2242	2.8572	3.344
			Cot.	6.0					
								Average of last two,	3.343
			Decane (Di-iso-amyl).						
53	1	0.7436	Par.	88.1	19.8	3.5607	0.3856	3.1751	4.270
			Cot.	3.6					
54	1	0.8176	Par.	112.3	20.0	3.9931	0.5001	3.4930	4.272
			Cot.	9.7					
55	2	0.7839	Par.	111.4	19.7	3.8341	0.4930	3.3411	4.262
			Cot.	7.4					
56	3	0.8210	Par.	120.0	20.2	4.0252	0.5179	3.5073	4.272
			Cot.	8.3					
57	3	0.8040	Par.	122.0	19.9	3.9667	0.5351	3.4316	4.268
			Cot.	6.2					
								Average,	4.269
			Methyl Alcohol.[a]						
58	1	1.4337	Sug.	95.1	19.7	3.0344	0.1513	2.883	2.011
59	1	1.4462	Sug.	103.3	19.6	3.0510	0.1587	2.892	2.000
60	1	1.6788	Sug.	94.3	20.2	3.4975	0.1464	3.351	1.996
61	1	1.8720	Sug.	112.8	20.3	3.9382	0.1771	3.761	2.009
62	1	0.7207	Gel.	43.0	17.7	1.5490	0.1020	1.447	2.008
			Cot.	18.0					
								Average,	2.005
			Ethyl Alcohol						
63	1	0.9749	Par.	102.0	20.1	3.0581	0.4511	2.6070	2.674
			Cot.	7.9					
64	1	1.1711	Par.	111.0	20.3	3.6156	0.4862	3.1294	2.672
			Cot.	6.4					
65	1	0.8960	Par.	104.5	19.9	2.8576	0.4606	2.3970	2.675
			Cot.	7.0					
66	2	1.0400	Par.	115.5	19.6	3.2887	0.5117	2.7770	2.670
			Cot.	8.7					
								Average,	2.673

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[a] These combustions were on the whole the least satisfactory of all, but they are probably at least as good as other published work concerning this substance. The result is only about 0.1 % less than the usually accepted value, which depends chiefly on Thomsen's results.

TABLE I (*continued*).

Expt. No.	Sample.	Weight. G.	Ignition material in mg.	Final temp. ° C.	Obs. rise in temp. ° C.	Total correction. ° C.	Corr. rise in temp. ° C.	Rise per gram. ° C.
			Propyl Alcohol.					
67	3	1.1434	Par. 128.1 Cot. 9.0	19.9	4.0190	0.5649	3.4541	3.021
68	3	0.7576	Par. 124.4 Cot. 10.9	19.2	2.8455	0.5522	2.2933	3.027
69	4	0.8417	Par. 120.7 Cot. 12.7	19.3	3.0916	0.5424	2.5492	3.022
70	4	0.6696	Par. 114.7 Cot. 6.5	19.8	2.5317	0.5048	2.0269	3.027
							Average,	3.024
			Butyl Alcohol—Normal.					
71	1	0.7000	Par. 139.0 Cot. 10.0	19.1	2.8823	0.6126	2.2697	3.242
72	2	0.7781	Par. 114.1 Cot. 6.0	19.4	3.0251	0.5010	2.5241	3.244
							Average,	3.243
			Isobutyl Alcohol.					
73	1	0.8628	Par. 113.2 Cot. 6.5	19.9	3.2942	0.4999	2.7943	3.239
74	1	1.0774	Par. 103.7 Cot. 7.5	19.9	3.9423	0.4571	3.4852	3.235
							Average,	3.237

Heats of Combustion of the Several Substances.

As already stated, the above results with sucrose, benzoic acid and naphthalene were used as standards in calculating the heats of combustion of the other substances. The samples of sugar were evidently nearly but not exactly alike. The two samples, 1 and 3, prepared here, gave results almost precisely identical. The average of all the results with each standard substance was taken as the value corresponding to that substance. According to the values furnished by the Bureau of Standards, the heat capacity of our calorimetric system in 20° calories is calculated from the results with these 3 substances as follows.

	Rise of temperature per gram (in air). Degrees.	Combustion heat (B. of S.).[a]	Heat capacity of system in 20° calories.
Sucrose	1.4831	3949	2662.9
Benzoic acid	2.3778	6329	2661.7
Naphthalene	3.6181	9622	2659.4
		Average,	2661.3

[a] Bureau of Standards, *Circ.* 11, 2nd Ed., 16 (1915).

