COMBUSTION CALORIMETRY AND THE HEATS OF COMBUSTION OF CANE SUGAR, BENZOIC ACID, AND NAPHTHALENE

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PART 1

I. INTRODUCTION

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°, 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°. 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.

Accurate determinations of the heat of combustion of a solid may be made by means of a calorimetric bomb of one of the several recognized types. These various bombs, while differing in mechanical details, consist essentially of a thick-walled metal vessel which can be opened for cleaning and the insertion of the substance, and closed tightly against 30 to 100 atmospheres pressure by means of a cover clamped or screwed in place. There is provision for filling the bomb with oxygen under pressure and for igniting electrically the charge of combustible.

The heat liberated by the combustion within such a bomb is measured by determining the rise of temperature of a known mass of water in which the bomb is immersed.

Apparatus of the above kind is now in use in many commercial laboratories and by users of fuel for the determination of the heats of combustion of fuels as a basis for purchase.

As is often the case where the same operations are repeated many times by the same observer, the relative accuracy (precision) of determinations made under such circumstances is often high, while the agreement between results found at different laboratories (i. e., true accuracy) is sometimes less satisfactory. In order to make it possible for different laboratories to express results of calorimetric determinations on a uniform and comparable basis, it was deemed desirable to determine accurately the heats of combustion of some chosen substances which can be reproduced with the requisite degree of purity and which can be used for calibrating the various forms of bomb calorimeters in use in commercial laboratories as well as by scientific investigators. This made necessary a careful study of the methods which are in use or which may be adapted for use in fuel calorimetry.

II. METHODS OF BOMB CALORIMETRY

Measurements of heat energy may be carried out by means of observations on the change of state or on the change of temperature of substances. Since only the latter method seems to be applicable to the problems in hand, that method only will be considered here.

Since there are no perfect heat insulators any calorimetric observation must necessarily involve a correction term to allow for heat transfers which take place within the calorimetric system, or some method must be used for eliminating such heat transfers. To reduce such corrections to a simple and determinate form it is well to consider a calorimetric system as consisting of two essential parts, first, a limited region containing a mass of known heat capacity the temperature of which is either uniform throughout or has some other known distribution as regards space and time; second, a surface surrounding and inclosing this region, and having a temperature either uniform and constant or at least known as regards space and time. The inclosed region will be spoken of as the "calorimeter" and the inclosing surface or vessel as the "jacket."

Four methods are applicable to the measurement of heats of combustion by means of a calorimetric bomb: First, the rise of temperature of the calorimeter, containing a stirred liquid, may be observed while the jacket temperature is kept constant; second, the temperature of the jacket may be kept the same as that of the calorimeter and only the initial and final temperatures measured (this method has been perfected by T. W. Richards at Harvard); third, the temperature of the calorimeter may be kept constant, as, for instance, by supplying cold water at the same time that the heat is being supplied (this method was used by Hesehus, of St. Petersburg, 1888); fourth, the temperature rise of the bomb itself may be measured, depending upon metallic conduction to equalize the temperature throughout its mass. This method has recently been applied by Féry to a specially constructed bomb for fuel combustion.[1] It might be applied with the jacket at a constant temperature or with the jacket at the same temperature as the bomb (calorimeter).

Of these four methods the first two are the only ones which have yet been largely used, and the first is the one which has been and probably will continue to be most used. This method was

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[1] Nernst has made use of a similar method during the past few years for the determination of specific heats, and similar apparatus has been in use at the Bureau of Standards for about the same length of time.

adopted for the present investigation, and the discussion of the sources of error on a later page will show that it affords about the same accuracy as the second method.

III. FACTORS AFFECTING ACCURACY

1. Temperature Measurement.—By far the most commonly used instrument for measuring temperatures in calorimetric experiments is the mercury-in-glass thermometer. The unavoidable errors of elastic aftereffect, of irregular capillary pressure and sticking of the mercury meniscus are not decreased by making the scale open and the bulb large as in calorimetric thermometers and with thermometers having a scale covering 10° or 15° and graduated to 0.02° the accuracy of a single measurement of a 2° temperature interval is hardly better than 2 or 3 parts in 1000. If a carefully calibrated Beckmann or other metastatic thermometer is used, the accuracy may possibly reach 1 part in 1000, the precision being somewhat higher in both cases. Some better method of temperature measurement is therefore necessary for precision calorimetry. This may be found in the adoption of either thermoelectric [2] or electrical resistance methods. The former has been brought to a high degree of perfection by White, of the Carnegie Geophysical Laboratory, while the latter has been developed to a very satisfactory condition at the Bureau of Standards and by Jaeger at the Physikalisch Technische Reichsanstalt. By either method an accuracy of 1 or 2 parts in 10 000 in the measurement of the above-mentioned temperature interval is attainable.

2. Stirring of the Calorimetric Liquid.—Vigorous stirring of the calorimetric liquid is necessary to keep the calorimeter at a uniform temperature throughout while heat is being rapidly supplied to it. There are two distinct functions of a stirrer, mechanically more or less incompatible: First, the whole mass of liquid in a calorimeter must be circulated, so that there are no stagnant portions; and second, there must be thorough mixing of the different portions of the liquid in order that a measurement of its mean temperature may be given by a thermometer of convenient size. Two forms of stirring apparatus are in general use, the ring stirrer,

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[2] Constancy of Thermoelements, White, Phys. Rev., 23, p. 449; 1906.

or some modification of it, having a reciprocating motion, and the screw-propeller stirrer. The former mixes thoroughly the smaller portions of the liquid but produces little positive circulation, so that certain portions of the liquid may be left nearly stagnant. It also has the disadvantage that the shaft alternately enters and leaves the surface of the liquid, thus promoting evaporation. The screw-propeller type of stirrer, on the other hand, properly applied, produces a rapid circulation of the whole mass of liquid, but may not so thoroughly mix the different portions—i. e., may permit definite stream lines. Such a stirrer can be mounted on a very small shaft and in such a way as not to promote evaporation.

A careful comparative study of the two methods of stirring, made at the Bureau of Standards by E. F. Mueller,[3] showed that the screw propeller produced temperature equilibrium throughout the mass of liquid in about half the time required when the other form of stirrer was used, and that the inequalities which persisted after a given time are very much less with the screw propeller. The energy dissipated by the screw propeller may be also much less than for the reciprocating stirrer. The screw in these experiments was mounted in a calorimeter shaped to adapt it to this type of stirrer. The design was similar to that described on page 210.

3. Heat Transfer Between Calorimeter and Jacket.—Heat transfer between a calorimeter and its jacket may take place in four ways—by conduction, convection, radiation, and evaporation (or condensation). Under ordinary calorimetric conditions some-

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[3] Mr. Mueller's experiments were made with the ring stirrer, as provided with the Peters calorimeter, and with the screw propeller in the calorimeter mentioned above. The temperatures at various positions in the calorimeter, during and after a period of heating electrically, were determined by means of a differential copper-constantan thermobattery consisting of five elements. One set of junctions was kept fixed while the other was placed in different positions. With the ring stirrer, differences of temperature of 0°.5 were observed one minute after the heating current had been switched off. These differences were reduced to 0°.001 only after from 7 to 10 minutes. Experiments with the screw stirrer, running at normal speed, gave differences of temperature during the first minute of from 0°.06 to 0°.08, or only about one-tenth as great as with the ring stirrer. These differences were reduced to 0°.001 within about 5 or 6 minutes after shutting off the heating current. It was also found that with the screw stirrer there was only a very small portion of the calorimeter which showed this lag in coming to temperature equilibrium, while with the ring stirrer a considerable part of the water was involved in the lag. The calorimeter, B. S. 7602, described on page 212, has a screw of larger diameter, which is run at slower speed than the one examined and the temperature of the water, as indicated by the resistance thermometer, appears to reach equlibrium to 0°.0002 within one minute after heating has ceased, when there is no large mass of metal, such as a bomb, which may cause a lag apart from that due to the stirring.

thing like one-fifth of the heat is transferred by radiation, about four-fifths by convection and air conduction, and only a very little by evaporation.

In the calculation of corrections for the transfer of heat it is generally assumed that Newton's law of cooling holds over the small range of temperature in question. That this assumption is only approximately true has been shown repeatedly by experiment and can be seen from theoretical considerations. In so far as radiation is involved the heat transfer is proportional to the difference of some higher power (about the fourth power) of the absolute temperatures of the two surfaces.

The heat transfer by convection and air conduction can hardly be considered from a theoretical basis, because it depends largely upon the shape and size of the surfaces involved. For small temperature differences, however, Newton's law is a very close approximation.[4] The transfer of heat by conduction and convection is nearly proportional to the temperature difference after steady state is reached.

With the heat transfer by evaporation and condensation, however, conditions are very different. If a free liquid surface forms part of the calorimeter and no corresponding free liquid surface is present at the temperature of the jacket, there will be no transfer of heat by evaporation so long as the calorimeter temperature is sufficiently below that of the jacket, as there will be no condensation of vapor on the warmer surface, and there will be no vapor lost to the space outside if the jacket is closed; but when the temperature of the calorimeter rises above that of the jacket, vapor is condensed on the cooler surface of the jacket and supplied from the free liquid surface, taking heat from the calorimeter. There is thus only a very small loss of heat from the calorimeter, due to the formation of enough vapor to keep the surrounding space saturated at the rising temperature until the temperature of the calorimeter is near that of the jacket, then there is increasing loss of heat by evaporation as the temperature rises. Since this heat

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[4] Some later observations have shown that this is by no means as nearly true when there is a considerable air space between the calorimeter and the jacket as it is in the present calorimeter, where the air space is reduced to a uniform width of about 1 cm.

transfer does not follow a simple law, it should be prevented so far as possible.

Observations have shown that the assumption of Newton's law or that $\frac{d\theta}{dt} = -k(\theta - \theta_0)$ where θ is the temperature of the calorimeter, θ_0 the temperature of the jacket, t the time, and k a constant, is justified for ranges of a few degrees in temperature provided k is determined from observations taken at the two temperatures between which the formula is to be applied. In most calorimetric measurements, however, the principal quantity observed is a temperature change produced mainly by energy liberated or absorbed within the calorimeter, while the above equation, representing the assumption usually made, takes account of only such temperature changes as are produced by convection, air conduction, radiation, etc. The complete differential equation for the temperature in a calorimetric observation would be $\frac{d\theta}{dt} = f(t) - k(\theta - \theta_0)$ where $f(t)$ is the rate of temperature change produced by the energy supply which is the subject of the experiment. The integral of this is the main quantity to be measured and is usually much larger than the term $k\ (\theta - \theta_0)$, which is a correction term. The assumption $k = \text{constant}$ permits the simple solution:

$$\theta = \theta_0(1 - e^{-kt}) + \int_0^t f(t)dt$$

when $\theta = 0$ and $f(t) = 0$, at time $t = 0$. The temperature at any time is simply the original temperature plus the temperature change due to the heat supplied plus the cooling correction. However, if k is a function of time, the equation can not in general be solved. The solution would take the form

$$\theta = \theta_0(1 - e^{-\int k(t)dt} + e^{-\int k(t)dt} \int_0^t e^{k(t)dt} f(t)dt)$$

in which $k\ (t)$ occurs in the main term, so that even an approximate solution is not easily obtained. The value of k can in general be determined only at times when the term $f(t) = 0$ and the fact that observations taken under these conditions indicate that the assumption $k = \text{constant}$ is sufficiently accurate, by no means proves that the same assumption is justified when $f(t)$ is large, i. e., when the rate $\frac{d\theta}{dt}$ is large.

It will be seen in the following discussion that k in the above equation is a function of the time, $k(t)$, to an extent which can not be neglected unless certain conditions are fulfilled. Of the four modes of heat transfer, radiation alone can physically correspond to the condition $k(t) = \text{constant}$ (i. e., k independent of time). The effect of evaporation can be eliminated. The effect of conduction and of convection on $k(t)$ will be considered separately.

