force lines can take place, quite apart from the fact that individual stages in any one condensation process may have the power of metastable existence. The phenomena of geometric isomerism belong to the former category, while the highly colored unstable nitrophenol ethers of Hantzsch and Gorke and similar compounds belong to the latter.

If two differently condensed fields are obtained from one set of force lines, it is possible that the two condensed fields may be opened differently by solvents, and, therefore, the two substances will have different reactivities. Such differences usually are accounted for by attributing different primary structures to the compounds, but it would seem that this is entirely unnecessary.

Summary.

1. The existence of molecular force fields due to the electromagnetic fields of the constituent atoms is dealt with. It is shown that these force fields afford an explanation of chemical reactivity and reaction.

2. To the closed force fields and their opening up by the influence of solvents or light may be attributed all the phenomena of chemical reaction. Ionic dissociation is one special case of the whole.

3. In the existence of definite stages in the opening up of a given complex field, each with its power of absorbing definite light rays, is to be found the explanation of differently colored derivatives from the same compound.

4. The theory leads to the existence of intermediate stages in a chemical reaction and such stages have experimentally proved to exist.

5. When a compound is dissolved in a solvent an equilibrium is set up between the opened-up and non-opened-up molecules of the solute. Such a system has the power selectively of absorbing light rays, the effect of the light being to increase the number of opened-up molecules and thus to shift the equilibrium towards the reactive side. Some preliminary experiments on the photocatalysis of the reaction $Hg(CN)_2 + 2KI = HgI_2 + 2KCN$ afford considerable support to this view.

6. The theory would also seem to afford a reasonable explanation of allotropy, magnetic rotation, stereoisomerism, optical rotatory power, and generally the phenomena of isomerism as a whole.

LIVERPOOL, ENGLAND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE AND THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE HEATS OF COMBUSTION OF AROMATIC HYDROCARBONS AND HEXAMETHYLENE.

BY THEODORE W. RICHARDS AND FREDERICK BARRY.

Received January 30, 1915.

During the last ten years, extensive series of thermochemical investigations have been carried on in the Harvard laboratories with the help of the adiabatic calorimeter, which has been modified in various ways to meet the requirements of different sorts of problems.[1]

One of the earliest of these investigations was concerned with the measurement of heats of combustion,[2] and yielded results proving the efficacy of the adiabatic principle. In a second research of similar character, the effective procedure already developed for the complete burning of organic liquids in the explosion bomb was further improved;[3] and the method was shown to be capable of such a degree of precision as to permit a quantitative comparison of the heats of combustion of isomeric substances, magnitudes heretofore often indistinguishable. The present paper describes further measurements of such constants; the outcome shows a distinct gain in consistency and accuracy even over the immediately preceding Harvard work. The concordance of the values obtained in some of the series of measurements, as recorded in this paper, indicates a degree of precision comparable with the accuracy of much exact quantitative analysis—even in some accepted determinations of atomic weights. The investigation seems at least to have clearly shown that heats of combustion may now be determined, by a method at once simple and facile, with a precision limited only by the efficacy of processes of purification with respect to the material used and by the possible accuracy of thermometric measurements when mercury instruments are employed. The data here submitted indicate that these limitations do not stand in the way of very exact measurement.

An accumulation of data of this degree of trustworthiness should lead to comparisons of a very interesting and suggestive character. If the corresponding heats of vaporization, heat capacities, and heats of formation of the products of combustion can be determined as accurately, general inductions may perhaps be drawn from such data concerning the relationships between molecular configuration, and changes of free energy and internal energy. Among the many aspects of the general connection between chemical structure and physical property, none can be more interesting or important than this.

When so many data are necessary, ease and speed of experimentation are imperative. On this account, the simplicity of the method as here described is evidently one of its important advantages. The mercury

---

[1] For a résumé of the earlier part of this work, see Richards, THIS JOURNAL, **31**, 1275 (1909). The method was first proposed in a paper by Richards, Forbes and Henderson, *Proc. Am. Acad.*, **41**, 1 (1905); *Z. Physik. Chem.*, **52**, 551 (1905).

[2] Richards, Henderson and Frevert, *Proc. Am. Acad.*, 42, 573 (1907); *Z. Physik. Chem.*, **59**, 532 (1907).

[3] Richards and Jesse, THIS JOURNAL, **32**, 268 (1910). Other applications of the method are to be found in papers by Richards and Jackson, *Z. Physik. Chem.*, **70**, 414 (1909); Richards and Burgess, THIS JOURNAL, **32**, 431 (1910); Richards, Rowe and Burgess, *Ibid.*, **32**, 1176 (1910); Richards and Mathews, *Ibid.*, **33**, 863 (1911); Richards and Rowe, *Z. Physik. Chem.*, 84, 585 (1913)

thermometer, which has been decried by some commentators, has the great merit of direct and convenient reading. Moreover, this instrument suffers from less suspicion of inaccuracy arising from thermal conduction than the electric instruments; and is of course wholly free from the very persistent and subtle errors due to stray electromotive forces. It is true, of course, that the mercury thermometer has its own errors, which must be carefully guarded against, but the most disturbing of these is the change of the zero point, which does not come into consideration in differential work of this thermochemical type. Moreover, all the work described in the present paper is relative, so that by using the thermometer over the same range and under the same conditions with the different substances to be compared, the thermometric errors may be almost entirely eliminated. Its simplicity enables a single experimenter without assistance to carry out the work of combustion with the adiabatic calorimeter, and the work may be done with a minimum loss of time from maladjustment and from accident.

One must bear in mind also the fact that a higher degree of accuracy than to within 0.001° is not warranted by the purity of most organic substances, and that the mercury thermometer in good hands can easily reach this degree of precision. Of course, where great *sensitiveness* is required, a modern electrical resistance thermometer or multiple thermoelement can easily outdistance the mercury-in-glass instrument; but, on the other hand, one must not confound sensitiveness and accuracy. An example of this danger is afforded by a recent publication by W. P. White,[1] in which the temperatures are given to within 0.0001°, although the accompanying diagram shows that readings made on different days deviated as much as 0.01°. The correspondence of the results with the empirical curve, moreover, was often even much worse than this, although this does not clearly appear in White's abbreviated statement.[2] This paper was the best authority on this subject at the time when the work to be described was performed. It is doubtless true that, since that time, this experimenter and others have obtained better results with the thermoelement than the unsatisfactory showing of this paper of 1910;[3] and the platinum resistance-thermometer may be yet better; but taking all things into consideration, after extended and intimate experience with a thermoelectric thermometer kindly made for us by Dr. White, we decided that the time had not yet come (1911) for the application of either highly sensitive but precarious instrument to the problem in hand.

---

[1] *Phys. Rev.*, 31, 162 (1910).

[2] The discrepancy referred to will be found on calculating the values, especially those corresponding to 40.0000° and 82.0000°, as pointed out to us by Prof. A. W. Rowe.

[3] W. P. White, THIS JOURNAL, 36, 2292 (1914).

The investigations here described had two distinct aspects; first, the actual measurement of the heats of combustion of certain homologous and isomeric hydrocarbons; secondly, a study and criticism of the method employed, for the purpose of estimating and of controlling or eliminating the possible sources of error inherent in it.

Preparation of Materials.

Particular attention was paid to the purity of the hydrocarbons to be studied. Both natural and artificial compounds of carbon are liable to serious contamination with impurities, either of a similar kind or of widely different character, such as bromides or chlorides, some of which may find their way into the substance during the course of its preparation. For the purpose in hand, of course, the radically dissimilar impurities are usually more prejudicial than the similar ones, and the worst of all impurities, weight for weight, is water, because it has no heat of combustion whatever. In order to eliminate as much as possible these dangers, especial precautions were taken. The details for each substance are discussed below.

Benzene.—This substance was made from a commercially pure sample derived from coal tar. It was shaken with successive portions of sulfuric acid until the acid remained quite colorless after three successive agitations. The last traces of acid were removed by means of a solution of sodium hydroxide, and this, in turn, by repeated washing with water. The benzene thus prepared, after thorough drying with calcium chloride and with sodium, showed no traces of thiophene or its homologs on applying the delicate indophenin test with isatin and sulfuric acid, although the same reagents gave with the original material a deep blue coloration. The complete chemical separation of thiophene is neceesary in the first place because it cannot be separated either by distillation or crystallization.[1] The sodium used for the final drying of the benzene was washed free from petroleum (under which it had been kept) with scrupulous care, because the paraffins of petroleum have a widely different heat of combustion from aromatic compounds of like boiling point. The metal was dried and cut in the air, washed for a long time with purified benzene, again cut and dried and pressed into wire through a clean press previously washed with benzene, the first portions of the wire being rejected. The dried liquid was crystallized with the greatest care, especial pains being taken to prevent access of the moisture of the air. During the first three crystallizations a slight change in the freezing point was noted as the freezing progressed; but in the fourth and fifth, the substance

---

[1] The boiling points are: benzene, 80.2°; thiophene, 84°. Thiophene separates with benzene when this is crystallized, in a solid solution which is 42% as concentrated as the original liquid solution. Bijlert, *Z. phys. Chem.*, 8, 343 (1891); Beckmann, *Ibid.*, 22, 609 (1897).

gave a melting point constant to within 0.003° during the freezing of a large part of the liquid. This constancy in the freezing point indicates a presence of less than 0.01% of water.[1] The final value of the melting point of benzene was found to be 5.484°, a value very close indeed to that (5.483°) since found by Shipley and one of us in an investigation dealing especially with the subject.[2]

Toluene.—Pure toluene was prepared by fractionation of the commercial distillate. This material was first agitated with several portions of sulfuric acid, and otherwise treated by a procedure similar to that followed in the first purification of benzene. The product was free from olefenes and from thiophene and its homologs. It was dried with carefully prepared sodium which had been freed from paraffin oils by evaporation, and by long continued soaking in toluene.

