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DESCRIPTION OF A BOMB-CALORIMETER AND METHOD OF ITS USE.

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THE apparatus of which an account is here given was first described in 1895.[1] The present description is, in part, a revision of one published in 1897.[2] Experience since the latter article was written has led to further improvements in the bomb and accessory apparatus. A number of the improvements have been devised by Mr. Blakeslee, formerly mechanician of Wesleyan University; others were suggested by Dr. F. G. Benedict, who has had much to do with its use, and by Messrs. Dinsmore and Singleton, of Middletown, Conn., by whom the apparatus is now made.

The bomb is a modification of that of Berthelot.[3] The latter is most excellent; the only objection to it is its great cost, which is due to the large amount of platinum in the cover and lining.

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[1] "A New Form of Bomb-Calorimeter," by W. O. Atwater and Chas. D. Woods. Report of the Storrs (Conn.) Experiment Station for 1894, p. 135.

[2] "Improved Forms of Bomb-Calorimeter and Accessory Apparatus," by W. O. Atwater and O. S. Blakeslee. Report of the Storrs (Conn.) Experiment Station for 1897, p. 199.

[3] "Sur la force des matières explosives," I, 225 and *Ann. chim. phys.*, (6) **6**, 546.

Various modifications of the Berthelot apparatus have been devised to obviate the expense of the platinum. Mahler uses a bomb of forged steel, with enamel lining. Hempel uses, for the determination of heats of combustion of coal, a simple bomb of steel without lining. In accordance with suggestions by one of us (W. O. A.) during a sojourn in Dresden, Professor Hempel most kindly had a bomb made by the mechanicians who make the bombs of his devising, and lined by Heraeus of Hanau with a thin sheet of platinum. Thanks to Professor Hempel's painstaking care, added to his inventive skill and his familiarity with the subject, the bomb proved very efficient. With modifications from time to time, it has gradually assumed its present form. The principle is the same as in Berthelot's bomb, but whereas the cover of Berthelot's fits into the cylindrical cup like a very wide stopper, the cover in this, as in Mahler's, rests directly on the upper edge of the cup.

The purpose of the present article is to describe the bomb and accessory apparatus and the method of their use in the determination of the heats of oxidation of foods, feeding-stuffs and products of animal metabolism, a kind of work for which the apparatus has been in almost constant use in this laboratory for some ten years. Experience here and elsewhere shows that the apparatus may be advantageously employed for determining sulphur and phosphorus in organic compounds, as well as for determining the heats of combustion of coal and other fuel materials, but the special ways by which it is best employed for these purposes will be more fitly described at another time.

The method of determining heats of combustion is essentially the procedure of Berthelot as modified by Stohmann.[1] It has been gradually developed in this laboratory under the hands of Messrs. C. D. Woods, F. G. Benedict, O. F. Tower and the authors.

I. DESCRIPTION OF THE APPARATUS.

The method consists essentially in burning the substance in excess of oxygen at high pressure in a bomb immersed in water, the heat of combustion being determined by the rise in the temperature of the water. The apparatus consists of:

(1) The calorimeter proper, including the bomb, a britannia-metal cylinder to hold the water in which the bomb is immersed, a thermometer and a stirrer. The term *calorimeter system* is here

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[1] *J. prakt. Chem.*, **147**, 503 (1889). See also Berthelot: "Traité pratique de calorimètrie chimique," p. 128.

used to denote the bomb and contents, the metal cylinder and the immersed parts of the thermometer and stirrer, together with the water.

(2) Two concentric protecting-cylinders of "indurated fiber" with cover. These enclose the calorimeter system and insulate it so as to prevent rapid passage of heat between it and the outside air.

(3) Accessory apparatus, including a clamp and spanner for closing the bomb, appliances for filling the bomb with oxygen (bomb-support, coupling and manometer), a mould and press for moulding powdered substances, which are to be burned, into pellets, electrical appliances for igniting the charge, and machinery for operating the stirrer.

The Bomb.

The bomb consists of three parts: A cylindrical *cup* to contain the substance to be burned and the oxygen for combustion, a *cover* to close the cup, and a threaded ring or *collar* to hold the cover tightly on the cylinder. With these is a metal capsule to hold the substance. The parts are shown separately in Fig 1, and in cross-section, as put together, in Fig. 2.

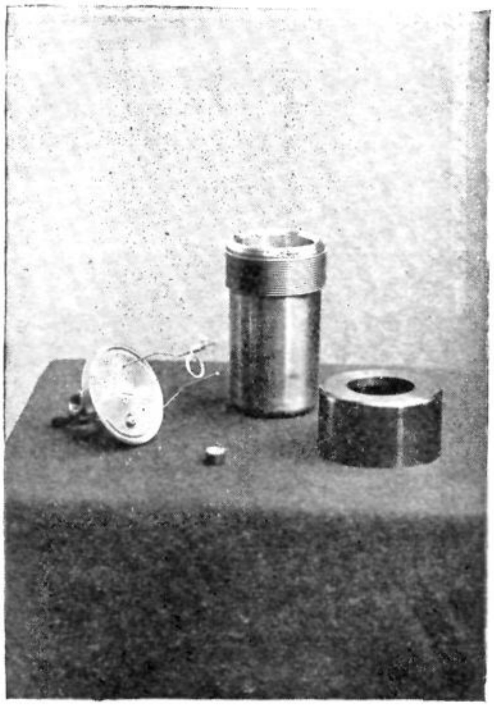

Fig. 1.—Parts of the bomb. Cup, cover with capsule holder, capsule and collar.

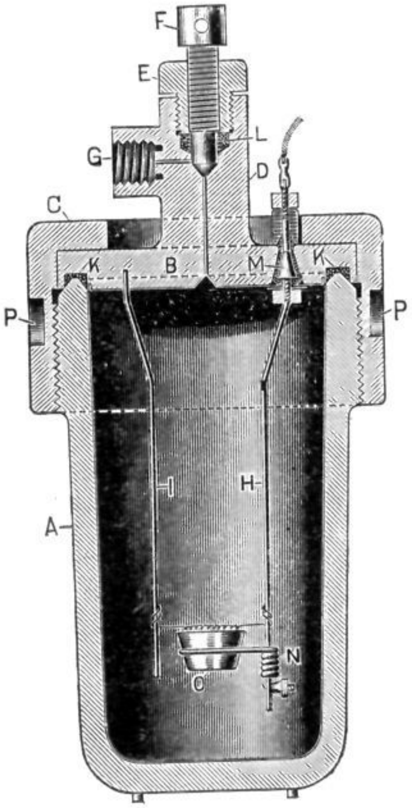

Fig. 2.—Cross-section of the bomb.

The cup is of Hotchkiss gun tool steel, kindly furnished by the Bethlehem Iron Company, which has favored us with tests of "oil-tempered forgings made from the same steel, and at about the same time the bars were made" which were used for the later bombs. These latter tests "were many in number, and an average taken from them gives the following results":

Tensile strength	85,514 lbs. per sq. in.
Elastic limit	47,366 " " " "
Extension	23.82 per cent.
Contraction	43.05 per cent.

The cover (B), collar (C), and screws (E, F) are of the best tool steel.

In the apparatus as now made the inside dimensions of the cup are, approximately: Depth, 12.7 cm.; diameter, 6.3 cm. at top and 5.9 cm. at bottom. The wall is approximately 0.6 cm. in thickness. The weight of the whole bomb is not far from 3,200 grams, and its capacity nearly 380 cc.

The cover is lined on the bottom with platinum and is provided with a neck (D). Into this fits, at the top, a cylindrical screw (E), into which in turn fits a valve screw (F). In the neck (D), where the bottom of the cylindrical screw (E) rests, is a shoulder fitted with a packing of lead (L). The pressure of the valve screw on this packing makes a tight closure upon the part of F which it surrounds. On the side of D is an opening (G), into which may be screwed the coupling connecting the tube with the receptacle which holds the oxygen used for the combustion (see Fig. 8). The coupling, when screwed in, thrusts against a washer of lead at the end of G, which insures perfect closure. A narrow passage runs horizontally to a point just above the valve seat in the center of D. A similar passage runs from the apex of the valve seat perpendicularly downwards through the cover. These two passages provide a channel for the oxygen to pass into the interior of the bomb. This channel may be tightly closed by the valve screw, the lower end of which is conical and thrusts against the inner surface of D, the angle of which at the place of contact corresponds to that of the tip of the screw. Between the top of the valve seat and the bottom of the packing (L), the valve screw fits so closely in the cover as to prevent the lead of the packing from working downward and thus obstructing the small gas passages. After continued use, the valve of the bomb may be found to leak a little on account of corrosion of the conical end of the valve screw by nitric acid and moist oxygen. It should then be reseated by an expert mechanician. The lead washer (G) and valve packing (L) will require to be replaced after long use.

The upper edge of the cup (A) is beveled on both sides; the apex is rounded and fits into a gasket (K) of lead, which is held in a recess or groove in the cover (B). With use, the metal gradually flows out of the groove under the heavy pressure so that the gaskets have to be replaced occasionally. The gasket may be removed from the groove in the cover by cutting it nearly in two *with the tool provided for the purpose and prying it up in such way* as to sever it. In using the tool, great care must be taken not to injure either the platinum lining of the cover or the sides and bottom of the groove. Attempts have been made to substitute harder metals for lead in the gaskets, but lead has been found most satisfactory as least liable to injure the platinum lining against which it presses. Extra gaskets are furnished with the bomb. In closing the bomb, it is important that the friction between the cover and collar should be reduced as much as possible. The surfaces of contact of the two pieces should, therefore, be well oiled.

The platinum wires (H) and (I), inside the bomb, serve to hold the capsule (O) containing the substance to be burned and to conduct an electric current for igniting it. Of these two wires, one (I) is screwed into the cover; the other (H) passes through a conical hole in the cover and is insulated from the metal. The method of insulating the wire is shown in Fig. 3. In the bomb cover, a section of which is shown at a, is a conical hole. The larger end of the hole is on the inside of the cover. Into the hole fits the conical enlargement (b) of the German silver rod (c) which projects above the cover and serves for the electrical connection. The platinum wire (d) is gold-soldered into the lower

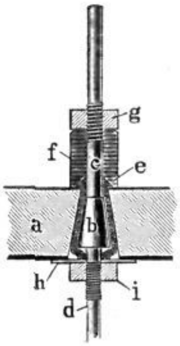

Fig. 3.—Method of insulation.

end of the cone, thus making a continuous conductor (c, b, d). To insulate this conductor, a piece of rubber tubing of $^3/_{32}$ inch (2.5 mm.) inside diameter is pushed down over the cone until it projects 1 to 2 mm. beyond the base. The free end of the tubing is threaded through the hole in the bomb cover and drawn up until the cone is in place; the surplus rubber tubing is then cut off at e, and over the rod (c) is placed the hard rubber sleeve (f) and the nut (g) is tightened down until the conductor (c, b, d) is firm in the cover. A mica disk (h) is placed over the platinum wire (d), and held against the lining of the cover by the platinum nut (i). This disk serves both to protect the insulating rubber from combustion and to prevent the nitric acid formed in the bomb from penetrating into the conical hole in the cover and causing leakage of current and corrosion of the German silver and steel. If a little space at the large end of the cone is left unfilled by the end of the rubber tubing, it is filled with a mixture of fine asbestos fiber and shellac, which is allowed to dry before the mica disk (h) is secured in place. Whenever the insulation of the wire becomes poor, the rubber covering of the conductor should be replaced by a new one.

