CIRCULAR
. OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 11

THE STANDARDIZATION OF BOMB CALORIMETERS

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Accurate determination of the heats of combustion [1] of solids, liquids, and gases are usually made by means of a calorimeter of

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[1] The heat of combustion at constant volume of a substance containing only the elements carbon, hydrogen, and oxygen may be defined as the number of heat units liberated by the combination, in an inclosure of constant volume, of unit mass of the substance with oxygen to form carbon dioxide and water, the substance and the oxygen being initially at the same temperature, the products of combustion being cooled to the initial temperature, and the water formed by combustion being condensed to the liquid state. To be exact, the temperature at which the reaction takes place should also be specified, but the change of the heat of combustion with change of initial temperature is so small that this is not necessary for a temperature range between 15° and 30° C, temperatures at which experimental results are usually obtained. In practice also the initial and final temperatures are not usually the same, but differ by from 2° to 4° C. The effect of this difference is also small and is usually neglected, except that it is partly taken account of when the heat capacity of the combustible charge is included in that of the calorimeter. The term "heat of combustion" is also commonly used to denote the heat liberated by the oxidation of substances containing other oxidizable elements, such as sulphur, nitrogen, etc. When the term is so used, the definition must be extended so as to define the condition of the final oxidation products, as, for example, if sulphur is present, whether the resulting product is sulphur dioxide or sulphuric acid.

the Berthelot bomb type. In these calorimeters a known quantity or mass of the combustible is burned in oxygen under high pressure in a closed container or 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 (*a*) the mass of combustible, (*b*) the mass of water, including the equivalent mass, or water equivalent of the bomb, container, and accessories, (*c*) the rise of temperature, and (*d*) the so-called "radiation correction," i. e., the correction for heat transfer or *thermal leakage* between the calorimeter and its surroundings.

1. CHARACTERISTICS OF BOMB CALORIMETERS

Several makes of bomb calorimeters, including all the necessary equipment for measuring heats of combustion, are to be found on the market and a question often arises as to the relative accuracy of these equipments. The differences between the various makes are in general not of such a nature as to greatly affect the accuracy of the results obtained with them, but are rather differences in mechanical design which affect the convenience of manipulation, the cost of manufacture, etc.

Certain suggestions may be useful in the design or selection of a calorimetric equipment. The three essential parts of a bomb calorimeter equipment are:

(*a*) The bomb or container in which the combustible charge is burned.

(*b*) The calorimeter proper or vessel containing water in which the bomb, thermometer, and stirring device are immersed.

(*c*) The jacket used to protect the calorimeter from effects of variations in room temperature, air drafts, etc.

The following conditions should be realized so far as practicable:

(*a*) The **bomb** should be of sufficient strength to withstand a pressure of at least 500 or 600 atmospheres. The outer surface should be nickeled or otherwise finished so as to be protected from corrosion. The shape should be such as to allow free circulation of water between the bottom of the bomb and that of the calorimeter, as well as on all sides of the bomb. The inner surface of the bomb may be of platinum, gold, enamel, or other material not

easily attacked by the products of combustion. Linings may for convenience be made removable, but such removable linings should not be used in bombs intended for combustions of gases unless they are so arranged that none of the combustible gases can find their way between the lining and the body of the bomb. Of the materials so far used platinum is perhaps the best and most durable, although it is also the most expensive. Gold has not been extensively used, but might prove 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 small amount of exposed metal and the products of combustion may be still too small to be of importance. Nickel linings are attacked by acid formed during combustion and should only be used when the corrections for acid formed can be disregarded. Certain alloys, said to be very resistant to attack by products of combustion, have been used for the construction of bombs, which thus require no special linings. If the claims made for such bombs are justified, these bombs should be entirely satisfactory.

(*b*) The **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 may usually be omitted 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 more efficient than the other type and does not promote evaporation, as it has no reciprocating parts entering and leaving the water. Such a screw propeller should preferably have no bearing in the water of the calorimeter, and the metal parts, such as the shaft and the tube, which extend out of the calorimeter, should be separated from the metal parts above by some heat-insulating material to reduce the conduction of heat. It is important that the stirrer

run at a constant speed, and this should be provided for in the design of the apparatus.

