of platinum black upon the surface of the electrode markedly increases the proportion of impurity. With clean electrodes the average per cent. of impurities is 0.004. A fairly large discrepancy thus remains between the ratio of silver and iodine determined by direct combination and by coulometers.[1]

In "Atomic Weights"[2] E. F. Smith outlines the researches upon atomic weights carried out in the John Harrison Laboratory of the University of Pennsylvania.

CAMBRIDGE, MASS.

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

IMPROVEMENTS IN CALORIMETRIC COMBUSTION, AND THE HEAT OF COMBUSTION OF TOLUENE.

BY THEODORE W. RICHARDS AND HAROLD S. DAVIS.

Received December 21, 1916.

This paper is one of a series, the object of which is to secure further knowledge of a more precise nature concerning the heats of combustion of typical compounds of carbon, and further development of the methods of determination.[3] The work herein described followed directly after that detailed in the recent communication published with Dr. Frederick Barry; and the methods and apparatus resembled in most respects those already explained. Having profited by the experience of the earlier work, we were able to improve upon some of its details. Especial emphasis will be laid upon the improvements.

The method depends on the successive combustions of toluene and of a standard substance in the Berthelot bomb as modified by Atwater and Benedict, in oxygen under about 22 atmospheres pressure. The rise of temperature of the calorimeter containing the bomb was paralleled in the environment, so that no correction for cooling was needed. That this adiabatic method is capable of giving excellent relative results is shown by the series of investigations conducted at Harvard University, while the accuracy of its absolute results is proved by the recent careful work of the Bureau of Standard by H. C. Dickinson and his assistants.[4] The general assemblage of apparatus is adequately described and depicted in the most recent of the preceding papers, and the reader is referred to this as regards minutiae.

The details in which improvements were instituted were as follows: the mode of sealing the bomb, the mode of providing for the well-regulated

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[1] See Report for 1914.

[2] Monograph, University of Pennsylvania.

[3] For references, see Richards and Barry, THIS JOURNAL, **37**, 993 (1915).

[4] *Bull. Bur. Stand.*, 11, 243 (1914).

and complete combustion of the volatile substance; the mode of ignition; the automatic control of the temperature of the environment by a special synthermal regulator; and the analysis of the residual gases for traces of unburned carbon monoxide. These several topics are discussed in order below, and finally the results for naphthalene and toluene are given. Other substances also were burned, but the details concerning these will be reserved for another communication.

The Closing of the Bomb.

The bomb was sealed by a washer of lead, N, sunk into a suitable circular slot and covered by a continuous round plate of gold foil, K (0.4 or 0.5 mm. thick), which protected the whole inside of the cover of the bomb. The foil was soft enough to conform perfectly to the double rim of the lower part of the bomb, without breaking; the lead was soft enough to secure complete closure, and the gold wholly protected the lead. If the gold foil is pressed closely against the steel top of the bomb, there is little danger of its melting; and if an accident happens, the foil is readily replaced. Accordingly, this method was uniformly used in the present research.

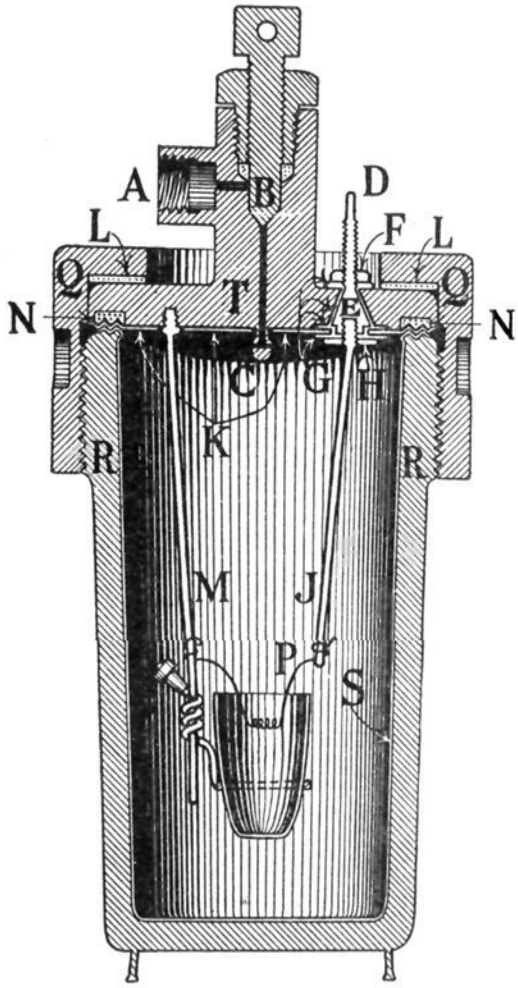

Fig. 1.—New Features in Calorimetric Bomb.