4. Conduction and its Effect on k (t).—Although the amount of heat transferred between calorimeter and jacket by conduction other than through the air is usually small, under certain conditions the effect on k may be very large. For example, if two objects placed on opposite sides of a plate of insulating material are at different temperatures, the rate of heat transfer between them—therefore the rate of temperature change of either with respect to the other (neglecting outside influences)—will become sensibly proportional to the temperature difference. If, however, the temperature of either is changing rapidly, due to an external cause, the rate will no longer be even approximately proportional to the temperature difference.

The most common cause of errors due to conduction is the presence of a sheet of poorly conducting material interposed between the calorimeter and the jacket, as when the calorimeter is supported on a rubber or cork block, or when an attempt is made to reduce the heat transfer by using some form of insulating material, as was often done up to a few years ago. Since the conductivity of such materials is always small, compared with that of the metallic sheets in contact with them, the temperatures of the surfaces may be taken, for the purposes of this discussion, as approximately the same as the measured temperatures of the calorimeter and the jacket, respectively. The distribution of temperature in such a layer and the rate at which heat is leaving the calorimeter at any time may then be determined from the following considerations:

A sheet of material of thickness c bounded by plane surfaces x_0 and x_1, is initially at temperature θ_0. If x_0 and θ_0 are each taken as 0 for convenience, and the temperature of one of the surfaces x_1 is then caused to rise from θ_0 to θ' in such a way that $\theta = \theta'(1 - e^{-\alpha t})$, the temperature distribution in this plate is given by the following: [5]

$$(1) \qquad \theta = \frac{x}{c} \cdot F(t) + \frac{2}{\pi} \sum_{1}^{\infty} \left[\frac{(-1)^m}{m} \cdot \sin \frac{m\pi x}{c} \left(F(t) - \frac{m^2 a^2 \pi^2}{c^2} \int_0^t F(\lambda) \, e^{\frac{-m^2 a^2 \pi^2}{c^2}(t-\lambda)} \, d\lambda \right) \right]$$

Where a^2 is the *thermometric* conductivity of the material.

$F(t)$ is the temperature of the face $x_1 = c$, taken here as $\theta'(1 - e^{-\alpha t})$.[6]

The point of interest in this discussion is the rate at which heat is leaving the calorimeter at any time, as this determines the value of k for the portion of the surface in question. If θ' and c are each made unity, and the above expression for θ is differentiated with respect to x, the following expression for the temperature gradient at any point in the material is found:

$$(2) \qquad \frac{d\theta}{dt} = 1 - e^{-\alpha t} + 2 \sum_{1}^{\infty} (-1)^m \cos m\pi x \left(e^{-\alpha t} - e^{-m^2 \pi^2 a^2 t} \right) \frac{\alpha}{m^2 \pi^2 a^2 - \alpha}$$

The surface $x = 1$ is the surface in contact with the calorimeter, so that substituting this value of x and the appropriate values for a^2 and α, the above expression gives the temperature gradient in the material in contact with the calorimeter, which is proportional to the factor k for this portion of the surface.

For an example showing the effect of this kind of distribution of material, suppose that the calorimeter rests on a sheet of hard rubber 1 cm. thick. The temperature in the calorimeter used for the present investigation, when containing a bomb in which a

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[6] Byerly; Fourier's Series and Spherical Harmonics, p. 110.

[6] This equation represents quite approximately the temperature rise of a calorimeter containing a combustion bomb in which a charge is burned.

charge of combustible is burned, rises quite approximately according to the relation $\theta - \theta_i ; = (1 - e^{-\alpha t}) (\theta_1 - \theta_i)$ where $\alpha = 0.03$ and θ, θ_i and θ_1 represent, respectively, the temperature at any time, the initial, and final temperature. The value of a^2, the thermometric conductivity, for hard rubber is approximately 0.001 in cgs units. These quantities substituted in the above equation show that after 60 seconds the rate of heat loss is 2.75 times its final value, after five minutes the rate is 1.13 times the final value, and only after 10 minutes does it come to within 1 per cent of its final value. If the area in contact with such a sheet were a considerable part of the whole area of the calorimeter, the error introduced from this cause evidently would be a very serious one.

Such a distribution of material as here discussed will also have an effect on the heat capacity of the calorimeter, similar to that discussed on page 204 et seq.

This discussion shows that all nonconducting supports should be negligibly small or, since the thermometric conductivity $a^2 = \frac{K}{c\rho}$ (the absolute conductivity K divided by the specific heat (c) and density (ρ)), the material used for them should have a small density and specific heat. A form of support is therefore indicated, in which the smallest possible mass of insulating material is used, with the smallest possible area in contact with the calorimeter. The mass of such supports can readily be made negligible compared with that of the calorimeter.

5. Convection and Radiation, and their Effects on k (t).—Since the greater part (about 4/5) of the transfer of heat between a calorimeter and its jacket is generally due to convection and conduction in the intervening layer of air, it is important to consider the nature and rate of establishment of convective equilibrium. Evidently the establishment of complete equilibrium for any given temperature distribution requires time. Hence, if the temperature distribution is rapidly changing, this equilibrium will not be established, or rather will lag behind the temperature distribution over the surfaces and the observed value of $k(t)$ may be in error. This subject can not readily be treated from a theoretical basis and an experimental investigation of it is given on a later page.

With some distributions of material, however, the value of k may be dependent upon the time, because of both convection and radiation. Consider a calorimetric system in which certain masses of material, with considerable area and good conductivity, are interposed between the calorimeter and the jacket, such, for instance, as metallic shields to decrease radiation, or parts of the jacket not maintained at a definite temperature, but allowed to take up a temperature dependent upon the surroundings. It will be assumed that the rate at which heat passes between a calorimeter and its jacket is dependent upon the nature and form of the surfaces and the temperature differences, and not very much upon their distance apart unless this distance becomes small. In a calorimetric system of the usual dimensions the air space, as found by experience, should not be much less than 1 cm in width for this assumption to hold.

Suppose a mass m of material, the specific heat of which is c' and the superficial area is s, situated in the neighborhood of other surfaces, in the present case two, one of which is at constant temperature and the other at a temperature which may be changed. If the system is initially in a steady state and the temperature of one of the surfaces is suddenly changed to another steady value, the mass m will eventually take up some temperature differing from the initial one and depending upon the existing distribution of temperature in the system. Let this equilibrium temperature be θ_e, then the temperature θ of the mass m at any time will be given by a solution of the equation $\frac{d\theta}{dt} = -\phi(\theta - \theta_e)$; that is, $\theta = \theta_e + ce^{-\phi t}$. If $\theta = 0$ when $t = 0$, the equation gives $\theta = \theta_e(1 - e^{-\phi t})$. If ϕ' and ϕ'' are respectively the cooling constants of the mass m with respect to the calorimeter, and the jacket, and θ' and θ'' are the temperatures of the calorimeter and the jacket, the equilibrium temperature θ_e of m will be given by the relation

$$(\theta' - \theta_e)\phi' = (\theta_e - \theta'')\phi''$$

$$\text{(3)} \qquad \text{whence } \theta_e = \frac{\theta'\phi' + \theta''\phi''}{\phi' + \phi''} \text{ or if } \theta'' = 0,\ \theta_e = \frac{\theta'\phi'}{\phi' + \phi''}$$

For instance, if the calorimeter, the shield (m), and the jacket were concentric spherical surfaces, ϕ' would be nearly proportional to the solid angle subtended by the calorimeter at m and ϕ'' to the angle subtended by m at the jacket. If ϕ is nearly independent of distance, since the temperature of m at any time is $\theta = \theta_e(1 - e^{-\phi t})$ and the temperature of the calorimeter is θ', the rate of temperature change of the calorimeter due to the presence of m alone is as follows:

$$\left(\frac{d\theta'}{dt}\right)m = -h\phi' \, (\theta' - \theta) \tag{4}$$

where h is the ratio of the heat capacity of m to that of the calorimeter, and the change in θ' is small compared with the quantity $(\theta' - \theta)$. Substituting the values of θ and θ_e from the foregoing equations

$$\begin{aligned} \left(\frac{d\theta'}{dt}\right)m &= -h\phi' \left[\theta' - \theta_e \, (1 - e^{-\phi t})\right] \\ &= (-h\phi') \left[\theta' - \frac{\theta' \, \phi'}{\phi' + \phi''} \, (1 - e^{-\phi t})\right] \\ &= -h \left[\frac{\theta' \, \phi' \, \phi''}{\phi' + \phi''} \, (1 - e^{-\phi t})\right] \end{aligned} \tag{5}$$

The above equations show some interesting facts. If m is a sheet halfway between extended parallel surfaces of the calorimeter and the jacket and not too near either, $\phi' = \phi''$, the loss of heat from the calorimeter over this portion of the surface will, by equation 3, be half of what it would be if the sheet were not there, since the temperature difference between the calorimeter and m is only half that between the calorimeter and the jacket. This will be approximately true when the outside area of the calorimeter is not much less than that of the jacket. The errors which may be introduced, however, by an attempt to utilize this fact for reducing the rate of heat loss are evident from the following example:

A sheet of metal having a heat capacity of 0.8 calorie per cubic centimeter per degree, a thickness of 0.03 centimeter and polished surfaces from which heat will be lost by radiation, conduction, and convection at the rate of 0.0001 calorie per second per square centimeter per degree difference in temperature, will have a cooling constant $\phi = 0.012$ degree per second. Substituting this value of ϕ in the above equation for rate of temperature change, the rate four minutes after the calorimeter temperature is changed from 0° to 1° will be 10 per cent, and after eight minutes 1 per cent greater than the final value. The same sort of an effect is present whenever the temperature of either the calorimeter or the jacket is changed.

The above figures would apply approximately to a calorimeter placed within a thin metallic vessel, when the walls of the room correspond to the constant temperature jacket. The conditions may be even worse when the containing vessel is of insulating material, such as a fiber pail, the kind of vessel often used for this purpose. With any such arrangement the cooling constant is a function of the time to a serious extent.

Ordinarily for precise observations the calorimeter is surrounded by a double-walled metallic vessel containing a large mass of water, preferably kept stirred. The inner surface of this metallic vessel is properly considered as the constant temperature jacket. This outer vessel can, however, evidently be considered as m in the above treatment, the walls of the room being taken as the constant temperature jacket. The heat capacity of such a double-walled vessel is from 200 to 400 times as great as for the metallic sheet discussed above, and in this case ϕ (the reciprocal of the time lag) becomes so small (about 0.00003) that the term $(1-e^{-\phi t})$ is practically 0; i. e., the change of temperature in 10 minutes is about 2 per cent of the total change which would take place. This is generally unimportant and can be corrected for if necessary. Such a jacket as this, however, is often provided with a cover of thin hard rubber or other material which is not kept at the temperature of the jacket itself. The effect of such a cover on the value of k can be seen from the above considerations.

The foregoing discussion shows that although Newton's law may represent with sufficient accuracy the behavior of a calorimeter when no heat is being produced or absorbed within it, the additional assumption that the same expression may be used for the heat interchange between the calorimeter and its surroundings, when heat is being produced or absorbed within, is not in general justified. In order that this assumption shall be justified it is necessary that any mass of material between the calorimeter and the jacket which may possess an indefinite intermediate temperature shall be small or that the difference in temperature between it and either the calorimeter or the jacket shall be small.

6. Lag of Thermometer.—In the foregoing discussion it has been assumed that the thermometer immersed in the calorimeter measured at every instant the true temperature of the outer wall of the calorimeter. This is never strictly true on account of the so-called time lag of the thermometer and of the calorimeter wall. If the calorimeter liquid is vigorously stirred and the material of the walls is thin and of high conductivity, probably the lag of the outer surface behind the temperature of the liquid itself is negligible. The lag of mercurial thermometers, which are suitable for calorimetric observations, is, however, from 5 to 8 seconds. The time lag of a thermometer may be defined as the number of seconds intervening between the time that the uniformly rising temperature of a given medium reaches a certain value, and the time that the thermometer immersed in that medium indicates this same temperature. It is not a constant for a given thermometer but depends upon the nature and rate of stirring of the medium in which the thermometer is immersed. As the rate of stirring increases the lag of a given thermometer approaches a constant value. In the case of the resistance thermometers, to be described later, the lag has been reduced probably to less than 0.5 second, but since the corresponding lag of the galvanometer used in measuring the resistance is approximately two seconds, this practically determines the time lag of the temperature-measuring system.