In 18° calories (actually used by us) this becomes 2660.0,[1] which is taken as the heat capacity of our calorimetric system in calculating the results for the other substances. The individual averages upon which it depends are more divergent than is desirable, the extreme divergences from the mean amounting to about 0.07%. Evidently naphthalene in our hands yielded a larger heat of combustion in relation to sugar than it did at the Bureau of Standards, although even our value is distinctly less than that found by some Europeans. Benzoic acid falls between the two others. Whether or not the reason of the difference is to be found in incomplete combustion in some cases, we do not attempt to decide. If at any time the discrepancy is explained and one or the other of these substances is proved to be the best standard of reference, the results can easily be calculated into that standard by reference to the figures just given. We are inclined to think that naphthalene may be found the best substance, when its purification has been perfected and its heat of combustion certainly established.[2] The whole question of the true standard of reference is discussed at such length in the interesting recent papers by Swietoslawski[3] and by Roth,[4] as well as in one of the Harvard papers,[5] that further treatment at present is unnecessary. The establishment of a thoroughly trustworthy and generally recognized standard of reference is one of the desiderata of this kind of work. The Bureau of Standards and Swietoslawski have made important advance in this direc-

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[1] See Richards and Barry, *loc. cit.*, p. 1016, Cal. (18°) = (Cal. 20°) × 1.0005. As already stated, when there was a 4° rise of temperature, no correction is applied to these figures for the small amount of heat evolved electrically by the fine platinum wire in firing, because this small quantity appears in practically equal measure in each combustion, and is eliminated in the later calculation. Swietoslawski, in recalculating Zubow's results, used the 15° calorie, which is perhaps 0.07% greater than the 18° calorie.

[2] Naphthalene has a vapor pressure of 0.064 mm. at 20° according to Barker (*Z. physik. Chem.*, **71**, 235 (1910)). Care must, therefore, be taken that none evaporates after weighing, either outside or within the bomb. The loss of one liter of its vapor at 20° means a loss of about 2 cal. on burning.

[3] Three years ago, after our experimental work was finished, Swietoslawski published his interesting paper on the use of benzoic acid as the standard unit in the thermochemistry of organic compounds (THIS JOURNAL, **39**, 2595 (1917)). With the general conclusions in this article we heartily agree. Unfortunately our own determinations with benzoic acid were too few in number to use them alone as the basis of our heat capacity determinations. Moreover in each of them a correction had to be made for nearly a milligram of carbon remaining unburned. Therefore, for the present the average value given above seems to us the safest. Swietoslawski's very valuable recent paper, giving a recalculation of Zubow's work upon a satisfactory basis, shows that in general Zubow's results are reasonably close to ours. This paper appeared after the present contribution was submitted for publication, and hence cannot be considered in detail here. (THIS JOURNAL, **42**, 1312 (1920).

[4] Roth, v. Auwers (and Wallasch), *loc. cit.*, pp. 113–127, 162.

[5] Richards and Barry, *loc. cit.*, p. 1016.

tion, but evidently more remains to be done, as they themselves would doubtless agree.

The heat capacity of the calorimetric system having been thus determined, it may be used to calculate the heats of combustion of the several substances. The resulting values are given below, not only on the basis of the weighings in air (corresponding to the results given above as well as to the values given by the Bureau of Standards), but also upon the vacuum basis. Moreover the molal heats of combustion are recorded likewise in the following table, both in large calories and in kilojoules, the atomic weights used being the present international values, C = 12.005, H = 1.0076 and O = 16.000.

Table II.

Heats of Combustion in Constant Volume of the Several Substances, Including Reduction to Vacuum Standard.[a]

(The Heat Capacity of the Calorimetric System between 16° and 20° is taken as 2660.0, Cal. (18°)/° C., its materials having been weighed in air. 4.182 joules are taken as equivalent to the 18° Calorie.)