This purified material, which contained besides benzene and xylene probably no other noticeable impurities, was fractionated from a still of special construction, a description of which has been published elsewhere.[3] The product of 40 cc. which distilled within a range of less than 0.01° was called *toluene A*, and was dried at 100° over sodium and kept over sodium. Of the two other samples, prepared by redistillation of the other distillate, one called *toluene B*, distilled over about the same interval as *A*, and another, *toluene C*, which was much less pure, distilled over 0.1°. The boiling point of the purest sample was taken with great care and found, by means of calibrated Beckmann thermometer, to be 10.25° above the boiling point of water under the pressure of 752.6 mm. Since under this pressure the boiling point of water is 99.726°,[4] that of toluene is 109.98°. According to the data of Young,[5] this would become 110.31° at 760 mm. pressure.

Ethyl Benzene.—Two samples of ethyl benzene were prepared. One was made by the Fittig reaction from bromobenzene and ethyl bromide with sodium. These materials were themselves very pure to begin with, the bromobenzene having been made from thrice recrystallized thiophene-free benzene, and the ethyl bromide having been carefully purified by

---

[1] W. Hertz, *Ber.*, **31**, 2669 (1898); miscibility of benzene with water; also Paterno, *Gazz. chim. ital.*, **19**, 460 (1889), on lowering of the melting point.

[2] THIS JOURNAL, **36**, 1825 (1914).

[3] Richards and Barry, THIS JOURNAL, **36**, 1787 (1914).

[4] Weibe, *Z. Instr.*, **13**, 329 (1893) from the data of Regnault; Landolt und Bornstein, "Tabellen," 1912 Aufl. p. 365.

[5] Data in Crafts, *Ber.*, **20**, 709 (1887), and Young, *J. Chem. Soc.*, **81**, 777 (1902). Summarized in Young, "Fractional Distillation" (1903), pp. 14, 15. The boiling point here given is in accordance with the value submitted by Neubeck, *Z. physik. Chem.*, 1, 656 (1887), and by Kahlbaum, *Ibid.*, **26**, 603 (1898), which are respectively 110.3° and 110.4°. It does not agree with those given by Young, *J. Chem. Soc.*, **73**, 906 (1898) and by Timmermans, *Bull. Soc. Belg.*, **24**, 244 (1910). which are, respectively, 110.8° and 110.7°.

fractionation. Thus it was possible to prepare a sample of ethyl benzene which when fractionated showed only traces of the acrid compounds which usually contaminate this hydrocarbon, possessing an agreeable, ethereal odor, and being perfectly colorless. At first it distilled wholly within a degree, and upon fractionation, after complete drying, it yielded a product which redistilled within three-tenths of a degree. This substance was labelled *ethyl benzene B;* and that part of it which distilled within one-tenth of a degree, *ethyl benzene A*. The boiling point of *ethyl benzene A* was determined during the final redistillation, which was carried out in a still of the same general design as that used for the fractionation of toluene, but of smaller dimensions. A small Reichsanstalt standardized Anschütz thermometer hung suspended in the tube, visible through the mica-covered apertures which pierced the asbestos insulation of this tube at the desired points. The boiling point was 136.03° (mean temperature) at 761.1 mm. which becomes 135.98° at 760 mm. pressure.[1]

That all this trouble was worth while was shown by the combustion of a cruder sample made from the rejected residues in the fractionation of *ethyl benzene A*. It boiled over four degrees and yielded a result for the heat of combustion 0.4% lower than that of the pure product.

Another sample of pure ethyl benzene, labelled *ethyl benzene C*, was made by the condensation of benzene with ethyl bromide under the influence of aluminum chloride in the presence of finely divided mercury.[2] The substance was prepared with the same care as that observed in making the other material, and the product was equally well fractionated. Moreover, it distilled at almost the same temperature. It yielded, nevertheless, lower values for the heat of combustion, as will be seen; but there is every reason to believe that the discrepancy was due to the presence of a trace of bromine, because an appreciable quantity of bromide was found in the bomb after the combustion. It is uncertain whether all of the bromine could be recovered in the bomb, and also in what way this substance was originally combined, hence the exact correction for the presence of this bromine is impossible; but an approximate correction is made below, which shows that the amount of the impurity was of the same order as the difference between the two series of results.

Mesitylene.—The specimen of this substance, prepared as usual from acetone, was carefully fractionated. Fifty per cent. of the raw material distilled within 0.3°. After five distillations half of the ma-

---

[1] Cf. R. Schiff, *Ann.*, **220**, 92 (1883), who gives the boiling point of ethyl benzene as 135.7° at 758.5 mm. This value reduces to the mean 135.8° at 760 mm. Perkin, *J. Chem. Soc.*, **69**, 1191 *et seq.* (1896) gives the boiling point as 135.5°.

[2] Radziewanowski, *Ber.*, **28**, 1138 (1895).

terial had been brought within the range 0.2°. The corrected boiling point of the portion taken at the peak of the accumulation in the distillate was 164.72° at 760 mm., including all corrections.[1] Three samples were burned: (A) having a boiling point between 164.6° and 164.7°, (B) having a boiling point 0.1 of a degree higher; and (C) 0.2 of a degree lower. In spite of these different boiling points, it will be seen that all of the material gave essentially the same quantitative results. The thermometer had been standardized by the Reichsanstalt.

Pseudocumene.—A specimen of this substance (1,2,4-trimethyl benzene) made by rectification of the commercial distillate furnished by a competent German firm, showed a fairly constant boiling point near 169°. After drying over sodium on the steam bath, it was fractionated by eight distillations, a fraction being finally obtained which redistilled within a range of 0.1°, as in the case of mesitylene. The boiling point of this material averaged 169.27° corrected to 760 mm. This specimen was labelled *pseudocumene A*. Here again we thought it worth while to test the heat of combustion of a distillate with a lower boiling point in order to determine as before if the inevitable impurities might have a perceptible effect upon the heat of combustion. No important difference was, as a matter of fact, observed. The boiling point of the pseudocumene, as we have found it, lies between the values given by Warren and Perkin, which are, respectively, 169.8° and 168.2°.[2]

Normal Propyl Benzene.—This substance and all the following substances were prepared from benzene or of substances made from benzene which had been carefully purified in the manner already described. They were in every case carefully fractionated and dried by distillation from sodium, just before being used for combustion, and were usually kept sealed in glass tubes or preserved in tightly clamped glass-stoppered bottles. As all but one of the hydrocarbons were made either by the Fittig or Friedel-Crafts synthesis, exceptional precautions were taken that the final products might be freed from halogen, because the halogen derivatives have much lower heats of combustion than the hydrocarbons. That this purpose was accomplished was shown by tests according to the Carius or the Pringsheim method.[3] Moreover, the residues in the bomb after combustion were tested with silver nitrate and nitric acid. In no case was more than a very slight opalescence observed, corresponding to an amount too small to have any perceptible effect upon the heat of combustion. The absence of these halides leads one to hope that the corresponding alcohols from which they were made were also absent. Alcohols are

---

[1] Schiff, *Lieb. Ann.*, **220**, 94 (1883) gives 164.5° and Perkin, *Loc. cit.*, 164.1°.

[2] Warren, *Z. Chem.*, **1865**, 666; Perkin, *Loc. cit.*

[3] Pringsheim, *Ber.*, **36**, 4244 (1903); *Ibid.*, **37**, 2155 (1904).

especially troublesome, because they form mixtures having constant boiling point with alkyl halides and with the hydrocarbons.[1]

Normal propyl benzene was synthesized from bromobenzene and normal propyl bromide with sodium. The reaction was retarded by cooling with ice in order to minimize molecular transposition. The product, having been once distilled, was treated with washed and dried ether and magnesium turnings to which a small quantity of activated magnesium had been added, together with a crystal of iodine, to catalyze the reaction. This mixture was refluxed for three hours, then treated with water and separated. The bromobenzene boiled at 156.2°. Afterwards the product was boiled with alcoholic potash, washed with water, dried and fractionated. The final product boiled with great constancy within 0.1°, at 158.0° under 760 mm. pressure. Schiff[2] gives the boiling point as 158.5° at 751.6 mm.

Every test showed this hydrocarbon to be entirely free from halogen. It might have contained a small quantity of isopropyl benzene, but its odor and the constancy of its boiling point militiates against this possibility. Even if much isopropyl benzene had been present, no measurable change would have been caused in the heat of combustion.