(c) 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 measured and kept uniform. It is also advantageous to have this temperature controlled by means of a thermostat. 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 preferably be of polished metal and it, as well as the calorimeter surface, should be kept clean and bright. 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 between the room and the space inclosing the calorimeter. A cover of such highly conducting metals, if of sufficient thickness and in good contact with the metal top of the calorimeter jacket, serves as a very fair approximation to a completely isothermal inclosure for the calorimeter. With some types of bombs, however, such a cover is not feasible on account of the long valve stem at the top of the bomb. When the highest accuracy is required, the cover should be double walled and so arranged that the jacket water circulates through it.

During recent years the "adiabatic" calorimeter, which is so arranged that the temperature of the jacket may be continuously kept very nearly equal to that of the calorimeter, thereby avoiding or minimizing the radiation correction, has been extensively used in research laboratories.* A calorimeter of this type requires more elaborate equipment than the ordinary type and requires also some sort of manipulation, either automatic or manual, in order to maintain equality of temperature between calorimeter and jacket. If this equality of temperature is not well maintained, the accuracy attained may be less than that with which a cooling correction may be easily determined and applied. The method is admirably suited for use in research laboratories, but in its application to commercial instruments used in technical

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* Richards, Henderson, and Frevert, Proc. Am. Acad. of Arts and Sciences, 42, p. 573, 1907; Richards and Barry, Jour. Am. Chem. Soc., 37, p. 993, 1915; Benedict and Higgins, Jour. Am. Chem. Soc., 32, p. 461, 1910; Dickinson and Osborne, Bull. Bureau of Standards, 12, p. 23, 1915; Farrington Daniels, Jour. Am. Chem. Soc., 38, p. 1473, 1916.

testing serious difficulties are encountered, and so far as is known to the Bureau no adiabatic calorimeter is on the market.

The name adiabatic has been applied to another type of calorimeter in which a Dewar flask is used as the calorimeter vessel and is supposed to provide sufficiently good insulation to render thermal leakage negligible. Tests made at the Bureau have shown that calorimeters of this type have a coefficient of thermal leakage of the order of one-third that of ordinary calorimeters of the same size. When such a calorimeter is treated as adiabatic—i. e., when no correction is made for thermal leakage—it is practicable to keep the error due to thermal leakage below 0.5 per cent of the heat measured by choosing the initial temperature of each experiment, so as to make the final temperature approximately constant. Obviously, the accuracy could be increased by making a radiation correction. In addition to the limitations common to all calorimeters, the accuracy attainable with Dewar flask calorimeters is limited by the indefiniteness of the temperature of the surroundings (outer wall of flask) unless the flask is in a water bath, and by accidental variations in the amount of the inner wall included in the water equivalent.

For use to an accuracy of the order of 0.5 per cent calorimeters of this type are satisfactory and convenient if properly made. However, if higher accuracy is desired, a cooling correction becomes necessary, and equally careful use will probably yield as accurate or more accurate results with a well-designed water-jacketed calorimeter.

2. METHODS OF CALIBRATION

The use of a bomb-combustion calorimeter for determining the heats of combustion of fuels, etc., requires a knowledge of the total heat capacity or "water equivalent" of the calorimeter as it is used. This water equivalent includes the heat capacity of the calorimeter itself (i. e., the vessel which contains the water), of the water which it contains, of the bomb and its contents, and of parts of the thermometer, stirring device, and supports for the calorimeter. If a floating cover is used on the calorimeter, this also is included in the water equivalent.

The heat capacity of the water is its mass (observed weight corrected for buoyancy of air) times its specific heat. The specific heat depends somewhat upon the temperature and is here taken

as unity at 20° C, so that *the calorie is defined as the heat capacity of 1 gram of water per degree centigrade, at a temperature of 20° C.*

In the previous edition of this circular the calorie was defined as the heat capacity of 1 gram of water per degree centigrade at 15° C, instead of at 20° C as here used. There is a growing tendency to express results of calorimetric measurements in terms of the 20° calorie on account of the fact that this temperature more nearly represents average laboratory conditions and the fact that the heat capacity of water changes much less rapidly with temperature in this region. For these reasons the 20° calorie has been adopted for this and future editions of this circular.

