[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE HEATS OF COMBUSTION OF THE OCTANES AND XYLENES.

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Received January 10, 1910.

Julius Thomsen sought, long ago, to obtain clues concerning the constitution of organic substances from the comparison of their heats of combustion. This endeavor, although it failed of a wholly satisfactory outcome, nevertheless showed certain relationships between the several members of homologous series and unmistakable differences due to variations in structure. Enough regularity is manifested in these results to show that the idea is worthy of further study.

The first step is obviously to seek among the older results for possible causes of the incompleteness in the relationships. This may be due either to the inadequacy of the theory or to the imperfection of the experiments. Turning to the first, one must admit at once that the heat of formation does not exactly represent the free energy of the change involved in the building up of the substance from other constituent elements; and therefore that it cannot represent the work which may actually be done by the chemical affinity. Yet nevertheless because in most cases where aqueous solutions are not concerned, free energy change is not very far from total energy change, a close relationship would be expected; moreover not only the free energy but also the bound energy must be supposed to have some relation to chemical structure. Hence if each of its constituents has a precisely regulated magnitude, the total energy change itself should be significant, although its significance might not be so easy to interpret as if it were simpler in its nature.

On the other hand, the experimental part of Thomsen's investigations was, as is well known, not wholly satisfactory and was undoubtedly inadequate in many cases. His universal burner gave too high results with all liquids having boiling points much above room temperatures, and the higher the boiling point the greater was the error. On the other hand, the results of Berthelot and Stohmann were probably too low in the cases of the more volatile liquids, because in these cases some of the liquids undoubtedly failed to burn. Hence, without further light upon the subject, one would be inclined to give more weight to Thomsen's figures with the lower-boiling substances and to shift the weight gradually over to Berthelot's and Stohmann's, as the boiling point rises. Compromises of this sort, however, cannot but be unsatisfactory; and the facts point clearly toward the need of further experimental work free from the inaccuracies of that now available. The precision needed is indeed of a high order, for differences of structure often cause but slight variations in the total magnitude of the heat of combustion of the substances; and upon these slight variations the inference wholly depends.

For example, it will be seen later that the greatest deviation between the heats of combustion of various octanes is no greater than one-third of one per cent. and if the magnitude of the variation is to be certain within one-tenth of its value, the several observations must be determined to within less than two one-hundredths of one per cent., a degree of precision which has never been approached in thermochemical work of this kind.

It was with the hope of obtaining more precise knowledge of these important quantities that E. Fischer and Wrede,[1] in Berlin, and Richards, Henderson and Frevert, in Cambridge, began the revision of thermochemical data, using quite different methods, which seem to give about equally reliable results. The German experimenters used the electrical resistance thermometer and comparatively small temperature changes, applying the usual correction for cooling. On the other hand, the American experimenters contented themselves with good mercury thermometers and arranged the conditions so that these thermometers could be read with precision and could yield sufficiently accurate results, eliminating the cooling correction by causing the environment of the calorimeter to change in temperature at the same rate as the inner vessel itself. Both groups of experimenters have attempted only to determine a comparatively small number of a few typical substances. The work of revising the data is therefore only at its very beginning.

The present research consists of a continuation of the earlier Cambridge work. The method used in that work was chosen for the continuation because it is much more speedy in execution than that used in Germany. The electrical thermometer, admirable as it is in many respects, is an exceedingly complicated instrument, and the calculation of a single temperature from the observed data requires much patience. The complete calculation of a single calorimetric determination by this method requires several hours. This is in addition to the laborious preparation, and adjustment of the sensitive electrical instrument. On the other hand, the adiabatic Harvard method is simple in the extreme. The temperature change is read off from the thermometers at once and the only corrections which have to be applied are those easily calculated figures which give the error of the mercury thermometer at each reading. The correction for cooling is non-existent. Hence it is easily possible for a single experimenter by the Harvard method to conduct and calculate three determinations in a single day, whereas it would hardly be possible for him to do more than one a day by the more elaborate method. If this more elaborate method yielded more accurate results, the difference in time ought not seriously to influence the experimenter, but be-

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[1] Fischer and Wrede, *Kgl. Preuse, Acad. Sitzber.*, 19, 20, 21, 687 (1904). An important correction of the detail is to be found in *Z. physik. Chem.*, 53, 161 (1903).

cause apparently the range of error is about the same in both cases, the advantage of the quicker method is very obvious.

The object of the research and the method of attack having thus been clearly outlined, it becomes necessary to justify the selection of the individual substances to be chosen for experimentation. Obviously the compounds should be complex enough to allow of considerable differences in structure and yet, on the other hand, not so complex as to complicate too greatly the interpretation of the results. The theoretical problem is greatly simplified by avoiding the presence of more than two elements. Moreover the compounds should be capable of being prepared in a state of very great purity, free from other substances which could seriously influence their heats of combustion. Among the incalculable number of organic compounds, these deciding criteria narrow greatly the range of choice; and from the theoretical point of view there seemed to be no question that the simpler hydrocarbons are the compounds most suitable to serve as a starting point. Among these the octanes seemed to be, on the whole, the best, because their molecular complexity is enough to allow of great variety of arrangement, but not so great as to confuse the relationships. The difficulty of obtaining them in a pure state seemed in the first place to be a serious barrier, but Dr. Latham Clarke, during the summer of 1906, kindly undertook the working out of methods for this purpose. He became greatly interested in the problem from the point of view of organic synthesis and was able, in the course of several years, to prepare larger quantities than had ever been made before of these hydrocarbons and of great purity. Most of those which he prepared had indeed never been isolated by previous experimenters. It is our hope that in the course of time all of the isomeric octanes may be prepared and investigated. The present paper contains results for only five, the others having not yet been prepared in sufficient quantities for calorimetric experiments.

In order to refer the determinations to a satisfactory and perfectly definite standard, under the somewhat new conditions involved in this new series of experiments, it was desirable to repeat the determinations made with sugar and benzene by Richards, Henderson and Frevert, in the research already mentioned. These two substances serve admirably for calorimetric standards because they are so easily obtained in a pure state. They typify respectively the solid and the volatile liquid; methods which will serve for these two substances can easily be made to serve for most others among the combustible organic substances. As will be seen, the value obtained by the earlier experimenters for sugar was confirmed, and the anomalies in the combustion of benzene have been explained and corrected so that for this substance yet more satisfactory results are to be chronicled than were reported in the earlier paper.

The investigation showed that not only must the substance be confined in flexible glass bulbs, but that special pains must be taken with regard to the form of the containing capsule and the details of manipulation in order to insure complete burning. When the proper conditions have been established, the presence of nitrogen in the compressed gas of the bomb does not prevent the complete combustion of the hydrocarbon. It will be seen that the results finally obtained showed a very satisfactory agreement among themselves. Without the high degree of precision made possible by the devices to be described, the data could not have been accurate enough to form the basis of any important conclusions; because, as has been said, the variations from which inferences must be drawn are small in proportion to the total magnitude to be measured.

Apparatus.

During the first part of the work the adiabatic calorimeter was essentially like that used by Richards, Henderson and Frevert.[1] It consisted of a large silver calorimeter holding about 4.4 liters, in which was immersed the calorimetric bomb. This was surrounded below and on all sides by a jacketed vessel and covered with a copper pan. Both of these receptacles contained alkali to which acid was added in order that the temperature of the surroundings of the calorimeter should keep pace with that of the calorimeter itself. The temperature of this solution was easily and quickly changed. The air space between the silver calorimeter and the copper jacket was made as small as possible, the two vessels being insulated thermally from one another by pieces of cork. The complete insulation was tested electrically just before each experiment. The first diagram (Fig. 1), taken from the earlier paper, depicts the arrangement in section.

The method of carrying out the determinations was so nearly similar to those described in the earlier paper that details are unnecessary. In one essential point, however, an alteration was introduced, namely as to the rate of stirring. On account of the experience recently gained in other thermochemical work in the laboratory (namely that carried out by Dr. L. L. Burgess and one of us concerning the heat of solution of metals),[2] the agitation of the liquid in the calorimeter was more thorough than in the earlier experiments. On this account a correction had to be determined and applied for the heat gained through friction. This correction will be discussed later.

In the later experiments the method of jacketing the calorimeter was modified in a fashion which greatly increased the convenience of experimentation. It may be remembered that Richards and Forbes[3] made calorimetric determinations of the heat of amalgamation of metals in a

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[1] *Proc. Am. Acad.*, **42**, 573 (1907): *Z. physik. Chem.*, **59**, 532 (1907).

[2] In press at present.

[3] *Publication of the Carnagie Inst.*. No. 56.