Near the lower end of H (Fig. 2) is a platinum wire bent in the form of a ring to hold the capsule, and coiled about the wire, to which it is held by a platinum thumb-nut. When a combustion is made, the two platinum wires are connected by a very fine iron wire which passes over the capsule and is heated by the electric current. The part directly above the substance to be burned is wound into a spiral, thus furnishing a larger quantity of iron to be ignited and, falling, to ignite the substance in the capsule.

Linings of Cup and Cover.—Both cup and cover are lined with platinum or gold-plated copper. The lining of the *cover* is sweated onto the steel. A platinum plug fitted into the vertical passage by which the gas enters serves to protect the steel surfaces of the valve seat and oxygen-channel from corrosion by the dilute nitric acid which condenses on the lining of the cover and which might otherwise be carried out into the channel when the valve is opened. The oxygen is admitted through the plug by a tubular passage, the outlet of which is horizontal, so that the current of gas may not blow directly upon the substance in the capsule.

The lining of the *cup* is made from a single sheet of metal which is spun to fit the steel cup accurately. It can be easily removed from the latter by placing the fingers of the left hand inside the lining, and the thumb against the threads of the cup (which maybe wrapped with cotton to protect the thumb), and drawing outward upon the lining, at the same time tapping the steel cup with a wooden mallet. The lining should be removed occasionally and any rust that may have formed on the inner surface of the steel polished off. Before the lining is put in again, the steel cup should be wiped out with a cloth moistened with oil.

For the lining, platinum has been used and has proved entirely satisfactory not only here but in other laboratories, but its high cost is an objection, and numerous attempts have been made to find a cheaper substitute. The Mahler bomb, which is in use in many laboratories, has a lining of enamel. So far as we are informed, it is found satisfactory save that it is apt to crack and scale off. We have found that aluminum linings, spun from the purest metal we can obtain, are attacked by the nitric acid to such an extent as to interfere with the accuracy of the determinations. Attempts to electroplate the inside surface of a steel cup with platinum or gold have been made by Berthelot[1] and also by Professor H. W. Wiley, chief of the Bureau of Chemistry, U. S. Department of Agriculture, but the results have been unsatisfactory, the lining either having proved porous and thus permeable to the oxygen and nitric acid, or having blistered, probably on account of the unequal expansion of the steel and the plating.

The most satisfactory substitute we have found for the platinum lining is one of copper heavily electroplated with gold. A cup was spun for us by the Middletown (Conn.) Silver Company from No. 20 Brown & Sharp gauge (0.8 mm.) sheet copper and electroplated by the International Silver Company of Meriden, Conn. A light plating of silver, two of gold of about 1 dwt. (1.5 grams) each, and finally three of gold of about 2 dwts. (3 grams) each were applied, each plating being thoroughly burnished before the next was deposited. This lining was used for four months or more. It was only after some 300 combustions had been made in it that blisters formed in the gold plating in two places on the bottom of the cup, and not until after the 400th determination, that copper could be detected in the bomb rinsings (which always contain free nitric acid). The same lining was then replated with gold and was in good condition after use in over 500 additional

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[1] *Ann. chim. Phys.*, (5), **23**, 161.

determinations, when it was destroyed by an accident. Other linings of this description are now in use in different laboratories and while, at present, any positive conclusion as to their durability would be premature, it seems probable that, at least with occasional replating, a copper lining might serve for several thousand determinations.

In devising this gold-plated copper lining we have profited, particularly as regards the necessity of burnishing repeatedly during the deposition of the gold, by the experience of Mr. Henry J. Williams, of Boston, who has constructed and patented a calorimeter having a spherical bomb of aluminum bronze, electroplated internally with gold and externally with nickel. Mr. Williams' apparatus appears to have many excellent features. Its cost is, however, much beyond that of even the platinum-lined apparatus here described.

We have planned to use gold-covered copper ("rolled plate") instead of platinum for the lining of the cover but have as yet no experience in its use.

We find it a very decided advantage to have the lining and especially that of the cup easily removable. The low cost of gold-plated copper makes it easy to have two linings, so that if one gives out, it can be easily removed and repaired while the other is used in its place.

Metal Capsules.—The sample for combustion is held in a frustum-shaped metal capsule which is supported in the bomb as shown in Fig. 2. We employ capsules of three sizes: the small size, which is 1 cm. deep, 1.4 cm. in diameter at the base, and 1.6 cm. in diameter at the top, is used in most cases; the medium size, 1.7 cm. deep, 1.5 cm. in diameter at the base, and 2.2 cm. in diameter at the top, is employed for the combustion of urine absorbed in cellulose absorption blocks; the large size, 2 cm. deep, 1.5 cm. in diameter at the base, and 2.5 cm. in diameter at the top, is used in the combustion of milk upon asbestos (see below).

Until recently we have used exclusively capsules of platinum of the two smaller sizes. Those of the smallest size with a thickness of 0.15 mm. weigh only about 2 grams. They serve the purpose but are too thin for durability. A thickness of 0.20 to 0.25 mm. would be preferable. Those of the larger, *i. e.*, medium size, with a thickness of 0.35 mm. and weighing 7 grams, we find very satisfactory for use with the cellulose blocks employed for determining the heat of combustion of urine. As the platinum capsules are rather expensive, we have recently used capsules of nickel. They are spun from $^1/_{64}$ inch (0.4 mm.) sheet nickel by the Goodwin & Kintz Company of Winsted, Conn., cost but a few cents each, and have thus far proved very satisfactory. To prevent their cracking, they are annealed and hammered and are so shaped that the sides join the base with a curve instead of a sharp angle. Before using, they are heated in the Bunsen flame until the surface is oxidized. When so treated, they withstand further oxidation for a considerable time even at the high temperature attained in the bomb.

Iron Wire.—The ignition of the sample in the bomb is brought about by means of a small coil of iron wire heated to ignition by an electric current. A spool containing about 25 grams of 0.007-inch (0.18 mm.) wire is furnished with each apparatus. This quantity, if cut into lengths of 2.5 inches (6.3 cm.) will suffice for about 2,000 combustions. By use of a simple "wire-measure," devised by Mr. Osterberg of this laboratory, a large number of wires of equal length may be prepared at one time. This measure consists of a cylindrical piece of hard wood, 2 cm. or more in diameter, having a longitudinal groove 0.6 cm. wide and 1 to 1.5 cm. deep. The cylinder may be conveniently prolonged into a handle. The wire is wound about this measure in as many turns as desired. By inserting one blade of a pair of shears into the groove, all the turns are easily cut at once. The pieces of wire, so cut, are made into coils by winding upon a pin or needle, leaving a half-inch of straight wire on each end. If the aggregate weight of the first ten pieces cut at one time is the same as that of the last ten of the same lot, the average weight of the twenty may be assumed to represent the weight of each piece of the lot.

Thermometer.—The thermometer used in determinations of heats of combustion must be capable of measuring small differences of temperature with as high a degree of accuracy as possible, since the chief source of error in the determination lies in these measurements, as explained below. At the same time, if the calorimeter is to be used in an ordinary laboratory room, the thermometer must be one that can be used over a considerable range of actual temperature. In specific terms, it must be capable of making measurements of temperature differences of 2° to 3.5°, accurate to a few thousandths of a degree, at an initial temperature of 12° and also at an initial temperature of 25° or even higher (the initial temperature of the calorimeter being 2° or 3° below the room temperature). The requisite accuracy and adaptability are combined in "metastatic" thermometers of the Beckmann type. We have used for the most part a thermometer of this type made by Fuess of Berlin-Steglitz. It has a large bulb about 5 cm. in length and 1 cm. in diameter and contains about 32 grams of mercury. The scale is 23 cm. in length, divided into 6°, graduated to hundredths and capable of being read to thousandths with the aid of a lens. We have also used the Beckmann thermometer manufactured by Goetze of Leipzig.

With thermometers of this type, in addition to the ordinary correction for variations in the bore of the capillary, a second correction is evidently necessary for the reduction of the degrees of the scale to true centigrade degrees, for it is obvious that when the thermometer is set for use at a low temperature, the quantity of mercury in the bulb will be greater and the expansion per true degree, therefore, greater than when it is set for a higher temperature. Our Fuess thermometers have been calibrated by the Physikalisch-technische Reichsanstalt. By interpolating between the data of the certificate furnished by the Reichsanstalt we construct tables giving the caliber correction for each 0.1° and the "correction for setting" for each degree. For use in the laboratory, these tables can be most conveniently mounted on cards. Since the correction for setting is most conveniently used in a form different from that given in the certificate, we think it worth while to illustrate how the one is derived from the other.

The certificate accompanying one of our thermometers states that when the thermometer is set at 0° and heated to 6° (with the mean temperature of the projecting thread of mercury at 15°), 1° of the scale is found equivalent to 0.991° C.; when the thermometer is set at 25° and heated to 31° (projecting thread, 22°), 1° of the scale is equivalent to 1.002° C.; and when the thermometer is set at 50° and heated to 56° (projecting thread, 26°), 1° of the scale is equivalent to 1.013° C. The correction for 1° rise on the arbitrary scale is, therefore, —0.009° when the zero of the thermometer corresponds to 0° C. and +0.002° when it corresponds to 25° C., and since the change of the correction between 0° and 25° is the same as between 25° and 50°, *viz.*, +0.011°, we are justified in assuming that the change for each degree amounts to $0.011^\circ \div 25 = 0.00044^\circ$. For any setting of the thermometer between 0° and 50°, therefore, the correction to be applied for each degree of observed rise of temperature is $-0.009^\circ + 0.00044n^\circ$ where $n =$ the true temperature to which the zero of the thermometer corresponds. The values of this correction for each degree are calculated to the nearest ten-thousandth of a degree and entered in the table of corrections. We determine the corrections for the Goetze thermometer by comparison with a Fuess which has been calibrated as above described.

For the reason that there is some danger of breaking thermometers of this type by improper handling, particularly in the case of the Fuess thermometer with its very heavy bulb, we give, for the benefit of the inexperienced, the following directions for changing the setting:

To set a thermometer of the Beckmann type for use at a temperature higher than that at which it has last been used, the bulb is warmed in the hand or in water until the mercury fills the whole of the capillary tube and a part of the upper reservoir. A portion of the mercury is then shaken off into the upper reservoir. This separation of the mercury may be effected by holding the thermometer vertically in one hand and either (1) tapping the outer tube ("envelope") near the reservoir smartly but not violently with the fingers of the other hand; or (2) striking the hand which holds the thermometer vertically against the other hand. Of the two methods, the former will usually separate a smaller portion of mercury than the latter. The thermometer should never be held in a horizontal or oblique position when jarred in either of these ways, as the inertia of so large a mass of mercury may produce so severe a transverse strain in the glass envelope as to break it.