The numerical values of heats of combustion expressed in 20° calories are about 1 part in 1000 greater than when expressed in 15° calories.

If the Btu were defined as the heat capacity of 1 pound mass of water at the same temperature (i. e., 20° C = 68° F), calories per gram would be convertible into Btu per pound by multiplying by the factor 1.8. In view of the facts that standard measurements in the English system of units are generally referred to 60° F (or 62° F in case of length standards), that weights of fuels are usually expressed as pounds weight (i. e., uncorrected for buoyancy of the air), and that common usage in the English system of measurements should perhaps have relatively more weight in definition than strict scientific accuracy, the Btu is here defined as the heat capacity of 1 pound weight of water per degree Fahrenheit at 60° F. To convert calories per gram to Btu per pound, according to the foregoing definition, it is necessary to multiply by 1.798 or divide by 0.556.

The water equivalent of a calorimetric outfit may be measured independently by several methods—as, for instance, by determining the heat capacity of its separate parts individually or by supplying heat, measured electrically, and determining the rise of temperature of the calorimeter, bomb, water, etc., as used. But in practice it is much more convenient to determine the water equivalent by the combustion of known amounts of some material, the heat of combustion of which has previously been determined accurately in a calorimeter calibrated by one of the methods referred to above.

The advantages of this procedure are that the calibration of one or two calorimeters can be performed with great care and to a high degree of accuracy in a laboratory possessing the equipment required for this kind of work, and after the heats of combustion of certain suitable materials have been thus determined these materials can be used in various laboratories under the same conditions which prevail in making fuel combustions. In this way the results obtained in different laboratories using the same standard samples are made more concordant and probably much more accurate than if each calorimeter were calibrated independently either at the laboratory in which it is to be used or even at a special testing laboratory—as, for instance, the Bureau of Standards. This is true because by the use of standard samples in the laboratory where the calorimeter is to be used, and by the same observers who are to use it, the minor details of observations are duplicated in both standardizations and fuel combustions, thus eliminating this source of small discrepancies; also because by the frequent use of standard samples it is possible to guard against errors such as might be introduced by changes in the apparatus or in the amount of water used and which might otherwise escape notice.

3. STANDARD MATERIALS

Among the materials available for standard combustion samples, sucrose or cane sugar, benzoic acid, and naphthalene have been most generally adopted. While any of these substances as procured from dealers in chemicals may be sufficiently pure for commercial calibrations, it is not safe to rely upon samples thus obtained, and the Bureau of Standards, after an extended study of the methods of preparation and the heats of combustions of these substances, is prepared to supply tested samples of any of these materials, as explained in the schedule of fees, page 18.

Sucrose is neither volatile nor strongly hygroscopic, but is rather difficult to ignite and occasionally 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 6330 calories, and burns more readily than sugar. The results obtained by different observers with this substance are also more concordant than with either sucrose or naphthalene.

Naphthalene is quite volatile, but not hygroscopic; it has a heat of combustion of about 9620 calories, a little higher than that of most coals, and it ignites and burns very readily. In its use some care is necessary to avoid errors due to sublimation.

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 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 have already been published.[2] The heats of combustion of other substances are being determined in the laboratories of the Bureau with a view to testing their suitability for use as standard combustion samples.

4. 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. A small amount of nitrogen is usually present in the oxygen, and an additional 3 per cent to 4 per cent is added when oxygen at 30 to 20 atmospheres pressure is admitted to the bomb originally containing air. It has recently been shown[3] that the presence of at least 5 per cent of nitrogen is desirable, since it has the effect of promoting the oxidation of the sulphur which is contained to some extent in most coals. Where coals are high in sulphur this amount of nitrogen should be present.

[2] Bulletin of the Bureau of Standards, 11, p. 189; 1914 (Scientific Paper No. 230).
[3] Regester, Jour. of Ind. and Eng. Chem., vol. 6, No. 10, p. 812; 1914.

(*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 usually be determined sufficiently well by inspection, as the presence of a few tenths of a milligram of soot can be readily detected. Some bombs are so constructed that the gaseous products of combustion can be conveniently removed and analyzed.