DE	Steel conical plug.
F	Steel nut holding plug in place.
G	Mica insulation.
H	Platinum nut protecting mica and clamping J.
J	Platinum rod for firing-connection.
K	Gold lining to cover protecting lead washer N.
L	Phosphor-bronze ring to prevent friction of screw cap Q on steel lid T.

The detrimental effect of the friction of steel screw-cap against the movable steel cover was greatly diminished by the use of a thin, smooth, flat ring of phosphor-bronze, L, between these two parts. Thus rupture of the platinum lining was avoided, and the closure greatly facilitated.

The insulation of the wires for conveying the current necessary for the ignition was improved by making the conical piece E (passing through the cover) of steel, not platinum, and insulating this from the cover by a thin layer of mica, G. A stout thread and nut, F, likewise insulated, on the outside, permits forcing the strong steel cone so firmly into place that the arrangement is wholly gas-tight. Into the base of this cone a thread is tapped for the stout platinum wire J used to conduct the current, and the iron of the cover is protected by a wide platinum nut, H, which is insulated from it by mica. Thus the platinum wire is very firmly held in place and yet may be easily unscrewed, and the insulation of the steel cone remains undisturbed indefinitely. Fig. 1 records all these improvements.

Other precautions concerning the makeup and treatment of the bomb were similar to those already described in previous investigations.

Mode of Enclosing and Igniting Volatile Liquids in Thin-Walled Glass Bulbs.

For enclosing the liquids to be burned, very thin bulbs, holding about 1 cc. and weighing about 0.4 g., were blown from a piece of ordinary soft glass essentially in the way illustrated in the preceding communication.[1] They were about 1.8 cm. in diameter and 0.5 or 0.6 cm. thick, being much flattened on both sides to give flexibility (necessary on account of the pressure in the bomb) which was tested by pressing with the fingers. The volume of each bulb was easily found by immersion, and the method of filling was essentially that previously described. The bulb should not only yield under the pressure, but should be thin enough to burst easily. Otherwise the violent explosion may lead to incomplete combustion, and to injury to the apparatus. Typical very thin bulbs filled with benzene or toluene were found to burst with slight explosion at a temperature of about 50° in an oil bath—a circumstance which may explain the occasional projection out of the crucible and incomplete combustion of some of the sugar at first used to ignite the liquid. Accordingly, instead of sugar about 0.1 g. of paraffin was used for this purpose; it was melted around the inside of the mouth of the weighed crucible by a hot glass rod outside of the crucible. A weighed wisp (about 0.5 mg.) of cotton wool was attached to the paraffin, while the spot was heated locally by means of the rod applied outside of the crucible. A minute coil of very fine platinum wire enveloping the projecting cotton served to ignite it and the paraffin. The heat from the burning ring of paraffin burst the bulb through the expansion of the liquid, and the vapor of the liquid rose into a ring of flame at the mouth of the crucible and was completely burned. This method is so easy to adjust and is so convenient that it is a distinct improvement over the method formerly used. The result was of course corrected for the accurately known heats of combustion of the paraffin and of the shred of cotton wool.

The method of Roth and his collaborators[2] was also tried, and often found to give good results, with complete combustion, especially in the

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[1] Richards and Barry, *Loc. cit.*

[2] *Ann. Chem.*, **385**, 104 (1911).

case of high-boiling liquids; nevertheless, this method, either in its original form or modified in several ways, was, on the whole, found to be less convenient in our hands than that described above.

Method of Ignition.