White [7] has shown that the lag of the thermometer introduces no error in the results of a calorimetric observation, provided the same thermometer is used throughout the observation. The subject of thermometric lag has been considered in detail by Harper.[8]

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[7] Phys. Rev., **21**, p. 562; 1910.

[8] This Bulletin, **8**, p. 659; 1912 (Reprint No. 185).

7. Boundary of the Calorimeter.—The heat capacity of a calorimeter at a given temperature may be defined as numerically equal to the number of heat units required to raise the temperature of the calorimeter 1° at this temperature.

The discussion on pages 198 to 203 indicates the effect of matter distributed between the calorimeter and the jacket, on the time required for the establishment of temperature equilibrium. It is evident, however, that such matter, independently of the time it takes to reach equilibrium, affects the heat capacity of the calorimeter as defined above. Referring to page 200, it will be seen that when the temperature of the calorimeter rises from 0 (that of the jacket) to θ', the temperature of the conducting mass between the calorimeter and the jacket eventually rises from 0 to $\frac{\theta'\phi'}{\phi'+\phi''}$ and if its mass is m and its specific heat is c, an amount of heat $mc\,\frac{\theta'\phi'}{\phi'+\phi''}$ has been taken from the calorimeter in establishing such temperature equilibrium. The heat capacity of the calorimeter is therefore increased by an amount $\frac{mc\phi'}{\phi'+\phi''}$ on account of the presence of the mass m, since $\frac{\phi'}{\phi'+\phi''}$ is the rise of temperature of m per degree rise of temperature of the calorimeter. If the mass m is in the form of a sheet or rod of uniform section extending between the calorimeter and the jacket (considering conduction only)—i. e., neglecting radiation—$\phi'=\phi''$ and the amount to be added to the heat capacity is $\frac{1}{2}\,mc$.

It is necessary in practice to have certain masses, such as a thermometer stem, stirring shaft, and electrical connections, which extend from the calorimeter. If such parts pass through the jacket and are kept at the temperature of the jacket where they enter it on the side toward the calorimeter, their effect on the heat capacity is that just discussed, i. e., neglecting the effect of radiation, etc., which would, in general, be small, there must be added to the heat capacity a correction, $\Sigma\frac{1}{2}mc$.

If, however, such extensions from the calorimeter are long and the outer portions reach equilibrium with the surrounding air—i. e., if they pass out through free openings in the jacket—

the amount which needs to be added to the heat capacity of the calorimeter to correct for them can be computed in the following manner:[9]

If the calorimeter is at a given temperature and the portion extending from it into a medium at a different temperature is uniform in section and the temperature can be taken as uniform over any cross section, after equilibrium is reached, the temperature at any distance, x, from the calorimeter is given by a solution of the equation

$$\frac{d^2\theta}{dx^2} = a^2\theta \qquad \text{where } a^2 = \frac{HP}{KA}$$

in which H is the surface emissivity (about 0.0001 cal. for polished nickel or copper).

P is the permimeter of the section,
K is the absolute conductivity,
A is the area of the section.

If the outside temperature is 0 and that of the calorimeter is θ', the required solution is

$$\theta = \theta' e^{-ax}$$

If the temperature of the calorimeter was initially 0 and was raised to θ', the temperature of the extending rod is also raised, and the heat necessary to raise the temperature of any section dx from 0 to θ is

$$\theta \rho c A\, dx$$

where ρ and c are the density and specific heat of the material. The total amount of heat Q taken from the calorimeter is, substituting for θ the value given above,

$$Q = \int_0^\infty \theta' \rho c A e^{-ax} dx$$

$$= \frac{1}{a}\theta' \rho c A = \theta' \rho c A \sqrt{\frac{KA}{HP}}$$

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[9] In this discussion it is assumed that the heat capacity of the calorimeter before correcting for any extended or extraneous matter is the heat capacity of the material comprised within the constant temperature surface which has been defined as the calorimeter.

but the heat required to raise the temperature of unit length of the material from 0 to θ' is $\theta'\rho cA$, so that a length $\sqrt{\frac{KA}{HP}}$ of this material must be considered as a part of the calorimeter, i. e., the heat capacity must be increased by $A\rho c\sqrt{\frac{KA}{HP}}$ on account of the presence of this extended portion.

For example, a copper wire of circular section 2 mm in diameter dipping into a calorimeter would add to the heat capacity an amount equal to nearly 7 cm of the wire, i. e., about 0.2 gram of water, since H for bright copper is 0.0001, K is 0.9, and $\frac{A}{P}=\frac{r}{2}$.

8. Richards's Method of Avoiding Cooling Corrections.—This method, as mentioned before, consists in causing the temperature of the jacket to be continually equal to that of the calorimeter. A consideration of the foregoing discussion as to the effect of various distributions of material on the cooling rate and heat capacity of the calorimeter, will show that most of the errors and uncertainties would remain nearly the same in this as in the foregoing method of procedure, but the errors due to these causes can be made negligibly small in either case. The relative accuracy of the method of constant jacket temperature and the method of varying jacket temperature reduces nearly to a question of the accuracy of observing a rapidly rising temperature relatively to that of keeping the temperature of a second mass of liquid always the same as the rapidly rising calorimeter temperature. The time lag of the thermometric device has been shown to introduce no appreciable error. The Richards method has the apparent advantage that the initial and final temperatures are constant while in the other method they are slowly changing. This is not advantageous with mercurial thermometers but is so with resistance thermometers or thermocouples. Even if there is some advantage in constant initial and final temperatures it would seem that this advantage may be offset by the unavoidable errors in causing the temperature of one bath to remain constantly equal to that of another, which is changing rapidly in a manner which can not always be readily predicted. In order to maintain the required condition of temperature equality it is necessary either to know the form of the arbitrary function representing the rise of temperature of the calorimeter or to follow it with some thermometric device, constantly adjusting the jacket temperature to it; but these operations are equivalent respectively to the thermometric problem of plotting the mean form of the arbitrary temperature rise or plotting its form for a given observation. Any error in maintaining the required temperature in the jacket therefore seems to be added to the errors inherent in the constant jacket temperature method, unless the temperature difference between the calorimeter and the jacket is determined at frequent intervals and a cooling correction applied. When a chemical reaction takes place similarly at the same time in the calorimeter and jacket, the varying jacket temperature has advantages in convenience and perhaps in accuracy. When correction is made for temperature difference, as described above, this method is also advantageous where very large temperature intervals are used or where long-time intervals are required or where electrical calibration methods are used in such a way as to permit of raising the temperature of the calorimeter and the jacket at the same, nearly linear, rate.

9. Lag of Convection Currents.—The effect of the time lag of convection currents in the air has been referred to previously. (See p. 199.) This lag can not be computed from present knowledge of the properties of the air layer, and its magnitude has theretofore been largely a matter of conjecture. The uncertainties in calorimetric measurements from this cause may be negligible, but seem not to have been investigated.

If it is assumed that the heat transmitted between two surfaces near together is proportional to the mean temperature gradient in the layer of air between them, then, if the temperatures of two different portions of the air layer, one near each surface, can be determined, the rate of heat transfer between the two surfaces at any time may be computed from this observed temperature difference. Such measurements of the temperature of the air can be made by measuring the resistance of very fine wires exposed to the air. Moreover, if platinum wires, the surface of which is nearly like that of the calorimeter and jacket, are used for this purpose, the effect of radiation on their temperature should not affect the validity of the assumption that the difference of temperature between the wires is proportional to the heat transfer between the surfaces, since this assumption would be true for the effect of radiation alone.

A differential thermometer was built to fulfill the above necessary conditions. The thermometer consisted of two platinum wires 0.05 mm in diameter and about 20 cm long stretched between small ivory supports in such a way that when placed between the calorimeter and jacket the two wires were about 1 mm distant respectively from the surface of the calorimeter and the surface of the jacket. The two wires were connected in adjacent arms of a Wheatstone bridge, so that the difference of their resistances was directly measured.

A series of observations was made with this differential thermometer and the results are shown on Fig. 10, explained on page 222. This series of observations showed that during the middle period the differential thermometer indicated a given temperature difference two and one-half seconds later than did the calorimeter thermometer. The effect of an error of two and one-half seconds in the time of all observations during the middle period would be to introduce an error of about 7 parts in 100 000 in the results. But the lag of convection currents seems to be somewhat, if not entirely, analogous to that of calorimetric thermometers, which itself produces no error in the results. For this reason it is assumed that the lag of convection currents in the present calorimeter produces no error greater than 7 parts in 100 000.

The above experimental method required that the thermometric lag of the differential and the calorimeter thermometer be the same, as was the case in this instance since the same galvanometer was used with both, and the lag of either thermometer of itself was negligible.[10]

IV. PRINCIPLES OF CALORIMETRIC DESIGN

1. General Requirements for a Stirred Liquid Calorimeter.—Such a system should consist of a calorimeter the outer surface of which has always at all points the same temperature as has the

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[10] The lag of the differential thermometer computed from the heat capacity of the wire and the energy required to hold it at a given temperature, above that of the air, is of the order of 0.01 second. The lag of the calorimetric resistance thermometer has been discussed.

liquid within, and a closed jacket which has always and at all points a temperature either constant or equal to that of the surface of the calorimeter, or a temperature uniform over the surface and which is known at all times. The calorimeter should be separated from the jacket by a distance of about 1 cm and held in place in such a way that the materials between them shall have a negligible or at least calculable time lag in coming to temperature equilibrium. These materials should also have a heat capacity negligible, or as small as possible, since their heat capacity enters as a rather uncertain addition to that of the calorimeter. The liquid within the calorimeter should be the standard substance—water—and should be so well stirred that its temperature is always sensibly uniform throughout. The amount of energy used in stirring should be constant and as small as possible. The entire surface of the calorimeter should be in contact with the liquid and no considerable part of the liquid surface should be exposed to permit evaporation, or if any part is so exposed, its temperature should never exceed that of the jacket, unless conditions are carefully considered to make sure that the effect of evaporation is negligible.

2. Size of the Calorimeter.—The choice of size for a calorimeter is determined by the relative accuracy attainable in the measurement of certain quantities. The heat capacities of similar calorimeters are proportional to L^3 where L is a linear dimension, the cooling surface to L^2, and the rise of temperature to L^{-3}. Taking the supply of energy to be constant, as must be done in the present case, for a given combustion bomb, the percentage heat interchange is proportional to L^{-1}. The ratio of the heat loss to the total heat supplied is inversely proportional, therefore, to the dimensions. In addition the assumption of Newton's law of cooling is probably more nearly correct for small temperature differences. From this it appears that the controlling factor in determining the dimensions of a calorimeter, once the supply of energy is known, is the accuracy of the temperature measuring device. The dimensions should be such that the temperature rise is as small as can be measured with the required accuracy, with the thermometric apparatus to be used.

V. THE CALORIMETRIC SYSTEM USED

The principles stated in the previous pages have been applied in the construction of two calorimetric outfits and in the adoption of methods which are to be described. Figs. 1 and 2 show sectional views of the elevation and plan of the second of these calorimeters, B. S. 7602, with its jacket and immediate accessories. The earlier form was similar to this, except for details which have greatly increased the convenience of operation and have somewhat increased the precision of observations.

1. The Calorimeter Proper.—The calorimeter C is made of thin copper, in the form shown in Fig. 3, to facilitate stirring. The extended portion which contains the stirrer S, Fig. 2, is separated from the main body of the vessel except near the top and bottom, forming a tube, the bottom of which is inclined and curved so as to direct the downward stream from the stirrer smoothly into the main body of the calorimeter. The stirrer S consists of a thin shaft of gold-plated steel on which is mounted a screw propeller made entirely of copper, except for a trifle of solder, and gold plated. The part of the calorimeter over the stirrer is closed by means of a copper cover having an opening only large enough for the stirring shaft. The stirrer thus always remains in the calorimeter.