To set the thermometer at a *lower* temperature, the mercury contained in the upper reservoir is brought into the upper part of the reservoir by inverting the thermometer and tapping the brass knob at the top gently on the table. The mercury will remain in the upper part of the reservoir when the thermometer is reinverted, *i. e.*, brought into normal vertical position with the bulb downward. The bulb is then warmed until the mercury in the capillary tube has joined that in the upper reservoir, then cooled until more or less of the mercury originally in the reservoir has been drawn into the capillary tube. The mercury remaining in the top of the reservoir is now separated and brought to the bottom by one of the methods described above. With practice, the shifting of the mercury from capillary tube to reservoir, or *vice versa,* is easily and quickly accomplished.

Lens and Tapper for Thermometer.—The use of a lens to magnify the divisions of the thermometer scale is essential. A Coddington lens of 1 inch (25 mm.) focal length (magnification = 10), made and mounted by the Bausch & Lomb Optical Co., Rochester, N. Y., has proved very satisfactory for this purpose.

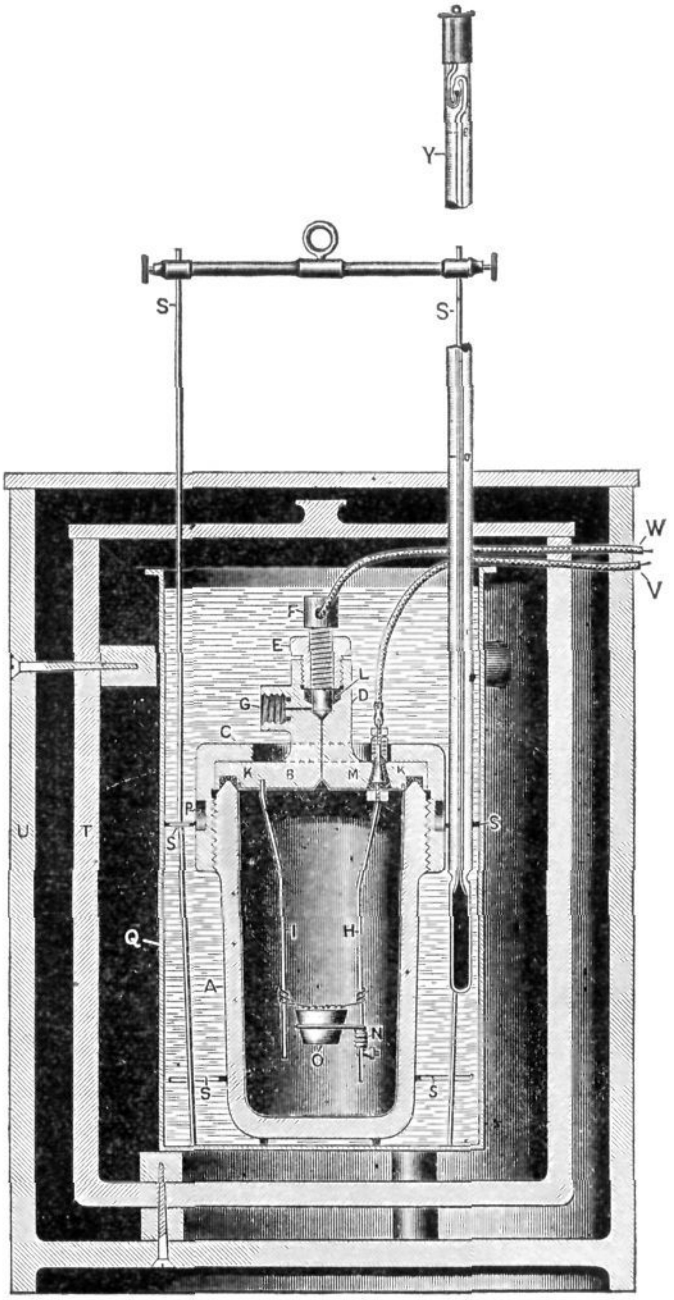

Fig. 4.—Bomb-calorimeter ; apparatus as used for actual determinations of heats of combustion.

For the prevention of errors of parallax, it is provided with an eyehole and with a grooved adapter which fits against the envelope of the thermometer and serves to keep the principal axis of the lens at right angles to the thermometer scale.

To prevent lagging of the mercury in the capillary, the thermometer should be tapped on the brass cap, rather than on the glass envelope. A most useful and convenient tapper for this purpose is the hammer of a small electric bell which can be operated by a battery of two dry cells.[1] By means of a conveniently placed switch, the observer sets the hammer in motion a few seconds before each reading and stops it again after the reading is taken.

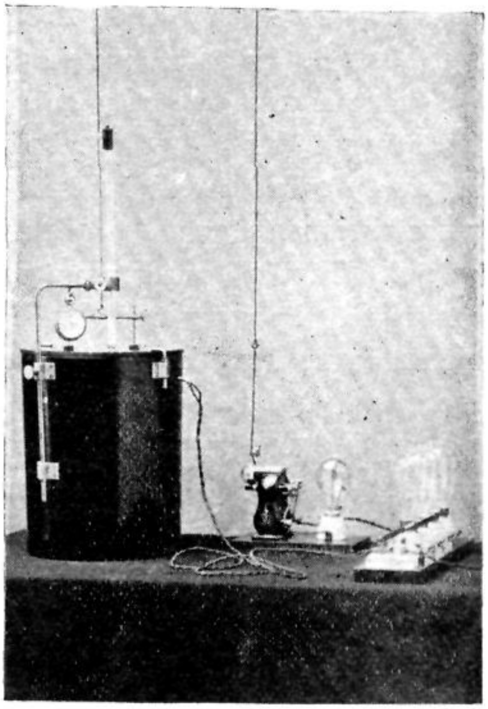

Fig. 5.—Bomb-calorimeter ready for a combustion.

Apparatus Mounted for Use.—The bomb, when ready for a combustion, is immersed in water contained in a metal cylinder. This cylinder is surrounded by concentric cylinders or pails of "indurated fiber," leaving air spaces to prevent undue passage of heat between the water and the outer air. The arrangement is shown in cross-section in Fig. 4 and, as it appears during a combustion, in Fig. 5.

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[1] Such a tapper for a Beckmann thermometer was employed by Loomis (*Physical Review*, **1**, 206 (1894)) and also by Orndorff and Cameron (*Am. Chem. J.*, **17**, 517 (1895)).

Calorimeter Cylinder and Stirrer.—The cylinder is of britannia-metal 13 cm. in diameter, 23 cm. high, and holds, with the bomb, not far from 2 liters of water. A stirrer (SS), moved by a small motor or other agency, keeps the water in motion and insures the mixing needed for equalizing its temperature. This stirrer consists of two perforated annular pieces of sheet-brass connected by two brass rods which project out of the calorimeter and are there attached by thumb-screws to a nickel-plated cross-piece. A groove is cut in one side of the annular brass pieces to admit the thermometer. The calorimeter cylinder stands on cork supports which prevent it from coming in contact with the bottom of the pail. The interior of the britannia-metal cylinder should be kept clean and free from sediment.

The Outer Cylinders.—The diameters of the indurated fiber pails (U and T, Fig. 4) are such as to leave an air space of about 1 cm. between the two pails and one of 3 cm. between the inner pail and the calorimeter cylinder. The covers of the pails are of hard rubber. They are provided with holes for the two rods of the stirrer and for the thermometer. An adjustable standard attached to the outer pail (Fig. 5) bears an arm provided with a clamp for the support of the thermometer (Y, Fig. 4). On the arm is a hook upon which a watch may be conveniently hung near the thermometer. A second standard, with arm for support of the electric hammer for tapping the thermometer, may be adjustably attached to the main standard by a thumb-screw clamp. The current for igniting the iron wire over the substance to be burned in the capsule (O, Fig. 4) is conveyed by the rubber-covered wires (V, W), of which one is connected with the valve-screw of the bomb and the other with the insulated platinum wire (H) which passes through the cover.

Accessory Apparatus.

Apparatus for Moving Stirrer and for Igniting the Charge for Combustion.—The most convenient source of power for operating the stirrer we have found to be the direct or alternating current of the city electrical circuit, with suitable motors of about 1/20 horse-power. The same current serves to ignite the charge. As yet, no perfectly satisfactory substitute for these currents has been found. Six cells of the Edison-Lalande batteries have most nearly filled the requirements.

By means of a worm gear fastened directly to the armature shaft of the motor, the speed is reduced, a final regulation being made, if necessary, by a rheostat, until the speed is such as to cause the stirrer to rise and fall about forty to fifty times per minute. With the apparatus as here described, it is important that the rate of stirring should not be less than 40 strokes (revolutions) to the minute. The connection between the motor and the stirrer is effected by means of a cord which is connected with the motor crank, passes upward to the ceiling or a shelf, over two pulleys, and thence down to the stirrer.

To heat the fine iron wire to incandescence, and thereby ignite the substance, requires a current of 3 or 4 amperes. If a 110-volt current is available, the necessary current may be obtained by switching it through four 32-candle power, 110-volt lamps in parallel. In case a 55-volt current is used, the 110-volt 32-candle power lamps would be replaced by a similar number of 16-candle power, 55-volt lamps. Lamps are especially desirable as resistances since they indicate to the observer whether the circuit is actually completed by the closing of the switch and whether it is broken by the fusion of the iron wire.

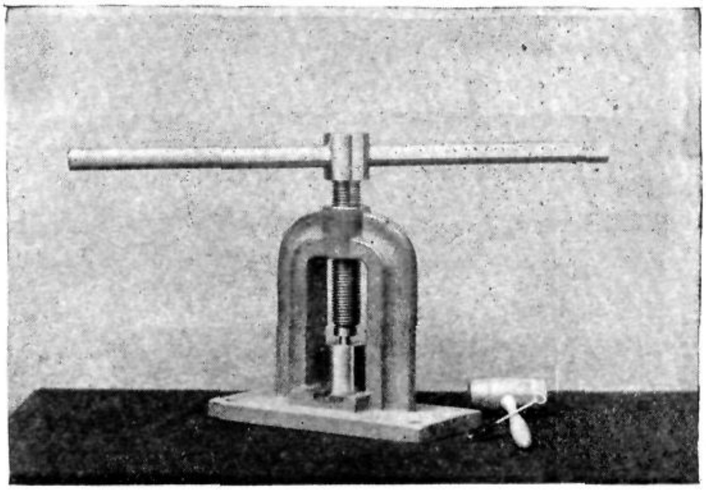

Fig. 6.—Pellet press.

Pellet Press and Mould.—Solid materials to be burned are usually pressed into small pellets, so that they may easily be held in the small platinum capsule within the bomb. This pellet form is advantageous, also, in preventing the mechanical losses of loose material, which might occur either before or after ignition, and so insuring the complete combustion of all the material. The mold resembles an ordinary "diamond mortar". The press (Fig. 6) is so constructed that a pressure of 50 pounds (22.5 kilos), applied at the extremities of the screw arm, gives a pressure of over 10 tons (9,100 kilos) on the pellet pin. In practice, such a pressure is rarely needed.