Iron wire, heated by an electric current to start the combustion, has several disadvantages. The amount of iron burned and the stage of its oxidation are uncertain. Moreover, drops of fused oxide are sometimes driven against the platinum, and frequently destroy the crucible or the lining of the bomb. Very fine platinum wire, used by Zubow and Roth, is decidedly better. In detail, the method used by us was as follows: 7–10 cm. of very fine platinum wire were wound in a spiral about 1 mm. in diameter, and attached to the ends of two supports directly above the crucible. Within the spiral was placed a weighed shred of filter paper or (better) cotton wool, dipping into the substance to be ignited first—as already described. A current of approximately 0.8 ampere ignited the cotton wool in about one-fifth of a second. The variations in the amount of heat obtained from the current in this time are wholly negligible in results like these, where one substance is measured by comparison with another treated in the same way.

Although the hygroscopic condition of cotton varies, for our purpose, using such small amounts, is may be considered as constant.

The Automatic Control of the Temperature of the Environment.

In a recent communication from this laboratory an automatic device, or "synthermal regulator," for causing the environment around the calorimeter to follow the temperature of the calorimeter itself, is described.[1] The present investigation was well in progress before this synthermal regulator was perfected, and, in the meantime we had evolved another quite different device (much simpler, and not so generally applicable as the other) which served the present purpose sufficiently well.

The general impression seems to exist that combustion within the calorimetric bomb is explosive and instantaneous.[2] According to our experience, this by no means the case, especially with solid substances. We found the rate of combustion to be quite variable, depending partly upon the nature of the substance, partly upon the state of aggregation, and partly upon the oxygen pressure. Thus benzoic acid or naphthalene in powder, or a volatile liquid, causes the temperature of the calorimetric system to rise very quickly when it is burned; but if the solids are compressed into hard tablets, the temperature rise is slow and steady and may require over three minutes for completion. This difference can be accounted for only by differences in the time actually required for the burning of the substances in the bomb. This conclusion is entirely in accord with that of

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[1] Richards and Osgood, THIS JOURNAL, 37, 1718 (1915).

[2] Stohmann, *J. prakt. Chem.*, 39, 514 (1889).

Benedict and Fletcher,[1] based upon the measurement of the pressures developed during the combustion of solid substances.

In the case of a liquid we found again that much depends upon its condition. If a bulb containing benzene broke before the ignition (indicated by the smell of the liquid in the gases before combustion), the rise of temperature on ignition was rapid, and the combustion incomplete. Evidently something partaking of explosion had taken place. This was doubtless the case in Stohmann's work and led to his thinking that all combustions in the bomb were explosive. Such an outcome is obviously to be avoided. Combustion so dangerously rapid as to be explosive was also noticed when our hermetically sealed glass bulbs were too thick, so as to need considerable pressure for their breaking, and likewise when the bulbs were completely wrapped in cotton wool, which was then ignited. In the latter case the containing crucible was often blown to pieces. On the other hand, when benzene, for example, is burned in small glass test tubes, according to the method of Roth, the temperature rises very slowly, sometimes for even fifteen minutes, showing that the rate of combustion is very slow. If the tube is too thick or too narrow, some of the liquid at the bottom of the tube may escape combustion.

Both extremes are avoided if the liquid is enclosed in a very thin bulb and ignited by a ring of paraffin around the top of the small crucible, as already explained. Then the rate of combustion, as shown by the rate of rise of temperature, is rapid but equable, and is determined chiefly by the volatility of the liquid; even methyl alcohol does not burn with the velocity of an explosion. The rise of temperature in the bomb seems then always to correspond to a curve of a certain definite type illustrated as *a* and *b* in Fig. 2, which records actual observations made with the help of an assistant observer. In every case the curve begins and ends somewhat in exponential fashion, with an almost straight line between, as one would expect. The differences between the different substances lay chiefly in the different inclinations of the straight line.