(*c*) The **charge** of a standard combustion sample should be 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. Failure to observe this precaution may lead to errors due to incomplete combustion. 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 preferable to use iron wire, although a small correction must be made for its heat of combustion (1600 calories per gram). A piece of No. 34 Brown & Sharpe gauge iron wire from 1 to 3 cm long may 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 of wire.

(*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 not advisable 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, accom-

panied by evolution of heat within the bomb. In any case it is important to close the firing circuit with a switch for only about one second, or as short a time as will serve to ignite the charge. When possible, an ammeter should be used in the circuit to indicate how much current is used and when the fuse wire has burned out. Small ammeters which will serve for this purpose can be bought for from $1 to $5.

(*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 usually serves only to maintain the *same* mass in all the observations (both calibrations and fuel combustions), and in this case it is not necessary to reduce to weight in vacuo.

(*g*) The **stirring** of the calorimeter water during an observation should be effected by some mechanical stirring device which can be made to run at a constant speed. Two types of stirrers in common use are described on page 5.

The amount of energy supplied by stirring should not be excessive. This may be determined by adjusting the temperature of the calorimeter to equality with that of the jacket and allowing the stirrer to run continuously for 10 minutes. If the temperature of the calorimeter rises more than about one hundredth of a degree in this length of time, the rate of stirring is excessive.

(*h*) **Temperature measurements** are usually 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 either of the graduated-stem type, with a scale covering a 10° to 15° C. range of temperature, graduated into 0°.05 or 0°.02 intervals; or of the Beckmann type, in which the scale covers a range of 5° or 6° C., graduated into 0°.01 intervals, 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 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 Circular No. 8. If an accuracy greater than about one or two parts in a thousand is required, recourse must be had to some instrument more accurate than the ordinary mercurial thermometer. An electrical resistance thermometer equipment affording greater accuracy has been put on the market. Such an equipment is more expensive than a mercurial thermometer. Thermometers of this type, which have been constructed at the Bureau of Standards, have been described in a recent publication.[4]

(*i*) A **cooling correction** or so-called radiation correction must be applied to calorimetric observations because 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 always proportional to the difference in temperature between the calorimeter and its jacket. This assumption is warranted provided the jacket is supplied with a cover (as described on p. 6) 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 the temperature of the calorimeter is not allowed to rise more than about a degree centigrade above that of the jacket, thereby avoiding any significant amount of evaporation from the calorimeter. A convenient method of computing the cooling correction is described under "Computation."

(*j*) The **lag of the thermometer** used in measuring temperatures has often been assumed to introduce an error requiring correction, but it may be shown that no such correction is required [5] under the usual conditions of combustion-bomb calorimetry.

(*k*) The formation of **nitric acid** from the nitrogen contained in the oxygen used for filling the bomb supplies an amount of heat equivalent to about 230 calories per gram of acid formed, and this amount is to be subtracted from the apparent total amount of

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[4] Bulletin of the Bureau of Standards, **9**, 483; 1913 (Scientific Paper No. 200).

[5] W. P. White, Physical Review, **31**, p. 562, 1910; and Bulletin of the Bureau of Standards, **8**, p. 659, 1912 (Scientific Paper No. 185).

heat due to the combustion. The amount of nitric acid formed can be found by titration, provided no other acids are present, which is substantially true for observations made with the standard combustion samples herein described.

5. MANIPULATION

(*a*) **Preparation of Sample.**—The material to be used for standardization should be removed from the container and compressed into a briquet of nearly the required weight, keeping the container closed except while removing the sample. The briquet should then be weighed (preferably in the crucible in which it is to be burned). If naphthalene is used, the briquet should be immediately placed in the bomb to avoid excessive sublimation.

(*b*) **Preparation of the Bomb.**—The firing wire, if of iron, should be measured and connected between the platinum terminals, using, if necessary, a piece of platinum wire somewhat heavier than the iron wire, to make the connection. The platinum and the iron must both be clean to insure good electrical connections. About 0.5 cc of water should be placed in the bottom of the bomb to saturate with moisture the oxygen used for combustion. When the crucible is put in place in the bomb, the firing wire should touch the briquet but not the crucible.