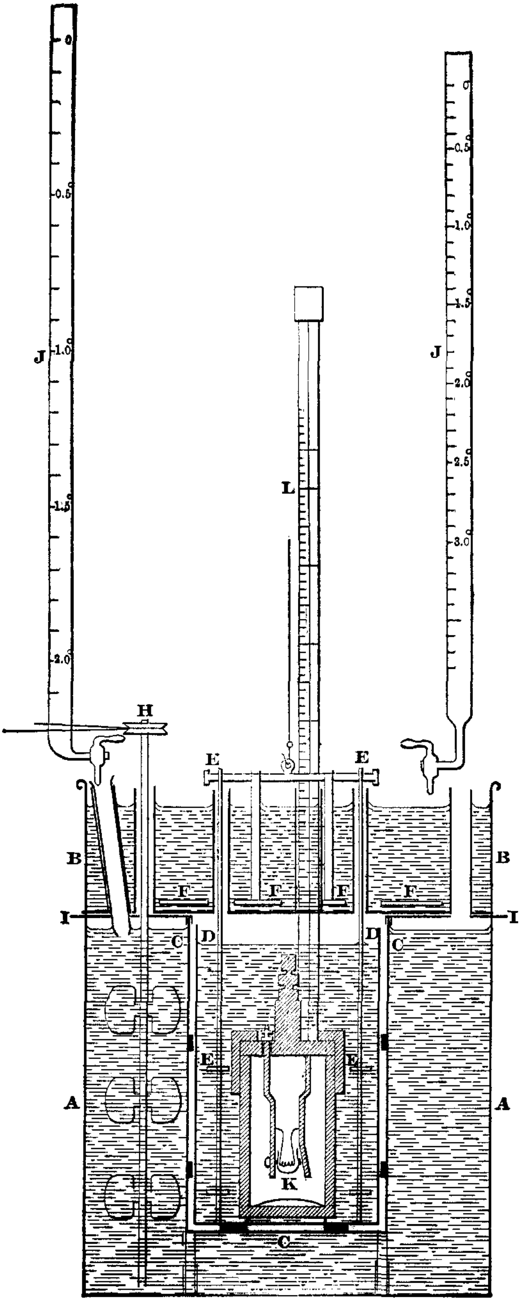

Fig. 1.

A. Outer vessel. B. Covering vessel. C. Nickel-plated copper can. D. Silver calorimeter. E. Stirrer for calorimeter. F. Stirrer for covering vessel. H. Stirrer for outer vessel. I. Copper cover. J. Burettes. L. Crucible containing substance to be burned. L. Thermometer.

calorimeter wholly enclosed in a single jacketing vessel, which was immersed below the surface of the liquid in the outer vessel. Dr. F. Wrede suggested the extension of the use of this kind of calorimeter for the bomb also. The obvious advantage of having only one jacketing vessel to regulate in temperature was found practically to outweigh the difficulty in keeping the apparatus water-tight. We succeeded in arranging the other experimental details so that this method of completely immersing the can surrounding the calorimeter will always be used in the future, in preference to the older apparatus involving a separate lower vessel and a movable pan above. The second diagram (Fig. 2) represents the arrangement.

A brief description of the essential features of the new apparatus is in place. To the top of the inner copper can C was soldered a flat projecting flange of copper of the same thickness as the can itself, and to the under edge of this flange was soldered a ring made from rectangular brass rod 1/8 inch thick and 1/4 inch high. As may be seen in the figure, this ring was separated from the side of the can and thus any possible thermal lag of the heavier mass of metal does not affect the inner vessel. The cover to this can consisted of a circular piece of sheet copper bearing tubes for the thermometer and stirrer and having on its upper edge a brass ring similar to the one soldered beneath the flange. When the calorimeter and its contents had been placed in the vessel (C), the cover was put on and a gasket of black sheet rubber was placed between the flange and the edge of the cover. These were then clamped together by means of several small brass clamps, sealing the can perfectly water-

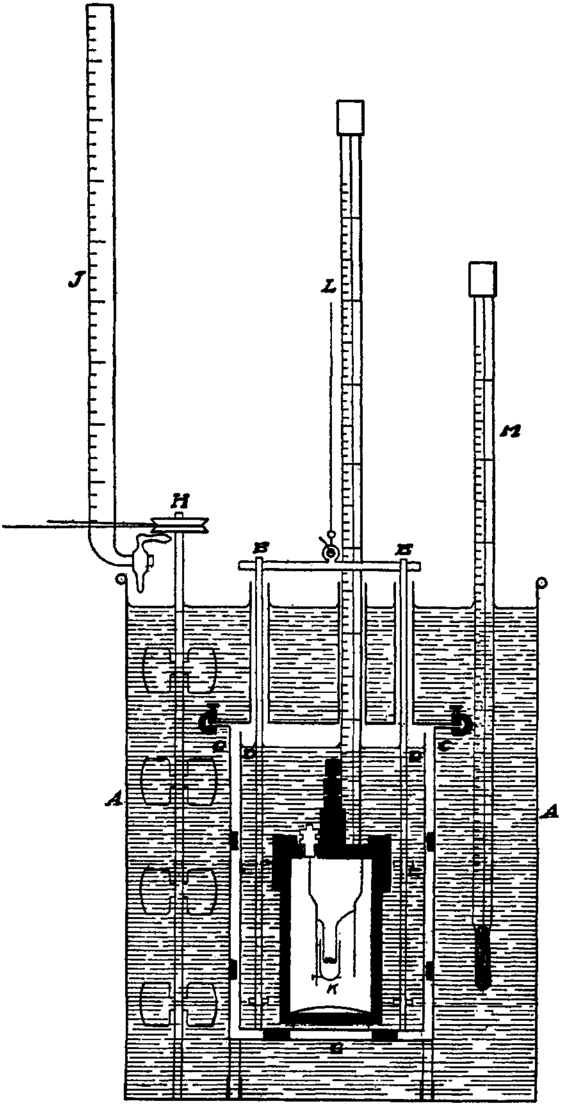

Fig. 2.
Vertical Section.

A. Outer vessel.
C. Nickel-plated copper can.
D. Silver calorimeter.
E. Stirrer for calorimeter.
H. Stirrer for outer vessel.
J. Burette.
K. Crucible containing substance to be burned.
L. Thermometer for calorimeter.
M. Thermometer for outer vessel.

tight. The whole arrangement was then completely submerged in the alkaline liquid in the outer vessel. With this arrangement one burette only is necessary, and only two thermometers must be compared. Determinations on sugar with this apparatus gave results identical with those obtained by the use of the older apparatus; that is to say, the advantage of this new form consists not so much in increased accuracy as in greater ease of operation.[1]

For accurate work the temperature of the outer jacket must be kept within 0.1° of that in the calorimeter. In following the rise, the acid was introduced in the immediate neighborhood of a rotary triple propeller driven by an electric motor at the rate of about 250 revolutions a minute. In this way equilibrium was established throughout the whole outer bath within a few seconds after the introduction of a quantity of acid. The sulphuric acid was run into the outer jacket (and into the cover also, in the earlier experiments) from the burettes graduated in terms of the volume of acid necessary to raise the vessels and their content 0.1°. The temperatures were observed at the same time by the thermometers.

As may readily be seen from the above description, the operator of the earlier form of apparatus was compelled at the same time to manipulate two burettes and to read the three thermometers in the calorimeter, the outer vessel and the cover. Since there was generally a rise of about 2° in the two minutes following the combustion, this requires rapid reading and manipulation; nevertheless, after some experience has been acquired, the task is not nearly so difficult as might at first sight be supposed. The second form of apparatus, in which the calorimeter was wholly beneath the solution in the larger vessel, does away with one burette and one thermometer.

The inner vessel (C) which held the calorimeter proper was in each case a can of heavy copper, nickel-plated and well burnished on the inside. Its walls were about of the same thickness as those of the silver calorimeter, so that the lag in heating each might be approximately the same. It was supported by metallic legs 5 centimeters high, so that there was plenty of room for the circulation of the alkaline solution beneath it.

The calorimeter itself (D) was a can of spun silver, 1357 g. in weight and of 4432 cc. capacity. It was placed within the can (C) and was insulated from it by pieces of cork. In the older form of apparatus, the air space between the silver and the nickel surface was about 3 millimeters thick; in the later form it was about 5 millimeters thick. The

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[1] Of the experiments recorded in this paper, those marked experiments 7–11 and 30–45, inclusive, were made with this "submarine" form of apparatus: all the others were made with the older form.

complete insulation was tested electrically before each calorimetric experiment.

The bomb was the one used by Richards, Henderson and Frevert. It was of the Atwater type, made by Singleton and Dinsmore, Middletown, Connecticut.[1] The inside of the bomb and the bottom of the cover were lined with spun platinum. To prevent possible heat effects from the oxidation of the lead gasket (used for sealing the bomb) during combustion, Richards, Henderson and Frevert protected the gasket by means of strips of gold foil.[2] In the earlier stages of the present work also, this method was used, but the accurate fitting of the gold strips is a tedious task, and, moreover, when the task was completed, it was necessary to use great force to screw down the top of the bomb sufficiently to prevent leakage. It was finally found that heavily gold-plated gaskets would answer the purpose. The gaskets were given three coats of gold, each coat being well burnished before the next was applied. The coating was not enough wholly to prevent oxidation, but the amount oxidized in a single determination was not enough to affect the heat of combustion appreciably. This was shown by the fact that the results of determinations on sugar with the gaskets protected by gold foil agreed well within the experimental error with those made with the gold-plated gaskets.

Instead of the capsule generally used for holding the substance to be burned, platinum crucibles were substituted. At first a larger crucible weighing 16 grams was used, but later it was found desirable to substitute a smaller crucible weighing 6 grams. The differences in heat capacity caused by this and other slight changes in the system were duly considered in the calculation.

Two thermometers were used for this work, both of the Beckmann type, graduated to 0.01°. One had been made by Fuess, and had a bulb containing about 75 grams of mercury and a very wide thread. The other was from Goetze, and had a smaller bulb and a narrower thread. Both were carefully standardized by comparison with two Baudin thermometers which had been calibrated by the French Bureau des Poids et Mèsures. The thermometers were also compared with two other thermometers of the Beckmann type which had also been separately standardized against the Baudin thermometers. The agreement was excellent. The Fuess thermometer had been standardized by the German Physikalisch-Technische Reichsanstalt, and this verdict agreed with the comparison with the French thermometers. No difference in the results obtained by the two thermometers could be detected.

