DEPARTMENT OF COMMERCE AND LABOR

CIRCULAR
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 11

THE STANDARDIZATION OF BOMB CALORIMETERS

[1st Edition]
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The heats of combustion of solids, also of liquids and gases when high accuracy is required, are determined by means of the so-called Berthelot bomb calorimeter. In these calorimeters a known quantity or mass of the combustible is burned in oxygen under pressure, in a closed bomb. The heat given off during combustion is taken up by a known mass of water in which the bomb is immersed. Combustion in this case takes place at constant volume and the quantities to be measured are the mass of combustible, the mass of water including the equivalent mass, or water equivalent, of the bomb, container, and accessories, and the rise of temperature.

1. TYPES OF BOMB CALORIMETERS

Several makes of bomb calorimeters, including all the necessary equipment for combustion determinations, are to be found on the market. A question often arises as to the relative accuracy of these various calorimeters and it may be said that the differences between them are very largely such as to affect only the convenience of manipulation, the cost of production, and the durability of the bombs. Certain refinements are introduced in some of the makes which tend to reduce the accidental errors of observation, but any of these different instruments properly calibrated and in the hands of a careful observer will give satisfactory results in determining heats of combustion of fuels.

Certain suggestions may be useful in the selection of a calorimetric equipment. The following conditions should be realized so far as practicable:

The bomb should be of sufficient strength to stand a pressure of at least 500 or 600 atmospheres. The outer surface should be nickeled or otherwise finished so as to be protected from rust or corrosion. The shape should be such as to allow free circulation of water between the bottom of the bomb and that of the calorimeter.

The lining of the bomb may be platinum, gold, enamel, nickel, or other metal not easily attacked by acids. These linings may for convenience be made removable, but such removable linings should not be used in bombs intended for combustions of gases. Of the above materials platinum is the best and most durable, although it is also the most expensive. Gold has not been extensively used, but might prove about as good as platinum. Enamel is satisfactory as long as it lasts, but it is liable to chip and crack from contact with hot particles of coal or fuse wire which are sometimes thrown out of the crucible. These linings may last for many hundreds of combustions or may be injured badly in the first few combustions. They may be still usable for work not of the highest accuracy when badly chipped, as the errors introduced by the reaction between the exposed metal and the products of combustion are too small to be of importance in any but the most precise investigations. Nickel linings are slightly attacked by the nitric acid formed during combustion, but the error introduced from this cause is probably always negligible in fuel combustions.

The calorimeter vessel or "calorimeter" should be as small as practicable while providing for total immersion of the bomb and proper stirring of the water. Highest precision requires that the calorimeter be fitted with a floating cover or its equivalent, but the use of such a cover is inconvenient and is not necessary in fuel calorimetry. Two forms of stirrer are in common use, the reciprocating stirrer and the screw-propeller stirrer. A screw propeller when mounted in a tube so as to give a positive circulation of the water is far more efficient than the other type. Such a screw propeller should preferably have no bearing in the water of the calorimeter, and the metal parts, such as the shaft and tube, which extend out of the calorimeter, should be separated from the metal parts above by a piece of hard rubber or other material to reduce the conduction of heat.

The jacket which surrounds the calorimeter should be a double-walled metallic vessel containing water between the walls. This water should preferably be stirred, so that its temperature can be kept uniform and measured. There should be no material between the calorimeter and the inside of the jacket except the smallest practicable insulating supports for the calorimeter. The inner wall of the jacket should be polished or white enameled and it, as well as the calorimeter surface, should be kept clean. The jacket should have a cover, preferably of copper or aluminum, making good contact with the top of the jacket in order to prevent convection currents. When the highest accuracy must be attained, the cover should be double walled and so arranged that the jacket water circulates through it. The stirrer should be supported from the jacket and should run at a uniform speed.

2. WATER EQUIVALENT

The total heat capacity of a calorimeter, as used, includes the heat capacity of the water and of the bomb, its contents, the container, thermometer, stirring attachments, and part of the supports. The heat capacity of the water is its mass (weight in vacuo) times its specific heat. The specific heat depends somewhat upon the temperature and is here taken as unity at 15° C, so that the calorie is defined as the heat capacity of one gram of water per degree centigrade, at a temperature of 15° C. Likewise the BTU is here taken as the heat capacity of 1 pound of water per degree Fahrenheit at a temperature of 60° F. The heat capacity of the bomb and accessories can not be sufficiently well determined by calculation from the weight. A bomb calorimeter therefore practically requires standardization in the condition in which it is to be used.