In molding a pellet, care should be taken to adjust the mold exactly under the screw of the press before turning the latter down and not to exert so great a pressure on the screw as to distort the pin and cause it to stick in the block. A little oil should be used between the end of the screw and the top of the pin, and both block and pin should be kept clean and free from grit. To remove the pellet, the screw is slackened, the mold slid out and inverted and the head of the pin pressed against the table. If the pellet cannot be removed in this way, the mold may be placed again under the screw of the press with the projection at the base *at right angles* to the groove of the press. By turning down the screw, the steel disk can be made to drop into the groove and can be easily pushed aside so that the pellet can be forced out in the same way. With a few substances (especially cane-sugar) it is necessary to wash and dry the mold after making each pellet, as otherwise some of the finely powdered substance may adhere to the inner surface of the mold and make the pin stick. The press screw is closely fitted and care must be taken not to injure it by turning it down its full length with any force, as might be done, for instance, by setting it rotating rapidly when the mold is not in place.

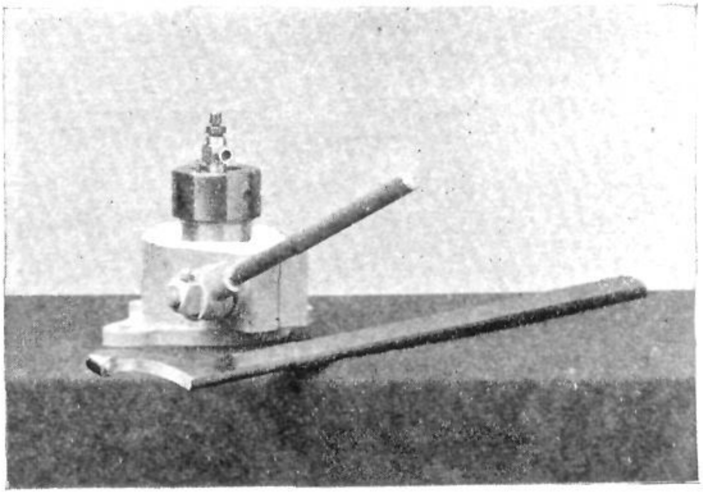

Fig. 7.—Clamp and spanner.

Clamp and Spanner.—To hold the bomb securely, while the collar is being screwed down, a clamp or vise (Fig. 7) has been devised, consisting of a fixed and a movable jaw enclosing a nearly cylindrical but slightly tapering space for the reception of the cup of the bomb. The jaws are drawn together through a maximum distance of about 0.5 cm. by a lever with a very coarse half-thread. A paper lining in the clamp will prevent the cup's slipping, and protect it from being marred. The spanner is about 1 meter in length and is provided with a steel pin of about 1 cm. diameter, which fits into a hole in the bomb collar. In using the spanner, care should be taken to fit the pin down its full length into the hole in the bomb collar; otherwise the edges of the hole may be worn away.

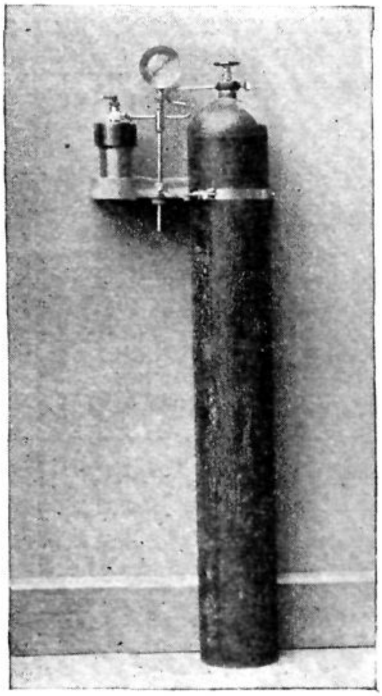

Fig. 8.—Appliances for filling the bomb.

Bomb Support, Manometer, and Couplings for Filling Bomb with Oxygen from Oxygen Holder.—The oxygen used in this laboratory is furnished by the S. S. White Dental Mfg. Co., of Philadelphia, in cylinders about 125 cm. long and 18 cm. in diameter. These cylinders contain about 8 lbs., 8 oz., or 3850 grams oxygen, a quantity which should suffice for over 250 determinations. Brass coupling tubes are used to connect the cylinder with the manometer and with the bomb, which is supported, during the filling, upon a cast-iron shelf, as shown in Fig. 8.

The graduations of the manometer enable one to ascertain when the supply of oxygen is nearly exhausted. When the pressure falls to 35 or 40 atmospheres, another cylinder of gas is ordered.

General Test of the Apparatus.

The general condition of the apparatus should be tested from time to time by check combustions. Benzoic acid and cane-sugar are convenient substances for this purpose, because they are easily obtained pure and their heats of combustion are accurately known (see p. 692). The benzoic acid has the advantage over the sugar that the pellets do not clog the pellet mold and that no kindler other than the iron wire is needed for the ignition.

II. METHOD OF USE OF THE APPARATUS.

Quantity of Substance To Be Used.

As explained below in the discussion of the accuracy of the method (p. 694), the quantity of material burned in the bomb should be such as will yield from 4000 to 7000 calories.

The following are suitable quantities of ordinary foods and feeding-stuffs:

Fats, oils, butter and very fat meats—as pork, fat mutton and fat beef	0.5 to 0.7 gram.
Leaner meats—as veal, fish, etc., and dried residue of milk	0.7 to 1.0 gram.
Vegetable products consisting mostly of starch, sugar, cellulose, etc., with more or less of proteids and not much fat—as sugar, starch, flour, meal, potatoes, fruits, seeds of cereals, legumes, etc., fodders and feeding-stuffs, including hay, straw, meals, etc	1 to 1.5 gram.

Of substances which we have found convenient for tests of the accuracy of the determinations, the following are suitable quantities:

Naphthalene and camphor	0.5 to 0.7 gram.
Benzoic acid and hippuric acid	0.7 to 1.0 gram.
Cane-sugar and glycocoll	1 to 2.0 gram.

Preparation of the Material for Combustion.

Solids.—Solids in general are powdered and pressed into cylindrical pellets in the pellet mold as described above. The material is weighed approximately before, and accurately after, molding. Food samples are used ordinarily in the "partially dried condition". The methods followed in this laboratory in preparing such samples have been previously described.[1] Fatty sub-

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[1] Report of preliminary investigations on the metabolism of nitrogen and carbon in the human organism, by W. O. Atwater, C. D. Woods and F. G. Benedict. Bull. 44, U. S. Dept. Agr., Office of Experiment Stations, 1897.

stances, such as dried milk, are weighed directly into the capsule without molding.

With some substances, special devices are required to secure ignition. A crystal of naphthalene serves as a kindler for such substances as sugar and glycocoll. The naphthalene may be inserted between two turns of the coiled iron wire with one edge touching the substance in the capsule. Or, instead of a coil, the wire may be formed into a loop, resembling one of the forms of wire office clips used for holding sheets of paper together, and the naphthalene placed in the loop, which should touch the substance in the capsule.

Substances which are still more difficult to ignite, *e. g.*, creatin and creatinin, may be enclosed in gelatin capsules, such as are used with volatile liquids (see below).

Fats, such as butter, may be ignited with naphthalene, or, preferably, by use of a small quantity of fibrous asbestos, such as is used in Gooch crucibles. The asbestos is placed on the fat in such position that the burning iron wire may fall upon it. In this way too rapid cooling of the wire is prevented, and local ignition of the fat ensured.

Oils.—Oils are absorbed in fibrous asbestos. The metal capsule is half-filled with asbestos, ignited in a Bunsen flame, cooled in a desiccator and is weighed before and again after addition of the oil.

Volatile Liquids.—Volatile liquids, *e. g.*, alcohol, may be enclosed in gelatin capsules.[1] We have found the "Beekman ideal" capsule No. 00, which weighs from 0.11 to 0.19 gram, very convenient for the purpose.

Urine.—The heat of combustion of urine cannot be satisfactorily determined by simply burning the solid residue, because a portion of the organic matter after carbonizing becomes encased in the fused ash and is thus protected from oxidation.[2] We have met with the same difficulty in attempting to burn urine dried on asbestos fiber according to the method used for the combustion of milk (see below). The difficulty is obviated by absorbing and drying the urine in cylindrical blocks of cellulose as proposed by Kellner.[3] Suitable blocks are Carl Schleicher and Schüll's "No. 573" which are 15 mm. in height and 14 mm. in diameter and

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[1] Berthelot uses collodion capsules for this purpose ("Traité pratique de calorométrie chimique," p. 160).

[2] See Kellner: *Landw. Versuchst.*, 47, 296 (1896).

[3] *Loc. cit.*

weigh about 0.7 gram. As the block and the dried urine are burned together, the quantity of heat due to the combustion of the cellulose must be estimated. It is scarcely practicable to determine once for all the specific heat of combustion[1] of the cellulose and to calculate from the weight of a block the heat that will be produced by its combustion, because the blocks contain varying quantities of moisture and are not easily dried to constant weight without danger of decomposition. If, however, a considerable number of blocks, say 50 or 100, are heated in the same drying oven at 95°-100° for three or four hours, they may then be assumed to have reached a uniform condition as to dryness and incipient decomposition. Determinations of the specific heats of combustion of three or four of the lot may, therefore, be made and the average result used for those burned with the urine. As the cellulose is very hygroscopic, the blocks should be kept in stoppered weighing bottles in desiccators over sulphuric acid and weighed in the same bottles. It is more convenient to have the weighing bottles large enough to hold several blocks.

The urine is prepared for combustion according to the following method, which was suggested by and is similar to that proposed by Tangl.[2] The weighed cellulose block is placed in an evaporating dish of 50 or 60 cc. capacity and the urine added from a 20 cc. pipette calibrated specially for urine.[3] One or two pipettefuls, *i. e.*, 20 or 40 cc., are taken according as the specific gravity is greater or less than 1.022. The weight of the urine is calculated from its specific gravity and the delivering capacity of the pipette. The urine is evaporated to dryness at 50°-60°. Repeated tests have shown that there is no appreciable loss of nitrogen in drying at this temperature. When dry, the block is transferred to the metal capsule and the urine residue remaining on the dish transferred to the capsule by wetting with water and wiping out with small quantities of fibrous asbestos held in bone-tipped forceps. After drying again at 50°-60°, the block is ready for combustion. The cellulose blocks will yield 2200-3000 calories each and the heat of combustion of urine ordinarily lies between 75 and 200 calories

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[1] A convenient term for the heat of combustion per gram.

[2] *Arch. f. Physiol.*, Leipzig, 1869, Suppl. Bd., p 251.