The immediate practical problem was to match this rise in the calorimeter by a similar rise in the environment. Since the rise in temperature of the calorimetric environment (caused by adding sulfuric acid to the alkaline outside bath) is directly proportional to the amount of acid added, a device was needed for delivering very little acid at first, then rapidly increasing the amount, then for some time adding acid at a nearly constant rate, and finally diminishing the stream until it is reduced to nothing. These differences in rate of flow could easily be attained by constructing an apparatus for delivering acid automatically under different pressures. To attain the first part of the curve the level of the acid must run uphill; to parallel the straight line in the middle, the liquid must

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[1] Benedict and Fletcher, This Journal, **29**, 740 (1907).

be delivered from a larger reservoir of nearly constant level; to get the last part of the curve, it must rapidly sink in a fine delivery tube. The necessary dimensions of the several tubes were found by trial, and an apparatus

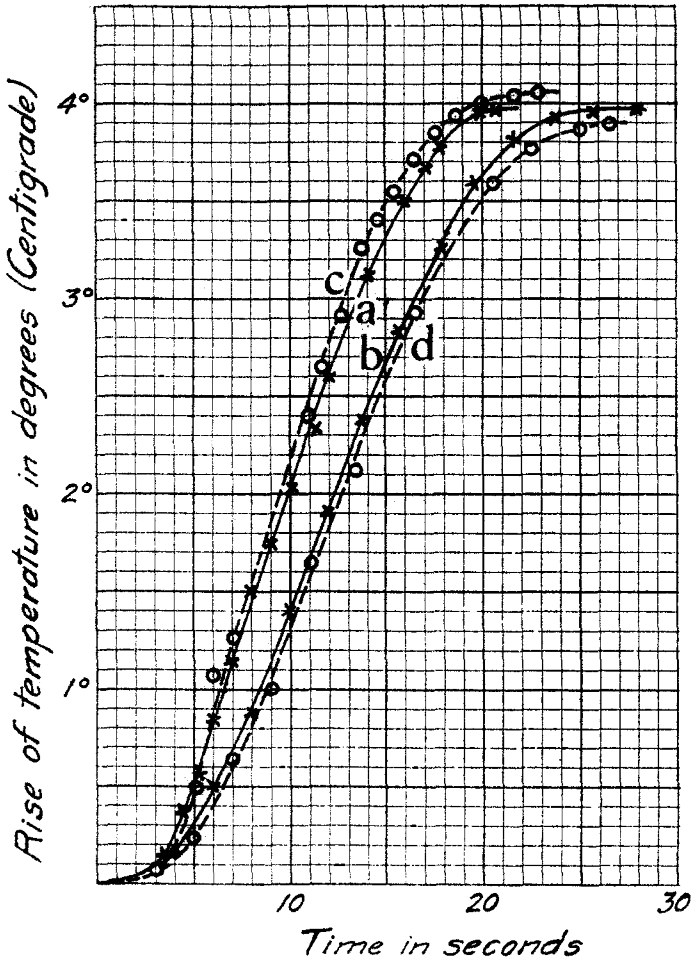

Fig 2.

Continuous lines *a* and *b* represent temperatures in calorimeter as indicated by thermometer in combustions of two different speeds.

Broken lines *c* and *d* indicate rise of temperature in environment as produced by apparatus to be described and illustrated in Fig. 3.

like that shown in Fig. 3 was found to serve the purpose excellently. The tube to the right had to be long and zigzag because its inside diameter could not be greater than 4 mm., on account of the small capillary constant of concentrated sulfuric acid.

After the apparatus had been made, minor adjustments could be completed by raising or lowering the end of the tube or by tilting, so as to give widely varying curves of delivery. Also, the total rate of delivery could be simply changed by a stopcock at the orifice, which can slow down or quicken the whole process, without altering the general nature of the curve. The dotted lines shown in curves *c* and *d* correspond to rates of flow obtained from the same delivery tube by simply changing the position of the stopcock E (Fig. 3), to which was attached a pointer operating over a scale.

For each substance with each method one or two preliminary trials determined the general inclination of the curve. Previous experiments with alterations in the stopcock showed the inclination corresponding to each position on its scale. Therefore, for any particular substance, when all was ready for the combustion, the stopcock E had simply to be set at the appropriate point, and at the moment of ignition M and N fully opened. The acid was then delivered automatically at a rate suitable for the case in hand.

As before stated, with very volatile liquids the thickness of the bulb and the amount of substance affect the rate of combustion, so that even after preliminary trials one could not always set the stopcock before-hand at exactly the right point. Nevertheless, even in such cases the automatic supply tube was still a great convenience, for at worst the amount of acid delivered was nearly right, and slight differences could be soon adjusted by an auxiliary buret or a little cold water. Moreover, the pointer attached to the stopcock E could be moved after the beginning of the combustion to fit the particular exception in hand, when its nature had been manifested. The diagram (Fig. 2) shows how closely the temperature changes in the calorimeter can be duplicated in the environment.