Other methods of making propyl benzene, such as condensation of benzyl chloride with ethyl bromide and of iodobenzene with normal propyl iodide, were attempted, but were not as successful.

Isopropyl Benzene.—Two samples of isopropyl benzene were prepared, one by the condensation of isopropyl iodide and benzene by the Freidel-Crafts reaction; the other from isopropenyl benzene, made by the Grignard reaction from acetophenone after the method described by Klage.[3]

The Freidel-Crafts material was prepared in the simplest possible way, by the use of anhydrous aluminum chloride alone. The use of mercuric chloride and metallic aluminum as catalyzer was abandoned; because of the suspicion that mercury alkyl compounds might thus be formed. The reaction ran slowly for two days in a closed flask, then rapidly when refluxed for three hours; it was stopped by a bath of ice water, and hydrochloric acid was added to separate the emulsion.

The product was freed from hydriodic acid and iodine and from hydrochloric acid by repeated washings in sodium hydroxide solution, was carefully dried and then distilled. The distillate was boiled with alcoholic potash for fifteen minutes, dried again and fractionated in the still used for the fractionation of ethyl benzene. The finally chosen fraction

---

[1] Ryland, *Am. Chem. J.*, **22**, 384 (1899); Young and Fortey, *J. Chem. Soc.*, **83**, 45 (1903). For a summary of these results, see Young, "Fractional Distillation" (1903), pp. 67, *et seq.*

[2] *Ann.*, **220**, 93 (1883).

[3] A. Klage, *Ber.*, **35**, 2640 (1902).

boiled at 152.85–153.15° under 765 mm. pressure,[1] and redistilled almost wholly within the same range. The product, which probably contained no isomeric hydrocarbon, yielded, after complete combustion under 20 atmospheres of oxygen, a residue which showed only a negligible opalescence when tested with silver nitrate and nitric acid. It was, therefore, a very pure product. This material was labeled *isopropyl benzene A*.

A second sample of isopropyl benzene was made by a radically different method with equal care. Acetophenone was added very slowly to the Grignard reagent at the temperature of melting ice; the ether was distilled off, and the residue then refluxed for six hours on the steam bath. The product, isopropenyl benzene, was then reduced by three times the reaction-quantity of sodium in absolute alcohol; and after the reaction, the product was washed and separated with dry ether, dried with anhydrous sulfate and twice distilled. The resulting liquid, of somewhat rancid odor, boiled at 152–153°. It was treated with alkaline permanganate until it showed no color-change after long standing, and until a sample added to a dilute solution of bromine and chloroform showed no evidence of further oxidation. This purified material was then fractionated in the usual way, and yielded a final fraction of 3 cc., which boiled at 152.5–152.8° under 751.4 mm. pressure. It was distilled from sodium and yielded a final distillate of about 2 cc. This product was called *isopropyl benzene B*. It is to be noted that the boiling points of these two products were fairly close together, although not identical.

Tertiary Butyl Benzene.—This hydrocarbon was synthesized from pure benzene and a residual sample of isobutyl bromide by the Freidel-Crafts reaction. The isobutyl benzene formed is under these circumstances wholly converted to the tertiary by molecular transformation.[2] The hydrocarbon thus made having once been distilled and thoroughly dried, was fractionated, and a final distillate was at length obtained which came over wholly within 0.2°. Its boiling point at 751.4 mm. pressure was 168.8–169.0°.[3] The yield of this pure substance from 410 g. of benzene, and 100 g. of isobutyl bromide was about 10 g. Upon combustion, the resulting water gave no opalescence whatever with silver nitrate.

Cyclohexane was prepared in a pure state from very pure benzene by the Sabatier-Senderens reduction.[4] The benzene was vaporized at 65°

---

[1] Cf. Perkin (*Loc. cit.*) who gives the b. p. 152.9°. The b. p. given above reduces to the mean 152.3° at 760 mm.

[2] Schramm, *Monatshefte*, **9**, 615 (1888); Gossin, *Bull. soc. Chim de Paris*, **41**, 446 (1884).

[3] Cf. Schramm (*Loc. cit.*) who gives the b. p. of this substance at 736 mm. as 167–167.5°. Data are not available with which to convert these boiling points accurately to 760 mm., and thus to compare them.

[4] *Compt. rend.*, **133**, 321 (1901).

in a current of pure hydrogen, which had been made free from all usual contamination, and carefully dried by passage over red hot copper gauze and solid potassium hydroxide. The mixed vapor was led at 160° through a coiled tube three meters in length packed with iron-free pumice, on which finely divided nickel had been deposited. This had been prepared in such manner that it was free from chlorides and other negative catalysts. The composition of the condensed vapor was tested by freezing-point determinations made after each attempted reduction. Only after the mixture has been passed eight times through the reducing coil was the reduction thus shown to be complete.

The approximate freezing points of these mixtures are of interest: the first condensate began to freeze at +4°, the second at —4°, the third at —21°, the fourth and fifth below —22°, the sixth at +2°, and the seventh and eighth at about +6.3°. Thus the first was almost pure benzene, and as more and more of the substance was converted into cyclohexane the freezing point passed through the eutectic point (below —22°) and finally rose as the benzene was eliminated.

From 800 cc. of benzene, about 120 of cyclohexane were thus made. A greater yield could have been obtained by the use at all times of a condenser packed in a freezing mixture, for there was much loss through evaporation. The material thus made was twice crystallized, while mechanically stirred, in a Beckmann freezing-point apparatus similar to that used for the crystallization of benzene. The bath was kept very constant at a temperature slightly above the freezing point of benzene; and care was taken that the cyclohexane was not contaminated with water. About a quarter or a third was rejected at each freezing, hence about 60 g. remained of the pure material. The product of the first crystallization was labeled *Cyclohexane B;* that of the second, *Cyclohexane A.* After having been carefully dried, cyclohexane A was distilled in a side-tube still which held a standardized thermometer wholly enclosed, and showed a boiling point of 80.8° under 760 mm. pressure, which remained constant within visible limits (*i. e.*, at least to within 0.03°). The melting point of this material was found with great care by comparison with that of pure benzene, the procedure being precisely similar to that by which the melting point of benzene had been determined. It was found to be 0.485° above that of benzene, or 5.97°.

In spite of our care, it is not impossible that a trace of benzene remained in this susbtance. Accordingly, its heat of combustion may be slightly lower than the true value, but we believe that more care to avoid this difficulty was taken in the present case than in previous investigations of others.

Cyclohexane burns with such violence in the bomb as to cause trouble in the thermal measurement. In one case, which of course had to be rejected, the insulted electrode was blown out of the bomb. The two determinations which are later given, however, are probably not more than 0.1% in error.

Sucrose.—Pure sugar was made from the commercial granulated material by successive crystallizations. It was dissolved in 50% redistilled aqueous ethyl alcohol and crystallized by the addition of more alcohol and by cooling. The precipitate was thoroughly centrifuged, and the process of precipitation was repeated four times. It was dried under reduced pressure, repulverized in agate, and dried again. It was kept over fused potassium hydroxide in a desiccator, and was so dry that it acted like a powdered silicate, and did not adhere either to pestle or platinum vessel. This purest sample was labeled *Sugar A*. A similar less pure sample was prepared in the same way, with only three instead of four crystallizations, but its heat of combustion was identical within the limits of experimental error; hence its purification was really sufficient—the further treatment received by sample *A* had been an act of supererogation. In the course of the crystallization of this sugar, all the precautions which would be observed in a most accurate investigation upon atomic weights were taken. These are well known and recognized, and it is perhaps unnecessary to detail them here. It is enough to say that, both as regards purity of the liquids, care in filtration and all the other minutiae of the work, every effort was used to prevent the ingress of impurity.

The Bomb and the Details of Combustion.

The apparatus employed has been in part described in the publications already cited, but certain additional features require explanation. The bomb used was of the Atwater type,[1] wholly lined with platinum. Because leaden gaskets around the rim are easily corroded, and because electroplating of the lead with gold or covering it with strips of gold foil had proved troublesome and unsatisfactory, we used a gasket of pure, soft annealed gold. In the later determinations the whole top of the bomb, in addition, was lined with a circular sheet of pure, soft gold, which covered the gasket as well as the center.

The bomb itself had been altered in two respects. After use during several years the lining had become worn at the edge which bore upon the gasket. This edge was planed down, and a ring of triangular cross sections was cut out of it in such a manner that a double edge was presented to the gasket (Fig. 1). The alteration insured a more complete closing of the bomb by moderate pressure, and prevented leakage. To the bottom of the bomb, legs of heavy wire were attached, a centimeter in length; and thus an easy circulation of the calorimeter water beneath

---

[1] This instrument, together with its accessories, is described in detail by Atwater and Snell, THIS JOURNAL, **25**, 659 (1903).

the bomb was secured. The instrument thus altered was found to be satisfactory in every way.[1]

The calorimetric vessel was a cylindrical can of pure spun silver, brightly polished on the outside. This vessel was somewhat smaller than those previously used in similar researches; thus the heat capacity of the calorimetric system was reduced, with the result that the temperature-rise per gram of material burned was nearly half again as great as in former measurements.[2] The calorimetric stirrer was of the usual vertical reciprocating type, consisting of two perforated rings firmly attached to slender vertical supporting rods; and provided with thin guiding wires which prevented engagement with the collar of the bomb. The supporting wires were cut to such a length that they never left the calorimetric system and were insulated from the outer attachments by thin rods of vulcanite. As a result of this modification no heat was lost to the system by conduction, while the sucking in of outside air remained minimal.