The thermometers were standardized and all the determinations were

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[1] Atwater and Snell, THIS JOURNAL, **25**, 659 (1903).

[2] For details, see Richards, Henderson and Frevert, *Loc. cit.*, p. 576.

made in a room provided with such regulating devices that the temperature could be kept very constant. Therefore no corrections are necessary for effects of differences in room temperature on the projecting threads of the thermometers.

The oxygen used was supplied by the Linde Air Products Company, of Niagara Falls. It had been obtained from liquid air, and was free from carbon dioxide and from chlorine. Samples of each tank used were analyzed volumetrically for oxygen. The purity ranged in general from 97.5 per cent. to 98.2 per cent. of oxygen.

The Heat of Combustion of Sugar.

Two of the samples of sugar prepared for the work of Richards, Henderson and Frevert were still available for this work. These samples had been crystallized with all the necessary precautions: one (Sample A) from water, and the other (Sample B) from a mixture of water and ethyl alcohol of such proportions that the heat of combustion of the mixture was the same, gram for gram, as that of sugar itself. The concordance of the determinations on these two samples showed that not enough water was included in the crystals to be detected by thermochemical means.

The details of a combustion of sugar will serve to illustrate the method. The manipulation was similar except in a few minor points for the other substances burned.

About two grams of sugar in powdered form were weighed into the platinum crucible, and the crucible was placed on its support. This support consisted of a platinum ring attached to a heavy platinum wire projecting downward from the cover of the bomb and in metallic contact with it. Between this wire and a similar one, insulated from the bomb, was suspended a coil of fine iron wire, of measured length, the bottom of which just dipped into the sugar. If this wire is protected from the oxygen by being buried too deeply in the sugar, it is sometimes difficult to ignite the sugar by the passing of an electric current. In order to avoid a correction for the evaporation of water formed during the combustion, a little water, less than a cubic centimeter, was placed in the bomb. The cover was now placed on the bomb, and the latter was sealed by screwing down the steel cover cap. In the earlier experiments, oxygen was run in until the gauge registered 35 atmospheres; later, as will be seen, a lower pressure was employed.

The water for the calorimeter was measured in a graduated flask, delivering a definite amount of water at 20°, and brought to the temperature at which it was desired to start the experiment. The alkaline solution in the jacket and the cover were adjusted to the same temperature. The bomb was placed in the calorimeter, and two insulated copper wires for the introduction of the electric current were attached to the platinum wires from which the fine iron coil was suspended. After the water had been poured into the calorimeter, the cover was put in place. The well-insulated electric connecting wires passed through the copper tubes in the cover provided for the wires of the calorimeter stirrer. When the thermometer and burettes were in place, the stirrers were started and the temperatures of calorimeter, jacket, and cover were equalized to within 0.01°. Readings were made every minute with the aid of a good hand lens, the thermometer being tapped by an electric vibrator immediately before each reading. When constancy had been obtained, the electric circuit was completed and the burning of the iron wire caused the combustion of the sugar. During the first rapid rise the temperatures of the outer vessels were kept from 0.05–0.1° higher than that of the calorimeter. This was done because the thermometer in the calorimeter had a slightly geater lag than that outside, and also in order to give time for the complete distribution of the heat in the jacket and cover. Richards and Burgess have shown that it is safer to keep the outer jacket a little too warm than a little too cold.[1] After the first two minutes the rise was very nearly complete and the temperatures were adjusted to within one or two hundredths of a degree. In five or six minutes the maximum temperature was reached, although readings were continued several minutes longer.

The stirring (at the rate of 68–74 strokes per minute) was much more energetic than in previous work, and caused a slight warming effect. In two blank trials of 30 and 40 minutes respectively the heating effect for 10 minutes was 0.0030° and 0.0033° with an average of 0.0031°. Thus, for experiments which lasted 7 or 8 minutes after the combustion was started, a correction of —0.002° was subtracted from the observed rise, and in those others which took 9 or 10 minutes the correction applied was —0.003°.

One centimeter of the iron wire weighed 0.00194 gram. The water equivalent of the system having been about 3760 grams, the rise due to the burning of 1 centimeter was calculated, from the heat of combustion of iron to the magnetic oxide, to be 0.0009°. Probably some ferric oxide forms also, augmenting this value slightly. The electrical heat needed to raise 1 centimeter of the wire to the point of combustion (perhaps 800°)[2] must have been enough to raise the calorimetric system through approximately an additional amount of about 0.00005°, so that the total amount to be subtracted from the thermometer reading for each centimeter of wire was approximately 0.001°, allowing for the small amount of electrical heat which must have been generated in other parts

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[1] *Loc. cit.*, in press.

[2] Fischer and Wrede assumed 600° as the temperature of ignition. *Z. physik. Chem.*, *Arrhenius Jubelband*, **69**, 233 (1909).

of the apparatus. This was verified by four experiments in which no sugar was burned, the combustion of the usual length of wire changing the temperature of the system 0.014°, 0.014°, 0.015°, and 0.015°, respectively, results very closely in agreement with the calculated value.

After an experiment was ended and the gas had been allowed to escape, the interior of the bomb was carefully inspected for indications of incomplete combustion. No carbonaceous matter was found, except in a single preliminary experiment. This determination was, of course, rejected. No tests were made for carbon monoxide, since Richards, Henderson and Frevert found no traces of this gas upon repeated analyses.

A degree of acidity in the water in the bomb after combustion, capable of being neutralized by 4.0 cubic centimeters of a certain alkaline solution, indicated a quantity of nitric acid whose heat of formation must have raised the calorimeter 0.001°.[1] Corrections were duly made for this source of error.[2]

The following table records the results of a preliminary series of combustions. In these experiments the conditions were identical with those just detailed, the heat capacity being exactly the same, equivalent to about 3760 grams of water, and the same thermometer being used. Thus all the figures in the final column are comparable with one another and with the results of Richards, Henderson, and Frevert, where the same heat capacity was used, except for the fact that in the present case the weight of the sugar was reduced to the vacuum standard.

COMBUSTION OF SUGAR.
Preliminary Series.

Expt. No.	Weight sugar (in vacuum). Gram.	Observed rise of temperature (corrected for thermom. errors).	Correction for stirring.	Correction for iron wire burning.	Correction for HNO_3 formed.	Corrected rise due to sugar.	Corrected rise in temperature per gram sugar.
1	1.7577	1.868°	—0.002°	—0.015°	—0.003°	+1.848°	1.051°
2	2.0796	2.213	—0.002	—0.023	—0.004	+2.184	1.050
3	1.8473	1.964	—0.003	—0.015	—0.003	+1.943	1.052
4	1.9460	2.071	—0.003	—0.015	—0.004	+2.049	1.053
5	2.1769	2.306	—0.002	—0.015	—0.002	+2.287	1.050

The average rise of temperature in this calorimetric system for the combustion of 1 gram of sugar is thus 1.0512. For the same system, Richards, Henderson and Frevert found 1.0504 (or 1.0498, if allowance is made for the correction of the weight of sugar to vacuum, as has been done in the present calculation). The difference, about 0.13 per cent.,

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[1] The standardization of this solution was effected by the use of Thomsen's equation, $2N + 5O + H_2O + Aq = 2HNO_3Aq_3 + 29.8$ cal., assuming the heat capacity of the system to be equivalent to 3,760 grams of water.

[2] During the rise of about 2° enough water is evaporated to raise the aqueous pressure of the confined air space immediately above the surface of the water by 2 mm. of mercury. This causes a cooling effect in the neighborhood of 0.0001°, an amount entirely negligible.

is a small deviation, but one nevertheless greater than the probable accidental error of either average. A slight constant error is indicated; we are inclined to think that this may lie in the fact that in these later determinations the stirring of the calorimetric solution was far more rapid than in the earlier ones. The work of Richards and Burgess has shown that unless the agitation of the solution is so great that the rise of temperature of the solution is equably distributed throughout the whole calorimeter, a thermometer placed near the bottom of the calorimeter will register a temperature below the average value. Therefore the environment will not be kept warm enough, and some heat will be lost. The error thus caused is just about of the same magnitude indicated by the difference between the two series of experiments, and of course the later ones are far more trustworthy because this cause of uncertainty was removed. Incidentally it may be noted that this cause is by no means peculiar to the adiabatic method of calorimetry. It affects the cooling correction calculated by the Regnault-Pfaundler method quite as much as it affects the actual reading of the thermometer in the adiabatic method. Hence it is probable that in most calorimetric work the liquid has not been adequately stirred.

The proportions of water and metal in our calorimetric system were such that for temperatures between 0°–30° the decrease in the specific heat of water with rising temperature is about offset by the increase of the specific heat of the metal parts. Therefore there is little error in this respect in comparing the results of the present determinations done between 17.7–20.2° (at an average temperature of 19°) with those of Richards, Henderson, and Frevert, performed at an average temperature of 21.4°. Indeed it has been calculated with a good degree of approximation that the heat capacity of the system at 25° differed by less than 0.03 per cent. from that at 20°.

After the experience had been gained by the conduct of these preliminary determinations, liquids were studied, especially benzene and a number of esters. In the course of this work much further experience in calorimetry was gained, and in particular it was found that a smaller crucible was far more satisfactory than that of the large size. Accordingly, because sugar is a substance of great importance as a standard of reference, it was thought worth while to make another series with sugar, in which all the experience gained in the course of the work came into play. In this series of six determinations the heat capacity of the system had been somewhat less than in the preliminary experiments, because 10.5 grams of steel had been cut off the bomb in providing new holes to engage the spanner, 10 grams of platinum had been removed in substituting a smaller platinum crucible, and 9.2 grams less water were used in the calorimeter. The water equivalent of these changes amounted in all to 10.73 grams (which was 0.29 per cent. of the total water equivalent), and this system was used in the first two experiments recorded in the series given below. The other four involved a still somewhat smaller heat capacity, because in these last the pressure of the oxygen was only 20 atmospheres instead of 35 atmospheres. This change involves a further loss of water equivalent of 1.1 grams, or about 0.03 per cent. In the final column given below all the results are reduced to the same standard by adding 0.0003° to the figures in the last column obtained from Experiments 6 and 7 for 1 gram of sugar.