Since it is important to avoid, so far as possible, evaporation of the calorimeter liquid, the main portion of the calorimeter, which must be accessible, is provided with a cover (Fig. 3 L) which fits the calorimeter vessel closely and has three openings, one for the thermometer and two for leads to the bomb or to the resistance coil M used in calibration. From the previous discussion it is evident that this cover should be in contact with the water. The cover is therefore made in the form of an inverted open dish with collars soldered around the necessary openings. The material is very thin copper.

All the copper surfaces are nickeled and polished to reduce radiation. There are no parts such as hooks or handles extending from the calorimeter and no part except the small cover at S and the necessary margin of a few millimeters at the top which is not in contact with the stirred liquid. The temperature of the outer

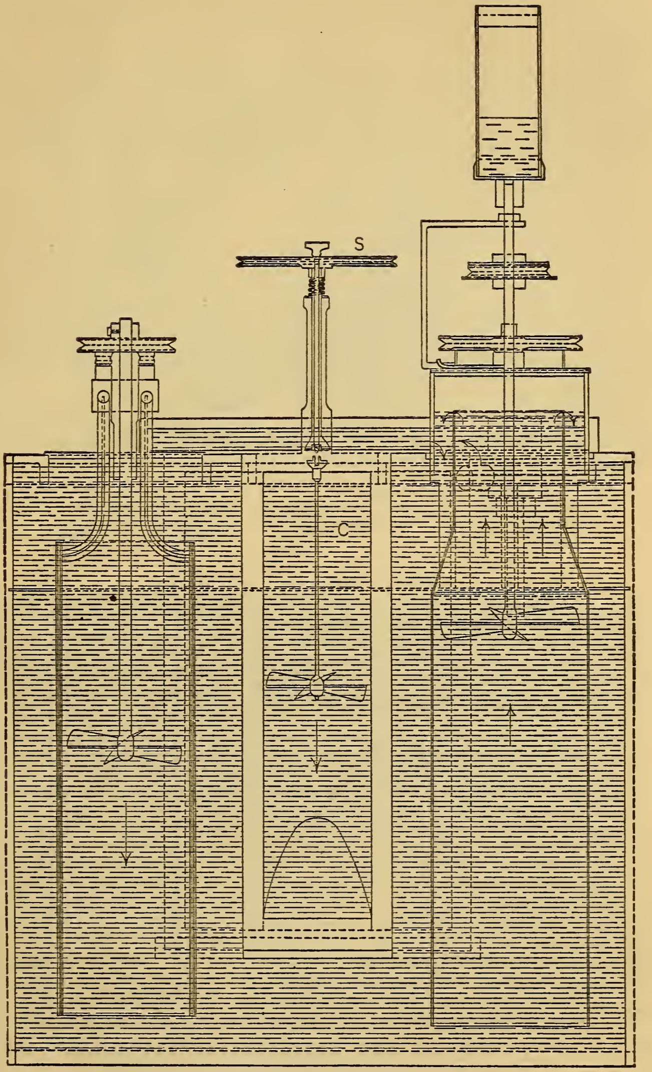

FIG. 1.—*Section of calorimeter and jacket*

surface can not, therefore, differ greatly from that of the liquid within.

During the process of building the calorimeter and the coil M (Fig. 3) which is used with it, the materials, almost entirely copper, which entered into the construction, were carefully weighed in order that the heat capacity of these parts which are not removable might be known from the mass and specific heat of the materials.

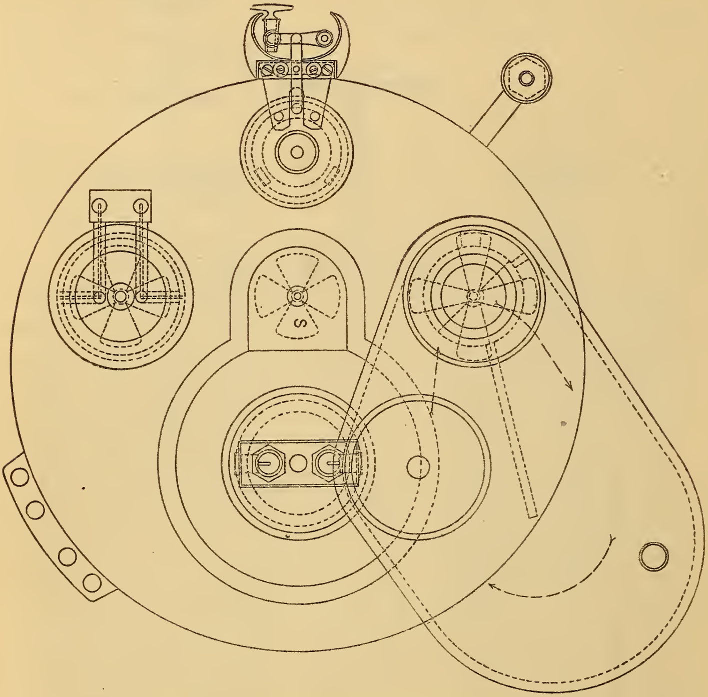

FIG. 2.—*Plan of calorimeter and jacket showing bomb in place*

2. The Constant Temperature Jacket.—The required constant temperature surface is supplied by the inner surface of the water jacket (Figs. 1 and 3). The distance between this and the surface of the calorimeter is approximately 1 cm at all points.

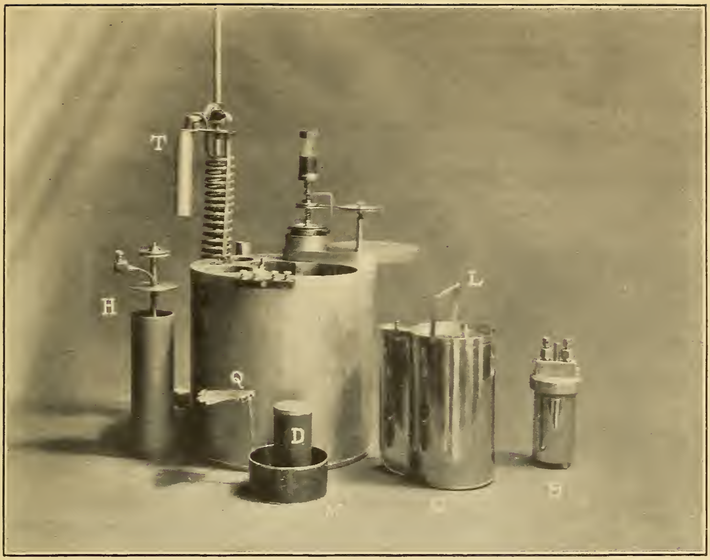

FIG. 3.—*Parts of calorimeter B. S. 7602 and accessories*

T, thermostat. H, heating coil for jacket. M, heating coil for calibration of calorimeter. Q, current and potential leads in flat plate. D, displacement buoy. C, calorimeter. L, handle for same. B, bomb B. S. 6316

FIG. 4.—*Assembled calorimeter B. S. 7602, showing stirring motor and calorimetric resistance thermometer*

The jacket must be so arranged that its temperature can be controlled, or at least measured. For convenience as well as accuracy it is desirable that this temperature be kept constant, unless it is desired to make observations by the so-called adiabatic method, in which case the temperature of the jacket must be under control. To provide for either condition the water jacket, as shown in Fig. 1, is provided with a cover through which the water is circulated, a heating coil, H, Fig. 3, having a capacity of at least 2 kilowatts and a thermostat, T, which may be used to maintain any desired temperature from room temperature up to 90° C. (See also Fig. 4.)

3. Supports and the Space between Calorimeter and Jacket.—It was shown that material between calorimeter and jacket may seriously affect the accuracy of the calorimetric measurements. The present construction is intended to reduce the amount of this material and its effect to a minimum. The surrounding air layer is reduced to a thickness of 1 cm and a mass of about 1.5 g, its heat capacity is therefore about 0.3 g.

The largest mass of material in this space is that required for supporting the calorimeter. The supporting pieces (three in number) are each made up of a brass cone soldered to the bottom of the jacket, and a small ivory tip about 2 mm in diameter cemented into the end of the cone and resting against small plates (one with with a hole, one with a slot, and the third plane) on the bottom of the calorimeter. The thermal conductivity of the ivory tips is small, and their total mass is not over 0.1 g, so that their effect on the cooling rate is too small to be significant. The brass cones, while they have a considerable mass, have a heat conductivity so great compared with the amount of heat which they can receive by radiation, convection, etc. (about 0.0001 calorie per square centimeter per second per degree temperature difference), that their temperature is at all times measurably that of the jacket,[11] hence their effect is entirely negligible, both as regards cooling rate and heat capacity.

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[11] If a brass rod 2 mm in diameter were soldered to the jacket and extended for 1 cm inside, the temperature at the extremity would differ from that of the jacket by only 5 per cent of the difference between that of the jacket and that of the air within. For the cones the extremities are even nearer the jacket temperature.

The steel stirrer shaft which enters the calorimeter ends just above it in a thin hard-rubber sleeve, which fits tightly over it and tightly within a larger steel piece. The latter couples to the steel shaft which has its bearing in the jacket cover and serves as the only support for the stirrer. (See Fig. 1, elevation.) The stirrer touches nothing within the calorimeter but water. It is evident that since the heat conductivity of steel is many times greater than that of the hard-rubber sleeve, the temperatures of the two metal parts will remain very nearly the same as the temperatures of the calorimeter and the jacket, respectively. The heat capacity of the rubber sleeve, some of which should be added to that of the calorimeter, is insignificant.

Aside from the stirring shaft and the calorimeter supports, the thermometer stem with its four copper leads, and the leads to the heating coil or to the firing terminals of the bomb, are to be considered.

The stem of the thermometer is of thin glass and its effect may be neglected, provided that the proper amount of it is added to the heat capacity of the calorimeter. The leads, however, are inclosed within this glass tube and extend from the calorimeter through the cover to the outer air. They therefore conduct heat between the calorimeter and the room. In this respect, therefore, the jacket is not strictly an isothermal surface and the cooling rate of the calorimeter is to a slight extent dependent upon conditions outside of this surface. The magnitude of this effect will be discussed later.

The coil leads and firing leads, where they pass over the top of the jacket, are in the form of wide, thin copper strips insulated with mica. They rest in good contact with the top of the jacket and are protected from the effect of the room temperature by a felt cover.

4. Accessories.—(*a*) *Thermometric.*—The platinum resistance thermometer shown in Fig. 6 represents one of four similar thermometers which were built especially for calorimetric work of this kind and are described in this Bulletin, volume 9, page 43, 1913. They resemble in general construction the two thermometers described in this Bulletin, volume 3, page 641, 1907, but have been