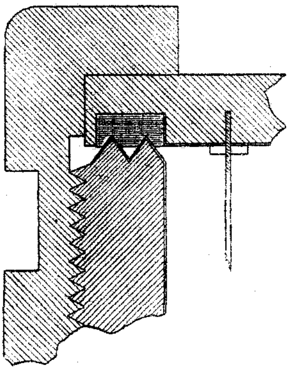

Fig. 1.—Section of edge of bomb (actual size). Showing double ridge pressed against gold washer.

The calorimeter was surrounded everywhere by a narrow air-jacket, being held by small pieces of cork within a slightly larger vessel of brightly polished nickel-plated copper, the walls of which were about the same thickness and conductivity as its own. The insulation was carefully tested electrically before and after each determination. This copper vessel, nicknamed a "submarine," was provided with a water-tight cover, pierced with tubes for the necessary entering parts of the apparatus. The cover, made of cast brass, was heavier than those formerly employed, and was supported by a correspondingly heavy rim of brass soldered to the jacket, which carried five swivelled thumb-nuts symmetrically arranged and permanently attached. Both cover and rim were perfectly plane on the bearing surface, so that the joint, protected by a gasket of

---

[1] A number of trial combustions were made with a Kröcker bomb of German manufacture. It was easily handled, and would in all probability have been a satisfactory instrument had it been constructed in accordance with the published and advertised design. As actually made, however, the lead gasket intruded into the bomb-chamber to such an extent that it was very badly corroded; moreover, the rim of the exposed part of the cover was of unprotected bronze; and the construction of the electric connection was flimsy and mechanically bad.

[2] By this alteration also, the surface of evaporation was reduced. Even in former work, however, in which larger vessels were used, error from heat absorbed by evaporation of the calorimeter water had been calculated to be negligible. See Richards and Jesse (*Loc. cit.*).

soft rubber, was easily made tight by gentle pressure and never leaked in consequence of the distortion of cover or rim, during several months of continuous use. In a practical way, this modification was important for obvious reasons. The somewhat lower conductivity of the cover (due to its greater thickness), was a matter of no moment, since the surface is small, and even with the greater thickness, the conduction of heat is very rapid. The whole calorimetric system, together with its protecting jacket, was held underneath a bath of dilute caustic alkali, the temperature of which could be regulated by the addition of sulfuric acid from a buret graduated as usual in tenths of a degree. The powerful stirrer and other mechanism of this external apparatus has been so often described that no further explanation is needed. The bath thermometer, placed on the opposite side of the bath from the acid-intake, was like the calorimetric instrument, and gave strictly comparable readings. Insulated ignition wires were led from the bomb electrodes through the chimneys in the cover of the calorimeter jacket which accommodated the stirrer. These chimneys were stopped above by cotton wool, loosely wired in place, in order to prevent circulation of atmospheric air. The stirring machinery was rigidly mounted, in such a manner as to insure fairly constant speed—a matter of first importance, as experience showed. The appended diagram shows the entire apparatus, drawn approximately to the scale (Fig. 2).

The calorimetric thermometer (maker's No. 11258) was one which had been made especially for this and similar work. It had been filled under an atmosphere of pure hydrogen, and the movement of the thread was prompt and regular. The scale, which was divided in hundredths of a degree, covered the temperature interval from 15.3 to 20.5°; the length of the 1/100° interval was about 0.8 mm., and intervals of 0.0005° could be readily estimated with a lens. Before reading, the thermometer was softly and evenly tapped upon the side; violent tapping, especially upon the top, may cause the column to jump and remain fixed several thousandths of a degree above its true point. This simple precaution is a very important matter. The best procedure for this particular instrument having been found, it was always practiced. The temperatures were always read to within 0.0005°, and the corrections were calculated also including the fourth decimal place, but this outcome was rounded off to the nearest unit in the third decimal place in the final recording of the results. The thermometer was read always with a very slowly rising temperature, never when the thread was falling. .

This instrument has been four times standardized: by the Reichsanstalt in 1909 (P. T. R. No. 37900); by the United States Bureau of Standards in 1909 (B S. No. 5506); and at a very great number of points by the authors in collaboration with Dr. A. W. Rowe in comparison with the

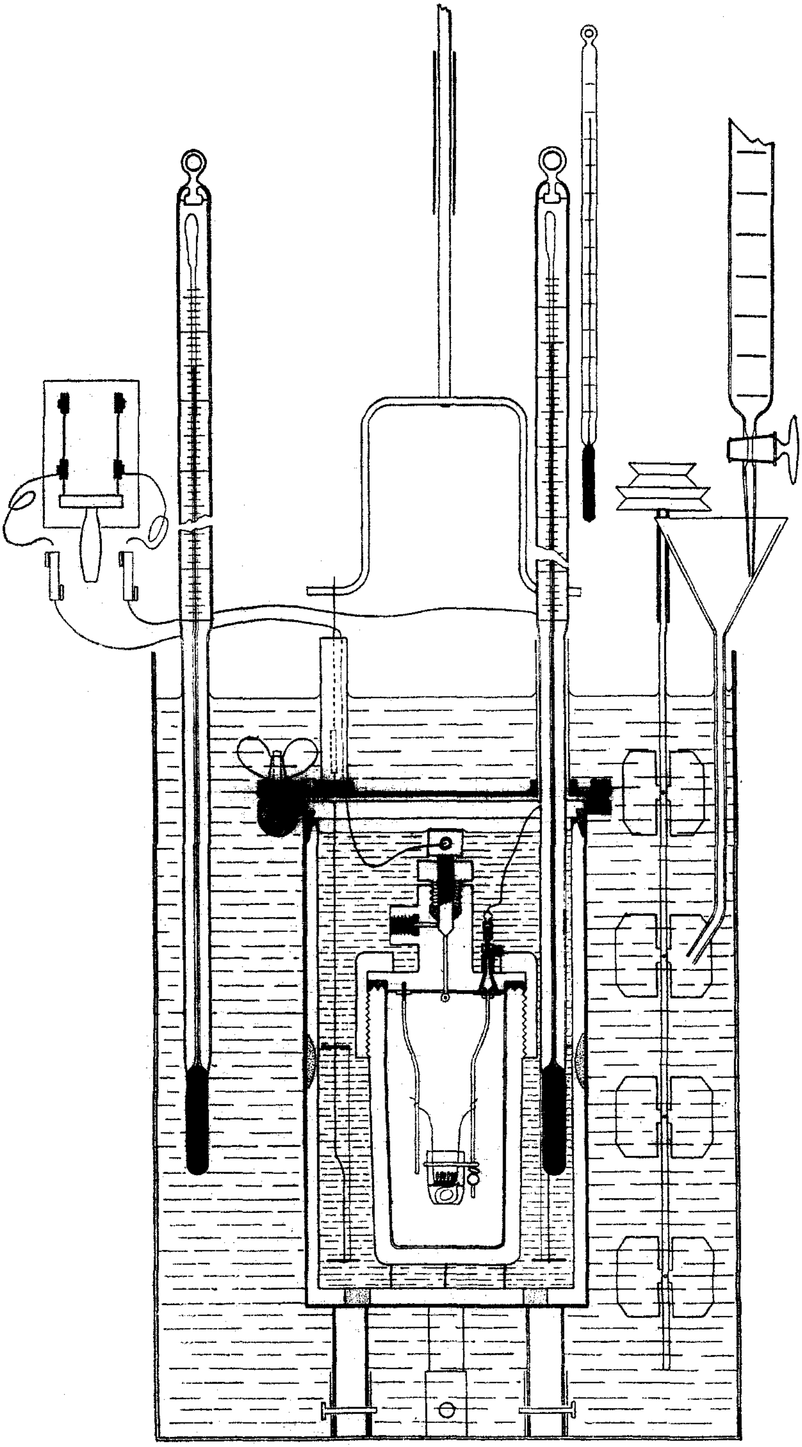

Fig. 2.—Complete assembled apparatus for calorimetric combustion. (In section.)

Baudin instruments 15200 and 15276 of the Bureau International des Poids et Mesures, and finally with the help of Dr. T. Thorvaldson. The Reichsanstalt work had been very crudely done, perhaps through a misunderstanding; on the other hand, the results of the Bureau of Standards at Washington corresponded fairly well with our own comparison with the Parisian Standard. The results are expressed in terms of the Parisian Standard as given by the Baudin instruments, but, as a matter of fact, it does not greatly matter which of these standards were used, as the work was wholly relative, and almost the same range was used for each experiment. If in the future it is found during the course of a critical study of the thermometric scale[1] now in progress here, that small corrections are in some cases necessary, these may easily be applied at any time. After some delay we have thought it best not to withhold the publication of this paper longer on this account.

It is worthy of note that such uncertainty as exists is not due to the mercury-in-glass thermometer used by us, but rather to the *standard to which it is referred.* This same uncertainty would apply to any other means (such as the electrical ones) of employing this same standard.