[3] A pipetteful of urine is delivered into a tared weighing-bottle and weighed. The quotient of the weight by the specific gravity gives a value for the delivering capacity of the pipette. A number of such determinations are made with urine of different specific gravities and the results averaged. The results obtained with the urines of different specific gravities, though agreeing substantially among themselves, differ materially from that obtained by calibrating with water.

per gram, that of urine of specific gravity 1.022 being in the neighborhood of 110 calories. The heat set free in the combustion will, accordingly, vary from 4400 calories (110 × 20 + 2200) to 7400 calories (110 × 40 + 3000), and at least 50 per cent. of this will come from the combustion of the urine.

For drying the urine it is desirable to have a self-regulating oven. An oven surrounded by a water-jacket, provided with a mercury thermostat, serves the purpose admirably. It will be found advantageous to provide a shelf in the oven with perforations into which the metal capsules may be set.

A serious difficulty in the determining of the heat of combustion of the unoxidized material of urine is the tendency to decomposition of urea and perhaps other compounds by which more or less of the potential energy is set free. We have found the danger of such loss of energy from urine on standing to be much greater than might be suspected, nor have we yet found a convenient way for preserving it for any considerable time with certainty that no loss occurs. We have been in the way of adding about 5 cc. of commercial formalin to 800 cc. of urine, keeping it in a refrigerator and making the combustion as soon as possible.

The drying of urine *in vacuo* at room temperature, as elaborated by Cronheim,[1] is probably the safest course. Preliminary experiments, made a number of years ago in this laboratory, but not published, indicated the success of the method but the length of time required renders its use extremely difficult when a large number of samples are to be prepared.

Milk.—For the combustion of milk, a metal capsule of the largest size is loosely filled with fibrous asbestos upon which the milk is then absorbed and dried. About 5 grams of milk should be used and care should, of course, be taken to secure a representative sample.

About 20 to 25 grams may be taken from the supply, after thorough mixing, and placed in a small stoppered flask or other weighing-bottle, from which the 5-gram portions for the individual combustions may be weighed out. The milk in the weighing-bottle should, of course, be mixed by shaking immediately before each portion is poured out.

Milk may also be dried and burned on the cellulose blocks used with urine, but the asbestos method described above has two ad-

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[1] "Conservirung des Harns für analytische und calorimetrische Zwecke," *Arch. f. Anat. u. Physiol.*, Phys. Abth., Sup., 1902, p. 262.

vantages. The correction for the combustion of the cellulose is avoided and the number of weighings is decreased.

Filling the Bomb.

The bomb cover being supported upon a ring-stand, the capsule containing the pellet is placed in position in the platinum ring. The ends of the coil of iron wire are wound around the vertical platinum wires (one turn only) and the coil adjusted so that it touches the substance to be burned but not the capsule. The naphthalene (if any is to be used) is placed in position. The cover is now placed on the bomb and a little oil dropped upon the top to prevent its turning with the collar, which is then screwed on and tightened by means of the clamp and spanner. The bomb is now ready to be filled with oxygen. With its valve slightly open, it is placed in position on the iron shelf (see Fig. 8) and connected with the manometer which is kept permanently connected with the oxygen cylinder. The valve of the oxygen cylinder is then opened cautiously. When the manometer indicates a pressure of 20 atmospheres, the oxygen is cut off, the bomb-valve closed, and the bomb disconnected from the manometer.

Leakage of gas from the bomb may occur either at the soft metal gasket (K) or at the conical tip of the valve-screw (F) (Fig. 2). Gas escaping at the gasket will usually make an audible sound. If the gasket is not too much worn, the leak may be stopped by screwing the collar tighter. A leak at the valve can be easily and quickly detected by placing the moistened finger over the opening (G). When the valve-tip or the conical shoulder into which it fits becomes corroded so that the valve cannot be closed by gentle pressure, it must be reseated carefully in a lathe to secure a proper fit. If, in filling the bomb, leakage occurs at L (Fig. 2), the cylindrical screw (E) should be tightened a little to press the packing (L) tightly around the valve-screw.

Arranging Apparatus for the Combustion.

The calorimetric water should now be put in the britannia-metal cylinder. Both the quantity and the temperature of this water are to be regulated. In order to facilitate the calculations, it is better to make the quantity always the same and such that the total hydrothermal value of the calorimeter system will be a round number, such as 2000, 2100 or 2200 grams. (Our custom is to make it 2100 grams.) In order to reduce to a minimum the correction for the influence of the surroundings upon the temperature of the system, the water in the cylinder should be made cooler than the surroundings of the system (as measured by an ordinary thermometer placed in the inner air-space) by about the expected rise in temperature, or a little more. For example, if the quantity of substance to be burned is such as will yield about 6300 calories and the hydrothermal value of the system is to be 2100 grams, the rise expected will be 3° and the water in the cylinder should be made 3°-3.2° cooler than the air of the inner air-space. The insertion of the bomb, which is at room temperature, will decrease this temperature difference by about one-sixth, the hydrothermal value of the bomb being about one-sixth that of the whole system, so that after the combustion the temperature of the system will be a little above that of the surroundings.

It is, obviously, more convenient to adjust the temperature of the water first and the quantity afterwards. The desired temperature can be readily obtained by mixing cooler water with that used in the preceding combustion (or with a portion of it). Water is then poured out of the cylinder until approximately the desired quantity remains; the cylinder, containing water and stirrer, is placed upon a tared balance, accurate to 1 gram, and small quantities of water are added or removed until the correct weight is obtained. The tare required is, of course, the desired hydrothermal value (*e. g.*, 2100 grams) minus the hydrothermal equivalent of the apparatus and plus the weight of the cylinder and stirrer.

The cylinder, containing stirrer and water, is now put in place inside the outer cylinders and the two conducting wires are joined, respectively, to the valve-screw and to the insulated conductor. The covers are put on and adjusted so that the stirrer will run smoothly, the thermometer is inserted and the stirrer set in motion. As soon as the different parts of the calorimeter system have assumed a common temperature, which usually requires two or three minutes, the mercury will begin to rise at a uniform rate, and the readings of the "initial" or precombustion period may begin.

The room temperature may have changed so much since the apparatus was last used that the thermometer must be reset. In that event, the water should be stirred a little after the insertion of the bomb and its temperature determined with an ordinary thermometer, so that the actual temperature to which the zero of the reset thermometer corresponds may be known within half a degree.

Temperature Changes in the System.

If the calorimeter system were absolutely insulated thermally, only two temperature observations would be necessary for the determination of the heat of combustion of a substance. One of these could be made at any time after the system had come to internal temperature equilibrium after the insertion of the bomb and before the ignition of the substance, for the temperature would remain absolutely constant during this interval of time, whatever might be its length. This observation would give the *initial* temperature of the system. The second observation, that of the *final* temperature, could be made at any time after the heat from the combustion had distributed itself uniformly throughout the system, for then the temperature would again remain constant.

But it is, of course, impossible to insulate the system completely and, consequently, external influences are continually affecting its temperature. The most obvious and doubtless the most important of these external influences is the temperature of the medium surrounding the system. This medium may be regarded as made up of (1) the air of the inner air-jacket, (2) the walls of the inner indurated fiber cylinder, and (3) the air and walls of the outer air-jacket and the air of the room. Interchange of heat occurs between the system and (1) the air of the inner jacket by convection and radiation, (2) the indurated fiber cylinder by radiation, and (3) the air of the outer air-jacket and of the room by conduction through and convection by the rods of the stirrer. All of these interchanges may fairly be assumed to obey Newton's Law—that the rate of warming or cooling of a body is proportional to the difference of temperature between the body and the surrounding medium.

Less important external influences are (1) the production of heat by the friction and, in case of imperfect adjustment, by the impact of the stirrer, and (2) the evaporation of water from or condensation of water upon the system. The motion of the stirrer being regular, the quantity of heat produced by friction and impact (which is of course very small) is the same for any one minute as for any other. The amount of water condensed or evaporated during an experiment is without doubt very small in any case. At the same time it must be remembered that the latent heat of water vapor at 20° being about 600 calories per gram, 1 calorie of heat is withdrawn from the system (and rendered latent) for every 0.0017 gram water evaporated. Conversely, the condensation of 0.0017 gram water upon the system would impart 1 calorie to it. Now *condensation* can not occur at all except when the air of the inner air-space is so nearly saturated with moisture that its dew-point lies within 3° of its actual temperature, because the initial temperature of the calorimeter system is never more than 3° lower than the temperature of the surrounding air. The air of the inner air-space is practically completely enclosed by the inner fiber cylinder with its cover, so that very little air will diffuse in or out. Its volume is about 5.11 liters. This quantity of air, if saturated with moisture, would contain:

At 23° C	0.0204×5.11 gram.[1]
At 20° C	0.0171×5.11 gram.
Difference	$0.0033 \times 5.11 = 0.017$ gram.
Heat of vaporization	$0.017 \times 600 = 10$ calories.
At 30° C	0.0300×5.11
At 27° C	0.0255×5.11
Difference	$0.0045 \times 5.11 = 0.023$ gram.
Heat of vaporization	$0.023 \times 600 = 14$ calories.

If the initial temperature of the calorimeter were 27° (which is as high as it would be necessary to make it on a warm day in summer) and the air of the room (at 30°) were completely saturated with moisture, the quantity of heat imparted to the calorimeter by the condensation of all the moisture, from the air of the inner jacket would be 14 calories. In winter the initial temperature of the system does not exceed 20°, therefore the quantity of heat imparted to the system by condensation of moisture cannot be more than 10 calories. Moreover, even in the extreme cases now under consideration, the heat imparted to the system *during the experiment proper* will be very much less than the quantities mentioned, because the experiment proper is preceded by a "settling period" of at least two or three minutes and an "initial period" of five minutes, during which time the greater part of the moisture of the air will have been deposited and the dew-point will have fallen in consequence, so that the temperature of the system will have little more than begun to rise on account of the combustion of the substance in the bomb when it passes the dew-point of the air and

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[1] See Smithsonian Phys. Tables, 2d ed., Washington, 1903, p. 155.

the deposition of moisture ceases. When we consider, further, how rarely the difference between the temperature of the air of a room and the dew-point will be as small as 3°, it is clear that the danger of error arising from the condensation of moisture upon the surface of the calorimeter system is insignificant.[1]

Evaporation of water, involving abstraction of heat from the calorimeter system, will occur much more commonly. This will be a slower process than that of dew-deposition and it seems probable that the 5.11 liters of air in the inner air-jacket will not become saturated with moisture in the length of time required for a determination, and it may safely be assumed that the difference in the amount of evaporation per minute will not vary materially in the course of the fifteen or twenty minutes required for the completion of the observations necessary for the determination of a heat of combustion.