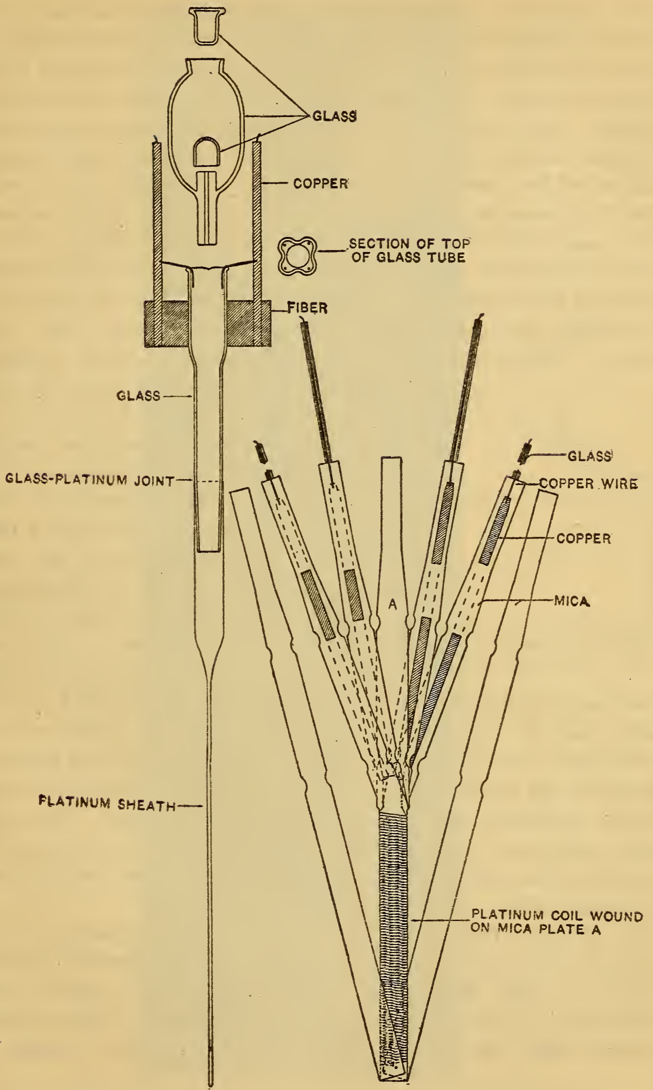

FIG. 5.—*Diagrammatic sketch of parts of thermometer, separated to show construction*

greatly improved over that form. In these later thermometers the resistance coils are of the purest platinum wire 0.1 mm in diameter, wound on a flat mica strip. The coil thus formed is about 8 mm broad, 8 cm long, and between 0.7 and 0.8 mm thick, including the sheath. The leads to this coil are of thin copper and compensated for heat conduction as described in the above-mentioned papers. Instead of four leads, arranged as in the Callendar form of resistance thermometer, these later thermometers are of the Siemens form, made with three or four leads (two of each form), with the leads connected in such a way that one of them is in the battery circuit of the bridge while the coil and one lead are in one arm of the bridge and the remaining lead in the adjacent arm. (See Fig. 7.) When four leads are provided, one of them is simply left open when the thermometer is used with the Wheatstone bridge. The advantage of four leads connected in this way is that such a thermometer can be used with the Wheatstone bridge, a Kelvin double bridge, or a potentiometer, interchangeably. The coils and leads of these thermometers are inclosed in thin tubes (two of the thermometers with platinum tubes and two with silver) 7 mm in diameter and 18 cm long, which are flattened except at the upper end. At this end they are slipped over previously platinized glass tubes and soldered in place. The glass tubes end above in a chamber which contains P_2O_5 to keep the coil free from moisture. The construction of these thermometers is shown in Figs. 5 and 6.

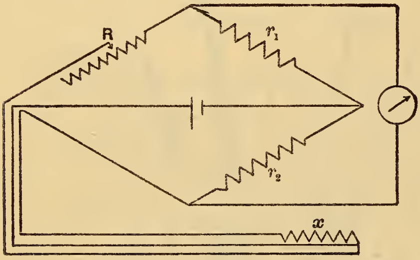

FIG. 7.—*Wheatstone bridge and thermometer circuit*

(*b*) *Bridge.*—The bridge used with these thermometers is one designed and built especially for resistance thermometer measurements. A brief description of it is given in the paper above referred to. The later observations were made with a bridge recently built on the same general lines but with a number of

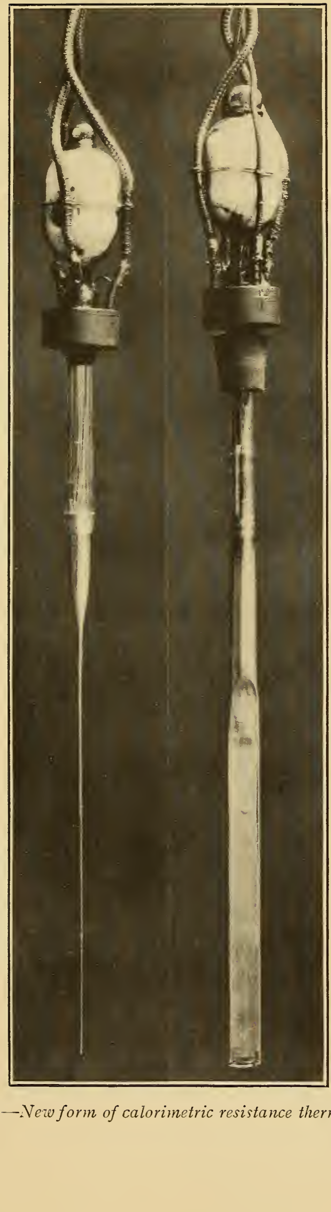

Fig. 6.—*New form of calorimetric resistance thermometers*

decided improvements. This bridge will be described in a future publication. The galvanometer which has been used is a Weston instrument of the moving coil type having a sensibility of 5 mm per microvolt when connected in series with the resistance (45 ohms) necessary for critical damping. The complete period is five seconds.

(*c*) *Chronograph.*—For observing during the period when the temperature is rising rapidly it has often been found convenient to use a chronograph. The instrument used is of the tape form in which the tape has a speed of 1 cm per second. The same chronograph was used in the electrical method of calibration, to be described later (Fig. 8).

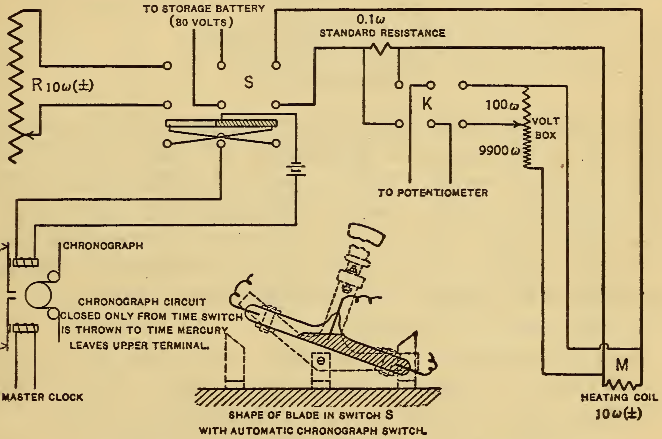

FIG. 8.—*Diagram of circuits for energy measurements*

(*d*) *Speed regulator.*—With the earlier calorimeter a small friction governor was used to control the speed of the stirrer, but with the later one a constant speed induction motor is used with a speed indicator sensitive to 1 per cent or 2 per cent. The indicator is shown in Fig. 1.

5. Heat Capacity.—The calorimeter here described was built with such care as to the weight and quality of materials that the heat capacity of its metal parts, nearly all pure copper, is known about as well as the specific heat of pure copper is known. The total value of this heat capacity is less than 1.5 per cent of that of the water which the calorimeter contains. The specific heat of copper has been determined by the substitution of a 5-kg cylinder of electrolytic copper in place of the bomb; also by observations made with a special calorimeter by Dr. D. R. Harper, and which are to be published in another paper. The results of these tests are given below and are probably reliable to within 0.5 per cent.

TABLE 1

Specific Heat of Copper

0°	25°	50°
0.0906	0.0917	0.0928

PART 2

The remainder of this paper deals particularly with the problem, stated at the beginning, of determining the heats of combustion of some organic solids. For the purpose of this determination the calorimeter must be used in connection with some form of calorimetric bomb. This requires, therefore, the determination of the heat capacity of the particular bomb to be used. The heat capacities of four bombs have been determined, but only two of them were used to any extent.

No. 1, of the Kroeker type, is of steel with a cover of bronze and a fixed platinum lining, and was made by Julius Peters, of Berlin. It has a capacity of about 275 cm³. (See Fig. 9, p. 219.)

No. 2 is similar to No. 1 except that it has a lining of porcelain enamel.

No. 3 is of a special cast bronze, spherical in form, with a lining of electrolytically deposited gold, and was made by Henry J. Williams, of Boston. It has a capacity of about 600 cm³.

No. 4 is of steel, made in the form of two hemispheres. It has a removable platinum lining, and was made by the Emerson Instrument Co., of Boston. It has a capacity of about 400 cm³.

VI. METHODS OF EXPRESSING RESULTS

The unit of heat in the cgs. system is generally defined as that quantity of heat which will raise the temperature of the unit mass of water 1°, the mean temperature being either 15° or 20° C; or as one one-hundredth of the amount of heat required to raise the temperature of unit mass of water from 0° C to 100° C. These define, respectively, the "fifteen degree calorie," the "twenty degree calorie," and the "mean calorie."

Although the 15° calorie and the 20° calorie have each been adopted by many experimenters, the former by perhaps the larger number, several advantages may be urged for the adoption of the 20° calorie. Perhaps the most important of these is the much smaller rate of change in the heat capacity of water at the latter temperature. This heat capacity reaches a minimum at about 30°, and its rate of change with temperature at 20° is only about one-third as great as at 15°. For this reason results can be obtained in the neigh-

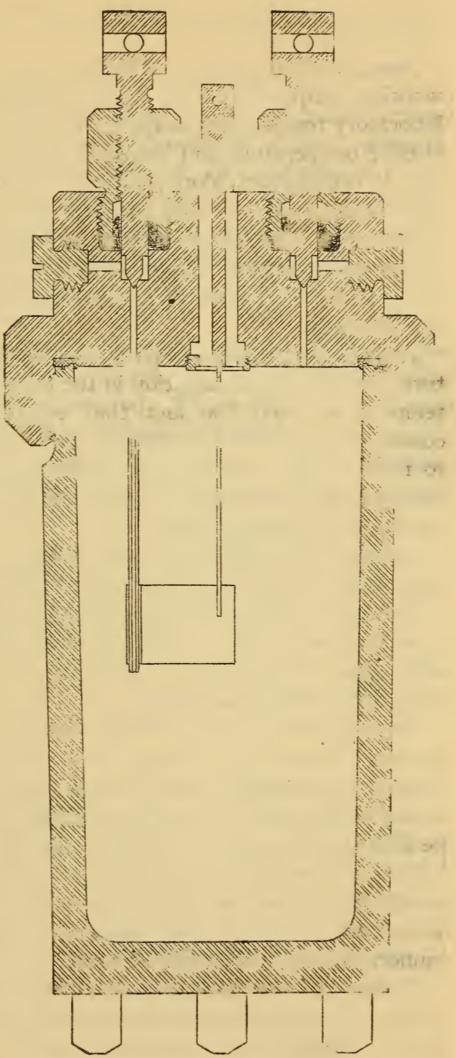

FIG. 9.—*Section of bombs, B. S. 6316 and 6216₂*

borhood of 20° with considerably greater consistency than in the neighborhood of 15°.

Another advantage lies in the fact that 20° is a more convenient working temperature than 15°. In many places the customary laboratory temperature is approximately 20°, while in summer the outside temperature and humidity are such as to make it impossible to use an open calorimeter at 15° without a means of reducing the temperature and humidity of the air. On the other hand, it is usually a very simple matter to maintain a calorimeter at a temperature several degrees above that of the room. Results obtained at 20° can be more accurately expressed in terms of the 20° calorie.

In view of the greater convenience of 20° as a working temperature, smaller rate of variation in the heat capacity of water at this temperature, and the fact that calorimetric observations are commonly made at temperatures near this, it appears desirable to follow what seems to be a growing tendency among experimenters and adopt the 20° calorie as the basis for expressing the results of this investigation.

Although the calorie has been adopted as the primary unit of heat, the extreme precision with which electrical measurements can be made has led to the use of the joule expressed in electric units, as a calorimetric unit. Such use involves the acceptance of a specific value for the ratio J of the joule to the calorie, when results are to be expressed in calories.

The adoption of such secondary units is hardly justifiable unless greater comparative accuracy can be obtained thereby. The present investigation seems to show that this is not true to any considerable extent. It seems, therefore, that the calorie should be adopted for work of this kind, and in this case the incidental values of J, which will be found as shown later, will serve as an excellent check on the other measurements by comparison of these values with those of other observers, taking care that the same numerical values are assigned to the electrical units used.

In view of these considerations it has been decided to express the results of the present investigation directly in terms of the calorie, but in finding the heat capacity of the several bombs, to make the fullest use of the methods applicable for calibration in terms of the joule.

VII. ELECTRICAL CALIBRATION APPARATUS

The electrical method of calibration consists essentially in supplying a measured amount of energy electrically to the calorimeter, and measuring the temperature rise, with all conditions as nearly as possible those of the experimental work for which the calorimeter is intended. The results of such observations give directly the heat capacity of the calorimeter and its contents, in joules per degree, but to make use of this very accurate method to the fullest extent in determining the heat capacity of a combustion bomb in calories per degree it should be possible to make a determination first with the bomb in place in the calorimeter and then a similar observation with the bomb removed. The removal of the bomb invloves a change in conditions respecting both the heat capacity and the form of the temperature-time curve. In order to eliminate these two effects and make the conditions nearly the same in the two cases, the approximate volume and heat capacity of each bomb were determined and for each of the different types a very light copper buoy was made, of such a size that it would displace just enough water in the calorimeter so that, when it was substituted for the bomb and the water level was made the same as with the bomb in place, the total heat capacity of the calorimeter would remain nearly unchanged. The shape and position of the buoy were much the same as of the bomb, so that the conditions of stirring were little affected.