	Rise of temp. in cal. system. ° C.	Comb. heat per 1.0000 g. (weighings in air).	Density.	Comb. heat per 1.0000 g. (weighing substance in vacuum).	Mol. wt.	Heat of combustion per mol. (weigh. in vac.).	
						Large Cal.	Kilojoules.
Sucrose	1.4831	3945	1.61	3943	342.23	1349.4	5643
Benzoic acid	2.3778	6325	1.32	6320	122.08	771.55	3227
Naphthalene	3.6181	9624	0.97	9614	128.11	1231.6	5151
Benzene	3.769	10026	0.88	10014	78.076	781.85	3269.7
Toluene	3.822	10167	0.87	10155	92.095	935.23	3911.1
Tertiary butyl benzene	3.927	10446	0.87	10434	134.16	1399.8	5854
Cyclohexanol, $C_6H_{11}(OH)$	3.343	8892	0.96	8882	100.12	889.3	3719.0
Di-isoamyl	4.269	11356	0.73	11339	142.22	1612.6	6744.0
Methyl alcohol	2.005	5333	0.79	5326	32.035	170.61	713.4
Ethyl alcohol	2.673	7110	0.79	7101	46.056	327.04	1367.7
Propyl alcohol	3.024	8044	0.80	8033	60.075	485.80	2031.6
Butyl alcohol	3.243	8626	0.81	8615	74.095	638.33	2669.5
Isobutyl alcohol	3.237	8610	0.80	8599	74.095	637.14	2664.5

[a] Attention may be called to another very small correction, namely, the correction for the heat rendered latent in evaporating water in the bomb between 16° and 20°. In our bomb (containing 375 cc.) about 1.4 mg. of water must have been evaporated for 4° rise in temperature, or for the output of 10700 cal. Hence, each value should be raised $100 \times 0.0014 \times 540/10700 = 0.007\%$. This is so small as to be less than the experimental error, and is, therefore, not applied above.

The comparison of these results with those of others is interesting and leads to the conclusion that the heats of combustion of some of these substances are now known, at least relatively, with considerable accuracy. The best method perhaps of tracing the comparative values is to state the heat of combustion of volatile substances, such as benzene and toluene (which offer the greatest difficulties) in relation to some one standard substance, such as sugar, which has been the most often used. Benzene was found by Berthelot[1] to give out 2.52 times as much heat as sugar, gram for gram, on burning. Stohmann's[2] value, obtained in one way, was 2.5325, and in another 2.5275. Richards, Henderson and Frevert[3] concluded that 2.534 was the minimum value, but found that nitrogen in their bomb interfered with complete combustion and believed the true value to be higher. One of us, in collaboration with R. H. Jesse, Jr.,[4] verifying this prediction, found the value corrected to the vacuum standard 2.5382 (almost identical with our present value 2.5397, which we believe to be very near the true one). The later finding (in collaboration with F. Barry) of a lower value 2.533,[5] again raised suspicions of incomplete burning. At that time no determinations of the carbon monoxide in the residual gases were made; but there can be little question that the deficiency in the last named value is due to this cause, because our present repetitions of the methods which yielded it (involving the auxiliary use of sucrose, combustions 31, 32 and 33) yielded results more than 0.1% too low until corrected for the carbon monoxide found in the residual gases (on the average 2.5 cc. per combustion). Seemingly trivial details in manipulation may determine whether or not the flame of the burning liquid reaches the cool walls of the bomb in such a way as to have its combustion partially inhibited. The method employing a ring of naphthalene, used almost exclusively in the present work, is doubtless much superior to that in which a small heap of sugar is the auxiliary substance. That the trouble was due to incomplete burning of the volatile liquid and not to other faulty procedure is shown by the fact that the results of Richards and Barry on toluene (2.5769 times sugar) were almost identical with the figures which we have just detailed (2.5754 times sugar). The most recent values of Roth and von Auwers[6] for benzene, 10,012 (±2) per g. and for toluene 10,146 (±6) based upon their electrical calibration of the calorimeter as well as upon the burning of benzoic acid (assuming Fischer and Wrede's[7] value as correct) are apparently very near ours (which are, respectively, 10,014 and 10,155). Unfortunately, the agreement is not quite as close as it seems, since their calculation assumes the heat of combustion of a gram of the standard benzoic acid (weighed in vac.) to be

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[1] M. Berthelot, *loc. cit.*

[2] Stohmann, *ibid.*

[3] Richards, Henderson and Frevert, *Proc. Am. Acad.*, 42, 573 (1907).

[4] T. W. Richards and R. H. Jesse, Jr., THIS JOURNAL, 31, 288 (1910).

[5] T. W. Richards and F. Barry, *loc. cit.*

[6] W. A. Roth and K. von Auwers, *Ann. chim.*, **407**, 109 (1914).