It should be noted that the instrument used in this work was always kept at temperatures near that of the room—it was never cooled to zero. Thus it was spared the internal upheavals which are caused in glass by any considerable changes of temperature.[2]

The hydrocarbon to be burned was dried with scrupulous care, and was sealed into small glass bulbs, previously weighed, in such manner that at room temperatures the bulb was completely filled. To make this possible the bulbs were made very thin, and were flattened on opposite sides; so that under high pressure they yielded until the liquid itself bore the strain, and at the higher temperatures they expanded readily under the internal tension (Fig. 3). The bulbs were filled by alternate heating and cooling, caused by contact with and removal from a piece of heated metal. A general heating of the bulb was dangerous, since under these circumstances the liquid evaporated almost explosively and often burst its fragile container. After filling, each bulb was kept at 16.7° in a water bath until constant in temperature; the liquid in the capillary was boiled out quickly by a small flame to a point close to the bulb; this was then chilled in cold water and sealed by a hot flame at the point from which the liquid had been thus withdrawn.[3] The bulbs were cleaned carefully and were

---

[1] See THIS JOURNAL, **37**, 81 (1915).

[2] These and other precautions are discussed in a recent paper by one of us, *Orig. Comm. 8th Intern. Cong. Appl. Chem.*, 1, 416 (1912).

[3] The bulbs without their attached capillaries weighed from 0.3 to 0.5 g. They were designed to hold somewhat less than a gram of material; in every case such a quantity as would cause a rise in temperature of 3° when burned in this calorimetric system. According to the value of the heat of combustion of the material being used,

dried in a desiccator under reduced pressure. This process tested their ability to remain unbroken when placed in the partially exhausted tube. They were weighed to within 0.05 mg. with carefully standardized weights; the weight was checked after a sufficient interval and was reduced to the vacuum standard. Leakage could always be detected by odor and by inconstancy in weight; of course all leaky bulbs were rejected.

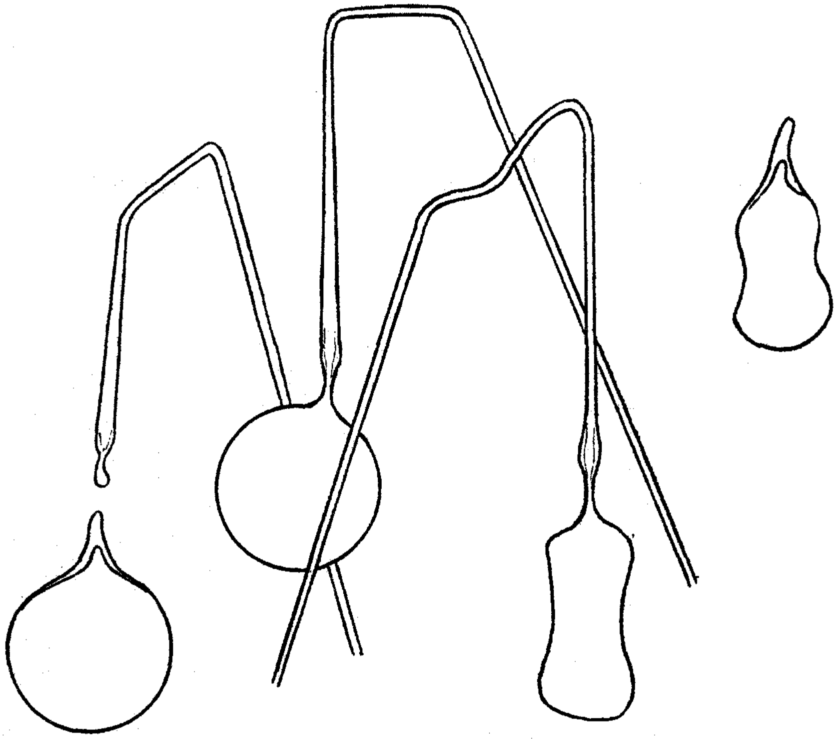

Fig. 3.—Glass bulbs for containing volatile liquids in various stages of preparation. (Somewhat larger than actual size.)

The bomb was prepared substantially as in the latest of the previous investigations. A small, narrow, platinum crucible replaced the usual capsule; the bulb, placed at the bottom of this, was covered by a thin circular plate or shelf of glass (a microscope slide-cover), from which a small piece had been snipped to allow the easy escape of vapor.[1] Pure

the bulbs were selected for size, which is, of course, easily measured by immersion. While the liquid was being boiled out of the capillaries, and during sealing, the bulbs were kept at the desired temperature in a thimble beaker, filled with water. The capillary protruded through a thick mica cover. Care had to be taken against forming tarry matter in the capillary by partial combustion, and against leaving residual liquid in the detached capillary. Loss of glass by volatilization in the blow pipe flame was negligible.

[1] Richards, Henderson and Frevert, Richards and Jesse, *Loc. cit.*

sugar in small quantity, usually less than 0.1 g., was spread evenly upon the little glass shelf; it was weighed by difference, and the weight reduced to the vacuum standard. The ignition wire of pure iron was cut to constant length (a procedure found to be as accurate as weighing), was coiled, and adjusted in such a way that several turns of the helix just touched the sugar. This precise adjustment was found necessary to prevent incomplete combustion and the formation of charred particles by spattering.[1] In consequence of the arrangement of the materials to be burned, the heat from the ignited sugar burst the bulb below it, and the vapors from the bulb had to pass through a zone of flame before they escaped into the combustion chamber. This favored completeness of combustion. Only occasionally when the bulb broke under pressure before ignition was the odor of unburned hydrocarbon detected in the open bomb.[2] Such trials were rejected.

Before the bomb was closed, 1 cc. of water was always introduced. This was in amount more than sufficient to insure the saturation of the enclosed air with water vapor before combustion, and thus to cause the complete condensation of the water formed by the reaction.

In order to diminish the amount of nitric acid formed during the combustion, the bomb, having been closed, was exhausted by air to a pressure of about 20 mm. of mercury. To the same end, as well as in order to reduce another correction, the ignition wire was made as short as seemed practicable; for the formation of nitric acid, *ceteris paribus*, seemed to result more from the combustion of the iron than from the burning of the hydrocarbon.[3]

The best oxygen pressure was found in these measurements to be in the neighborhood of 20 atm. Under a greater pressure the bulbs were likely to burst; moreover, at 30 atm., odoriferous gaseous products were formed. In all combustions the fairly constant pressure of 20 to 23 atms. was maintained, the variation in which could not have altered sensibly the heat capacity of the system.[4]

The colorimeter water, at a determined initial temperature somewhat

---

[1] This procedure, the general method, involving which was applied in previous investigations, has been here described in some detail, since of all involved it required the greatest nicety in manipulation; and determined in greatest measure the success of each operation.

[2] By the dilution of a known quantity of benzene vapor with successive additions of air, it was demonstrated that the odor test for unburned hydrocarbon was more than sufficiently sensitive to serve for the detection of all but quite negligible quantities. The benzene was chosen for this test because of its relatively faint odor.

[3] This was shown by the parallel variation which was always observed between the corrections applied for wire burned and for nitric acid formed.

[4] The oxygen used was made from liquid air. It had been analyzed for oxygen, and was found to contain never more than 2.5% of inert gas, largely argon. Subsequent tests showed it to be free from halogen.

below 16.5°, and always the same in amount was weighed to within ±0.2 g.—an accuracy more than adequate.

The apparatus having been assembled and tested for insulation and correct adjustment, the whole calorimetric system was brought to thermal equilibrium in the neighborhood of 16.5°. The approximate temperature range expected had been estimated by calculation from the weights of the materials used; while the initial temperature had been selected in accordance with this value, usually so as to cause the final temperature to be near 20°. Effort was made to have both temperatures come upon smooth stretches of the curve of thermometer-calibration. The thermometer was cooled a trifle below the chosen point before immersion, so that initial readings could be taken on a rising thread. Equilibrium having been once established, observations were made at short intervals for 15 or 20 minutes, while the system was kept as closely as possible adiabatic. The rate of temperature rise due to stirring at the initial temperature was thus determined. Simultaneously, readings of the stem temperature and of the actual rate of stirring were recorded. This done, the charge was ignited and the temperature rise within was paralleled in the bath outside by the addition to the bath of sulfuric acid from the buret. It was found to be in no way difficult to hold the thermometer registrations of the bath temperature within 0.1° of those indicated by the calorimeter thermometer during the minute or more occupied by the rapid change of temperature; while toward the end, this correspondence could be maintained within 0.010 to 0.02°. Calculation, based upon blank experiments in which the rate of heat interchange was measured while differences of several tenths of a degree were maintained between the calorimeter and bath, indicated a much wider margin of safety in manipulation. The effective distribution of acid in the outer alkaline bath is an essential precaution. The rotary bath-stirrer completed 320 r. p. m., and was found to distribute the acid evenly in less than four seconds. The thermometric lag, occurring to the same extent with both instruments, is eliminated from consideration.