1. Heating Coils.—In order to supply energy to the water electrically and not to introduce a large mass of material of uncertain heat capacity, three closed heating coils were built as follows: A strip of "Advance" resistance ribbon, 3 mm wide and about 8 m long, with a resistance of 10 ohms, was wound over thin mica insulation on a cylinder of 0.2 mm copper, then covered with another layer of mica and closed with a second layer of copper 0.1 mm thick, soldered at the edges. One of these coils is 10 cm in diameter. Another is of a diameter to fit closely over either of the two Peter's bombs, covering most of their cylindrical surfaces. The third is about 12 cm in diameter and was built for the calorimeter, B. S. 7602. The current and potential leads of the first and second coils are brought out through small glass tubes. These leads branch near the surface of the calorimeter water so that the potential is measured across only that part of the coil which is immersed in the water.

In building the third heating coil it was recognized that if the portion of a current lead adjacent to the jacket is at the jacket temperature and the portion entering the calorimeter is at calorimeter temperature, the potential lead should be connected at such a point that the thermal conductivity between this point and the calorimeter is the same as that between this point and the jacket. To satisfy this condition the leads must be in very good thermal contact with both jacket and calorimeter and the ends next the heating coil must not be appreciably affected by the heating of the coil, otherwise the temperature gradient will depend upon the current in the coil. The above conditions are quite approximately realized by making the leads in the form of wide, flat copper strips insulated with mica, and resting firmly against the upper surface of the jacket, is shown at Q an Fig. 4, by interposing a few centimeters of thin copper ribbon of low resistance between the leads and the resistance ribbon as wound on the coil and by connecting the potential leads at the proper median points.

The form of temperature-time curve, observed when the close-fitting coil is used, is markedly different from that observed when the open coil is used, as may be seen from the figures given later (Fig. 10 a–b). When the open coil is used and a current passed through it for a given time, the temperature of the calorimeter water rises almost linearly until the current is cut off, then very soon reaches a steady condition. When the close-fitting coil is used, however, the temperature rises less rapidly at first, showing that much of the heat is being taken up by the metal of the bomb, and after the current has been cut off the temperature continues to rise for a considerable time while the metal of the bomb is losing its heat to the water. The form of this curve is much the same as that observed when a charge of combustible is burned within the bomb. The curve obtained with the copper buoy in place of the bomb is almost identical with that obtained with

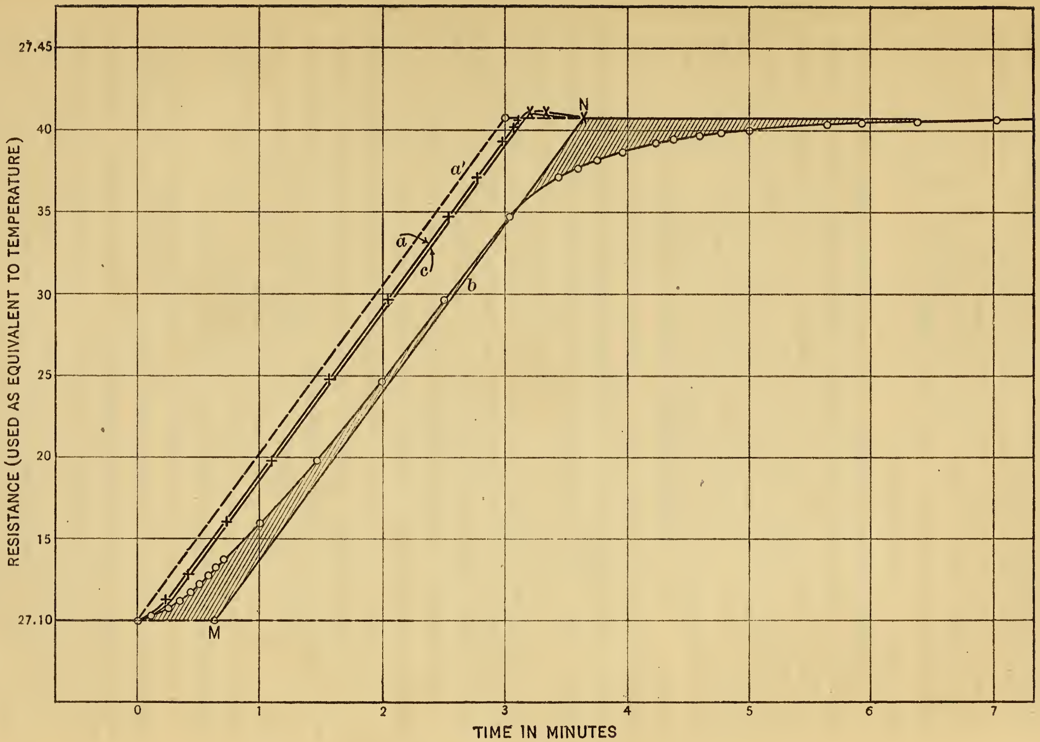

Fig. 10.—*Typical time-temperature curves for electrical calibrations.*

the open coil and the bomb, so that for comparisons with and without the bomb the open coil is the better. It is interesting to note, later, that the results obtained with the open and the close-fitting coils and the bomb are in perfect agreement with each other, though the cooling corrections to be applied in the two cases are very different.

2. Electrical Measurements.—The electrical measurements consisted of a determination of temperature by means of an accurate resistance thermometer used in connection with the special resistance bridge, referred to in the earlier part of this paper, and a determination of current and voltage during the time when the heating current was flowing through the calorimeter heating coil. The arrangement of the thermometer and bridge circuits is shown in Fig. 7. Since measurements must be made with a changing temperature the method used was to set the bridge resistance to a given value and note the time when the galvanometer deflection became zero. The arrangement of circuits for measurement of current and voltage and for recording the time is shown in Fig. 8. The adjustable resistance R was made equal to the resistance of the heating coil in the calorimeter, so that on throwing the quick-break switch S no change was made in the current taken from the storage battery, and by using a battery which was partly discharged it was possible to keep the current constant to well within 0.01 per cent for the time (usually 3 to 5 minutes) during which it was flowing through the heating coil. Measurements of current and voltage were taken alternately by throwing the switch K, which connected the potentiometer with either the standard 0.1 ohm or the volt box. All the resistances in the bridge, potentiometer, and volt box, and the standard 0.1 ohm were often calibrated and were accurate to 2 parts in 100 000.

For the measurement of time the tape chronograph was used in connection with the Riefler clock kept by the division of weights and measures. By the arrangement of switches shown in Fig. 8 the operation of throwing the switch S automatically closed the chronograph circuit. The chronograph tape traveled about 1 cm per second, so that times could be read easily to 0.01 or 0.02 second. The quick-break switch S, which operates the main current circuit and the chronograph circuit, is so made that there is not more than 1 or 2 mm of motion between the opening of the circuit on one side and the closing of the circuit on the other side. The time required to move this distance evidently enters as an error in the chronograph time interval, but since this error could not exceed a few thousandths of a second or a part in 100 000 it was neglected.

S is a three-pole switch with a glass tube partly filled with mercury mounted upon it in such a way that while the third pole serves to close the chronograph circuit on either side, the motion of the mercury opens the circuit immediately afterward, allowing only time for the chronograph to operate, and leaving the connections right for the next throw of the switch.

VIII. HEAT CAPACITY DETERMINATION

The method adopted requires a comparison of two sets of observations entirely similar except for the interchange of bomb and buoy. The procedure need be described for only one of the sets—e. g., when the bomb is used.

1. Procedure.—A suitable amount of distilled water, at a temperature a few degrees lower than that of the room, was poured into the calorimeter and weighed to tenths of a gram. The calorimeter was put into position in the jacket, the temperature of which had been lowered to within 2° or 3° of that of the calorimeter. The bomb was lowered into the calorimeter and brought the level of the water up to within 1 cm of the top. Different amounts of water were used with different bombs so that the upper surface of the water was always at nearly the same level. The heating coil M and the cover were put in place, 0.3 cc of oil was dropped on the surface of the water which was exposed in the openings of the cover, the jacket cover was turned into position, and the stirrer connected.

The main observations required two observers and can be divided into initial, middle, and final periods. In the initial period observations were made with the resistance thermometer. First, a series of four or five observations were made of the time when the galvanometer deflection was zero for settings on the bridge differing by 0.0001 or 0.0002 ohm, corresponding to approximately

0°001 or 0°002. Then after from five to eight minutes another similar series was taken, usually comprising more observations.

The middle period began at the end of this series when the second observer closed the switch S, Fig. 8, and began taking observation of current and voltage, as described on page 224 et seq. At the same time the observer at the bridge recorded on the chronograph tape the times when the galvanometer deflection became zero for various settings of the bridge at intervals of resistance corresponding to temperature differences of from 0°2 to 0°5, according to the rate of temperature rise. During this period the sensibility of the galvanometer was reduced and determined in terms of resistance so that galvanometer deflections could be observed and used to plot additional points on the time-resistance curve when desired. At other times the temperature observations during the middle period were made with a thermocouple, with junctions on the calorimeter and jacket, and connected directly to the galvanometer. At the end of 2, 3, or 4 minutes, as the case might be, the switch S was again thrown, cutting off the current from the heating coil and automatically recording the time on the chronograph. For convenience this switch was always thrown both on and off at an even minute—i. e., at the same second—so that any possible error in the contact device of the clock, such as eccentricity of the seconds wheel, was eliminated. A watch was used by the observer to indicate the second on which the switch was to be thrown, and to record the time of observations during the initial and final periods.

The final period may be considered as beginning when the rate of temperature change has become sensibly constant, as shown by equal time intervals between observations of equal resistance changes. When the rate had become sensibly constant, a series of observations, like those in the initial period, were recorded, and after several minutes another series. As the rate was always slow the time in these observations need seldom be known to better than one second and the watch was sufficiently accurate. These observations serve to determine the initial and final cooling rate.

After finishing a series of observations of this kind the temperature of the jacket was raised the same amount as the temperature of the calorimeter had been raised, and another similar series of observations was taken. In this way with a single filling and adjustment of the calorimeter as many as five observations were made. The whole set of observations was again carried out with all the conditions as nearly as possible the same, except for the substitution of the thin copper buoy in place of the bomb, and the two series of observations thus obtained served for a calculation of the heat capacity of the bomb. This is virtually a comparison of the bomb with a mass of water which is very nearly its equivalent in heat capacity.

2. Form of Records.—Table 2 shows the form in which the observations were made and the computation carried out.

The original record includes under "Amperes" and "Volts" the potentiometer readings corresponding to current and voltage, and under "on" and "off" the times of throwing on and off the heating current. The exact times are entered from the chronograph record. Under "Time" and "Resistance" are recorded the times and corresponding resistance readings on the bridge. During the middle period the bridge readings may often be omitted. The times (when required) during the middle period may be entered later from the chronograph record or may be observed with a watch. The weight of water used and other data are entered under the proper headings.