An electrical method[1] gives the highest accuracy, but is hardly necessary, except in the case of investigations on standard substances. A differential method depending upon observations taken with different amounts of water has sometimes been applied, but can not be used with any considerable accuracy. The most satisfactory and only practicable method of calibration for commercial calorimeters is by the use of standard samples, the heats of combustion of which have been carefully determined in calorimeters calibrated by electrical methods. Experiments have shown that the total heat capacity of an ordinary combustion calorimeter does not change appreciably with temperature between 15° and 25° C. This is due to the fact that the metal of the bomb and accessories has a relatively large positive temperature coefficient while the water has a small negative temperature coefficient throughout this range of temperature, and the two nearly neutralize each other.

3. STANDARD MATERIALS

Among the materials available for standard samples, sucrose or cane sugar, benzoic acid, and naphthalene have been generally adopted. Any of these substances can be obtained on the market of sufficient purity for most commercial calibrations, but standard samples of these materials are prepared for distribution by the Bureau of Standards.

Sucrose is not volatile nor strongly hygroscopic, but is rather difficult to ignite and sometimes does not burn completely. It has a heat of combustion of about 3950 calories, or only about half that of the average coal. The more exact value for each sample will be given in the certificate.

Benzoic acid is only slightly volatile, is not very hygroscopic, has a heat of combustion of about 6320 calories and burns more readily than sugar.

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[1] W. Jaeger and H. v. Steinmehr, Ann. d. Phys., **21**, pp. 23-63; 1906. See also Bulletin of the Bureau of Standards, Reprint No. 135.

Naphthalene is quite volatile but not hygroscopic; it has a heat of combustion of about 9610 calories, a little higher than that of most coals, and it ignites and burns very readily.

Of these materials probably the most satisfactory for work of the highest accuracy is benzoic acid, but for calibration of commercial calorimeters to an accuracy of 0.1 per cent naphthalene has some advantages. The loss by sublimation from samples of naphthalene made up into briquets will hardly exceed 0.1 or 0.2 per cent in an hour.

The details of the methods of preparation of these standard combustion samples and of the determination of their heats of combustion will be published in the Bulletin of the Bureau of Standards. The heats of combustion of other substances, with a view to testing their suitability for use as standard combustion samples, are being determined in the laboratories of the bureau.

4. MANIPULATION AND PRECAUTIONS

(*a*) The **oxygen** used for combustion should be as pure as is obtainable commercially and must be free from all combustible gases, such as hydrogen, carbon monoxide, and hydrocarbons. The small amount of nitrogen usually present, if it does not exceed about 5 per cent, introduces an error only by the formation of oxides of nitrogen which are approximately determined by titration for nitric acid. It is well to exhaust the bomb or to wash out the air with a little oxygen before filling, in order to remove the nitrogen contained in the air, which, if allowed to remain, would increase the percentage of nitrogen in the filled bomb by from 3 to 5 per cent.

(*b*) The **pressure** to which the bomb should be filled is usually from 20 to 30 atmospheres, depending upon the volume of the bomb and the charge to be burned, but in no case should the total amount of oxygen be less than three times that which will combine with the charge. With a smaller amount of oxygen there is danger of incomplete combustion. The completeness of combustion can generally be determined sufficiently well by inspection, as the presence of a few tenths of a milligram of soot can very readily be detected. Some bombs are so constructed that the gaseous products of combustion can be conveniently removed and analyzed.

(*c*) The **charge** is generally best prepared in the form of a briquet, both for ease of handling and to avoid danger of blowing the material out of the crucible when oxygen is admitted to the bomb. Samples should be weighed in the crucible and placed in the bomb immediately afterwards, particularly if volatile. Naphthalene in particular requires briquetting or fusing into a solid mass to reduce the rate of sublimation.