At the final temperature, which was approximately that of the environment, further readings were taken at intervals of two minutes until the rate of temperature rise became uniform; and thereafter at longer intervals for ten minutes or more. Thus the temperature rise due to stirring at the final temperature was determined. During this time also, the stem temperature and the rate of stirring were again recorded. The initial temperature had been read immediately before ignition. The final temperature was taken at any convenient time after the rise had become uniform. The time interval that had elapsed between these readings, usually about ten minutes, was known from the data; and the stirring correction was calculated for this interval from the observed rate at the final temperature, at which it was unaffected by the sucking in of air from the outside, since this was at about the same temperature. The two observed rates of evolution of heat from stirring were usually closely the same; normally, that taken at the lower temperature was slightly larger, perhaps because of the greater viscosity of the water, but in such degree that no important error could have resulted in basing the correction upon the other. A correction derived from either the initial or the average rate would have approximated the true value somewhat less closely than that from the final rate, since the temperature rise was much more rapid at the start. This method of reading initial and final temperatures on almost stationary but very slowly rising thread, which is moving at nearly the same rate at both times, quite eliminates thermometric lag as a factor of inaccuracy in the difference between the readings.

The correction for stirring was somewhat variable, depending upon the speed, and the size and shape of the annular space between the bomb and the calorimeter wall. By placing thermometers at different heights, it was found that no stirring rate less than 65 strokes a minute was effective in preventing a dangerously persistent thermal stratification within the calorimeter; in consequence, the usual rate employed was 70 strokes a minute. The rise of temperature due to stirring at this rate might have been reduced by using a larger calorimeter, as in former work, but the advantage thus gained would have been slight in comparison with that lost. Because of its variability, the stirring correction was determined in each case to within a small limit of error.

The correction for stem exposure was in these determinations very small, since at the initial temperature there was but slight exposure and since the final temperature was near to that of the environment. Its magnitude was invariably less than 0.001°.

The correction for heat developed from that portion of the iron ignition wire actually burned was calculated from the known heat of combustion to Fe_3O_4; the small pieces of unburned wire found attached to the electrodes after the bomb had opened were always measured and allowed for.[1] The calculated value of this correction was checked by determinations carried out according to the usual procedure, in which wire alone was burned, of a length double that used in the combustions. These measurements verified each other and the calculated correction within the limit of observation. They proved, incidentally, that the electrical heating of this wire to ignite it, which had been made as uniformly slight as possible and calculated to be negligible, was so in fact.

The quantity of nitric acid formed in each combustion was determined by titrating the washings from the bomb with standard alkali. From this correction for heat developed in its formation was calculated from

[1] Richards and Jesse, THIS JOURNAL, 31, 277 (1910).

known data. Since the oxygen used contained only a small percentage of nitrogen, and because the bomb had been partially exhausted of air before oxygen was let in, this correction was very small. Its effect on the calorimeter approximated 0.0001° per centimeter of iron wire burned. All errors in the determination of this correction were quite negligible.

No further observations on the method and procedure are necessary. The notes of each experiment were recorded essentially in the manner detailed in a previous paper.[1]

In order to effect economy of space in the following tabulation of results, the minor corrections, which depend upon the purely accidental nature of each particular experiment, are all algebraically added together in one column. The magnitudes of these corrections were about of the following order: Correction for calibration of the thermometer, +0.013°; stirring, —0.015°; for heat of combustion of wire, —0.018°. All these, together with the very small corrections for stem exposure and for nitric acid are included below in the column headed "Total corr." In all the tables except Table I, the rise of temperature due to the sugar taken to start the combustion (calculated from the outcome of Table I) is also included in this total correction.

The heat capacity of the system was increased 0.023% by slight alteration of the parts after the work described in Table VII; all subsequent work is corrected below, so as to reduce all to the original standard. The total heat capacity was equivalent to 2663.6 g. of water at first and 2664.2 later, as calculated from the rise of temperature caused by the combustion of sugar, assuming the Bureau of Standards' latest value (3945 cal. [18°] per gram weighed in vacuum) for the heat of combustion of the latter substance.[2]

The Quantitative Results and their Discussion.

TABLE I.—COMBUSTIONS OF CANE SUGAR (SUCROSE).[3]

	Wt. sugar in vacuo.	Temperature range.	Observed rise in temp.	Total corr.	Corrected rise in temp.	Rise per gram sugar (weighed in vac.).
1........	2.00257	16.8–19.8	2.9870	—0.0210	2.9660	1.4811
2........	2.00190	16.8–19.8	2.9855	—0.0205	2.9650	1.4811
5........	2.00085	16.8–19.8	2.9885	—0.0250	2.9635	1.4810
7........	2.0048	16.8–19.8	2.9910	—0.0215	2.9695	1.4812
8........	2.0023	16.8–19.7	2.9850	—0.0200	2.9650	1.4808
9........	1.93788	16.9–19.8	2.9010	—0.0315	2.8695	1.4810

Average rise per gram sugar.................................. 1.4810°
Extreme variation from the mean.................... 0.013%

---

[1] Richards, Henderson and Frevert, *Proc. Am. Acad.*, 42, 587 (1907).

[2] *Bull. Bur. Standards*, 11, 190 (1914) Paper 230.

[3] NOTE.—The determinations recorded in Table I comprise all that were completed in a continuous series, save three. Of these, two, Nos. 4 and 6 in the continuous series,

The exceptionally close agreement of the values given in this table show how accurately it is possible to conduct experiments of this kind with the adiabatic calorimeter and the mercury thermometer. It will be noted that the temperature range was almost the same in each case, hence fundamental errors in the calibration of the thermometer could not appear. Of course, results as good as this can be expected on comparing different temperatures range only if the thermometer is everywhere thermodynamically consistent with itself, and this seems to be too much to expect of our present thermometric scale.[1]

Feeling satisfied that the temperature rise during the combustion of sugar in our apparatus was hereby determined accurately enough for our purpose, we now proceeded to the thermally quantitative combus-

TABLE II.—BENZENE (A).

Determination.	Wt. hydrocarbon in vacuo. G.	Wt. sugar in vacuo. G.	Final temp.	Obs. rise temp.	Total corr.	Corr. rise in temp.	Rise per g. hydrocarbon.
1.........	0.79280	0.07040	19.8°	3.097°	−0.123°	2.974°	3.751°
2.........	0.84505	0.10025	20.0	3.331	−0.163	3.168	3.749
3.........	0.91350	0.08870	20.3	3.576	−0.149	3.427	3.751
4.........	0.89805	0.09145	20.3	3.528	−0.160	3.368	3.750
5.........	0.72885	0.11175	19.9	2.923	−0.189	2.734	3.752

Average rise per gram benzene.................................... 3.751°

Extreme variation from the mean............ 0.002° in 3.75° = 0.04%

TABLE III.—TOLUENE.[2]

1.........	0.81020	0.07970	20.0°	3.225°	−0.133°	3.092°	3.817°
2.........	0.63535	0.41145	20.0	3.052	−0.627	2.425	3.818
3.........	0.80995	0.10140	20.2	3.252	−0.160	3.092	3.817
4.........	0.77820	0.08515	19.8	3.114	−0.141	2.973	3.820
5.........	0.85460	0.06145	20.0	3.358	−0.098	3.260	3.815
6.........	0.77370	0.07605	19.8	3.072	−0.119	2.952	3.816
7.........	0.74047	0.12570	19.8	3.023	−0.197	2.826	3.817
8.........	0.78500	0.08130	19.9	3.128	−0.131	2.997	3.818

Average rise per gram toluene.................................... 3.8172°

Extreme variation from the mean............ 0.003° in 3.82° = 0.08%

Sample A was used in Nos. 6, 7, 8; Sample B, in Nos. 3, 4, 5; Sample C, in Nos. 1, 2.

were rejected because carbon or charcoal was discovered in the bomb after combustion. The other, No. 3 of the continuous series, was rejected because its temperature range was 1° lower than that of the others, and was such that the initial and final temperatures fell upon points that marked sharp and irregular changes in the slope of the curve of thermometric calibration.

[1] Richards and Thorvaldson, THIS JOURNAL, **37**, 81 (1915).

[2] The above record comprises all the results in an unbroken series of completed determinations, save one. This omitted result yielded the value 3.8470 for the rise per gram toluene, which showed a variation from the average of the preceding of nearly 1%. Such a discrepancy, which corresponds to a thermometric error of 0.024° or to a weighing error of 0.006 g., is far beyond any possible variation resulting from experimental error; and must be due to misreading, probably of weights.

tion of the volatile hydrocarbons, the results for which are given in the following tables. In each of these experiments, as already stated, the hydrocarbon was enclosed in a small, hermetically sealed bulb and the combustion was started by means of a small amount of sugar. The temperature rise due to this sugar is included with the other smaller corrections in the column headed "Total corr." It was in each case obtained by simply multiplying the weight of sugar by the factor 1.481°, just found, according to Table I.

TABLE IV.—ETHYL BENZENE (A).