(*c*) **Filling the Bomb with Oxygen.**—Oxygen from the supply tank is to be slowly admitted until the required pressure of about 20 atmospheres for the larger bombs or about 30 atmospheres for the smaller bombs is reached.

(*d*) **Calorimeter Water.**—The amount of water to be used depends upon the type of calorimeter. Distilled water is preferable, and the amount should be determined by weighing. The amount must be kept the same as that used in fuel combustions, or a correction applied for the difference in weight.

(*e*) **Temperature Adjustments.**—The initial temperature in the calorimeter should be so adjusted that the final temperature, after the combustion, will not be more than $1°$ C., preferably about $0°3$ C, above that of the jacket, under which conditions the total correction for heat gained from or lost to the surroundings will be very small when the rise of temperature is $2°$ or $3°$ C. The effect of evaporation will also be small.

(*f*) **Method of Making an Observation.**—The bomb, when ready for firing, is to be placed within the calorimeter, the firing wires connected, the cover put in place, and the stirrer and thermometer so placed as not to be in contact with the bomb or container. The stirrer is then started and after the rate of change of the thermometer reading has become uniform, not less than two minutes after the stirrer is started, temperatures are read at one-minute intervals for five minutes, and the charge is then fired, noting the exact time of firing. Observations of temperature are then made at intervals depending upon the method to be used for computing the cooling correction. When the rate of change of temperature has again become uniform, a series of thermometer readings is taken at one-minute intervals for five minutes to determine the cooling rate.

(*g*) **Titration.**—After a combustion the bomb is to be opened, after allowing the gas to escape, and the inside examined for traces of unburned material or sooty deposit. If these are found, the observation should be discarded. If the combustion appears complete, the bomb is to be rinsed out and the washings titrated to determine the amount of acid formed. A correction of 230 calories per gram of nitric acid should be subtracted from the total heat observed.

6. COMPUTATION OF RESULTS

The following method of computation is recommended, to take the place of the Pfaundler or other similar formulas for computing the cooling correction (radiation correction). This method, described in full elsewhere [6] is there shown to give an accurate determination of the cooling correction as based on the assumption of Newton's law of cooling. The method is conveniently applied in the following manner:

Observe (1) the rate of rise (r_1) of the calorimeter temperature in degrees per minute for five minutes before firing, (2) the time (t_1) at which the last temperature reading is made and the charge fired, (3) the time (t_2) when the rise of temperature has reached six-tenths of its total amount (this point can be determined by

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[6] Bulletin of the Bureau of Standards, **11**, p. 189; 1914.

adding to the temperature observed at the time of firing 60 per cent of the expected temperature rise and noting the time when this point is reached,[7] (4) the time (t_3) of a thermometer reading taken when the temperature change has become uniform some five minutes after firing, and (5) the final rate of cooling (r_2) in degrees per minute for five minutes.

The rate r_1 is to be multiplied by the time $t_2 - t_1$ in minutes and tenths of a minute, and this product added (subtracted if the temperature were *falling* at the time t_1) to the thermometer reading taken at the time t_1. The rate r_2 is to be multiplied by the time $t_3 - t_2$ and this product added (subtracted if the temperature were *rising* at the time t_3 and later) to the thermometer reading taken at time t_3. The difference of the two thermometer readings thus corrected, provided the corrections from the certificate have already been applied, gives the total rise of temperature due to the combustion.

7. EXAMPLE OF WATER EQUIVALENT DETERMINATION

Weight of benzoic acid sample [8] (6329 cal_{20} per gram)..............grams.. 1. 2007
Weight of water in calorimeter [9].......................................do.... 2700
Weight of water in bomb [9]..do.... 0. 5
Pressure of oxygen in bomb [9]..............................atmospheres.. 30
Weight of iron fuse wire (2 cm at 0.065 g per meter).................grams.. 0. 0013
Initial temperature observed.. 1°46
Approximate rise of temperature 2°50; 60 per cent of rise............ 1°50
Temperature to observe at $t_2 = 1°46 + 1°5$ .... 3°0
Temperature of outer jacket (constant)............................ 20°3