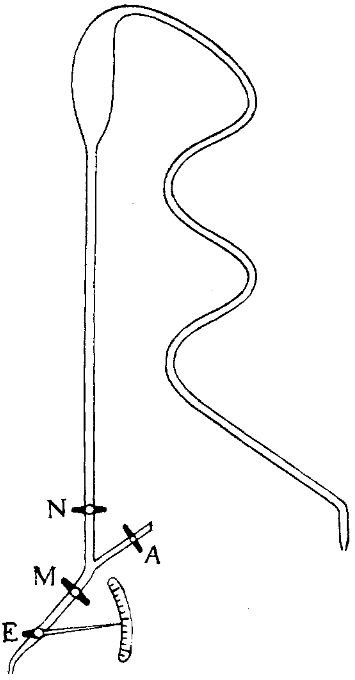

Fig. 3.

A	Stopcock for admitting sulfuric acid to apparatus in process of filling.
E	Regulating stopcock for determining rate of flow without altering general character of curve.
M	Stopcock for starting and stopping flow of acid into tank.

Incomplete Combustion.

In the recent work of one of us in collaboration with Dr. F. Barry, it was pointed out that the results of various experimenters for volatile liquids, especially benzene, have varied to a significant extent, suggesting that the combustion is sometimes incomplete. This error is an insidious one, which has hardly received enough attention in the past. To be sure, in one of the earlier Harvard investigations the gases remaining in the bomb after the combustion of sugar were repeatedly analyzed for carbon monoxide or other volatile carbon compound, and none was found.[1] Nevertheless, with volatile liquids the danger is much greater, as is indicated by the careful work of Auwers, Roth and Eisenlohr.[2] They showed that their test tube and capsule method gave much higher results, and, therefore, presumably more complete combustion, than results obtained by the older method, although these had agreed very well among themselves. Excellent agreement is shown by the results for benzene in the last Harvard research already quoted, although these values are 0.2% lower than others found at Harvard before. Hence mere agreement of the results is no proof of completeness of combustion; it shows only that the same degree of completeness (or incompleteness) was obtained in each case of a given series.

The final test is the actual analysis of the resulting gases for reducing carbon compounds, especially carbon monoxide. This we have now carried out after many combustions, and can definitely report that with volatile liquids the combustion as ordinarily conducted is often somewhat incomplete.

The arrangement of the apparatus was as follows: To the bomb, after each calorimetric combustion, was connected a train of tubes, in this manner: 2 U-tubes filled with concentrated potassium hydroxide solution and glass pearls; a Liebig absorption tube containing saturated barium hydroxide solution; a drying tube filled with phosphorus pentoxide; a tube of copper oxide heated to a dull red heat by electricity; a tube of phosphorus pentoxide, and finally, either a Liebig's potash bulb or a spiral filled with a definite quantity of 0.1 *N* barium hydroxide, which was afterwards titrated. Allowance was of course made for the residual gas in the bomb.

In very many cases, considerable quantities of carbon monoxide were thus found, often corresponding to errors of several tenths of a per cent. in results obtained by the older methods, although the combustions seemed otherwise complete. This discovery entirely explains the discrepancy in previous results for benzene of many experimenters. Fortunately, it was only with volatile liquids of this sort that any important incompleteness of combustion was found.

On the other hand, the combustion was found to be fairly complete

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[1] Richards, Frevert and Henderson, *Proc. Am. Acad.*, 42, 581 (1907).

[2] *Ann. Chem.*, 385, 102 (1911).

when volatile liquids were burned by the finally approved method of enclosing the liquids in very thin bulbs ignited by the ring of paraffin.

The gases from a combustion of benzene were also tested for oxidizable carbon compounds by bubbling through a weak solution of alkaline potassium permanganate, and for ozone by allowing them to impinge on starch-iodide paper. Both of these tests gave negative results.