The correction for the "external influences" may, therefore, be estimated on the assumption that the rate of warming or cooling of the calorimeter system in a given minute is proportional to the difference between the average temperature of the system for that minute and the temperature of the surrounding medium. Further, the temperature of the surrounding medium may be regarded as constant. The correction for the effect of external influences on the temperature of the system may, therefore, properly be determined according to the method of Regnault, which is based upon the assumptions just mentioned. This consists in estimating the effect produced on the temperature of the system by the external influences during each minute of the time intervening between the ignition of the substance and the reattainment of internal temperature-equilibrium after the combustion ("main" or "combustion" period of the determination) from determinations of the mean

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[1] It ought, perhaps, to be pointed out that this conclusion refers only to this particular form of apparatus. In calorimeters having no covers to separate the air of the air-spaces from that of the room, especially where by means of a water-jacket the temperature of the air-spaces is regulated so as to be always the same (whatever the temperature of the room), the question of dew formation may be of greater importance. Stohmann, when using his constant pressure calorimeter (in which, of course, the rise of temperature being more gradual than in a bomb calorimeter, the time during which dew deposition may occur is greater), endeavored to keep the temperature of the air-spaces constant between 17° and 18° and made the initial temperature of the system always about 16°. As the temperature was frequently lower than the dew-point of the atmosphere in summer, long interruptions of work were sometimes necessary in that season of the year (*J. prakt. Chem.*, **143**, 22 (1887)). In his description of the method of use of the bomb-calorimeter, Stohmann again refers to the danger of dew formation and recommends that the difference between the initial temperature of the system and that of the surrounding air be not made too great (*J. prakt. Chem.*, **147**, 519 (1889)).

temperature of the system during each minute of this period and of the mean temperature and the rate of change of temperature during two periods of five minutes each, one (the "initial" period) immediately preceding, the other (the "final" period) immediately following the main period. The correction is most readily calculated from the actual observations of the temperature of the system, made at the beginning and end of the initial and final periods and at intervals of one minute throughout the main period by means of the formula derived by Pfaundler (see p. 688).

The Thermometer Readings.—Readings may be begun at any time after the stirrer has been set in motion. They should be continued until there has been a *uniform* rise of temperature for five minutes, the differences between successive readings not varying by more than 0.002°. These five minutes constitute the initial or precombustion period.

Precisely at the end of the five minutes (*i. e.*, at the sixth reading of the initial period), the electric circuit through the fine iron wire in the bomb is completed by closing a switch. The resistance lamps are incandescent during the passage of the current and the extinction of their light indicates that the iron wire has been fused. This usually occurs within two or three seconds after the closing of the circuit. The switch should now be opened immediately to avoid error from the production of heat in the calorimeter by the passing of the current through the water.

Readings should be continued at intervals of one minute until the rate of fall of the mercury has become regular—an indication that internal equilibrium has been regained. This marks the end of the combustion period. In our routine work, however, we find it convenient, for the sake of uniformity in the calculations, to regard the combustion period as ending, in all cases, five minutes after the ignition. With an apparatus of the present model, it may safely be assumed that the system will return to equilibrium within five minutes, if the rate of stirring exceeds 40 revolutions per minute. After the final reading of the combustion period, the stirring is continued for five minutes (final or "post-combustion" period), at the end of which time another reading is taken.

Before each reading, the thermometer should be tapped with the electric hammer.

After the Combustion.

The bomb is now removed from the calorimeter and placed in the clamp. After the pressure has been relieved by opening the valve; the collar is unscrewed and the cover removed. The interior of the bomb and the lining of the cover are rinsed with water and the rinsings titrated to determine the nitric acid (see below). The quantity of iron, if any, remaining unoxidized must be deducted from the quantity originally taken. It may be determined by weighing or (more conveniently) by measuring its length on a millimeter or other finely graduated scale.

Determination of the Nitric Acid.

The temperature in the interior of the bomb during the combustion is so great as to bring about the combustion of some of the atmospheric nitrogen left in the bomb on filling and also of some of the nitrogen contained in the substance burned. The product of this combustion is nitric acid. The heat produced by the combustion of the nitrogen is, of course, to be deducted from the total heat measured. For the determination of the nitric acid we follow Stohmann in using a solution of normal sodium carbonate (Na_2CO_3) of 3.706 grams per liter. One cc. of this solution contains 0.003706 gram sodium carbonate which is equivalent to 0.004406 gram nitric acid, the heat of formation of which is 1 calorie.[1] Thus each cubic centimeter of sodium carbonate used in the titration represents 1 calorie set free in the calorimeter by the combustion of nitrogen. Methyl orange is used as indicator.

Calculation of Results.

To find the heat of combustion of the substance under investigation, it is necessary to determine the total quantity of heat liberated in the apparatus and to deduct from this total the quantities due to the "accessory combustions" of the kindlers and the nitrogen. To determine the total quantity of heat liberated, one must know (1) the hydrothermal value of the calorimeter system, and (2) the rise of temperature reduced to true degrees and corrected for the influence of the surroundings. The details of the calculation can be best explained by an example.

The following copy of a page of our laboratory book gives the observations made in a determination of the heat of combustion of cane-sugar with the calculations therefrom, arranged in the form we have found most convenient. At the top of the page are given

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[1] Molecular heat of formation of nitric acid from nitrogen, oxygen and water equals 14,300 calories. Berthelot: *Ann. chim. phys.*, (5), 6, 151 (1875); "Thermochimie," Vol. II, 107 (1897).

general data, such as the number and description of the sample, apparatus used, etc. Following this we have recorded the weighings of the sugar itself and of the iron wire and naphthalene and the titer of the nitric acid as found at the end of the determination.

SERIAL No. ....

Sample No. Description, *Cane-sugar.* Date, *July 13*, 1901.
Bomb No. *3*. Observer, *J. F. Snell.* Thermometer, No. *733*.

Capsule No. *1*.
Wt. caps. + subs. = *4.2501*
Wt. capsule = *2.8783*
Wt. substance, W = *1.3718*

CORRECTION FOR ACCESSORY COMBUSTIONS.
Wt. Fe *13.0 — 1.1 = 11.9* mgs. = *19.0* cal.
Wt. naphthalene = *6.4* " = *61.6* "
HNO_3 = *6.6* "
Correction for accessories = *87.2* "

	READINGS.		CORRECTED READINGS.
INITIAL PERIOD.	1	*1.018*	*1.015*
	2	*1.021*	
	3	*1.025*	
	4	*1.027*	
	5	*1.030*	
	$6\theta_0$	*1.032*	*1.029*
MAIN PERIOD.	$7\theta_1$	*2.300*	*2.3*
	$8\theta_2$	*3.650*	*3.7*
	$9\theta_3$	*3.678*	*3.7*
	$10\theta_4$	*3.662*	*3.7*
	$11\theta_5$	*3.653*	

FINAL PERIOD.
$\frac{\theta_5 + \theta_0}{2}$ = *2.3*
Sum = *15.7*
5θ = *5.1*
Diff. = *10.6*
Log. diff. = *0253*
Log. V′-V = *7324*
Colog $\theta'-\theta$ = *5820*
3397
Antilog. = + *.0219*
+ 5 V = − *.014*
Radiation correction = + *.0079*
16 *3.640* | *3.633*
Time *3.30*

INITIAL PERIOD.
Fall = − *.014*
Rate V = − *.0028*
Mean t°, θ = *1.022*

CORRECTED READING, θ_5 = *3.646*
θ_0 = *1.029*
$\theta_5 + \theta_0$ = *4.675*
½ = *2.3*

FINAL PERIOD.
Fall = + *.013*
Rate V′ = + *.0026*
V = − *.0028*
V′ − V = + *.0054*
Mean t°, θ' = *3.640*
θ = *1.022*
$\theta'-\theta$ = *2.618*

THERMOMETER CORRECTION.
T° air = *25.2*
T° water = *23.8*
1st reading = *1.0*
T° of zero = *22.8*
Corr. for 1° = + *.001*
Rise (degrees) = *2.6*
Ther. corr. = + *.0026*

FINAL CALCULATION.
θ_5 = *3.646*
θ_0 = *1.029*
$\theta_5 - \theta_0$ = *2.617*
Th. corr. = + *.0026*
Rad. corr. = + *.0079*
Corr. rise = *2.6275*
" " × 2100 *52.550*
= Total heat = *5517.8*
Accessories = *87.2*
Corrected heat = *5340.6*
Log. corr. heat = *73485*
Log. W = *13729*
59756
HEAT OF COMBUSTION PER GRAM = *3959*

Remarks:

Below the second horizontal line are given at the left of the page the thermometer readings. The last reading, No. 16, will be found near the foot of the page, below the calculation of the radiation correction. Corrections on account of variations in thermometer bore are applied to readings 1, 6, 11, and 16, and the corrected values given in the next column, with the exception of No. 11 $(\theta)_5$, which is placed for convenience in the third column and repeated in the fourth.

The total rise of the thermometer during the combustion period amounts to 3.646° — 1.029° = 2.617° of the arbitrary scale of the thermometer (see Column 4, "Final Calculation"). To this "apparent" rise of temperature, two corrections are to be applied:

(1) The degrees of the arbitrary thermometer scale are to be reduced to true degrees (thermometer correction).

(2) Allowance is to be made for the influence of the surroundings upon the temperature of the calorimeter during the combustion period (radiation correction).

Thermometer Correction (Column 4).—The temperature of the water at the beginning of the combustion was 23.8° C. The reading of the calorimeter-thermometer corresponding to this temperature is 1°. The zero of the thermometer corresponds, therefore, to 22.8° C. At this temperature, 1° of the arbitrary scale of the thermometer is equal to 1.0010 true degrees. A correction of + 0.001° is therefore to be made for each degree of apparent rise of temperature, or a total correction of $0.001 \times 2.6 = +0.0026°$.

Radiation Correction (Columns 1-3).—During the early part of the combustion period, the calorimeter, *i. e.*, the calorimeter system, is cooler than the surrounding air. The temperature is rising as the calorimeter system gains heat from the air. In the later part of the period, the calorimeter is ordinarily warmer than the air and its temperature is falling as heat passes from it to the air. According as the quantity of heat gained during the early part of the period is greater or less than the quantity lost later, the observed rise of temperature is greater or less than that properly attributable to the combustion and a subtractive or additive correction is to be made.

The correction is calculated by the Regnault-Pfaundler formula,[1]

$$C = nV + \frac{V'-V}{\theta'-\theta}\left(\frac{\theta_n + \theta_o}{2} + \sum_1^{n-1} \theta - n\theta\right),$$

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[1] Pfaundler: Pogg. *Ann.*, **129**, 113 (1866).

where n = number of time units (minutes) in combustion period.

V = rate of fall of temperature of calorimeter during initial period.[1]

V′ = rate of fall of temperature of calorimeter during final period.[2]

θ = mean temperature of calorimeter during initial period.

θ' = mean temperature of calorimeter during final period.

$\theta_1, \theta_2 \cdots\cdots \theta_n$ = temperature at end of first, second, ······ nth minutes of combustion period.

θ_0 = temperature at moment of ignition.

Applying this formula to our example, we find for the expression within the bracket 10.6° (see first column); for $V'-V$, 0.0054°, for $\theta'-\theta$, 2.618° and for nV, $5 \times (-0.0028) = -0.014°$ (see middle column); whence $C = + 0.0079°$ (see first column).