Determination.	Wt. hydrocarbon in vacuo. G.	Wt. sugar in vacuo. G.	Final temp.	Obs. rise temp.	Total corr.	Corr. rise in temp.	Rise per g. hydrocarbon.
1.........	0.83774	0.09761	20.3°	3.398°	—0.167°	3.231°	3.857°
2.........	0.75158	0.11322	19.8	3.086	—0.188	3.898	3.855
3.........	0.67529	0.10992	19.8	2.792	—0.189	2.603	3.855
4.........	0.90187	0.07334	20.4	3.617	—0.137	3.480	3.859
5.........	0.90102	0.08665	20.4	3.625	—0.151	3.474	3.856

Average rise per gram ethyl benzene.......................... 3.8565°

Extreme variation from the mean........... 0.0025° in 3.86° = 0.06%

TABLE V.—ETHYL BENZENE (C).

1.........	0.80760	0.13303	20.0°	3.323°	—0.217°	3.106°	3.846°
2.........	0.77136	0.17095	20.1	3.240	—0.273	2.967	3.847
3.........	0.75198	0.17611	19.9	3.184	—0.293	2.891	3.845

Average rise per gram ethyl benzene........................ = 3.846°

Extreme variation from mean............................ = 0.001°

Correction for bromide present[1]........................... = 0.008°

Corrected value.. 3.854°

TABLE VI.—MESITYLENE.

1........	0.94948	0.10076	20.2°	3.856°	—0.169°	3.687°	3.883°
2........	0.87078	0.09281	19.9	3.651	—0.164	3.487	3.883
3........	0.95053	0.12873	20.1	3.900	—0.211	3.689	3.881
4........	0.64775	0.13989	19.8	2.749	—0.235	2.514	3.881
5........	0.92360	0.10692	20.1	3.767	—0.181	3.586	3.883

Average rise per gram mesitylene............................ 3.882°

Extreme variation from the mean............ 0.001° in 3.88 = 0.03%

Sample A was used in Nos. 1 and 3; B, in Nos. 2 and 4; C, in No. 5.

TABLE VII.—PSEUDOCUMENE.

1........	0.92170	0.15390	20.4°	3.829°	—0.258°	3.571°	3.875°
2........	0.86005	0.11067	20.4	3.524	—0.193	3.331	3.873
3........	0.99240	0.09866	20.5	4.001	—0.160	3.841	3.871
4........	0.92585	0.10556	20.4	3.771	—0.186	3.585	3.872

Average rise per gram pseudocumene......................... 3.873°

Extreme variation from the mean........... 0.002° in 3.873 = 0.05%

Sample A was used in 2, 3 and 4; Sample B, in 1.

---

[1] The washings of the bomb in one case yielded 4.9 mg. of silver bromide, corresponding to 2.84 mg. of ethyl bromide, the heat of combustion of a gram of which (according to Berthelot's figures) is 7.4 Calories less than that of a gram of ethyl benzene. Hence the correction to be applied is 0.00284 × 7,400/2671 = 0.0078°.

TABLE VIII.—NORMAL PROPYL BENZENE.

Determination.	Wt. hydrocarbon in vacuo. G.	Wt. sugar in vacuo. G.	Final temp.	Obs. rise temp.	Total corr.	Corr. rise in temp.	Rise per g. hydrocarbon.
1........	0.73741	0.14909	20.2°	3.117°	—0.249°	2.868°	3.889°
2........	0.91483	0.15620	20.4	3.817	—0.260	3.557	3.888
3........	0.90782	0.16555	19.8	3.801	—0.269	3.532	3.890

Average rise per gram *N* propyl benzene.................... 3.889₀

Corrected for change in heat capacity of calorimetric system (+0.023%).. 3.890°

Extreme variation from the mean............ 0.001° in 3.9° = 0.02%

TABLE IX.—ISOPROPYL BENZENE (A AND B).

1........	0.82262	0.14734	20.2°	3.445°	—0.243°	3.202°	3.892°
2........	0.93195	0.16105	20.3	3.891	—0.262	3.629	3.894
3........	0.87228	0.15930	20.3	3.651	—0.257	3.394	3.891
4........	0.73131	0.19482	19.7	3.150	—0.309	2.841	(3.885)[1]
5........	0.82612	0.16830	20.3	3.483	—0.277	3.206	(2.881)[1]

Average risê per gram isopropyl benzene, Sample A............ 3.893°

Corrected for change in heat capacity of calorimetric system (+0.023%).. 3.894°

Extreme variation from the mean........... 0.002° in 3.9° = 0.05%

Sample A was used in Nos. 1, 2 and 3; Sample B, in Nos. 4 and 5.

TABLE X.—TERTIARY BUTYL BENZENE.

1......	0.89891	0.18351	20.0°	3.814°	—0.297°	3.517°	3.912°
2......	1.07954	0.18321	20.4	4.517	—0.294	4.224	3.913
3......	1.01951	0.15835	20.4	4.250	—0.258	3.992	3.916

Average rise per gram III butyl benzene..................... 3.913°

Corrected for change in heat capacity of system (+0.023%) .... 3.914°

Extreme variation from the mean.......................... 0.06%

TABLE XI.—CYCLOHEXANE.

1[2].....	0.92870	0.13580	20.2°	4.090°	—0.222°	3.868°	(4.165)
2......	0.62918	0.09031	19.8	2.797	—0.160	2.637	4.192°
3[3].....	...	...	..	..	..	..	4.189

Mean of 2 and 3.. 4.190°

Corrected for change in heat capacity (+0.023%)............ 4.191°

Extreme variation....................................... 0.07%

The study of the individual results in this long series of determinations shows that, although the results are sometimes not quite so concordant

---

[1] Sample B of isopropyl benzene, made by the Grignard reaction, was doubtless less pure than A, made by the Friedel and Crafts reaction. Accordingly the results with Sample B are not included in the average.

[2] The result of determination 1 (made in Sample B) is not included in the average. Hexamethylene B contained more benzene than hexamethylene A, which was used in Nos. 2 and 3.

[3] Immediate data mislaid at date of writing. It is known, however, that the measurement involved very closely the same temperature range.

as those with the sugar alone, they are, nevertheless, as closely concordant as the circumstances permit. In most cases the extreme variation from the mean is less than 0.002° in the final results, while in many cases the agreement is even better than this; and in no case do the variations cause the highest result with one isomer to overlap the lowest result with the isomer giving the larger output of heat. As regards the different preparations of substance, the discrepancy between the two samples of ethyl benzene has already been noted, and its cause explained. Unquestionably the samples of ethyl and isopropyl benzene, labeled *A*, purer than those labeled *B*, and the excellent results obtained with them will be used in the future discussion. As against this discrepancy it is interesting to note that in the cases of toluene, mesitylene, and pseudocumene, the different samples gave almost identical results in each case. This is doubtless because the impurities in these preparations were chiefly homologous hydrocarbons, which would have much less effect upon the heat of combustion than upon the boiling points that served as the criterion of purity. This comparison is especially instructive as showing the different effect of different kinds of impurities.

Let us now collect all these results for the rise of temperature caused by the combustion of one gram of these several hydrocarbons in a systematic table, and reduce the data to the usual standards, in the first place giving the ratio of the rise of temperature caused by each substance to that caused by exactly one gram of sugar, and in the next place giving the corresponding absolute value for the heat of combustion of one gram of each substance, based on the current absolute values for the heat of combustion of sugar.

Unfortunately the absolute value for the heat of combustion of sugar is not agreed upon by all authorities. The best of the earlier work has been done by Fischer and Wrede, who found as the absolute value 16.545 kilojoules (or kilowatt seconds).[1] A very careful study of the data concerning the mechanical equivalent of heat by Professor Harvey N. Davis, of Harvard, indicates that at 16° this is 4.1846, and at 20° 4.1800. Therefore, accepting this estimate, we may decide that the value over the range used in these experiments is closely 4.182, that is to say, one joule equals 0.23912 calorie. On this basis Fischer and Wrede's value for the heat of combustion of sugar becomes 3956 calories per gram.

On the other hand, the most recent work of the Bureau of Standards of Washington, published by Dickinson,[2] seems to have been very carefully performed, and to be worthy to supersede the German work. The value here given is 3949 calories (20°) per gram sugar weighed in air, or 3947 calories per gram weighed in vacuum. In 18°-calories this latter figure

---

[1] Fischer and Wrede, *Sitzb. kgl. preuss. Akad.*, 5, 145 (1908).

[2] *Bull. Bur. Stand.*, 11, 190 (July, 1914)

would become 3945. In the table below, the value given by the Bureau of Standards is used, but anyone preferring the other (Fischer and Wrede's) can easily add to each value 0.28%.

In the table below there are included also the results concerning xylenes obtained by one of us in collaboration with R. H. Jesse,[1] because this formed an integral part of the series. With these preliminaries the summarized table of results may be given:

TABLE XII.—SUMMARY OF DATA AND SPECIFIC HEAT OF COMBUSTION.