As regards the amount of nitric acid found: the amount varies with the pressure of oxygen, with the velocity and amount of combustion, and with the concentration of nitrogen in the bomb.[1] The effect of the burning of iron noticed in previous papers was, of course, absent, because the ignition was always started by fine platinum wire. Methyl alcohol in burning produced the most nitric acid, ethyl alcohol and butyl ketone and propyl alcohol next, cyclohexanol next, and the hydrocarbons and solids very little indeed; but even the maximum amount with methyl alcohol corresponded to less than 0.0005° in the temperature of the calorimeter, that is to say, enough to be neutralized by 4.5 cc. of alkali, having a concentration of 0.022 N. Methyl orange was used as indicator because of the presence of carbon dioxide. It must be borne in mind that in all our work the bomb was exhausted previous to filling with oxygen, and this gas contained little nitrogen; hence there was but little opportunity for the formation of nitric acid.

Heat Exchange between Bomb and Calorimeter.

In our preliminary experiments with benzene the effort was made to vary the conditions as much as possible in order thereby to attain knowledge concerning possible disturbing circumstances. This was precisely the opposite procedure from that adopted in the work with Barry, where the effort was made to have the conditions as similar as possible in order to find out whether the circumstances involved in thermometry and the other experimental processes could be repeated with precision, giving constant results under constant conditions.

As was to be expected, this varying of the conditions in the present series of experiments led to several interesting results. The most puzzling of these was the fact that in those experiments where the bulb was wrapped with cotton wool and hence the combustion was so rapid as to be explosive (often shattering the crucible), the rise of temperature was larger (3.778° per gram) than that normally shown by slow combustion (3.770°), even when the latter was proved to be entirely complete. Since there is no obvious reason why very rapid combustion could evolve a larger amount of heat than perfect slow combustion, it is clear that the difference must have been in the mode of interchange of the heat from the bomb into

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[1] This confirms earlier Harvard results and those of Auwers and Roth, *Ann. Chem.*, **373**, 239, 267 (1910).

the calorimeter. Systematic error in the adiabatic process had been ruled out, for long experience had shown this process to be satisfactory.

Moreover, combustions involving only a small range of temperature likewise usually gave somewhat higher results than those covering a large range of temperature.

A possible explanation for these irregularities is the following: When the combustion is rapid but not explosive, and considerable in amount, the *top* of the bomb naturally becomes hot. This must heat the water immediately above it, which might not be sufficiently stirred to distribute the heat promptly. Hence the thermometer bulb (about half-way down in the calorimeter) would fail to register the full rise of temperature, and some heat would be lost by evaporation and radiation from the warmer upper surface of the water in the calorimeter. Such results would be low. Slow combustions, especially those covering a less range, would involve less serious error in this way, because of less heating of the top of the bomb. They should give higher results. On the other hand, explosive combustions in which the crucible is shattered, would heat the whole bomb. Here the heat would be distributed over all the calorimeter water at once, and have its full effect.[1] These inferences all correspond with the facts. One may note that the divergences would be just as serious if one used the older method of correction for cooling, instead of the adiabatic method. It is possible that this source of error may have entered into previous work of others, and that it may account for some of the divergences in published results.

The lesson to be drawn from these considerations is as follows: Either the stirring must be so efficient as to prevent any thermal stratification in the calorimeter, or else the unknown substance to be burned must be treated in such a way as to burn at about the same rate and to give out about the same amount of heat as the standard substance to be burned. When the latter condition is maintained not only will all such errors be eliminated, because similar in both series, but also any possible errors in the calibration of the thermometer will become as little perceptible as may be. Attention was called some time ago to the need of active stirring in the calorimeter[2] because a thermal stratification within the calorimeter was noticed with a rate of stirring less than 65 strokes per minute; probably even this would not be enough with widely differing rates of combustion. In the determinations given below, this cause of error was obviated by a combination of both precautions: adequate stirring and equal combustion rate.

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[1] For the same reason the method of Roth, when very slow, usually gave higher results in our hands, because there the top of the bomb could never have got very warm.

[2] Richards and Barry, THIS JOURNAL, 37, 1011 (1915).

Source and Preparation of Materials.

Naphthalene was obtained from the Bureau of Standards; it had evidently been prepared by them with very great care, and gave every evidence of having a high degree of purity. It serves admirably for standardizing calorimetric determinations; we found it much superior to sugar.