These two experiments just mentioned were made before the experiments with liquids, while Experiments 8 to 11 were made at the very conclusion of the whole research. The essential identity of the two sets is pleasing. Because of the close agreement of the results, the final figures in the last column are given to the fourth decimal place.

COMBUSTION OF SUGAR.
Final Series.

No. Exp.	Thermometer.	Weight of sugar.	Obs. rise of temperature.	Corr. for stirring and iron burnt.	Corr. for HNO_3.	Corr. temp. change.	Temp. change for 1 gram sugar.	Temp. change for 1 g. sugar corr. to lowest heat capacity.
6	B	1.5703	1.669°	—0.013°	—0.002°	1.654°	1.0533°	1.0536°
7	B	2.1784	2.312	—0.015	—0.002	2.295	1.0535	1.0538
8	B	2.0045	2.132	—0.016	—0.003	2.113	1.0541	1.0541
9	B	2.0563	2.187	—0.017	—0.002	2.168	1.0543	1.0543
10	B	2.0780	2.310	—0.017	—0.002	2.291	1.0539	1.0539
11	J	1.8772	1.997	—0.016	—0.003	1.978	1.0537	1.0537
								1.0539

Thus with the new heat capacity (0.32 per cent. less than in the previous series) the rise of temperature caused by 1 gram of sugar is 1.0539°, the extremes being less than 0.04 per cent. divergent from this mean. The preliminary series recalculated over to the basis of the new heat capacity would give 1.0545°, a value slightly greater, but probably within the limit of error of the first crude set of experiments where the individual determinations varied somewhat widely. It seems probable that the value 1.0539° is a correct one, and it may be used in subsequent work as the basis of conclusions concerning the relative heats of combustion with other substances as compared with sugar.

The Heat of Combustion of Benzene.

Two of the samples prepared for the previous work were still available.[1] These samples had been purified by several careful crystallizations: Sample A was from Merck's best grade of benzene and Sample B from Kahlbaum's "thiophenfrei" material. These had been preserved in well protected glass bottles with good ground-glass stoppers. Never-

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[1] *Proc. Am. Acad.*, **42**, 578 (1907); *Z. physik. Chem.*, **59**, 538 (1907).

theless, because they had been standing in this way for over two years it was thought best to prepare another specimen. Accordingly a new sample (C) was purified from Kahlbaum's "thiophenfrei" benzene by four successive crystallizations. In each case only about a third of the liquid was allowed to solidify. The crystals were allowed to drain slowly so that adhering mother liquor should be washed off by the liquid formed through the melting of the crystals themselves. In a determination conducted with all the ordinary precautions, no difference could be detected between the freezing point of the fourth crop of crystals and that of the mother liquor from which they had been crystallized. Furthermore, the temperature remained constant until practically all the liquid was frozen.

It has been mentioned at the first of the paper that the earlier method of combustion was finally modified, and that a more trustworthy arrangement was made. Before describing the modifications it is worth while to record the results of new experiments with the use of the earlier method.

In brief, this old method was as follows: The benzene was sealed and weighed in a completely filled glass bulb with very thin walls. The bulb was placed in the platinum crucible within the bomb, on the top of a small weighed quantity of sugar, which was ignited as usual by the coil of iron wire. The burning of the sugar burst the bulb and inflamed the benzene. The remainder of the manipulation was precisely as described above in the case of cane sugar. The heat capacity was the same as that used in the earlier experiments, Nos. 1 to 5, with cane sugar, and the rate of stirring was the same. The following table contains the results of the combustion of benzene in this way, the larger crucible with a diameter at the top of about 35 centimeters having been used as the capsule for the combustion, and the oxygen containing about 5 per cent. of nitrogen.

COMBUSTION OF BENZENE.
Preliminary Series with Large Crucible.

No. of Exp.	Thermom.	Weight of benzene in vacuum. Gram.	Weight of sugar. Gram.	Correction for sugar burned.	Rise due to benzene.	Rise per gram benzene.
12	B	0.7108	0.2715	0.286°	1.887°	2.655°
13	B	0.7535	0.2359	0.248	2.003	2.658+
14	B	0.6049	0.2711	0.285	1.607	2.657+
					Average,	2.657°

Thus 1 gram of benzene is shown to raise the calorimetric system 2.657°. Richards, Henderson and Frevert found for the combustion of benzene with oxygen containing the same amount of nitrogen the value 2.655°.[1] The difference of 0.002° is not much beyond the limit of error of the average and is just what one would have expected as a

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[1] *Proc. Amer. Acad.*, **42**, 588 (1907).

result of better mixing of the liquid in the calorimeter. Thus if the ratio of benzene to sugar 2.657/1.051 = 2.528, found by the new investigation, is compared with the older ratio 2.655/1.0504 = 2.528 (or, if the weights of benzene and sugar are both corrected to the vacuum standard, 2.526), the essential identity of the results is seen to indicate that the experimentation was really identical and to verify the previous work as far as accidental errors are concerned. The error due to the inadequate stirring in the older work was a constant one, and affected the experiments with sugar and with benzene in like manner, hence it is essentially eliminated from the ratio.

It will be remembered, however, that the earlier experimenters found a higher result when the oxygen contained less nitrogen, showing that combustion with 5 per cent. of inert gas present had not been complete; and they were inclined to believe that even the highest value which they obtained, about 0.3 per cent. higher than the one just given, was not quite high enough. Pure oxygen was at that time not obtainable under this pressure, and the cause of the incomplete combustion was pointed out as a matter well worth further investigation. An important point in explaining the anomaly is the following fact demonstrated by repeated experience, namely that whenever the benzene vapor had a chance to become intimately mixed with the gases in the bomb before combustion took place (as for example, by the premature bursting of the glass bulb by the pressure of the oxygen), the combustion was always incomplete. Under these circumstances we have detected the odor sometimes of nitrobenzene and sometimes of phenol—substances which are notoriously hard to burn. Once after rinsing out the bomb and diluting the liquid as usual with sodium hydroxide, the solution turned yellow immediately before the color change in the phenolphthalein took place—a phenomenon which might have been due to the presence of paradinitrobenzene.

These observations clearly point to the inadequacy of the usual method of burning a volatile liquid absorbed in a mass of cellulose, because under these conditions some of the liquid inevitably evaporates prematurely. They also form an important step, as has been said, in the train of reasoning which guided us to a better result.

In the present work we have been fortunate enough to solve the difficulty and discover the cause of the incomplete combustion of the benzene as well as to show why this cause does not affect experiments with non-volatile substances like sugar. We will show also that the suspicion that the true value is yet higher than the highest value found before was correct. The answer to the riddle was found only after protracted investigation. In the search for further light and experience, other liquids, especially methyl butyrate, methyl isobutyrate, and ethyl propionate, were subjected to calorimetric combustion, and it was through experience gained in working with these less combustible compounds that the error in the results of previous investigators with all volatile liquids became manifest. Therefore it may not be out of place here to describe the various methods which were tried in the attempt to obtain complete combustion of the esters.

At first the earlier method just described was used. This method was, however, obviously inadequate, for after the bomb was opened a distinct odor of the ester, varying in intensity in different experiments but always recognizable, could be detected in the issuing gases. Moreover, in several cases there was a deposit of carbon in the crucible. It seemed possible that the carbon was formed from sugar protected from the oxygen by the molten glass of the bulb, hence in a few experiments the bulb was placed on a small staging of heavy platinum above the surface of the sugar. In this way the sugar should have a chance to become thoroughly ignited before the melted glass could fall upon it. The plan succeeded, indeed, in eliminating the carbon, but the odor of ester was still very distinct. Evidently, at the moment when the bulb burst, some of the vapor was projected upward at a rate greater than the rate of propagation of the explosion; and as the amount which thus escaped was evidently insufficient to form an explosive mixture throughout the bomb, it escaped combustion.

The amount left unburned would naturally be greater, the greater the concentration of nitrogen present, for the effect of an inert gas in retarding the rate of propagation of an explosive wave is well known.[1] It is conceivable that the retarding effect here was so great that some of the vapor escaped combustion entirely. Dixon[2] has shown that in some cases an excess of one of the reacting gases also has a retarding effect, but this cause of incomplete combustion does not seem to have affected our work, probably because in no case the pressure of the oxygen exceeded 35 atmospheres.

These considerations adequately explained the effect of increasing the concentration of the nitrogen, and furnished the leading idea in effecting improvement.

The following arrangement was then tried. The bottom of the platinum crucible was so distorted as to form on one side a depression large enough to hold the bulb. On the bottom of the crucible, now somewhat above the bulb, sugar was piled in such a way that the capillary was buried in it. It was hoped that, when the bulb burst, the liquid would be projected into the burning sugar. Also, since the sugar was on a higher level, the vapor rising upward would have to pass through

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[1] See Mellor, "Chemical Statics and Dynamics," pp. 466ff.

[2] *Phil. Trans.*, 184, 97 (1893). *J. Chem. Soc.*, **69**, 774 (1896): **75**, 631 (1899)

an area filled with flame. But here too there was evidence that part of the vapor escaped combustion.

