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

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The object of this investigation, which is part of a much larger program, was to secure further more precise knowledge of the heat of combustion of typical compounds of carbon, and further development of the methods of determination.[1] 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 consisted in the successive combustion of toluene and 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 colorimeter 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 investigation conducted at Harvard University; its absolute accuracy is proved by the recent careful work of the Bureau of Standards by H. C. Dickinson and his assistants.[2] The general assemblage of apparatus is adequately described and depicted in the most recent of the preceding papers, and the reader is referred to these 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 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, sunk in a suitable circular slot and covered by a continuous round plate of gold foil (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.

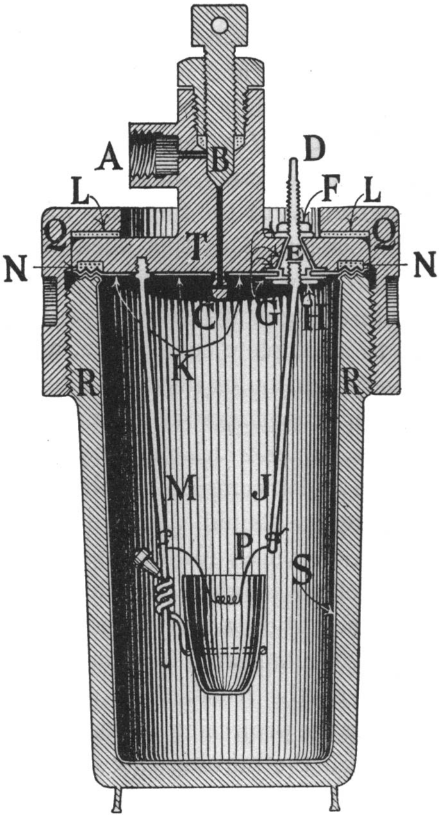

FIG. 1. NEW FEATURES IN CALORIMETRIC BOMB

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

The insulation of the wire for conveying the current necessary for the ignition was improved by making the conical piece (passing through the cover) of steel, not platinum, and insulating this from the cover by a thin layer of mica. A stout thread and nut, 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 used to conduct the current, and the iron is protected by a wide platinum nut, which is insulated from the cover 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. Figure 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.[3] These must be much flattened on both sides to give flexibility (necessary on account of the pressure in the bomb), tested by pressing with the fingers. The volume of each bulb is easily found by immersion, and it is filled essentially in the way previously described. The bulb should not only yield under the pressure, but should be thin enough to burst easily. Otherwise the violent explosion might 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 a water 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, melting it upon the inside of the mouth of the weighed crucible by a hot glass rod outside of the crucible. A weighed fiber (about 0.5 mgm.) of cotton wool was attached to the paraffin, while heated for a moment 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 ruptured 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 heat of combustion of the paraffin and shred of cotton wool.

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 at the ends of two supports directly above the crucible. As already stated, within the spiral was placed a weighed shred of filter paper or cotton wool, dipping into the substance to be ignited first, whether this was sugar, napthalene or paraffin. 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.

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 match the temperature of the calorimeter itself, is described.[4] The present investigation was well in progress before this synthermal regulator was perfected, and in the meantime we had evolved a quite different much simpler device which served the present purpose sufficiently well, although not so generally useful as the other.

The general impression seems to exist that combustion within the calorimetric bomb is explosive and instantaneous.[5] According to our experience, this is by no means the case, especially with solid substances. We find that the rate of combustion is very 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 napthalene in powder, or a volatile liquid cause the temperature of the calorimetric system to rise very quickly when they are 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. The dif-