	Rise of temp. caused by 1.000 g. substance.	Ratio of this rise to that caused by 1.000 g. sugar.	Absolute heat of combustion of 1 g.	
			Calories (18°).	Kilojoules.
Sucrose (Standard)	1.4810°	(1.0000)	(3.945)	(16.498)
Benzene (C_6H_6)	3.751	2.533	9.993	41.79
Toluene (C_7H_8)	3.817	2.577	10.166	42.51
Ethyl benzene A	3.857	2.604	10.273	42.96
Xylene ortho (R. & J.)	...	2.605	10.277	42.98
Xylene meta (R. &. J.)	...	2.605	10.277	42.98
Xylene para (R. & J.)	...	2.596	10.241	42.83
Mesitylene C_9H_{12}	3.882	2.621	10.340	43.24
Propyl benzene (normal)	3.890	2.627	10.364	43.34
Isopropyl benzene (cumene)	3.893	2.629	10.371	43.37
Pseudocumene	3.873	2.615	10.316	43.14
Tertiary butyl benzene	3.914	2.643	10.427	43.60
Hexamethylene (cyclohexane)	4.191	2.830	11.164	46.69

On comparing these results with the earlier results of others, it is noticeable, first, that the value for benzene is slightly lower than that found by Richards and Jesse five years ago, their value having been 2.538 instead of 2.533 times that of sugar. Nevertheless, our value as given below is decidedly higher than that found earlier by Richards, Henderson and Frevert, and recognized by them as having been too low because of incomplete combustion. The manner of experiment, excepting small details, was very similar in our case to that in the case of Richards and Jesse, and the difference of 0.2%—a quantity distinctly greater than the error of experimentation—needs further elucidation. The matter is, in fact, being studied further in the Wolcott Gibbs laboratory, and it is hoped that before long more light upon it may be obtained. It is possible, indeed, probable, judging from the variations among the Harvard results and also from the varying results obtained by others,[2] that the complete

---

[1] Richards and Jesse, THIS JOURNAL, 31, 294 (1910).

[2] See W. A. Roth's able discussion of this subject in the Landolt-Börnstein Tables, page 910, 1912. Roth used the factor 4.189 for the conversion of kilojoules to calories. Accordingly his figures are slightly different from ours as given above. Attention should be called to the error in the next to the last and the preceding column on that page. Instead of "const. vol." and "g. Kal pro gram" the headings should read "Konst Druck" and "Konst. vol.," respectively, like the corresponding columns on p. 911. Roth's work is very thorough and painstaking. In this connection, attention

combustion of benzene in the bomb is a difficult matter, and although the method adopted in the Harvard work has probably secured the best combustion heretofore attained, there is good reason to believe that the further treatment by passing the gases remaining in the bomb over a hot catalyzer is necessary in the case of a substance as volatile as benzene. This has, in fact, been done in a yet more recent research by one of the authors, helped by Dr. H. S. Davis, and before long the further results of this research will be communicated. The same objection does not apply so seriously to the higher boiling liquids, where the vaporization is less rapid and the chance for the escape of unburned carbon monoxide is much less.

Our results also for toluene are higher than those of Roth, and of ethyl benzene, higher than those of Jesse.[1] It is probable that less trouble was taken to dry the substances than in our case, and possibly also our combustion was more complete. For cyclohexane, our results are above those of Roth and below those of Zubow, who found respectively 11127 and 11231 for the heat of combustion of a gram,[2] instead of our value 11164.

On the other hand, our value for normal propyl benzene is somewhat below that given by Genvresse. All these results and others are recorded in Roth's recalculation, already quoted.

Incidentally it should be noted that these values, as given by the combustion of the material in a closed bomb, correspond to the reaction in constant volume.

It is now a matter of much interest to record these results in the usual standard, namely, in terms of the gram molecule. The molal heats of combustion are, of course, very easily calculated from the specific heats of combustion by multiplying in each case by the appropriate molecular weight.

This table is very interesting from many points of view. In the first place, the striking similarity of the heats of combustion of isomers is distinctly shown. In the eight-carbon isomers recorded above (of which there are four), the range is only between 4559 and 4543 kilojoules, a difference of only 1/3 of one per cent.; and in the case of the nine-carbon isomers, the range is not much greater, extending only from 5180 to 5208 kilojoules, a difference of a little over 0.5%. The increase of molal heat of combustion, due to the addition of CH_2, remains nearly constant throughout the series. Between benzene and toluene it is 651 kilojoules;

should be called to the interesting and comprehensive paper entitled "Thermochemische Untersuchungen," by W. A. Roth and Auwers, which has reached us too late for discussion here. The new values found by them for benzene, toluene and cyclohexane are very near ours (*Lieb. Ann.*, **407**, 109 (1914)).

[1] R. H. Jesse, Jr., THIS JOURNAL, **34**, 1340 (1912).

[2] See Landolt-Börnstein (1912).

between toluene and ethyl benzene, 644; between ethyl benzene and propyl benzene, 647; between propyl benzene and butyl benzene, 643—the average being 646. It is possible that the true average is slightly less than this, because the value of benzene given above may be slightly too low, as already stated.

TABLE XIII.—MOLAL HEATS OF COMBUSTION.

Formula.	Mol. wt. C = 12.000. H = 1.0078.	Absolute heat of combustion (in const. vol.) of 1 mol.	
		Calories (18°).	Kilojoules.
Benzene, C_6H_6	78.05	780.0	3262
Toluene, $C_6H_5CH_3$	92.06	935.9	3913
Ethylene benzene, $C_6H_5C_2H_5$	106.08	1089.8	4557
Xylene (*o*), $C_6H_4(CH_3)_2$	106.08	1090.2	4559
Xylene (*m*), $C_6H_4(CH_3)_2$	106.08	1090.2	4559
Xylene (*p*), $C_6H_4(CH_3)_2$	106.08	1086.4	4543
Mesitylene, $C_6H_3(CH_3)_3$	120.09	1241.7	5193
Propyl benzene (*n*), $C_6H_5C_3H_7$	120.09	1244.6	5204
Isopropyl benzene, $C_6H_5CH(CH_3)_2$	120.09	1245.5	5208
Pseudocumene, $C_6H_3(CH_3)_3$	120.09	1238.8	5180
Butyl benzene (tert.), $C_6H_5C(CH_3)_3$	134.11	1398.4	5847
Cyclohexane, C_6H_{12}	84.09	938.8	3926

The data are not yet plentiful enough to permit definite conclusions as to the effect of the more subtle features of the grouping upon the heat of combustion.

The six extra atoms of hydrogen in cyclohexane evolve 564 kilojoules upon burning as compared with benzene. The same amount of hydrogen gas would have evolved half again as much, but, of course, the situation is so complex that an exact interpretation of differences of this sort is as yet beyond our reach. It is hoped that this work may be continued, and not only further progress made with regard to compounds of this type, but also that the work may be extended to other compounds, so as to secure a great variety of accurate data upon which conclusions concerning the total energy relations of organic substances may be built. This is especially important, because, as is well known, many of Thomsen's carefully obtained data are vitiated by the defect of his "universal burner," and in many of the earlier results obtained from the bomb, the combustion was undoubtedly incomplete.

In concluding, we are glad to express our indebtedness to Dr. G. L. Kelley for generous assistance in developing the methods adopted and in directing an assistant employed in preparing and purifying some of the higher homologs; and also to the Carnegie Institution of Washington for the subsidy which alone has made the investigation possible.

Summary.

The principal results of this investigation may be summarized as follows:

1. The method of adiabatic calorimetry as applied to combustion in the Berthelot bomb has been further improved in several directions, making more accurate determinations possible.

2. The agreement among the results with any substance is close enough to show that the method is capable of all the necessary refinement.

3. The relative heats of combustion of sugar, benzene, toluene, ethyl benzene, normal and isopropyl benzene, mesitylene, pseudocumene and cyclohexane have been determined.

4. The striking similarity between the heats of combustion of various isomers appears. Nevertheless, real differences exist, and will doubtless some time, when more data are available, be capable of reference to differences in molecular stability and configuration.

5. The boiling points of these liquids have been carefully studied, especially those of exceptionally pure toluene (110.31°) and cyclohexane (80.8°); and the melting point of benzene also has been determined as 5.484°, while that of cyclohexane was found to be 5.97°.

CAMBRIDGE, MASS., 1911–1912; 1915.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF LEAD. THE ANALYSIS OF LEAD BROMIDE.

[SECOND PAPER.]

BY GREGORY PAUL BAXTER AND THORBERGUR THORVALDSON.

Received March 8, 1915.

Since the work by Baxter and Wilson[1] on the atomic weight of lead by the analysis of lead chloride some years ago, which yielded the value 207.09 (Ag = 107.880), the atomic weight of lead has been under almost continuous investigation in the Harvard Laboratory. Attempts were made by Mr. W. A. Worsham to synthesize the sulfate from the metal, but serious difficulties were met in the production of lead sulfate free from occluded matter, and in the drying of the sulfate, so that this method was temporarily given up in favor of the analysis of lead bromide. The latter substance, in spite of the fact that it is somewhat less soluble than lead chloride, is, nevertheless, sufficiently soluble for the purpose. Preliminary experiments in the preparation of pure lead bromide were carried out by Mr. Worsham. The investigation was then continued by the present authors, and finally was taken up by Mr. F. L. Grover. This paper presents the results of Dr. Thorvaldson's experiments, while the following one describes the completion of the research by Mr. Grover.

The method employed was the usual one in the case of metallic halides, with special modifications made necessary by the idiosyncrasies of lead

---

[1] *Proc. Amer. Acad.*, 43, 365 (1907); THIS JOURNAL, 30, 187 (1908); *Z. anorg. Chem.*, 57, 174 (1908).