After a few fruitless experiments with an entirely different method, whereby it was hoped to reduce the rate of vaporization of the ester and thus to obtain a slower combustion, the use of the thin-walled bulbs was again resorted to. The bulb was now placed in the bottom of a much narrower crucible. About half way up in this crucible and on top of the bulb was fixed a rectangular plate of thin perforated platinum foil, and sugar was put on top of this. By having this plate rectangular instead of disc-shaped, there was room for the passage of the vapor around the sides of the plate and at the same time there was plenty of oxygen for the combustion. In this way the sugar was ignited first, and when the bulb burst, the vapor was forced to pass up through the top half of the crucible, which was completely filled with flame. Thus complete combustion was obtained, so that no odor of ester could be noticed in the residual gas, and there was no carbon deposit within the crucible or bomb, but with 35 atmospheres pressure the combustion took the form of an explosion of considerable violence, as the appearance of the crucible testified. In order to reduce the rate of combustion, the concentration of oxygen was therefore diminished; with 20 atmospheres of oxygen everything went smoothly, although the temperature within the crucible was still sufficient to fuse the thin platinum foil, especially where the iron oxide came in contact with it. Afterwards platforms of ignited asbestos paper were substituted for the platinum. With the thick asbestos paper there was some tendency toward carbonization in the bottom of the crucible, but with thinner paper this tendency disappeared. The thin asbestos fused together into a globule with the iron oxide—perhaps forming an iron silicate. That this gave rise to no thermal effect was proved by a combustion of sugar alone in which a similar asbestos platform was used. The agreement of this determination with the previous ones also proved the absence of any carbonaceous matter in the asbestos which had escaped combustion in the lower temperature of the Bunsen flame. In this way seemingly complete combustions of the esters, which yielded concordant results, were finally obtained.[1]

Having thus mastered the technique of the combustion of volatile liquids, we returned to the work upon the hydrocarbons, which are far

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[1] Although we were not entirely sure of the purity of the esters, they were probably as pure as most organic liquids which have been used by other physico-chemical investigators. Therefore we venture to give, for what they are worth, our results on methyl isobutyrate. which are typical. This ester had proved harder to burn than the others mentioned above. Therefore when the method was perfected it was applied to this one first, in order to be sure that it was capable of dealing with the worst cases. In the determination given below no ester smell could be detected and there was no carbon in the bomb. The ester supplied by Kahlbaum had been carefully

more easily burned than esters. It was not a great surprise to find that the new method yielded results which were higher than those previously found, for the earlier results had been thought too low. In order to make sure, however, that the increase was not due to the presence of combustible matter in the asbestos, very thin glass platforms (made from microscopical cover-glasses) were substituted for the shelf upon which the sugar was to be placed. To review, briefly, the method of combustion for benzene, in its final form, was as follows: the benzene in a very thin glass bulb was placed in the bottom of a narrow platinum crucible, 2 cm. in diameter and 2.5 cm. high. A few millimeters above the bulb was fixed a small platform of thin glass bearing a weighed quantity of powdered sugar. The passage of a current through the coil of iron wire ignited the sugar, which in its turn burst the bulb and ignited the benzene at a moment when the whole top of the narrow crucible was filled with flame from the burning sugar. Thus none of the benzene vapor could escape ignition. The trouble with the old method had been that the larger crucible was too wide. Moreover, the sugar had been beneath the benzene instead of above it, so that some of the benzene escaped unconsumed. The amount which thus escaped was greater when there was more nitrogen present than when there was less. Obviously, with non-volatile compounds like sugar the width of the crucible would make no difference.

There follows a series of determinations carried out as described, with always the same quantity of water in the calorimeter.

In a few cases there was conclusive evidence to show that the glass bulb had been broken by pressure previous to the combustion. This fractionated and dried with calcium chloride. and the fraction boiling between 91.4°–92.0° at 754 mm. was taken. No impurity was detected in this particular sample.

The combustions were made with 8.0 per cent. nitrogen in the bomb.

DATA FOR THE HEAT OF COMBUSTION OF METHYL ISOBUTYRATE.

Therm.	Wt. ester in vacuum.	Observed rise corrected.	Correction for sugar burned.	Correction for iron wire, stirring and HNO_3.	Corrected rise due to ester.	Rise per gram ester
B..........	0.8806	1.739°	—0.126°	—0.020°	1.593°	1.809°
J..........	0.6546	1.358	—0.152	—0.020	1.186	1.812
J..........	0.5147	1.134	—0.135	—0.017	0.932	1.811
J..........	0.6532	1.454	—0.255	—0.018	1.181	1.808
					Average,	1.810

Since a gram of sugar caused a rise of 1.0539° in the same system, methyl isobutyrate on burning is seen to evolve 1.717 times as much heat as an equal weight of sugar. Hence the molal heat of combustion in constant volume of methyl isobutyrate is 2901 kilojoules or 694.0 calories. Thomsen found for the vapor 717.6 calories under constant pressure.

Favre and Silbermann find for methyl butyrate (liquid) 693.4 cal. (*Annales chim. phys.*, [3] 34, 441 (1852).

Heat of vaporization 7.9 cal. (Schiff, *Liebig's Ann.*, **234**, 338 (1886)).

was detected by means of the odor of the benzene in the small amount of oxygen always allowed to escape just before the combustion. Such experiments were of course rejected. Otherwise, all the experiments made are recorded in the following table:

HEAT OF COMBUSTION OF BENZENE.

Final Series.

Exp. No.	Sample.	Per cent. N_2.	Wt. benzene in vacuum.	Wt. sugar.	Change of thermometer corrected.	Correction for sugar burned.	Correction for iron wire and nitrogen burned and for stirring.	Rise due to benzene.	Rise due to 1 gram benzene (weighed in vacuum).
15	B	8.0	0.7763	0.2376	2.347	—0.250	—0.019	2.078	2.677
16	B	8.0	1.0144	0.1050	2.847	—0.111	—0.021	2.715	2.676
17	B	8.0	0.6443	0.2431	1.999	—0.256	—0.019	1.724	2.676
18	B	2.6	0.7480	0.3199	2.355	—0.337	—0.017	2.001	2.675
19	C	2.6	0.7365	0.2522	2.252	—0.266	—0.017	1.969	2.674
20	A	2.6	0.7360	0.2068	2.202	—0.218	—0.017	1.967	2.673
21	C	2.6	0.7618	0.2420	2.307	—0.255	—0.017	2.035	2.672
22	A	2.0	0.6860	0.2823	2.152	—0.298	—0.018	1.836	2.677
								Average =	2.6750°

Thus one gram of benzene weighed in vacuum evolves enough heat on combustion to raise the special calorimetric system employed 2.675°, the figure having a probable error of 0.0004. The extreme deviation from the mean amounts to less than 0.003°, which, although larger than in the case of sugar, is nevertheless as small as could be expected. considering the complication of the process and the fact that less than a gram of benzene was usually used in the combustion.

Not only is the series satisfactory as a whole, it is also convincing as regards the agreement in several samples of benzene. The average value for Sample B is 2.676°, for A 2.675°, and for C but slightly less, 2.673°. These differences are within the reasonable limit of error, especially since only two determinations of each were made with Samples A and C.

It is interesting to note that the presence of nitrogen has no longer any effect upon the completeness of combustion. Of the eight determinations in the table, the first three were made in the presence of 8 per cent. of nitrogen, whereas in the last five the per cent. of nitrogen was 2.6 or less. The amount of heat evolved in the first three, per gram of benzene, was 2.676, in the last five 2.674. This difference is not greater than the possible experimental error. It is in fact in a direction opposite from that which would have been expected if the difference had any significance. This is a very satisfactory evidence that the combustion was complete in every case, for if it had been incomplete with 2.6 per cent.

of nitrogen, it would have unquestionably been still less complete with 8 per cent.

The only effect of decreasing the nitrogen in our accepted experiments was to cause the correction of nitric acid formed to become noticeably smaller, so that in many instances where the nitrogen amounted to 2.6 per cent. or less, this correction amounted to practically nothing. The actual amounts of nitric acid found were as follows: with 8 per cent. of nitrogen, 0.04, 0.06, 0.03 gram, respectively; with 2.6 per cent. of nitrogen in only two experiments (the second and last) did the amount of nitric acid exceed 0.01 gram.

Circumstantial evidence supported this conclusion that complete combustion of the benzene had at last been obtained. No indications of incompleteness—neither deposited carbon nor residual odor—were perceptible in the bomb after combustion. No test was made for carbon monoxide, because Richards, Henderson and Frevert were unable to find any traces of this gas even with their less efficient method.

In order to show that the first rush of benzene vapor upon the bursting of the bulb in the moment of ignition had not so blown about the powdered sugar that part of it escaped combustion, the following test was made in one case (No. 21). After the combustion the bomb had been rinsed out with very pure water and the nitric acid titrated with sodium hydroxide solution, the sodium nitrate solution was evaporated to dryness in a tared platinum dish. The gain in weight of this dish amounted to 0.0008 gram more than the amount of sodium nitrate calculated from the quantity of sodium hydroxide solution used. Tests by the resorcinol method and with Fehling's solution (after treatment which would have inverted sugar) failed to show any traces of sugar. Even if the gain was really unburned sugar, the temperature rise due to it would have been only 0.0008°, which is beyond the limit of error of the thermometric readings.

Another experiment (No. 22), in which the sugar was compressed into pellets so that it could not be easily blown about, gave a result in perfect agreement with the rest of the series. Benedict and Fletcher[1] have shown that the only important effect of this treatment is a diminution of the speed of reaction.