(*d*) **Firing** of the charge is usually accomplished by means of an electric fuse of either fine platinum or fine iron wire. Platinum wire will ignite coal, but it is not certain to ignite substances such as sugar, benzoic acid, or naphthalene, which melt readily. For these materials it is better to use iron wire, although a small correction must be made for its heat of combustion (about 1600 calories per gram). A piece of No. 34 Brown & Sharpe gauge iron wire from 1 to 3 cm long can be connected to somewhat heavier platinum leads. The longer wires (2 or 3 cm) should be wound into a small spiral and mounted just above the briquet to be fired. A straight wire 1 cm long will ignite naphthalene, but for sugar it is better to use 3 cm.

(*e*) The **current** for firing should be obtained from storage or dry cells and should not be of more than 10 or 15 volts potential. It is never safe to use a high potential such as that of a 110-volt lighting circuit, even though the current is cut down by lamps in series, since with a high voltage there is danger of arcing, accompanied by evolution of heat within the bomb. Even when a low voltage is used it is important to close the firing circuit with a switch for only about 1 second.

(*f*) The **water** should be weighed out in the calorimeter, and if the absolute heat capacity of this water is to be known, the weighing must be reduced to vacuo. In practice, however, this weighing generally serves only to maintain the same mass in all the observations, and in this case it is not necessary to reduce to weighing in vacuo. The water must be well stirred during observations, and the rate of stirring should be kept constant.

(*g*) **Temperature measurements** are generally more subject to error than any other parts of the calorimetric determination, and yet they often receive the least attention. Mercurial thermometers used for this purpose are usually of the solid-stem type, with a scale covering a 10° to 15° C range of temperature, graduated in 0°.05 or 0°.02 intervals; or of the Beckmann type, in which the scale covers a range of 5° or 6°, graduated in 0°.01, adjustable for use at different temperatures by removing some of the mercury from the bulb to an upper reservoir. None of these thermometers can be relied upon to give true temperature differences to better than 0°.02 unless they have been tested and corrections are applied for errors of the scale, for the emergent stem, and, in the case of Beckmann thermometers, for the amount of mercury removed from the bulb. The methods of making these corrections are explained in certificates which accompany all thermometers tested at this Bureau; also in Bureau of Standards Circular No. 8. If an accuracy greater than about one or two parts in a thousand is required, recourse must be had to something more accurate than the mercurial thermometer. An electrical resistance thermometer equipment has recently been put on the market. Such an equipment is much more expensive than a mercurial thermometer and has not yet been very widely introduced. The accuracy attained with it is about two or three parts in ten thousand. Considerable work has been done in the laboratories of the bureau with platinum resistance thermometers especially adapted to calorimetric work. The bureau will be pleased to furnish information relating to this work to anyone contemplating the use of resistance thermometers.

(*h*) A so-called **radiation correction** must be applied to calorimetric observations on account of the transfer of heat between the calorimeter and its jacket. This heat transfer may take place by conduction, convection, radiation, or evaporation. Corrections are usually made on the assumption that Newton's law of cooling applies—i. e., that the rate of heat transfer is proportional to the difference in temperature between the calorimeter and its jacket. This assumption is very nearly true provided the jacket is covered and kept at a constant temperature; that it contains only a negligible amount of material, such as supports, between its inner surface and that of the calorimeter, and that there is no measurable evaporation from the calorimeter. The assumption is sufficiently accurate in ordinary cases provided the jacket is covered and the temperature of the calorimeter is not allowed to rise more than a degree centigrade above that of the jacket. When observations are made at equal intervals of time, the correction may be readily computed by the Regnault-Pfaundler formula.

(*i*) The **lag of the thermometer** used in measuring temperature has often been assumed to introduce an error requiring correction, but it may be readily shown that no such correction should be applied, because the error is automatically eliminated in applying the ordinary radiation correction.[1]

(*j*) The formation of **nitric acid** from the nitrogen contained in the oxygen used for filling the bomb, assuming that the products are oxidized to nitric acid, supplies an amount of heat equivalent to about 230 calories per gram of acid, and this correction is to be subtracted from the apparent total amount of heat due to the combustion. The amount of nitric acid formed can be found by titration provided no other acids are present, but if, for instance, sulphuric acid is formed from sulphur contained in the combustible the relative amounts of the two acids can only be determined by analysis. It is important to have some water, from 0.5 to 1.0 cc, in the bomb before filling under pressure, to saturate the oxygen with water vapor and to absorb the oxides of nitrogen formed.