Toluene was prepared from commercial toluene by shaking with successive portions of sulfuric acid until the acid remains colorless. Further agitation with mercury until it had ceased to pollute a clean mercury surface, washing with water and many times repeated distillation followed. The fraction which came over in the immediate neighborhood of 110.31° under normal pressure was retained as pure.[1]

Thermometers.

The mercury thermometers employed in this and in the previous research continued to give good service, as the excellent agreement of the results indicates. The chief difficulty with the temperature measurement was our uncertainty as to whether or not our standard of reference really represented exactly the true temperature scale.[2] Any other form of thermometer based on the same standard would have been equally uncertain. This uncertainty is the reason for the postponement of the publication of the results for other substances besides naphthalene and toluene—for the other substances were studied over varied ranges of temperature. In the results given below for naphthalene and toluene, the uncertainty is eliminated, because all the experiments covered approximately the same range, and any calibration would give about the same outcome as any other. Active endeavors are now in progress to settle the question of calibration definitively; when that is done the other results also will be corrected accordingly and published.

The twin thermometers in calorimeter and environing bath were conveniently read by means of two long adjoining mirrors placed behind them, the thermometers being placed with their backs to the observer. In this way the two columns appeared side by side, and the two could be compared at a single glance.

Since 1 g. of naphthalene, which evolves (according to the Bureau of Standards) 9622 calories, raised our system 3.616°, the heat capacity of the system must have been 2661 $\frac{\text{cal. } 20^\circ}{t^\circ \text{ C.}}$ — or 0.12% less than that used in the preceding research.

Execution of Determinations.

The details of combustion of organic substances in the apparatus have been so often described that they need not be reiterated. The bomb was in every case evacuated to within the pressure of a few millimeters

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[1] Richards and Barry, This Journal, **36**, 997 (1915).

[2] Richards and Thorvaldson, *Ibid.*, **37**, 84 (1915).

of mercury before oxygen was admitted. The gas used had been prepared by a commercial firm from liquid air, and was admitted from a cylinder under compression until the pressure in the bomb attained 20 atmospheres. The oxygen gave no test for chlorine or for carbon dioxide and contained very little nitrogen. The chief impurity was argon, of which it contained in the neighborhood of 2%. The same weight of water was used in the calorimeter in every case. The observations necessary were the following:

(1) The weight of material to be studied;
(2) The weights of auxiliary materials for ignition;
(3) The correction for stirring;
(4) The nitric acid formed in the bomb;
(5) The presence or absence of unburned carbonaceous material;
(6) The presence or absence of carbon monoxide in the residual gases;
(7) The initial and final temperatures, both of which, of course, must be corrected according to the careful calibration of the thermometers, if the range is not the same in determinations to be compared.

Data for the heats of combustion of the several auxiliary substances follow, in the form most convenient for the present purpose. Of these only paraffin and cotton-wool were used in the six determinations reported below.

QUANTITATIVE COMBUSTION OF AUXILIARY SUBSTANCES.

Substances.	Rise of temperature caused by 1 g. (weighed in air) with extreme variations from average.	Heat of combustion of 1 g. (weighed in air).
Paraffin (4 trials)	4.214° ± 0.0025	11210
Beeswax (2 trials)	3.859° ± 0.003	10266
Cotton-wool (4 trials)	1.51° ± 0.02	4020

There follows the record of the last three and most successful determinations of the heat of combustion of naphthalene, chosen as a standard substance, and of three determinations of the heat of combustion of toluene, contained in thin sealed bulbs. These determinations serve to indicate the consistency attainable by use of the precautions just described—a ring of paraffin encircling the inside of the top of the crucible in the toluene combustions, and those in both series being fired by fine platinum wire encircling wisps of cotton-wool.

In the tables, the weights have not been corrected to the vacuum standard. This correction is applied later. The amount of auxiliary material used to start the ignition is given in Column I. M. The correction for this, together with the correction for stirring, and that for nitric acid and any residual carbon monoxide[1] are all added together in a single quantity labelled "Cor." in the tables below.

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[1] This particular correction is easily calculated to be about 0.0009° per cc. of carbon monoxide.

NAPHTHALENE.