TABLE 2

Department of Commerce
BUREAU OF STANDARDS
Washington

Observer HCD
Computed by HCD

Date Jan. 27, 1913
Expt. No. 4

WATER-EQUIVALENT RECORD

				(r_1)	(r_2)	TIME	DIF.	RESISTANCE	NOTES
t_R	2-52-33		dR	.0088	.00151	2-44-10	12	28.22700	Bridge BS 7481 at 30°C.
t_M	2-55-31		dt	503	960	22	9	20	Calib. of 11-16-12
dt	2-58	=178	$\frac{dR}{dt}$	$.0^41749$	$.0^5157$	31	13	40	Ratio 100 R.
r_1	$.0^41733$		Cor.	$.0^40016$	$.0^5003$	44	12	60	Therm. Pt 4
r_1dt	+.00308		r	$.0^41733$	$.0^5160$	56		80	5 mil'amps.
R_1	28.23580		*a*	$.0^437$					
R_1cor	.23888		R_o			2-51-46	12	28.23500	
						58	13	20	
Potentiometer No. 1665			Cell No. 1506			52-11	11	40	
Volt Box No. 8325			Std. Res. No. 4997			22	11	60	
Temp.	19°5		Temp. 19°6			33		80	
	49.358			4.9380					
	56			75					
	53					2-53-03		28.24	
						08		.25	
						38		.30	
Mean	49.356		Mean	4.9378		54-07		.35	
Pot. Cor.	+1		Pot. Cor.	+1		37		.40	
Vltb. fctr.	0		Res. Std.	−90		55-06		.45	
			Vlt. bx. cur.			35		.50	
						56-04		.55	
Volts	49.357		Amperes	4.9289		35		.60	
Resistance	10.0138		Power	243276		57-03		.65	
						34		.70	
on	2-52-51.28	Time 300.01	Energy 72985			52		.73	
off	57-51.29								
t_R	3-02-00		Calorimeter No.	7602					
t_M	2-55-31		Bomb "	6316_1		2-59-33		28.74350	
dt	6-29	=389	Total Wt.	3500.0		3-00-02		40	
r_2	$.0^5160$		Tare	409.3		01-00		33	
r_2dt	.00062			3090.7		2-00		26	
R_2	28.74326		Vac.	3.2_8		3-00		17	
R_2Cor.	.74388		Cor. Mass	3094.0 H_2O		4-00		05	
R_1Cor.	.23888								
diff.	.50500		Total H_2O equivalent of			3-16-00		.74192	
Bdg.	00		Cal. Therm. Coil etc. at			17-00		83	
			32° = 53.9 Cal. ≎ 225.4 J			18-00		75	
dR	.50500								
K	1.01035								
dθ	5°1023								
Equiv.	14306 J								
Mn. Tmp.	32°1								

ROOM TEMP. THERM.		JACKET THERM.	
Time	Temp.	Time	Temp.
2-46	21.3	2-46	35.5
3-06	.4	3-06	.5

The resistances were read directly on the bridge; the coil corrections being small were entered under "Bdg" during computation. The time intervals between successive readings under "Dif." serve to indicate when the cooling rate has become uniform and to compute a correction to the time which corresponds to any chosen resistance.[12]

3. Computation.—Observations with the resistance thermometer, more particularly during the middle period, are more conveniently made at even resistances than at even time intervals. For this reason formulae such as Pfaundlers are not conveniently applied. A graphical method has been developed which, though somewhat laborious when worked out completely, leads to a very short and simple practical method of correcting for heat transfer, applicable in both electrical calibration and combustion observations with errors so small as to be neglible even in work of high precision.

Fig. 10 shows typical curves plotted with times as abscissae and resistances (instead of temperatures)[13] as ordinates. In this figure a' represents the curve which would be found, provided the heat

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[12] In a series of resistance-time observations, as above, it is often desirable to find a corrected value for one of the observations rather than a mean value for several of them. A series of time observations is made, which in general have a constant difference—i. e., a linear variation—but which show fortuitous errors of observation. It is desired to find the best value of time corresponding to the resistance measured immediately at the end of the initial period since by using this observation the cooling correction can be made smaller than if a mean were taken of a number of observations. The corrected value of the time can be conveniently computed from variations of the quantities in the column "Dif." as follows:

Let a_1, a_2, a_3, etc., be a series of observations such that β is the mean of the differences a_2-a_1, a_3-a_2, etc., any observation $a_n=a_{n-1}+\beta+x_{n-1}$ where x is the departure of the individual difference a_n-a_{n-1} from the mean difference β.

The corrected value for a_1 may be written as a' where

$$a'=\{a_1+(a_2-\beta)+(a_3-2\beta)+(a_4-3\beta)+--+[a_n-(n-1)\beta]\}\div n=\{a_1+a_2+a_3+---+a_n-\beta[1+2+3+---+(n-1)]\}\div n \qquad (1)$$

But the above series of a's is made up as follows:

$$a_1=a_1$$
$$a_2=a_1+\beta-x_1$$
$$a_3=a_1+2\beta-x_1-x_2$$
$$a_n=a_1+(n-1)\beta-x_1-x_2-----x_n$$

Substituting these values in (1) and simplifying

$$a'=a_1-(1/n)\{(n-1)x_1+(n-2)x_2--+x_{n-1}\} \qquad (2)$$

This formula is usually applied for $n=5$, and the value of β used to get the x's is from the mean of as many differences "Dif." as seem to be regular. The computation of a correction by this means can be made mentally in a few seconds after finding β.

[13] Resistences may be used in plotting the curves since the resistance-temperature relation is very nearly linear, and Newton's law of cooling may be assumed for resistances in the same way as for temperatures.

from the heating coil was instantly distributed to the water and provided the thermometric system had no time lag; *a* represents actual observations when the calorimeter was heated electrically with an open heating coil and with the calorimetric bomb in place; *c* represents observations taken at the same time with the differential thermometer in the air space between the calorimeter and the jacket; *b* represents observations taken when the calorimeter was heated by means of the heating coil which fitted closely the surface of the bomb. It should be noted that the curve *c* is displaced from *a* by two and one-half seconds. A series of 10 observations of this displacement, taken with various rates of temperature rise, all gave values of between two and three seconds.

Fig. 11 is a characteristic curve observed when a charge of combustible was burned in the bomb. The ordinates are resistances, as in the preceding figure. This figure is so drawn as to illustrate the method of computing cooling corrections, discussed below.

The cooling correction $A = \alpha\int_{t_1}^{t_2}(\theta-\theta_0)dt$

where

$\alpha =$ cooling constant of the calorimeter.

$\theta =$ temperature; θ_1, θ_0, θ_2, respectively initial, convergence, and final temperatures.

$t =$ time; t_1 and t_2 respectively initial and final times.

A time t_m may be found such that

$$r_1(t_m-t_1)+r_2(t_2-t_m)=\alpha\int_{t_1}^{t_2}(\theta-\theta_0)dt \tag{1}$$

$$=\alpha\int_{t_1}^{t_m}(\theta-\theta_0)dt+\alpha\int_{t_m}^{t_2}(\theta-\theta_0)dt$$

where

$$r_1=\alpha(\theta_1-\theta_0)$$

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$$r_2=\alpha(\theta_2-\theta_0)$$

---

[14] It may be shown that this is true, independently of the form of the curve, as, for instance, when the temperature rises above the final temperature θ_2, as in Fig. 10, *a*. If the line MN in Fig. 10 is so drawn that the shaded areas are equal, the middle point of this line may be taken as t_m.

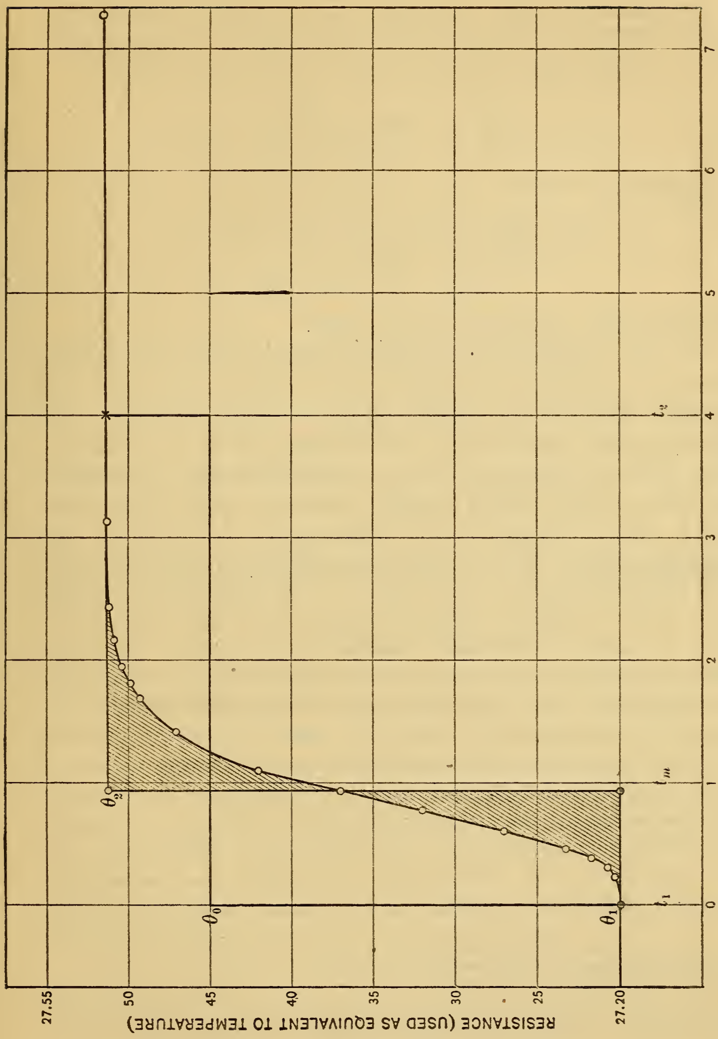

Fig. 11.—*Typical time-temperature curve for combustion observations*

The geometry of Fig. 11 suggests that the above condition (1) will be satisfied if t_m is so chosen that the shaded areas between the curve and the lines θ_1 and θ_2 are equal on either side of it.[15]

$$\text{(3)} \qquad \text{that is } -\alpha\int_{t_1}^{t_m}(\theta_1-\theta)dt+\alpha\int_{t_m}^{t_2}(\theta_2-\theta)dt=0$$

Adding (2) and (3)

$$\alpha(\theta_1-\theta_0)(t_m-t_1)+\alpha(\theta_2-\theta_0)(t_2-t_m)=A$$

or

$$A=r_1(t_m-t_1)+r_2(t_2-t_m)$$

which is a very convenient form to use.

It is only necessary to multiply the initial cooling rate by the time (t_m-t_1) and add the product to the initial temperature, and multiply the final rate by (t_m-t_2) and add the product to the observed final temperature. The difference of the two temperatures thus corrected gives the true temperature rise corrected for the effect of heat transfer between calorimeter and surroundings.

If a curve is plotted it is a simple matter to locate t_m, but experience shows that for electrical calibrations (with the open coil) the position of t_m with respect to the beginning and ending times is, for a sufficient rate of stirring, remarkably constant; in fact, for scores of electrical calibrations its position has never varied more than 2 seconds from the mean value, this mean being 8 seconds later than the middle point of the heating period. An error of 2 seconds would affect the result by about 6 parts in 100 000. In combustion experiments the agreement is not so good, as t_m depends both upon the time required for the charge to ignite after closing the switch and upon the total rise of temperature. But it was noted that the position of t_m with reference to the temperature for combustion observations was remarkably constant, the line t_m crossing the temperature-time curve always

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[15] The factors r_1 and r_2 are the rates of cooling at times t_1 and t_2, not the rates computed from observations covering periods of time respectively preceding t_1 and following t_2.

If θ_1' be the temperature at a time t_1' earlier than t_1, the observed rate r_1' will be $(\theta_1-\theta_1') \div (t_1-t_1')$ and the rate at time t_1 may be found from this by means of the relation $r_1=r_1'\left\{1-a\frac{\theta_1-\theta_1'}{2}\right\}$ which simply assumes that the change in rate is proportional to the change in temperature. The final rate r is found in the same way.

at nearly the same relative position. This fact suggested the following calculation, which is given in this connection although it applies more particularly to combustion observations.

If the heat generated were all distributed instantly to the walls of the bomb, the rise of temperature of the water would follow very nearly an exponential law corresponding to the cooling constant of the bomb in water—i. e., $\theta = 1 - e^{-kt}$—for unit rise of temperature from an initial temperature of 0°. As a matter of fact, the temperature does very nearly follow such a law beyond the first few seconds after firing. Assuming $\theta = 1 - e^{-kt}$, t_m may be found in terms of θ.