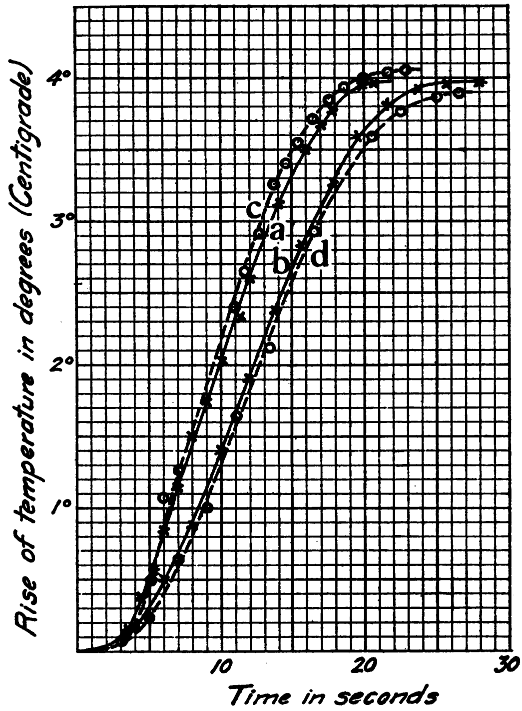

FIG. 2

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 figure 3.

ference can only be accounted for 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 Benedict and Fletcher,[6] based upon the measurement of the pressures developed during the combustion of solid substances.

The immediate practical problem was to match this rise in the calorimeter by an equal rise in the environment. Since the rise in temperature of the calorimetric environment, caused by adding sulphuric 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, in order to follow the carefully ascertained course of the rise of temperature of the calorimeter. These differences in rate of flow can 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 during the rapid rise, the liquid must be delivered from a larger reservoir of nearly constant level; to match 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 like that shown in figure 3 was found to serve the purpose excellently. The tube to the right hand had to be long and spiral because its inside diameter could not be greater than 4 mm., on account of the small capillary constant of concentrated sulphuric acid.

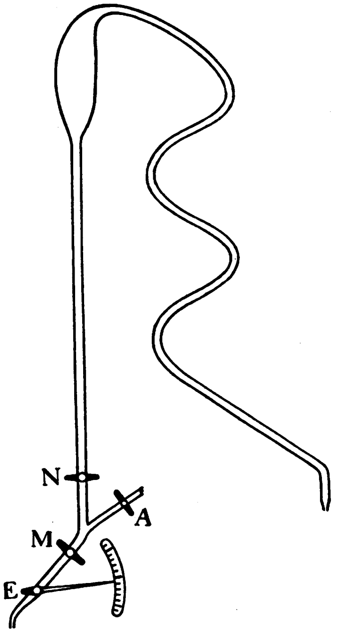

FIG. 3

A, stopcock for admitting sulphuric acid to apparatus in process of filling, *N* being open; *M*, stopcock for starting and stopping flow of acid into tank; *E*, regulating stopcock for determining rate of flow without altering general character of curve.

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.

Incomplete combustion.—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.[7] Nevertheless, with volatile liquids the danger is much greater, as is indicated by the careful work of Auwers, Roth and Eisenlohr.[8] The final test is the actual analysis of the resulting gases for combustible carbon compounds, especially carbon monoxide. This we have now carried out after many combustions, and can definitely report that with volatile liquids the combustion 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, as follows: 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 tenth normal barium hydroxide, which was afterwards titrated.

In very many cases considerable quantities of carbon monoxide were thus found, often corresponding to errors of several tenths of a per cent in combustions carried out by the older methods, which seemed otherwise complete. This discovery entirely explains the discrepancy in previous results of many experimenters for benzene. Fortunately, it is 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 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 compound by bubbling through a weak solution of alkaline potassium permanganate, and for ozone by allowing them to inpinge on starch-iodide paper. Both of these tests gave negative results.

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

Toluene was prepared from commercial pure toluene by shaking with successive portions of sulphuric 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.[9] Several samples from different sources were employed.

There follows the record of the last three (and most successful) determinations of the heat of combustion of napthalene, chosen as a standard substance, and of three determinations of the heat of combustion of toluene, conducted in the thin sealed bulb with a rim of paraffin around the top of the containing crucible, as already described. Since they were thus all made over about the same range of temperature any uncertainty in the calibration of the thermometer largely disappears from the result—nevertheless this was carefully calibrated. These determinations serve to indicate the consistency attainable by use of the precautions just described.

Napthalene

NO. OF EXP.	WEIGHT NAPTHALENE	WEIGHT OF COTTON FOR IGNITION	SUM OF ALL CORRECTIONS	t_1°	t_2°	CORR. RISE OF TEMPERATURE
			degrees	degrees	degrees	degrees
5	1.1537	0.008	0.0220	16.008	20.202	3.616
6	1.1002	0.0095	0.0260	16.036	20.043	3.618
7	1.1023	0.008	0.0222	16.046	20.059	3.615
Average..................						3.616

Toluene.