Applying the thermometer and radiation corrections, we have $2.617 + 0.0026 + 0.0079 = 2.6275$ as the rise of temperature in true degrees (see "Final Calculation" in last column). The total hydrothermal value (water + hydrothermal equivalent of apparatus) being 2100 grams, the quantity of heat set free in the apparatus must have been $2.6275 \times 2100 = 5517.8$ calories.

Correction for Accessory Combustions.—The weight of the iron wire was 13 mg. The quantity unburned was 1.1 mg. The quantity burned was therefore 11.9 mg. The specific heat of combustion of iron being 1601 calories, the heat of combustion of 11.9 mg. is $11.9 \times 1.6 = 19$ calories. The quantity of naphthalene burned was 6.4 mg., which yields $6.4 \times 9.63 = 61.6$ calories, the specific heat of combustion of naphthalene being 9628 calories. The heat from the combustion of nitrogen as determined by titration of the nitric acid is 6.6 calories. The total heat from accessory combustions is therefore $19 + 61.6 + 6.6 = 87.2$ calories.

Deducting this quantity from the total heat set free in the apparatus, we have $5517.8 - 87.2 = 5430.6$ calories as the heat due to the combustion of the sugar. The quantity of sugar burned was 1.3718 grams. The specific heat of combustion according to this determination is therefore $5430.6 \div 1.3718 = 3959$ calories.

It will be found convenient to have tables mounted on cards,

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[1] The change is actually a rise but for convenience in mathematical calculation it is here expressed as a fall in temperature. The value of V thus becomes negative.

[2] The change is generally a fall in temperature. Sometimes, however, the initial temperature of the water or the quantity of heat set free may be such that final temperature of the calorimeter will be lower than that of the surroundings, in which case there will be a rise of temperature and the value of V′ will be negative.

giving the heat of combustion of quantities of naphthalene weighing from 4 to 10 mg. and of quantities of iron weighing from 10 to 20 mg. The weights may be expressed to tenths of milligrams and the heat quantities to tenths of calories. If iron wire of uniform diameter is used, the quantities of iron may be more conveniently expressed in lengths instead of weights. The specific heat of combustion of naphthalene is 9628 calories and that of iron 1601 calories.

Heat Unit.

The unit in which the heat of combustion, as thus calculated, is expressed is the quantity of heat necessary to raise the temperature of 1 gram of water 1° at the temperature which the water has in the determination in question. (In the above example it ranges from 23.8° to 26.4°.) Since the variations in the specific heat of water between 15° and 30° are small,[1] it scarcely seems necessary to correct results obtained at any ordinary room temperature for the variation of the specific heat of water from its value at 15° or 20° C. No error of any consequence will be committed, for instance, by taking 3959 calories as the determined specific heat of combustion of cane-sugar, whether the calories be defined as the heat necessary to raise the temperature of 1 gram of water from 15°-16° or from 20°-21° C.

Reduction to Constant Pressure.

The heat of combustion determined in the bomb calorimeter is that at constant volume, while the heats of combustion customarily

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[1] The following table gives the results of determinations of the specific heat of water at 15° and 30° by different experimenters and different methods. The specific heat at 20° is taken as unity.

SPECIFIC HEAT OF WATER AT 15° AND 30° REFERRED TO THAT AT 20°.

Experimenter.	Method.	Specific heat of water. at 15°.	 at 30°.	Difference. 30–15°.
Bartoli and Stracciati[1]	Mixtures.	1.0005	1.0014	—0.0009
Ludin[2]................... ...	"	1.0009	0.9999	+0.0010
Rowland[3]	Frictional heating.	1.0014	0.9986	+0.0028
Griffiths[4]	Electrical heating.	1.0014	......	......
Callendar and Barnes[5]......	"	1.0010	0.9987	+0.0023

[1] Bartoli and Stracciati: *Estratti dal Nuovo Cimento*, Series 3, Vol. 32. (1891). We have derived the figures from a table by Pernet in Louguinine's *Bestimmung der Verbrennungswärme*, p. 18.

[2] Ludin: Inaugural Dissertation, Zurich, 1895. We have derived these figures also from Pernet's table.

[3] As corrected by Waidner and Mallory, *Phys. Review*, 8, 232 (1899).

[4] Value corrected by F. A. Wolff, Johns Hopkins Univ. Circular, June, 1898, cited by Waidner and Mallory, *Loc. cit.*, p. 235.

[5] Callendar and Barnes: *Phys. Review*, 10, 213 (1900).

tabulated and used are those at constant pressure. To reduce the molecular heat of combustion of a solid or liquid compound, $C_nH_pN_rO_q$, at constant volume to that at constant pressure, it is necessary to add $(\frac{1}{2} p - q - r)$ T calories where T = the absolute temperature of the calorimeter.[1] To reduce the *specific* heat of combustion at constant volume to that at constant pressure the term to be added is, therefore, $(\frac{1}{2} p - q - r) \mathrm{T} \div \mathrm{M}$, where M = the molecular weight of the substance. For carbohydrates, this correcting term is zero, *i. e.*, the heats of combustion at constant volume and at constant pressure are identical. For tripalmitin it amounts to + 15.6 calories, for tristearin to + 16.1 calories, and for triolein to + 15.2 calories. For protein it amounts to about + 3 calories.

With food materials in general, therefore, the heats of combustion obtained by the bomb-calorimeter should be increased by 15-16 calories for each gram of fat and by 3 calories for each gram of protein.

III. DETERMINATION OF THE HYDROTHERMAL EQUIVALENT OF THE CALORIMETER.

Now that the heats of combustion of many compounds are accurately known, the most convenient and satisfactory method for the determination of the hydrothermal equivalent of a bomb-calorimeter is to burn weighed quantities of such compounds in the bomb immersed in a known quantity of water.[2] From the observed rise of temperature and the known heat of combustion of the compound used, the total water value of the calorimeter system is calculated. Deducting from this the quantity of water used, we have the water value of the calorimeter itself.

The substances used in these determinations should be such as can easily be obtained pure and preserved without risk of change by deliquescence, oxidation, decomposition or otherwise. Their heats of combustion should have been determined in calorimeters whose hydrothermal equivalents have been learned by other methods.[3] Those which have been determined by several investigators, independently and with closely accordant results, are to be preferred. Stohmann selected hippuric acid, benzoic acid, cane-

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[1] See Berthelot: *Thermochimie*, **2**, 30 (1897).

[2] Stohmann: *J. prakt. Chem.*, **157**, 99 (1894).

[3] For descriptions of such methods see Stohmann, Kleber and Langbein: *J. prakt. Chem.*, **147**, 524 (1889); Berthelot: *Traité practique de calorimétrie chimique*, **144**ff.; Wiley and Bigelow: This Journal, **19**, 439 (1897).

sugar and camphor as suitable for the purpose, these being substances for whose heats of combustion fairly accordant values had been obtained in his own laboratory and that of Berthelot. We have used substances of which we had specimens known to be pure from previous determinations of carbon, hydrogen and nitrogen and which were at the same time substances with regard to whose heat of combustion Stohmann and Berthelot were in approximate agreement. The substances happen to be the same as those recommended by Stohmann, except that we have used glycocoll instead of camphor.

Camphor, hippuric acid and benzoic acid are ignited directly by the heated iron wire but with cane-sugar and glycocoll a kindler (a naphthalene crystal) should be used.

The following are the specific heats of combustion of the five substances in question.

Stohmann used his own figures in preference to those of Berthelot. We have used the average.[1]

	Stohmann.	Berthelot.	Tower.[2]	Average.
Glycocoll	3129.1	3133.6	....	3131
Cane-sugar	3955.2	3961.7	3958.7	3959
Hippuric acid	5668.2	5659.3	....	5664
Benzoic acid	6322.3	6322.1	....	6322
Camphor	9291.6	9288.0	....	9290

In order to check the accuracy of the bomb, it is customary in this laboratory to make a combustion of cane-sugar about every two weeks. The average of the last twenty combustions thus made is 3959.3 calories per gram. The minimum result was 3948 and the maximum 3967.

If m be the number of grams of substance burned, q_1 the heat of combustion per gram, the quantity of heat liberated by the combustion will be mq_1 calories. If, at the same time, q_2 calories are produced by the accessory combustions of iron wire, of nitrogen and of kindling material (such as naphthalene), the total heat, q, set free within the calorimeter will be $q = mq_1 + q_2$; and if t be in degrees centigrade, the observed rise of temperature (corrected for thermometer calibration and for influence of surroundings of

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[1] That Stohmann's methods of manipulation were more painstaking than Berthelot's is very plain to one who has seen both as actually carried out in their respective laboratories. At the same time, Stohmann's special refinements probably made but little difference in the actual results. W. O. A.

[2] Unpublished experiments made in this laboratory.

calorimeter), w the weight of water used, and a the required hydrothermal equivalent, evidently $q = (w + a)t$, whence

$$a = \frac{q}{t} - w.$$

The method of calculation is illustrated by the following example:

	Substance.	Quantity burned. Grams.	Specific heat of combustion. Calories.	Heat liberated by the combustion Calories.
	Cane-sugar	1.0177	3959	4029.0
Accessories	Iron	0.0201	1600	32.2
	Naphthalene	0.0078	9628	75.1
	Nitrogen (by titration of the nitric acid formed)			6.0
Total heat liberated, q				4142.3
Corrected rise of temperature, t				1.9751°
Weight of water used in calorimeter, w				1685 g.

whence, $a = \frac{4142.3}{1.9751} - 1685 = 412$ grams.

A number of determinations (at least three) of a are made in this way with each of three or four substances. The triplicate results with each substance should agree very closely with each other as should the several averages of these triplicates. If the latter do not differ by more than a few (*e. g.*, 5) grams, the average of these averages may be taken as the correct hydrothermal equivalent of the calorimeter.

To insure that the hydrothermal equivalent thus obtained shall be actually that of the apparatus as used subsequently for determinations of heats of combustion, the quantity of water used in the calorimeter in the determinations of the hydrothermal equivalent should be as nearly as possible the same as in the regular determinations. In the above example, for instance, 1685 grams of water were used, because we knew that the hydrothermal equivalent was not far from 415 grams and it was our intention to have regularly a total water-value (water + hydrothermal equivalent) of 2100 grams.

A tolerably close estimate of the hydrothermal equivalent may be made in advance of the accurate determinations by calculation from the weights and specific heats of the *materials* of which the calorimeter is constructed, only those parts being taken into account which share the temperature rise of the water. These are, of course, the water cylinder, the lower parts of the thermometer, the lower part of the stirrer, and the bomb with its contents. A statement of the weights of the component materials is furnished with each of the calorimeters here described. The following are the specific heats as nearly as we know them:

Material.	Sp. heat.	Source of figures.
Bomb:		
Tool steel	0.1087	Determined by Dr. Tower.
Hotchkiss gun steel	0.1114	" " " "
Platinum	0.032	Smithsonian Phys. Tables, 2nd ed., Washington, 1903, p. 296.
Lead	0.030	Smithsonian Phys. Tables, 2nd ed., Washington, 1903, p. 296.
German silver	0.094	Tomlinson: Proc. Roy. Soc., 1885.
Oxygen (constant volume)	0.157	Wüllner, "Experimental Physik," (4th ed.), III, 509.
Water-cylinder:		
Britannia-metal: 90 pct. tin	0.054	Smithsonian Phys. Tables.
7 pct. antimony	0.049	" " "
3 pct. copper	0.092	" " "
Stirrer:		
Brass	0.094	Kohlrausch, Phys. Meas.
Thermometer:[1]		
Mercury	0.033	Smithsonian Phys. Tables.
Glass	0.19	Kohlrausch, Phys. Meas.