After one experiment a light deposit of a brownish red powder was found on the walls of the bomb. This proved, upon examination, to be an oxide of iron, obviously without effect upon the value derived from the determination, because the heat of combustion of the iron was always allowed for.

After scores of combustions, the crucibles showed no visible signs of

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[1] THIS JOURNAL, **29**, 753 (1907).

having combined with carbon. The high temperature and the presence of an excess of oxygen undoubtedly prevented this cause of error.

The heat capacity of our calorimetric system has not yet been determined by the method of summing up the water equivalent of the component parts.[1] Thus the results in this paper are to be expressed as ratios, the standard being the temperature rise produced in our calorimetric system by one gram of sugar.

Expressed in this way, our final results are as follows:

Average rise produced in the calorimetric system by one gram of benzene	2.6750°
Average rise produced in the calorimetric system by one gram of sugar	1.0539°
Ratio benzene to sugar = 2.6750/1.0539	2.5382

This is now directly comparable to the results of Richards, Henderson and Frevert. Their ratio of the heats of combustion of like weights of benzene and sugar (when the oxygen was as pure as they could make it) was 2.534. If vacuum corrections for the weights of sugar and of benzene are applied, their value falls to 2.532. Our heat of combustion is thus about 0.26 per cent. higher. This difference was only to be expected, since these investigators clearly showed that their figure was probably less than the true one, on account of the effect of the nitrogen present under the conditions of the earlier experiments. Although the lowering of the heat of combustion was not exactly proportional to the per cent. of nitrogen present, one would have inferred by extrapolation from their experiments that the true value must be about 2.54, in close agreement with our new value 2.538.

Stohmann's ratio for the heat produced by benzene in comparison with that by sugar is 2.5225.[2] This ratio is based upon the determinations for benzene done with the Berthelot bomb. Stohmann also made some earlier determinations with the apparatus of Berthelot and Vieille (a modification of that of Favre and Silbermann), in which the benzene was burned from a lamp in a stream of oxygen. The average of these determinations gave the value 9.977 Calories per gram of liquid benzene at 17°. The ratio derived from this is 2.5275. Thus the results of Stohmann's two series are a little over 0.6 per cent. and 0.4 per cent.,

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[1] Richards and Rowe have recently devised a new method for determining specific heats (*Proc. Am. Acad.*, **43**, 473 (1908)) and are further perfecting it. It seems probable that with slight modifications their method can be used for the accurate determination of the heat capacity of a bomb. This method is more easily carried out in a chemical laboratory than is the electrical method of Jaeger and von Steinwehr (*Verhandl. d. d. physik. Ges.*, **5**, 50 (1903): *Ibid.*, **5**, 353 (1903); *Z. physik. Chem.*, **53**, 153 (1905))

[2] Stohmann and Langbein, *J. prakt. Chem.*. **45**, 313 (1892); **40**, 77, 81 (1889); Stohmann, Rodatz and Herzberg. *Ibid.*, **33**, 241 (1886).

respectively, lower than our ratio. Berthelot's[1] ratio is lower still, about 2.520. Julius Thomsen[2] burned benzene vapor, finding a result to which Stohmann applied corrections for the heat of vaporization, using Regnault's formula for the heat of vaporization, and Kopp's value for the molecular heat capacity of liquid benzene. Thomsen's value thus reduced to the heat of combustion in constant volume of liquid benzene at 17° is for a gram of benzene, 10.135 Calories, a value much higher than the others.

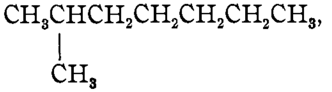
The most probable figure for sugar is that of Fischer and Wrede,[3] who found that a gram of sugar on complete combustion yields 16.545 kilojoules of heat energy. If we accept this value, a gram of benzene is found from our work to yield 2.5382 × 16.545 kilojoules = 41.99 kilojoules. If a kilojoule at 19° is taken as 4.179 Calories, the heat of combustion of a gram of benzene is 10.049 Calories, a result almost as high as Thomsen's.

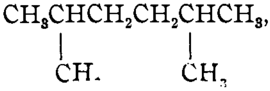
In the more usual and more generally useful standard, 1 mole or gram-molecule of benzene (78.05 grams) evolves 3278 kilojoules. or 784.3 Calories on combustion.

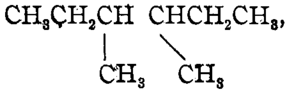
Heats of Combustion of the Octanes.

The next substances whose heats of combustion were studied were five isomeric octanes. These compounds were furnished us by Dr. Latham Clarke, of this laboratory, who is now engaged in an attempt to prepare all the possible isomeric octanes. The octanes burned were:

Normal octane,[4]—$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, boiling point 124.5°.

2-Methyl heptane or iso-octane,[5]  $CH_3\underset{\displaystyle CH_3}{CH}CH_2CH_2CH_2CH_2CH_3$, boiling point 116.0°.

2,5-Dimethyl hexane or diisobutyl,[6]  $CH_3\underset{\displaystyle CH_3}{CH}CH_2CH_2\underset{\displaystyle CH_3}{CH}CH_3$, boiling point 108.4°.

3,4-Dimethyl hexane or di-secondary butyl,[7]  $CH_3CH_2\underset{\displaystyle CH_3}{CH}\;\underset{\displaystyle CH_3}{CH}CH_2CH_3$, boiling point 116.2°.

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[1] Berthelot and Vieille, *Ann. chim. phys.*, [6] 10, 458 (1887); Berthelot, *Ibid.*, [5] **23**, 193 (1881).

[2] *Thermochemische Untersuchungen*, IV, 59 (Leipzig, 1886).

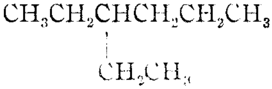
[3] *Z. physik. Chem.*, *Arrhenius Jubelband*, **69**, 234 (1909).

[4] Riche, *Ann.* (Liebig), **117**, 265: Schorlemmer, *Ibid.*, **162**, 280; **147**, 227; **152**, 152. Zincke, *Ibid.*, **152**, 15. Paterno and Peratoner, *Ber.*, **22**, 467.

[5] Clarke, THIS JOURNAL, **31**, 107 (1909).

[6] Wurtz, *Ann.* (Liebig), **96**, 365.

[7] Norris and Green, *Amer. Chem. J.*, **26**, 293.



3-Ethyl hexane,[1] $CH_3CH_2\underset{\substack{|\\ CH_2CH_3}}{CH}CH_2CH_2CH_3$, boiling point 115°.

Great care was taken by Dr. Clarke in the preparation of these compounds and they were undoubtedly purer than most organic liquids of this sort. The earlier preparations formed a small amount of black precipitate on standing over mercury, but the final specimens used in the combustion experiments were practically free from unknown contamination which caused this effect. Careful experimentation showed them to be free from sulphur and halogen, and they were dried by distillation over sodium.

Two samples of 2,5-dimethyl hexane, which had been prepared by different methods, were used. One sample had been prepared by the action of sodium on isobutyl iodide, $(CH_3)_2CHCH_2I$. The other had been prepared by treating acetoacetic ester with sodium and isobutyl iodide. By the action of a magnesium alkyl iodide, the ketone, resulting from saponification of the product obtained above, was reduced to the hydrocarbon. The first sample boiled 0.2° lower than the second and there were also differences of a few units in the fourth decimal place of the densities and in the fifth decimal of the refractive indices, but no differences in the heats of combustion could be detected. In the table, these samples have been marked A (b. p. = 108.3–108.5°) and B (b. p. = 108.1–108.3°). Dr. Clarke considers Sample A slightly purer.

The method of burning the octanes was essentially the same as that used for benzene, except for a slightly different arrangement of the sugar used to start the ignition. In the present case this substance was compressed into pellets, one of which was placed upon the glass plate above the bulb and another, much smaller, was fixed in the coil of iron wire suspended about a millimeter above the large pellet. Another minor modification made in the case of the latter experiments was the invariable use of flattened bulbs instead of spherical ones sometimes employed for holding the liquid. This was especially important because of the considerable compressibility of the octanes; for flattened bulbs are much more flexible than spherical ones, and the danger of their breaking when the bomb is charged with gas is much less.

With the octanes, as with benzene, whenever the bulb broke previous to the combustion, the burning was never complete. Each of these octanes has a characteristic odor and the presence or absence of any smell in the gases after combustion formed a very delicate test of the completeness of the combustion. Whenever the bulb did not break prematurely, the combustion was always complete.

The effect of the amount of nitrogen present in the bomb was tested

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[1] This substance has not been described in full by Dr. Clarke.

in the case of one octane (diisobutyl). Since combustions in which the concentration of the nitrogen exceeded 6 per cent. gave results identical with those with only 2 per cent., it was not thought necessary in the other cases to evacuate the bomb before running in the oxygen. The table following gives the rise per gram of octane in the same calorimetric system as that used in the final experiments with benzene. For the last three compounds given in the table the newer form of jacketing apparatus was used. The somewhat increased air space around the calorimeter can involve the heating of more air, but this amount in a system whose heat capacity is nearly 3800 calories is entirely negligible.

DATA CONCERNING HEAT OF COMBUSTION OF OCTANES.