[7] Fischer and Wrede, *Z. physik. Chem.*, **75**, 81 (1910). The very elaborate work of W. Swietoslawski (*J. Russ. Phys.-Chem. Soc.*, **46**, 935–75 (1914)) found a value as low as 6310 for the heat of combustion of benzoic acid. His recommendations concerning the use of the adiabatic calorimeter (*ibid.*, p. 1284) are excellent; but more of them had been anticipated at Harvard than he seems to have realized.

6325.5 cal., whereas ours takes this figure as 6320. Reduced to our standard, the results of Roth and Auwers become 10003 and 10137—results less than ours by 0.11 and 0.18%, respectively. Whether this difference is due to differences in the substances or to incomplete combustion in the German work it is impossible to say. The details of the work of Roth are carefully elaborated and it is clear at least that he got better results with his method than we were able to obtain until we analyzed the residual gases, a step which he did not take.

Further comparison of the new results with those of others, especially in view of the detailed discussion given by Roth in the paper so often quoted, may be omitted.

The new figures give another accurate basis for computing the effect on the heat of combustion of the familiar increment CH_2 of homologous series.

TABLE III.

Increase in Combustion Heat Due to CH_2.

(Substitution of CH_3 for H in alcohols and side chains.)

Difference between.			Kilojoules.
Ethyl alcohol-Methyl alcohol	= 1368.7	— 713.4	= 654
Propyl alcohol-Ethyl alcohol	= 2031.6	— 1367.7	= 654
Butyl alcohol-Propyl alcohol	= 2669.5	— 2031.6	= 638
Average of 3 differences in alcohols			= 649
Ethyl benzene-Toluene	= 4555.0	— 3911.1	= 644
Propyl benzene-Ethyl benzene	= 5202	— 455	= 647
Isopropyl benzene-Ethyl benzene	= 5206	— 4555	= 651
Tert. butyl benzene-Propyl benzene	= 5854	— 5205	= 652
Tert. butyl benzene-Isopropyl benzene	= 5854	— 5206	= 648
Average of 5 differences in aromatic substances			= 648

Evidently the addition of CH_2 produces on the average an increase in the heat of combustion of 648 kilojoules or 153.5 Cal.—a quantity almost identical with the provisional figures, 644 kilojoules reported by Richards and Jesse[1] and 646 reported by Richards and Barry.[2] This new value is different from that of Thomsen, 660 kilojoules or 158 Cal., doubtless because Thomsen's "universal burner" gave increasingly too high results with decrease in volatility.

The thermochemical effect disclosed in the above table refers to the substitution of the methyl group for hydrogen attached to a carbon singly bound to another: for in the aromatic compounds given, the additions are to the side chain. The effect seems to be slightly different when the methyl group replaces a hydrogen attached directly to the ring, as is shown by the following table—a table not full enough, indeed, to give a certain

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[1] Richards and Jesse, *loc. cit.*, p. 296.

[2] Richards and Barry, *ibid.*, p. 1019.

value to the average, but nevertheless serving as some indication of the differing effect.

Table IV.

Increase in Combustion Heat Due to CH_2 Added to the Benzene Ring.

Difference between

Toluene-Benzene	= 3911.1	— 3269.7	= 641
Xylene (*o*- or *m*-)-Toluene	= 4557	— 3911	= 646
Xylene (*p*)-Toluene	= 4541	— 3911	= 630
Mesitylene-Xylene (*m*)	= 5191	— 4557	= 634
			Average, 638

Further conclusions concerning the essential relations of these to one another and to other trustworthy data of the same kind are reserved for a later communication.

We take pleasure in expressing our indebtedness to the Rumford Fund of the American Academy of Arts and Sciences for the calorimetric bomb employed and to the Carnegie Institution of Washington for much of the rest of the apparatus.

Summary.

This paper gives detailed figures for the heats of combustion of the following substances in 18°-calories per gram (weighed in a vacuum): sucrose 3943, benzoic acid 6320, naphthalene 9614, benzene 10014, toluene 10155, tertiary butyl benzene 10434, cyclohexanol 8882, di-iso-amyl 11339, methyl alcohol 5326, ethyl alcohol 7101, propyl alcohol 8033, butyl alcohol 8615, isobutyl alcohol 8599.

It is hoped that in several respects most of these figures are more trustworthy than previous values, especially because more precaution was taken than usual to make sure that the combustion was in each case complete, and because the substances were in most cases very carefully purified and always carefully dried.

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