IV. ACCURACY OF THE METHOD.

Theoretical Discussion.

If m be the quantity of substance burned, $h = a + w$, the hydrothermal value of the calorimeter system, a being the hydrothermal equivalent of the apparatus and w the weight of the water, and t the rise of temperature of the system due to the combustion; then the specific heat of combustion of the substance, $q = \frac{ht}{m}$.

From this formula it is clear that errors making h or t too large or m too small will make q too large in the same proportion, and errors making h or t too small or m too large will make q too small in the same proportion. An error in a, the hydrothermal equivalent of the apparatus, will affect equally all determinations made with that apparatus, *i. e.*, will produce the same percentage error in each. Errors in m, w, or t, on the other hand, will affect only the individual determination.

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[1] We have found by examination of a broken Fuess thermometer of the kind used in this laboratory and described above, that the portion immersed in the calorimeter water consists of about 8.5 grams glass and 32.5 grams mercury.

Allowing a possible error of ±0.0002 grams in weighing the substance, we have a possible error in m and therefore also in q of ±0.02 per cent. when 1 gram, or of ±0.04 per cent. when 0.5 gram is used. Allowing a possible error of ±1 gram in the weighing of the water, the possible error in h, leaving out of consideration the constant error in a, is ±0.05 per cent. on a hydrothermal value of 2100 grams. The possible error due to t will, however, be greater. ±0.001° must be allowed on each reading of the thermometer or ±0.002° on the two readings necessary to determine a temperature difference. In addition, the correction for the influence of the surroundings upon the temperature of the calorimeter is uncertain. If we allow another ±0.002° (which is probably a liberal estimate) for error here, we have a possible total error of ±0.004°. In the measurement of temperature differences of from 1° to 4°, the maximum errors, on the above assumption, will be from 0.4 to 0.1 per cent.

It is clear, then, that for accurate results the greatest care is needed in the temperature measurements. To secure this accuracy:

(1) The quantity of substance burned should, if practicable, be large enough to give a rise of from, say, 2° to 3.5°. In other words, if the water-value of the calorimeter be made 2100 grams, a quantity sufficient to yield 4000 to 7000 calories or a little more should be used.

(2) The thermometer must be accurate and must be accurately read and corrected.

(3) The temperature of the air-space immediately surrounding the metal cylinder should be kept constant throughout each experiment so that the conditions may be correct for the application of the Regnault-Pfaundler "radiation correction" (see above). So far as we are aware, the most accurate experimenters in this field work in rooms of constant temperature, and some protect their calorimeters from radiation from the observer's body by enclosing them in metal cylinders having double walls with interspaces filled with water. According to our experience, however, the two indurated fiber cylinders of our calorimeter afford sufficient protection, and reasonably accurate determinations may be made in an ordinary laboratory room, provided the temperature is nearly constant during each experiment. We have, however, arranged a small room in the center of the basement of our laboratory for this special work.

Accuracy of Actual Determinations.

In the actual use of the apparatus, the accuracy attained is about what would be expected from the foregoing considerations. Thus, in thirteen determinations of the heat of combustion of benzoic acid, made by three observers in this laboratory, the average deviation of the individual results from the mean was ±0.16 per cent. and the maximum deviation —0.35 per cent. The minimum quantity of substance burned being 0.8 gram, we should anticipate a possible error of ±0.03 per cent. in the weighing. The minimum rise of temperature produced in the calorimeter being 2.5°, we should look for a possible error of ±0.16 per cent. in the determination of the temperature difference. Allowing a possible error of ±0.05 per cent. in the weighing of the water and leaving out of consideration personal error and error due to the use of different apparatus, we should expect to find a maximum error of $0.03 + 0.16 + 0.05 = \pm 0.24$ per cent. in the individual results. The actual maximum error was, as just stated, —0.35 per cent. The difference barely exceeds that between the specific heat of water at 15° and at 30° (see p. 690, foot-note).

That, in general, the actual determinations on solids and homogeneous liquids have very nearly theoretical accuracy is shown by the following comparison of anticipated errors, estimated in the manner just illustrated, with the actual deviations of the results of individual determinations from the average of those results.

Substance.	No of determinations.	No. of samples.	No. of observers.	Maximum error.		Mean error. Actual. Per cent.
				Anticipated. Per cent.	Actual. Per cent.	
1. Benzoic acid	13	..	3	±0.24	—0.35	±0.16
2. Hippuric acid	9	..	3	0.31	—0.39	0.22
3. Cane-sugar	18	..	4	0.38	+0.51	0.28
4. Cellulose blocks	15	5	3	0.38	+0.43	0.17
5. Commercial oils	84	40	1	0.29	+0.39	0.12
6. Beef	8	4	2	0.23	±0.20	0.07
7. Dried residues of milk	8	4	1	0.22	±0.14	0.11
8. Other foods of animal origin, *e. g.*, butter, pork, casein	10	5	2	0.29	±0.20	0.09
9. Vegetable foods and fodders, largely carbohydrate in composition	14	7	2	0.27	±0.18	0.10
10. Human feces	10	5	3	0.24	±0.25	0.12

This comparison indicates pretty clearly, we think, that with substances of these classes, there cannot be any very important sources of error other than those discussed above, also that the allowance of ±0.002° for uncertainty in the radiation correction is ample.

From the table, it would appear that the determinations on substances of mixed composition were actually more accurate than those on pure chemical compounds. The explanation of this is. doubtless, partly that in the case of the substances of mixed composition, the quantities burned were such as to set free larger quantities of heat, thus reducing the anticipated maximum error, and partly that on these substances the duplicate or triplicate determinations on each sample were made by a single observer with a single apparatus, while the determinations on benzoic acid. hippuric acid, cane-sugar, etc., were made by more than one observer with more than one apparatus.

With a substance of uniform composition, combustible without the aid of a kindler, it is a safe practical rule, in case only two determinations are ordinarily made, to make an additional determination whenever the duplicates vary from each other by 0.5 per cent. or more (*i. e.*, from their average by ±0.25 per cent. or more) and in case three or more determinations are made, to reject results varying from the average by over ±0.4 per cent.

Where a kindling substance is used, especially when, as in the combustion of urine on cellulose blocks, the kindler furnishes a considerable proportion of the total heat measured, greater latitude between duplicates must be allowed and lower accuracy of result accepted. If 20 cc. of urine (a little over 20 grams), having a specific heat of combustion of 110 calories, be burned with a cellulose block yielding 2200 calories, the maximum error anticipated will be ±0.4 per cent. in the determination of the temperature difference and about ±0.2 per cent. due to the use of the kindler, or about ±0.6 per cent. in all. Duplicates varying by less than 1.2 per cent. should, therefore, not be rejected, but an additional determination should be made in case the duplicates differ by over 0.5 per cent.

With milk, owing to the great difficulty of taking uniform samples, the variations between duplicates sometimes amount to 2 per cent. or more. Where such wide differences occur, a third determination is obviously necessary, but until a better method of sampling milk is devised, we must be content to accept less accurate results with this substance than we are able to obtain with solids and with liquids of uniform composition.

Verification by the Respiration Calorimeter.

Experimenters with the bomb-calorimeter have felt the lack of an absolute standard for verification of the accuracy of the results obtained by its use. Such a verification is found in comparative measurements of the heat of combustion of alcohol by the bomb-calorimeter and by the Atwater-Rosa respiration calorimeter[1] in this laboratory.

To establish the accuracy of this latter apparatus as a calorimeter, known amounts of heat are introduced electrically, and are measured by the apparatus. In the average of a large number of determinations, the disparity between the amounts introduced and the amounts as measured has been about 1 part in 10,000.

The accuracy of the apparatus for the determination of heat being thus shown, considerable quantities of alcohol are burned in the respiration chamber during long periods (about 40 grams per hour during periods of twelve to one hundred hours each) and the heat thus produced is measured and the heat of combustion per gram of alcohol is determined. Aside from the possibility of a slight error in the figure 0.592, which was employed for the latent heat of evaporation of water, it seems hardly probable that there can be any considerable error in the average of the results obtained. Omitting from consideration the experiments in which obvious disturbing factors influenced the results, and considering only the experiments of the past three years, during which earlier errors of various kinds were eliminated, eleven series of experiments performed during the years 1900-2 gave figures for the heat of combustion of alcohol which averaged 7090 calories per gram. The maximum and minimum figures were 7111 and 7048 respectively, the range of error being thus ±0.6 per cent. The average of six determinations with the bomb-calorimeter, corrected for constant pressure, was 7.095 calories, the maximum and minimum being 7110 and 7068 respectively, and the range of error ±0.4. In other words, the average of the determinations with the bomb differs from that with the respiration calorimeter by only 0.07 per cent.

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[1] U. S. Dept. Agr., Office of Experiment Stations, Bulletins 63, 69 and 109.

We thus have a standard to which the determinations by the bomb-calorimeter are referable and which shows them to be correct.

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PETROLEUM IN CALIFORNIA.

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WITHIN the last few years California has developed a new industry, that of petroleum. The knowledge that it existed is not new. Seepages occur in various parts of the State, and natural gas is found over a very large area. Immense deposits of asphaltum occur in the southern counties and were used by the early Mission Fathers. Attempts were made to distil the crude oil and in 1855, Pico erected a small refinery.

The discovery of oil in Pennsylvania produced great excitement, not only in the east but in California. Claims were located in all parts of the State and companies formed to work them. In 1865 there were sixty-five companies in existence with a nominal capital of $45,000,000. Oil properties were exploited in every county from Humboldt to San Diego, but there was no apparent success, owing to lack of prospecting, insufficient depth of wells, and to the opinion of eminent chemists and geologists that the oil would not be found in large quantities, and could not be refined.

Petroleum occurs in every part of the State, but as yet only the southern part yields any large quantity. Ventura, Los Angeles, Orange, Santa Barbara, Kern and Fresno Counties furnish practically all the oil that is produced, although in many other counties small yields have been obtained.

Los Angeles, in common with other districts, was exploited nearly forty years ago, but no oil was obtained. The wells were not bored deep enough. Nothing further was done for thirty years, until in 1892 a well 365 feet deep was sunk and yielded oil. In three years, more than 300 wells were drilled and most of them yielded oil. Other districts in the neighborhood were exploited, and hundreds of new wells located. The production of oil rapidly increased until in 1897 it had reached 1,400,000 barrels. The total amount of oil obtained from the Los Angeles district amounts to more than 9,000,000 barrels. About 1400 wells have been dug,