No. of exp.	Name of substance.	Designation of sample.	Weight octane vacuum. Gram.	Weight sugar vacuum. Gram.	Corr. total rise of temperature observed.	Corr. sugar burnt.	Corr. iron wire stirring HNO_3.	Rise due to octane.	Rise per gram octane.
23	Normal		0.4723	0.1903	1.655°	—0.201°	—0.018°	1.436°	3.040°
24	octane		0.4915	0.1933	1.718	—0.204	—0.019	1.495	3.042
								Average,	3.041
25	Diisobutyl	B	0.6112	0.1521	2.034	—0.160	—0.018	1.856	3.036
26		B	0.6293	0.1045	2.040	—0.110	—0.018	1.912	3.038
27		A	0.5298	0.1395	1.773	—0.147	—0.018	1.608	3.035
28		B	0.5939	0.1381	1.974	—0.145	—0.016	1.813	[3.054[1]]
29		A	0.4944	0.1273	1.656	—0.134	—0.020	1.502	3.038
30		B	0.6606	0.1966	2.234	—0.207	—0.020	2.007	3.038
								Average,	3.037[1]
31	2-Methyl-		0.4340	0.2475	1.599	—0.261	—0.018	1.320	3.041
32	heptane		0.3439	0.2100	1.286	—0.221	—0.017	1.048	3.047
								Average,	3.044
33	3,4-Methyl		0.4283	0.2940	1.628	—0 310	—0.018	1.300	3.035
34	hexane.		0.4681	0.2478	1.702	—0.261	—0.018	1.423	3.040
								Average.	3.038
35	3-Ethyl hexane.		0.3720	0.1428	1.296	-0.150	-0.017	1.129	3.035

[1] Experiment 28 is 0.6 per cent. higher than the values for the other experiments, an amount very much greater than can be explained by ordinary experimental error. It is included in the table. because no fault was found in it adequate to account for this discrepancy. The error was probably caused by a mistake in reading one of the thermometers. A single division of the scale (the hundredth of a degree) would have caused the error in question. and every one knows how easy it is to make such a mistake as this. Because of the consistent verdict of the other five experiments, we have not included the result of Experiment 28 in the average. Those who wish to retain it will use 3.040° as the average rise caused by a gram of diisobutyl instead of 3.037°, as given above.

No completed determinations are omitted from the table; all are given which were actually carried out, except those in which the bulb was known to have burst prematurely.

Thus the rises of temperature in our calorimetric system caused by the combustion of the five octanes, namely, the isomeric compounds, normal octane, diisobutyl, 2-methyl heptane, 3,4-dimethyl hexane, and 3-ethyl hexane, were found to be respectively, per gram of liquid, 3.041, 3.037, 3.044, 3.038, and 3.035. The differences are small, but seem to be really significant, because they are distinctly greater than the variations among the individual experiments on any one substance.

In order to express these results in terms of gram-molecules, it is necessary to compare these rises of temperature with those produced by a gram of sugar in order to transform the values into terms of energy. The following table contains these comparisons and gives in the first column the name of the substance, in the second column the rise in our system per gram as given above, in the third column these numbers divided by 1.0539 (the rise of temperature caused by a gram of sugar in the same system), in the fourth column the numbers in the third column multiplied by 16.545, in the fifth column these numbers multiplied by the gram-molecular weight, giving the heat of combustion of 1 mole in kilojoules, and in the last column the same data expressed in terms of calories.

In calculating these results, the molecular weight of the several octanes is taken as 110.11 and the equivalent of one joule is taken as 0.2393 calorie, the value based upon the work of Callendar and Barnes for the 19° calorie, the range over which our experiments were carried out:

HEATS OF COMBUSTION OF FIVE ISOMERIC OCTANES.
(In constant volume, measured at 20°.)

	Rise per gram.	Ratio octane to sugar.	Heat from 1 gram of hydrocarbon (kilojoules).	Heat of combustion of 1 mole in kilojoules.	Heat of combustion of 1 mole in calories.
Normal octane.........	3.041°	2.885	47.73	5256	1257
2,5-Dimethyl hexane...	3.037	2.882	47.68	5250	1256
2-Methyl heptane......	3.044	2.888	47.78	5261	1258
3,4-Dimethyl hexane...	3.038	2.883	47.70	5252	1256
3-Ethyl hexane........	3.035	2.880	47.65	5247	1255

The five octanes thus have similar heats of combustion, ranging from 5,247 to 5,261 kilojoules, or a range of about one-quarter of 1 per cent. Of the five measured, 3-ethyl hexane has the lowest heat of combustion and 2-methyl heptane the highest. As far as has been discovered by a search into the literature of the subject, no one else has ever determined the heats of combustion of these substances. The differences observed above may represent real differences between the respective energy contents of the five substances; but because only small quantities were available for individual experiments on account of lack of material, the uncertainties of the averages are greater than in the case of benzene. This is especially true with regard to 3-ethyl hexane, of which only one determination was made. Nevertheless it is clear that these isomers are very near together in their heats of combustion, the deviation from the mean value, 5,253 kilojoules, being less than 10 kilojoules on each side, or less than 0.15 per cent. The significance of the figures will be considered later in the summary of all the results.

The Heat of Combustion of the Xylenes.

The only determinations of the heats of combustion of xylenes that have been made before this research was begun were those of Stohmann.[1] He was far from satisfied with the purity of his material, some of which he prepared himself, while part was obtained from the most reliable commercial sources. He neglected in his paper to give boiling points or any other data which might indicate the degree of purity. The combustions themselves were probably more reliable than those of the more volatile hydrocarbons, because of the higher boiling point and less evaporation before combustion, but evidently the figures need thorough revision.

The preparation of pure xylene is by no means an easy matter, as is so often the case with organic compounds. The original material used for the following determinations was the best that Kahlbaum could furnish. The samples had been many times carefully fractionated by electrical distillation in the course of the previous work.[2] Just before being used in the present work the specimens were dried over anhydrous copper sulphate and again distilled. The boiling points, corrected for the projecting thread of the thermometer, were found to be in excellent accord with those found in previous investigations. The following table records these boiling points with the pressures in parentheses, as well as the boiling points given by Schiff[3] and Perkin.[4] Schiff's readings, like ours, were corrected for the protruding column. In Perkin's the thermometer was wholly immersed in the vapor.

BOILING POINTS OF XYLENE.

	Richards and Jesse.	Schiff.	Perkins.
Orthoxylene.......	143.9°–144.2° (763)	141.1° (756.2)	142.6° (760)
Metaxylene........	138.8°–139.2° (761)	139.2° (759.2)	139.3° (760)
Paraxylene........	137.8°–138.1° (754)	138.1° (761.2)	137.5° (760)

About the boiling piont of orthoxylene there seems to be some doubt, the values ranging from 141° to 144°. Neither Schiff's nor Perkin's

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[1] *J. prakt. Chem.*, **35**, 40 (1887).

[2] *Z. physik. Chem.*, **61**, 449 (1908); THIS JOURNAL, **30**, 8 (1908).

[3] *Ann.*, **220**, 92: **223**, 66.

[4] *J. Chem. Soc.*, **69**, 1249 (1896).

values agree very well with the present experience, but Woringer[1] has found 143.7°, a value not far from ours.

These substances were burned in the calorimetric bomb under exactly the same conditions as those used in the case of the octanes. Two of the determinations were vitiated by the premature bursting of the bulb containing the liquid. The experiment was nevertheless continued, to see what would happen, and in these cases a noticeable odor, resembling that of bitter almonds, could be detected afterwards. These, of course, were rejected. In all of the cases excepting the first combustion of paraxylene, the amount of nitrogen present in the oxygen was only two per cent. In this single case it was 6 per cent., but this difference caused no diminution in the heat of combustion. Therefore it is safe to assume that in all the cases the combustion was complete, especially as no odor or sign of deposited carbon was visible in any case. Only in two cases, the first combustion with metaxylene and the first combustion with paraxylene, was enough nitric acid formed to cause 0.001° change in the temperature. In these two cases this correction has been added to the correction for the iron wire burned. The stirring correction was in each case 0.002°, this also has been included with the other. The thermometer numbered B was used in all these determinations:

TABLE—DATA FOR HEAT OF COMBUSTION OF XYLENES.

No. of expt.	Substance.	Wt. xylene vacuum.	Wt. sugar.	Total corr. rise of temperature.	Corr. for sugar.	Corr. for wire for stirring and for HNO_3 found.	Rise due to xylene.	Rise per gram xylene.
36	Orthoxylene....	0.6365	0.2421	2.018	—0.255	—0.017	1.746	2.743
37		0.7429	0.3276	2.402	—0.345	—0.016	2.041	2.747
38		0.7307	0.2528	2.288	—0.266	—0.016	2.006	2.745
							Average,	2.745
39	Metaxylene....	0.6871	0.2534	2.171	—0.267	—0.018	1.886	2.745
40		0.7019	0.2008	2.156	—0.212	—0.016	1.928	2.747
41		0.6828	0.3314	2.238	0.349	0.016	1.875	2.743
							Average.	2.745
42	Paraxylene.....	0.5955	0.3190	1.985	—0.336	—0.018	1.631	2.739
43		0.6980	0.2786	2.220	—0.294	—0.016	1.910	2.736
44		0.7380	0.2924	2.342	—0.308	—0.017	2.017	2.733
45		0.5871	0.2260	1.859	—0.238	—0.016	1.605	2.734
							Average,	2.736°

Thus a gram of orthoxylene on burning caused a change of temperature in our calorimetric system of 2.745°; and metaxylene gave precisely

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[1] *Z. physik. Chem.*, **34**, 264 (1900).

the same quantity, within the range of error of our experiments. On the other hand, paraxylene evolved slightly less heat, the temperature in this case rising only 2.736°.