NO. OF EXP.	WEIGHT TOLUENE	IGNITION MATERIAL	CORRECTION	CO FOUND	t_1°	t_2°	CORR. RISE OF TEMPERATURE FOR 1 GRAM.
			degrees		degrees	degrees	degrees
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 1.0000 g. of napthalene in burning was capable of raising our calorimetric system by 3.616° and 1.0000 g. of toluene 3.821°, (or 1.0567 times as much as the same weight of napthalene) both substances having been weighed in air. According to the careful absolute determination of the Bureau of Standards 1 g. of naphtalene thus weighed evolves 9622 calories (20°) on burning. 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 only 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 (napthalene instead of sugar). Evidently, 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.

Both results are much higher than that found by Roth and Auwers,[10] 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 napthalene, instead of 1.0567. It is not impossible that either all our toluene contained a slight aliphatic impurity[11] (a rather unlikely contingency because we obtained samples from various 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.

Many other determinations of a variety of organic substances have been made here with the help of these improved methods and the matter will be pursued further, with especial reference to purity of materials. 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 effectively closing the bomb with less risk of injury to the platinum lining and cover; 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 calorimetric operation 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 are recorded, giving the value 10,155 calories (18°) per gram (weighed in vacuo). This is but a preliminary publication.

[1] For references, see Richards and Barry, *J. Amer. Chem. Soc., Easton, Pa.*, **37**, 1915, (993–1020).

[2] *Washington, D. C., Bull. Bur. Stand.*, **11**, 1914, (243).

[3] Richards and Barry, Loc. cit.

[4] Richards and Osgood, *J. Amer. Chem. Soc., Easton, Pa.*, **37**, 1915, (1718–1720).

[5] Stohmann, *J. prak. Chem., Leipzig*, **39**, 1889, (514).

[6] Benedict and Fletcher, *J. Amer. Chem. Soc.*, **29**, 1907, (739–757).

[7] Richards, Frevert, and Henderson, *Boston, Mass., Proc. Amer. Acad., Arts. Sci.*, **42**, 1907, (584).

[8] Auwers, Roth, and Eisenlohr, *Liebig's Ann. Chem., Leipzig*, **385**, 1911, (102–116).

[9] Richards and Barry, *J. Amer. Chem. Soc., Easton, Pa.*, **36**, 1915, (997).

[10] Roth and Auwers, *Liebig's Ann. Chem., Leipzig*, **407**, 1914, (154, 158).

[11] For example, 2-4 Dimethyl hexane, boiling point 110°, L. Clarke, *J. Amer. Chem. Soc., Easton, Pa.*, **30**, 1908, (1148). Octanes have higher specific heats of combustion than toluene. (Richards and Jesse, *Ibid.*, **32**, 1910, (292).

THE MASS OF THE ELECTRIC CARRIER IN COPPER, SILVER AND ALUMINIUM

By Richard C. Tolman and T. Dale Stewart

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In a previous article [*Physic. Rev.*, **8**, 97 (1916), these PROCEEDINGS 2, 189 (1916)] we have described some experiments in which a coil of copper wire was rotated about its axis at a high speed and then suddenly brought to rest, the ends of the coil being connected with a sensitive ballistic galvanometer which permitted a measurement of the pulse of current which was produced at the instant of stopping by the tendency of the electrons to continue in motion.

We have continued these experiments making use of three new windings of copper wire, and using two different windings each of silver and aluminium wire. These further experiments were made, not only because it seems desirable to subject so new a phenomenon to a more rigid test, but because it is also desirable to see if the mass of the carrier of electricity is the same in all different metals and how much it differs, if at all, from the mass of the electron in free space.

We now have a record of the results of 624 individual runs made on a number of different coils, using three kinds of wire, two different sizes, and two different kinds of insulating binder to hold the coils in place. The runs were made with various total resistances in the circuit, with various lengths of wire, and at various velocities, rotating sometimes in one direction and sometimes in the other. Not only was the pulse of electricity every time in the direction which would be predicted on the basis of a mobile *negative* electron as the carrier of electricity,