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[7] When the temperature rise is not approximately known beforehand, it is only necessary to take thermometer readings at 40, 50, 60 seconds (and possibly 70 seconds with some calorimeters) after firing, and from these observations to find when the temperature rise had reached 60 per cent of the total. Thus, if the temperature at firing was 2°135, at 40 seconds 3°05, at 50 seconds 3°92, at 60 seconds 4°16, and the final temperature were 4°200, the total rise (temperature at firing minus final temperature) was 2°07; 60 per cent of it was 1°24. The temperature to be observed was then 2°14+1°24=3°38. Referring to the observations at 40 and 50 seconds, the temperatures were, respectively, 3°05 and 3°92. The time corresponding to the temperature of 3°38 was therefore

$$40 + \frac{3°38 - 3°05}{3°92 - 3°05} \times 10 = 45 \text{ seconds.}$$

[8] The weight of the sample should be such as to give about the same temperature rise as is commonly uesd in fuel combustions.

[9] These weights to be kept the same in all observations, both calibrations and fuel combustions.

Temperature Observations by Beckmann Thermometer

Time			Temperature	Thermometer corrections from certificate	Corrected temperature
	h	m	s	Degrees C	Degrees C	Degrees C
	12	00	00	1.446	....	....
	12	01	00	1.450	....	....
	12	02	00	1.455	....	....
	12	03	00	1.459	....	....
	12	04	00	1.462	....	....
Charge fired (t_1)	12	05	00	1.466	−0.005	1.461
(t_2)	12	05	48	3.0	....	....
(t_3)	12	11	00	3.961	0.000	3.961
	12	12	00	3.960	....	....
	12	13	00	3.959	....	....
	12	14	00	3.958	....	....
	12	15	00	3.957	....	....
	12	16	00	3.956	....	....

$r_1 = 0.020 \div 5 = 0.0040$ per minute; $(t_2 - t_1 = 0.8$ minute),

Initial temperature $= 1°.461 + 0.004 \times 0.8 = \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ $1°.464$

$r_2 = 0.005 \div 5 = 0.001$ per minute; $(t_3 - t_2 = 5.2$ minutes),

Final temperature $= 3°.961 + 0.001 \times 5.2 = \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ $3°.966$

Total rise of temperature $(3°.966 - 1°.464)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ $2°.502$

Stem and setting corrections to thermometer$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ $+0°.002$

Total corrected rise of temperature$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ $2°.504$

Total heat supplied by benzoic acid sample, $6329 \times 1.2007\ldots\ldots\ldots\ldots$ 7599

Heat supplied by formation of nitric acid 230×0.020 (0.020 found

by titration)$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ 4.6

Heat supplied by combustion of iron firing wire, $1600 \times 0.0013\ldots\ldots\ldots$ 2.1

Total heat supplied$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ 7606

Water equivalent $(7606 \div 2.504)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ 3038

8. BASIS FOR EXPRESSING RESULTS

The heats of combustion at constant volume of the purest samples of sugar, benzoic acid, and naphthalene which have been produced at the Bureau were found to be as follows:

<div align="center">

Cane sugar	3949 ± 2
Benzoic acid	6329 ± 1
Naphthalene	9622 ± 2

</div>

20° calories per gram of the substance weighed in air against brass weights.

These figures represent the total heat of combustion when all the water formed by combustion is condensed to liquid water at a temperature sensibly equal to that before combustion.   Correction has been made for the heat of formation of whatever nitric acid is produced by combustion, for the heat of combustion of the iron firing wire, as well as for the heat produced electrically in heating the wire up to its ignition point.

9. SCHEDULE OF FEES

Schedule 39.—Calorimetry.

[Note: The Bureau's supply of benzoic acid is at present exhausted, and, while efforts are being made to obtain a new stock, it is impossible at present (June, 1917) to state when this material will be available for distribution.   When the stock is renewed, announcement to this effect will be made through the usual channels.]

(*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

> Note.—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 of the corrections to the accompanying thermometer.. 25. 00

The fees for testing calorimetric and Beckmann thermometers will be found in Bureau of Standards Circular No. 8.

S. W. STRATTON,
Director.

Approved:
WILLIAM C. REDFIELD,
Secretary.