There follows a table which translates these temperature changes into terms of energy, similar to the table already given for the five isomeric octanes. In this case, as in the other, the change in temperature produced by a gram of sugar is taken at 1.0539 in our system: the energy represented by the combustion of 1 gram of sugar as 16.545 kilojoules, the large calories as equal to 4.179 kilojoules. The molecular weight of xylene is taken as 106.023.

HEAT OF COMBUSTION OF THREE ISOMERIC XYLENES.

(In constant volume, measured at 20°.)

	Rise of temp. per gram.	Ratio of xylene to sugar.	Heat from 1 gram of hydrocarbon, kilojoules.	Heat of combustion of 1 mole in kilojoules.	Heat of combustion of 1 mole in calories.
Orthoxylene........	2.745°	2.605	43.100	4570.0	1093.5
Metaxylene.........	2.745°	2.605	43.100	4570.0	1093.5
Paraxylene.........	2.736°	2.596	42.951	4554.0	1089.8

The orthoxylene and metaxylene give the same molecular heat of combustion, namely, 4570 kilojoules, or 1093.5 large calories, while the heat of combustion of the para compound is 0.35 per cent. less. Stohmann found for all three values (reduced to the same standard as those employed above) 1084 large calories, or nearly 0.9 per cent. lower than our value for the ortho- and metaxylenes and more than 0.5 per cent. lower than the new value for the paraxylene. This figure is not surprising. Stohmann, as has been said, was much dissatisfied with his determinations, so much indeed that he left the individual experiments unpublished, contenting himself with giving the averages. His hypothetical method of calculating the value from benzene, phenols, etc., need not receive serious consideration, although they yield results not far from ours. A careful survey of the literature seems to leave no doubt that the values given in the above table are by far the most probable of any thus far published.

Theoretical Considerations.

It is interesting now to bring into a single table the several results for the heats of combustion of the various compounds studied in this paper with the idea of comparing them and interpreting their variations. Together with the heats of formation of the several compounds expressed in kilojoules there are given below the boiling points of the various compounds and the approximate latent heats of vaporization. For the xylenes these values have been determined by Richards and Mathews in an investigation soon to be published; but for all but one of the octanes no data are available, and it was necessary accordingly to compute these latent heats according to the rule of Trouton. There are given also in the last column of the table several approximate heats of combustion of the substances in a vaporized condition—simply the sum of the quantities in the two preceding columns:

HEATS OF COMBUSTION OF LIQUID AND OF VAPORIZED HYDROCARBONS.

(In constant volume, determined at 20°.)

	Boiling points.	Heats of combustion of liquids (kilojoules).	Approximate heats of vaporization.	Approximate heats of combustion of vapors (kilojoules).
Benzene	80.4°	3277	30.8[1]	3308
Orthoxylene	144.1	4570	37.5[1]	4607
Metaxylene	139.0	4570	36.1[1]	4606
Paraxylene	138.0	4554	35.6[1]	4590
Normal octane	124.5	5256	33.8[2]	5290
2,5-Dimethyl hexane	108.4	5250	32.0±	5282
2-Methyl heptane	116.0	5261	33.0±	5294
3,4-Dimethyl hexane	116.2	5252	33.0±	5285
3-Ethylhexane	115.0	5247	33.0±	5280

This table presents several interesting relations, the most important of which may be here briefly summarized:

On comparing the heat of combustion of the liquid benzene, 3277, and the average heat of combustion of the liquid xylenes, 4565, it is evident that the addition of CH_2 causes an increase in the heat of combustion of 644 kilojoules. This is not far from the number found by Thomsen, namely, 671.[3] It probably, more nearly than Thomsen's value, represents the average effect of the addition of CH_2 in a homologous series, because in each of his experiments the liquids with higher boiling points were increasingly in error because of the increasing heat from his "Universal Burner." Accordingly in his work the differences must have been too large. It is evident, nevertheless, that the position of the CH_2 makes an important difference in the result; probably the same value is not to be expected from an aromatic series as from an aliphatic series, and the values are entirely different when oxygen is present.

In spite of these qualifications, the conclusion that the following thermochemical reaction,

$$-\overset{|}{C}H_2 + O_2 = CO_2 + H_2O + 644 \text{ kj.},$$

holds true, at any rate in the case of aromatic substances when burnt in constant volume, is the least uncertain of all the theoretical inferences which may be drawn from the present work.

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[1] Observations by Richards and Mathews, as yet unpublished.

[2] Longuinine, *Compt. rend.*, 121, 557 (1895). The value computed independently by Trouton's rule for the heat of vaporization of normal octane was 34 instead of the value 33.8 found by Longuinine. This close agreement increases one's confidence in the other values calculated in the same way.

[3] This value is found from Thomsen's results from the aromatic hydrocarbons (*Thermochem. Untersuch.*, 4, 221) by subtracting from the average difference (161.8 Calories) corresponding to CH_2 the values 0.6 Calorie for correcting to constant volume, and 0.7 Calorie to allow for the difference of latent heat of evaporation caused by adding CH_2.

Because the heats of combustion of octanes on the average exceed those of the xylenes by 688 kilojoules, one might infer that each gram-atom of hydrogen in combination with carbon caused an increasing heat of combustion of 172 kilojoules. The addition of four hydrogens to each molecule of xylene to make an octane is nevertheless associated with important changes in the relations of the carbon atoms to one another, and these changes may be of considerable thermochemical effect. Hence it is not safe to conclude that a single gram-atom of hydrogen, even when united with carbon, will always increase the heat of combustion by 172 kilojoules, and the futher inference that because CH_2 adds 644 and H_2 adds 344 a single carbon would cause 300 kilojoules additional heat is likewise uncertain.[1]

Enough evidence has been collected to suggest the possibility of finding yet other interesting and fundamental relations and to make the collection of many more figures of the highest accuracy desirable. It will be necessary to investigate with the utmost precision a great number of typical cases of all kinds, in order to be sure of any generalization. In the fulfilment of this program, it is hoped that further careful work of this kind may be undertaken at Harvard University in the immediate future.

In conclusion it is a pleasure to express our indebtedness to the Carnegie Institution of Washington for generous pecuniary assistance in the prosecution of this work.

Summary.

In further prosecution of the revision of thermochemical data, the heats of combustion of benzene and a number of octanes and xylenes were determined with unusual care. The object in choosing these substances was to endeavor to trace the effect of constitution or arrangement upon the heats of formation of isomeric substances and thus to obtain a more definite idea of the relation of total energy change to structure. Octanes in particular were chosen because the molecule is large enough to admit of considerable variety in the isomeric compounds, but not so large as to confuse the relationships. Simplicity in interpretation is also gained by having only two elements present. The hydrocarbons were prepared in a state of great purity by Dr. Latham Clarke, according to methods worked out several years ago for this purpose. In the execution of this work the adiabatic method of calorimetry was used with great success and in general the precautions used in previous work of this kind were adopted throughout, with several new improvements. The volatile liquids were sealed in flexible flattened glass bulbs and ignited by means of small weighed quantities of sugar placed above the bulb on a glass shelf, the substances both being contained in a very small narrow platinum crucible. When conducted in this way, the combustion was in every case complete; with a wider crucible the combus-

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[1] See W. A. Noyes, "Organic Chemistry," pp. 44, 80, 85, 90, and 102.

tion was not always complete. The final results showed very satisfactory agreement among themselves.

In this way it was found that the heats of combustion of the following substances possess relative magnitudes, indicated by the numbers following the respective names: sugar, 1.0000; benzene, 2.5382; orthoxylene, 2.605; metaxylene, 2.605; paraxylene, 2.596; normal octane, 2.885; diisobutyl, 2.882; 2-methyl heptane, 2.888; 3,4-dimethyl hexane, 2.883; 3-ethyl hexane, 2.880. If the heat of combustion of sugar is taken with Fischer and Wrede as 16.545 kilojoules per gram and O = 16.000 is taken as the standard of molecular weight, the molal heats of combustion of the nine liquid hydrocarbons (in kilojoules, determined in constant volume at 20°) are as follows, respectively: benzene, 3,278; orthoxylene, 4570; metaxylene, 4570; paraxylene, 4554; normal octane, 5256; diisobutyl, 5250; 2-methyl heptane, 5261; 3,4-dimethyl hexane, 5252; 2-ethyl hexane, 5247 kilojoules. The deviations from one another, shown by the simple isomers, are comparatively small. The addition of CH_2 in aromatic compounds is seen to cause an increase in this heat of combustion of 644 kilojoules, or 154 Calories.

The differences between the isomers are so small that an attempt at definite explanation of their causes would be premature. Much more work of the most precise nature is necessary to afford firm basis for theory. It is hoped that this investigation will be continued, and that in the near future further data of this kind will be obtained in the laboratory of Harvard College, where these researches were made.

[Contribution from the Chemical Laboratory of Harvard College.]

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.

FIRST PAPER.—THE ANALYSIS OF SILVER PHOSPHATE.

By Gregory Paul Baxter and Grinnell Jones.

Received January 14, 1910.

Although phosphorus is one of the best known and most important elements, present knowledge concerning its atomic weight is somewhat inadequate. The early determinations of this constant by Dulong,[1] Pelouze,[2] Berzelius,[3] and Jacquelain[4] are widely discrepant and have no particular significance. Those by Schrötter, Dumas, van der Platts, and Berthelot, on the other hand, all give values not far from 31.0, and this value has been selected by the International Committee on Atomic Weights. Although these investigations have already been critically

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[1] *Ann. chim. phys.*, 2, 149 (1816).

[2] *Compt. rend.*, **20**, 1053 (1845).

[3] Lehrbuch, 5th Ed., **3**, 1188 (1845).

[4] *Compt. rend.*, **33**, 693 (1851).