No.	W. substance.	I. M.	Corr.	CO.	t_1.	t_2.	ΔT for 1 g.
5..........	1.1537	Cotton 0.008	0.0220°	...	16.008°	20.202°	3.616°
6..........	1.1002	Cotton 0.0095	0.0260°	...	16.036°	20.043°	3.618°
7..........	1.1023	Cotton 0.008	0.0222°	...	16.046°	20.059°	3.615°
						Average,	3.616°
			TOLUENE.				
6..........	0.9154	Paraffin 0.0982 Cotton 0.0036	0.4256°	None	15.961°	19.885°	3.822°
7..........	0.9986	Paraffin 0.0953 Cotton 0.003	0.4143°	2.0 cc.	15.553°	19.782°	3.820°
8..........	1.0566	Paraffin 0.0747 Cotton 0.0079	0.3348°	1.7 cc.	15.987°	20.357°	3.822°
						Average,	3.821°

Thus 1 g. of naphthalene in burning was capable of raising our calorimetric system by 3.616° and 1 g. of toluene 3.821° (or 1.0567 times as much as a gram of naphthalene) both substances having been weighed in air. According to the careful absolute determination of the Bureau of Standards 1 g. of naphthalene thus weighed evolves 9622 20°-calories.[1] Hence 1 g. of toluene must evolve 10,168 calories, the toluene being weighed in air. Corrected to vacuum and to 18° this would become 10,158, a value slightly less than that (10,166) found by Richards and Barry. A part at least of the difference may be due to the different standard of reference used in this case (naphthalene instead of sugar).

It is evident that the combustions in the earlier Harvard research must have been essentially complete, for such difference as exists is in the direction opposite from that which would have been caused by incompleteness of combustion in the earlier ones.

Both results are much higher than that found by Roth and Auwers,[2] who apparently did not test the residual gases for carbon monoxide after combustion, and found the gram of toluene to give only 1.0529 times as much heat of combustion as a gram of naphthalene, instead of 1.0564. A part (but not all) of the discrepancy may be due to the very high value for naphthalene found by them (9636 instead of 9622). On the other

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[1] *Bull. Bureau Stand.*, 11, 251 (July, 1914).

[2] Roth and Auwers, *Ann. Chem.*, **407**, 154, 158 (1914).

hand, possibly either our toluene contained a slight aliphatic impurity[1] (a rather unlikely contingency, considering our use of several samples from different sources) or theirs contained traces of some other contamination, since it is so very difficult to purify completely a compound of carbon, even by countless distillations, from substances with nearly the same boiling point. Crystallization is safer, and will be applied to this case in the near future.

Many other determinations of a variety of organic substances have been made with the help of these improved methods. The results will be communicated in the near future in a publication of the Carnegie Institution of Washington, to which we are much indebted for generous assistance in this work.

Summary.

In this paper there are described improvements in various details of the procedure of calorimetric combustion, to wit: means of effective closing with less risk of injury to the platinum lining and cover of the bomb; means of burning volatile liquids without loss; a method of automatically controlling the temperature of the environment about the calorimeter so as to make the combustion more convenient and more truly adiabatic; and means of evaluating the incompleteness of combustion if any volatile carbon compounds should remain unburned. New determinations of the heat of combustion of toluene (10,158 18°-calories or 42.47 kilojoules per gram, weighed in vacuum) are recorded.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE STRUCTURE OF THE SURFACES OF LIQUIDS, AND SOLUBILITY AS RELATED TO THE WORK DONE BY THE ATTRACTION OF TWO LIQUID SURFACES AS THEY APPROACH EACH OTHER.

[SURFACE TENSION. V.]

BY WILLIAM D. HARKINS, F. E. BROWN AND E. C. H. DAVIES.[2]

Received December 27, 1916.

In this paper data will be presented for the work done when the surfaces of two liquids come together to form an interface. The numerical value of this work in ergs per square centimeter is characteristic of each

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[1] For example, 2,4-dimethylhexane, boiling point 110°, L. Clarke, THIS JOURNAL, 30, 1148 (1908). Octanes have higher specific heats of combustion than toluene. Richards and Jesse, *Ibid.*, 32, 292 (1910).

[2] The experimental work of this paper was begun by E. C. Humphery in 1912, and was continued in 1913 by F. E. Brown. The delay in its publication has been caused by the fact that until recently we had not determined accurately the corrections in-