5. BASIS OF RESULTS GIVEN

Combustion bomb observations give the heat of combustion at constant volume and for saturation with water vapor at (nearly) constant temperature. Neither of these conditions is realized in the use of fuels, as for instance under a boiler, where combustion takes place at constant pressure and the products of combustion pass off at temperatures above the boiling point of water so that water vapor is not condensed. Observations with the bomb are therefore too high from both causes. The condensation of water vapor makes by far the largest part of this difference, and may be corrected for by determining the amount of water vapor condensed and subtracting its latent heat from the total heat observed in the bomb combustions. Evidently this amount will depend largely upon the relative amounts of carbon and hydrogen in the fuel, and theoretically, at least, the correction should be applied to make the results comparable for different fuels. The heats of combustion of standard samples are given for constant volume and for saturation with water vapor at nearly constant temperature.

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[1] W. P. White, Physical Review, **31**, p. 562; 1910.

6. EXAMPLE OF WATER EQUIVALENT DETERMINATION

Weight of benzoic acid sample	1.0007 g

(NOTE.—The weight of the sample should be such as to give about the same temperature rise as is commonly used in fuel combustions.)

Weight of water in calorimeter *	2700 g
Weight of water in bomb *	1 g
Pressure of oxygen in bomb *	30 atm
Weight of iron fuse wire (2 cm at 0.065 g per meter)	0.0013 g
Weight of nitric acid formed (found by titration)	0.020 g

Temperature Observations by Beckmann Thermometer

Before firing		**Middle period**		**After period**	
Reading	**Time**	**Reading**	**Time**	**Reading**	**Time**
1°431	11–55–00	2°05	12– 5–40	3°541	12–11–00
1.435	–56–00	2.75	– 6–00	3.540	–12–00
1.439	–57–00	3.25	– 6–20	3.539	–13–00
.....	....	3.40	– 6–40	.....	......
1.462	12–04–00	3.49	– 7–00	3.532	–20–00
1.466	–05–00	3.52	– 7–20	3.531	–21–00
Fired	–05–10	3.53	– 7–40		
		3.54	– 8–00		
		....	......		
		3.54	–11–00		

Temperature of outer jacket (constant)		16°3	
Reading of thermometer in calorimeter (at 12–05–00)	+1°466		
Correction to thermometer at this point	−0.005		
Corrected Beckmann reading		1°461	
Reading at beginning of after period	+3°541		
Correction to thermometer	+0.004		
Corrected reading		3°545	
Observed temperature difference		2°084	
Stem correction to thermometer		+0.002	
Radiation correction (computed from the customary formula)		+0.001	
Corrected difference of temperature			2°087
Heat of combustion of benzoic acid sample in calories per gram	6318		
Heat supplied by benzoic acid 1.0007×6,318		6322 cals.	
Heat supplied by formation of nitric acid equals 0.020×230=		4.6 "	
Heat supplied by formation of iron oxide equals 0.0013×1600=		2.1 "	
Total heat supplied			6329 cals.
Water equivalent of calorimeter as used equals 6329÷2.087=			3033 g

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* The same for all combustion determinations.

† For accuracy these temperatures should be obtained by means of a plot of several observations, or by some other device, so that they will depend not upon one but upon several thermometer readings.

7. SCHEDULE OF FEES

SCHEDULE 39

Calorimetry

(*a*) Standard combustion samples, of about 50 grams each, of sugar, naphthalene, benzoic acid, etc., accompanied by a certificate giving the heat of combustion of the sample, each	$2.00
On all orders for four or more combustion samples (alike or different) a reduction of 10 per cent will be made. Orders for samples should be accompanied by a remittance, which may be by check, draft, or post-office order, and should be payable to the Bureau of Standards.	
(*b*) Test of a combustion calorimeter (type of Berthelot, Mahler, Atwater, Peters, Williams, Emerson, Parr, Junkers, Sargent, Simmance-Abady, Boys, Fery, etc.), including a determination of the water equivalent for calorimeters of the bomb type and the corrections to the accompanying thermometers	25.00
(*c*) The fees for testing calorimetric and Beckmann thermometers will be found in Bureau of Standards Circular No. 8.	

S. W. STRATTON,
Director.

Approved:
BENJ. S. CABLE,
Acting Secretary.