For convenience, assume $\theta_1 = 0$, $\theta_0 = 0$, $\theta_2 = 1$, then for t_m to satisfy the condition of equal areas as given above:

$$\int_0^{t_m} [1 - e^{-kt}]\, dt = \int_{t_m}^{\infty} [1 - (1 - e^{-kt})]\, dt$$

integrating and simplifying

$$t_m = \frac{1}{k}$$

and substituting to get the value of θ, i. e., (θ_m) corresponding to t_m

$$\theta_m = 1 - e^{-\frac{K}{K}} = 0.63$$

Thus, if the time is observed when the temperature rise has reached 0.63 of its final value, this time may be used as t_m. A large number of observations for which the curves have been plotted give 0.57 to 0.62, always slightly less than that for the exponential curve, due, probably, to the fact that the temperature rise does not begin as soon as required by the assumption. (When gases are burned in the bomb the observed value for t_m is very nearly the same as the computed value, viz, 0.63.)

If the figure 0.60 were used in all these observations, the error introduced would in no case exceed 1 in 10 000.

When the total rise in temperature to be expected is approximately known it is only necessary to observe the time when 0.6 of that rise has occurred and to use this time as t_m. The degree of approximation which can be permitted must be determined for any given class of experiments.

The above method of computing the cooling correction is plainly independent of the units used for plotting the ordinates of the curve and is therefore applicable directly to observations taken with the differential thermometer or thermocouple in terms of galvanometer deflection, provided the deflection is nearly a linear function of the temperature difference.

The observations for the middle period have always been made with the thermometer in the calorimeter, and not with the differential thermometer, described on page 207. The data necessary for correcting these observations to a basis of the differential theremometer were obtained from a series of comparisons between observations made with it and the inside thermometer under conditions similar to the above. The curves plotted from these observations were almost identical with the curve Fig. 10, *a*, except that they were displaced on the average 10½ seconds from the ideal curve AB instead of 8 seconds, as is the average for curves taken with the thermometer in the calorimeter. From this it is concluded that a correction of 2½ seconds should be applied to all observations with the thermometer in the calorimeter. Under like conditions the displacement observed very seldom differs from the mean displacement of 8 seconds by more than 1 second, which corresponds to an error of about 0.00003 (3 parts in 100 000) in the observed temperature difference.

The computation of results on this observation sheet can be best explained by indicating the entries under each heading.

Under T_R and under R, five lines below, are entered, respectively, the corrected time and the corresponding resistance observed immediately before throwing on the heating current. The device for correcting the observation of time is explained in note 12.

Under t_m is entered the time corresponding to the vertical line in Fig. 10. In this case t_m is 10 seconds after the middle of the heating period.

dt is $t_m - t_R$.

r is the cooling rate determined from observations.

rdt is the product as indicated.

R_1 cor. is the sum of rdt and R the resistance which would have been observed at time t_m if the actual cooling conditions had been operative without any energy supply from the heating coil.

For the computation of the cooling rates r_1 and r_2 under dR and dt are entered differences in resistance and in time between a pair of observations as far apart as possible during the initial period. One of these observations is always that recorded under t_R and R.

$\frac{dR}{dt}$ is the apparent cooling rate.

"Cor." is a correction equal to $\alpha\frac{dR}{2}$, and is applied to reduce the coolihg rate $\frac{dR}{dt}$ to the correct value r_1 which it would have at the time t_R, i. e., for resistance R_1.

The "amperes" and "volts" are potentiometer readings with the indicated corrections applied. "Resistance" is the observed resistance of the heating coil entered as a check on the observations.

The following headings t_R etc., are like those at the top of the page except that they apply to the final period. t_m is the same in both cases, and R_2 cor. is the resistance for the time t_m if all the energy had been supplied before that, and existing cooling conditions had held.

R_1 is entered from above, dR is the corrected change in resistance, and K is a term depending upon the constants of the resistance thermometer, which reduces the observed difference of resistance to difference of temperature $d\theta$. The method of computing the table from which this term is obtained is described in Bureau of Standards Reprint No. 200.

The corrected weight of water and the calculated heat capacity of the fixed part of the calorimeter are given below. To find the heat capacity of the bomb it is only necessary to compare the results of observations including the bomb with those without it. If W is the heat capacity of the calorimeter, heating coil, and water, exclusive of the bomb, B is the heat capacity of the bomb and K is that of the displacement buoy and the additional water used when the bomb is not in the calorimeter; the two equations given below give the value of $K-B$ from which B can be determined by using an approximate value of J, since $K-B$ is made small.

$$W+K=\left(\frac{A_1V_1T_1}{\theta_1J}\right)$$

$$W+B=\left(\frac{A_2V_2T_2}{\theta_2J}\right)$$

This method of determining the heat capacity of the bomb alone does not require an accurate knowledge of the heat capacity of the fixed parts of the calorimeter nor of the electric heating element used, and the accuracy attainable is limited only by the precision of the measurements.

An accurate knowledge of the heat capacity of the calorimeter used for combustion experiments (not necessarily the same one as is used for determining the heat capacity of the bomb) must, however, be accurately known in order to express the results in calories. If, in addition to this, the heat capacity of the electric heating element is known, the former of the above equations also gives a value for J, the equivalent of the calorie in electrical units.

The following series of results from observations dated January 27 and January 28, 1913, is representative. Observed joules per degree for the calorimeter with 3093.8 g water (corrected to vacuo), heating coil 7602 and bomb 6316_1,

TABLE 3.

Temp.	15°	20°	25°	30°	35°
Joules.	14317	14309	14307	14306	14305

Observed joules per degree for the calorimeter with 3368.2 g of water (corrected to vacuo), heating coil and displacement buoy of copper equivalent to 4.1 g of water,

TABLE 4

Temp.	15°	20°	25°	30°	35°
Joules.	14334	14322	14317	14315	14314

The heat capacity of the bomb at each of the following temperatures is found from these observations to be equivalent to that of the following masses of water at the same temperatures.

TABLE 5

Temp.	15°	20°	25°	30°	35°
Mass.	274.7	275.7	276.3	276.6	276.7

Or in terms of 20° calories, using the variation in the heat capacity of water, as found from this set of observations,

TABLE 6

Temperature	15°	20°	25°	30°	35°
Specific heat of water	1.0009_1	1.0000_0	0.9994_8	0.9991_8	0.9991_1
Heat capacity of bomb	275.0	275.7	276.2	276.4	276.5

The value of J computed from this observation (taking the heat capacity of the calorimeter (p. 240) as 175.5 joules at 15°, and 176.8 joules at 35° of the coil (p. 242) as 47.8 joules, and of the buoy (p. 242) 17.1 joules, and of the 10 drops of oil used to prevent evaporation as 0.8 joule) is 4.181 joules per 20° calorie on the basis of the present electrical units.

The heat capacities of the bombs, particularly of 6316_1, have been determined at various times, the weights being somewhat variable on account of the wearing away of the lead washer used in the cover of the bomb.

A series of observations in 1910, in the earlier calorimeter, gives the following results:

TABLE 7

Bomb	Observations	Temperature			
		15°	20°	25°	30°
6316_1	80	272.7	274.9	276.3	276.7
6316_2	29	272.9	275.1	276.5	277.0
6428	57	....	401.9	403.3	404.5
Em. 549	5	....	402.4	405.0	406.7

A recent series of 15 observations in calorimeter No. 7602, with all the factors very carefully redetermined, gave the following results:

TABLE 8

Temp.	15°	20°	25°	30°
Bomb 6316_1	275.0	275.8	276.2	276.4

in terms of 20° calories at the temperatures given.

4. **Accuracy of the Various Measurements.**—The measurements of time were made to an accuracy of about 1 part in 20 000; of current, voltage, and weight to an accuracy of better than 3 parts in 100 000. The potentiometer, volt box, and standard 0.1 ohm have been tested at frequent intervals during the investigation.

The computations of heat capacity of the metal parts of the calorimeter aside from the bomb involve an uncertainty, mainly in the specific heat of copper, which uncertainty should amount to less than 1 part in 10 000 of the entire heat capacity. An error in this would affect all results to the same proportional extent.

The measurement of temperature enters into both the observed temperature interval and the temperature-time curve from which the cooling correction is computed. In fixing the temperatures (resistances) during the initial and final periods the error of the thermometer probably does not exceed 1 part in 10 000 of the interval measured.

The four thermometers built for these investigations and described in Reprint No. 200 were calibrated with great care by comparison with some of the primary standards of the Bureau of Standards in the same manner as were the thermometers described in Reprint No. 68, from the Bulletin of the Bureau of Standards. These four thermometers were also compared in 1910 with the two thermometers previously described in Reprint No. 68 and were finally calibrated by means of observations in sodium sulphate in the manner there recommended. The three methods are in agreement to within 0°.002 in 50°. Many later observations have confirmed these results to this order of accuracy. The one thermometer of the four which showed the greatest constancy is designated as Pt. 4, and has been used for most of this investigation. The resistance of this thermometer in ice has apparently not changed by 1 part in 100 000 during three years.

The constants of this thermometer are as follows:

$$R_0 = 25.1818, \qquad F.I. = 9.8525, \qquad \delta = 1.48$$

All four of these thermometers have been intercompared and they agree to within 1 part in 10 000 in defining any temperature interval between 0° and 100°.

The effect of errors in temperature measurement during the middle period on the cooling correction is very small since an error of 1 second in the position of the entire resistance-time curve involves an error of only 3 parts in 100 000, and it is an easy matter to observe any point on the curve with greater accuracy than 1 second. Errors in the determination of the cooling rates can only be determined from a study of the values found for the cooling constant from various observations.

The accuracy required in these observations is not high, since the total cooling correction ranges from 2 parts in 1000 to zero for combustion observations, where the final temperature may be from 0.°3 to 0.°5 above the equilibrium temperature. This procedure does not entirely eliminate the evaporation and condensation of water (see p. 195), and it is only justified by the observed fact that the rate of evaporation from the covered and oil-sealed surface of the calorimeter is negligibly small under these conditions.

5. Cooling Constant.—The observed cooling rate of the calorimeter at any time is the sum of 3 parts, first, the rate of the calorimeter proper represented by its cooling constant in degrees per second per degree difference in temperature between the calorimeter and the jacket; second, the rate due to energy supplied by the stirrer; and third, that due to heat conducted by thermometer leads, firing leads, etc., between the calorimeter and the space outside of the jacket. This latter part could be eliminated if it were practicable to secure sufficiently good thermal contact between these leads and the jacket.

When the jacket temperature remains constant and the cooling constant of the calorimeter is computed from the difference in rates before and after a combustion, divided by the change in temperature, the second and third factors are eliminated. A series of values taken from one month's combustion observations at a mean temperature of 25° gives 0.0000339, with a mean variation of 0.0000003 and a maximum variation of 0.0000007. Comparison of about 100 values of this constant obtained at temperatures ranging from 15° to 45° shows a change of about 0.6 per cent per degree, the constant increasing with the temperature. For a given calorimeter temperature, however, the cooling constant is independent of the difference of temperature between calorimeter and jacket to within the limits of observation (1 per cent or 2 per cent), for differences up to 5°.

However, when observations are made by the "adiabatic" method, as described later, it is necessary to know the magnitude of the stirring and lead conduction effects. These have been determined at several different times. The stirrer running at its normal speed of 300 rpm. causes a rise in temperature of 0°.0000040 per second, which corresponds to 0.057 watt, an amount of energy very much less than is usually dissipated in stirring, yet the rate of stirring is entirely sufficient.

The rate due to lead conduction is 0°.0000004 per second per degree difference in temperature between the jacket and the room. This corresponds to 0.006 watt.

6. Heat Capacity of Fixed Portions of the Calorimeter.—The various materials entering into the construction of the calorimeter, heating coils, and displacement buoys, together with their assumed specific heats and calculated heat capacity, are discussed below.

The calorimeter proper, including the calorimetric vessel, the cover above the stirrer, the stirrer and shaft, the main cover, and the immersed part of the thermometer, is made up of the following:

TABLE 9

	Weight	Specific heat		Heat capacity—	
		At 15°	At 35°	At 15°	At 35°
	g				
Copper	420.8	0.0920	0.0927	38.71	38.99
Solder	2.7	.05	....	.13	.13
Steel	3.6	.10	....	.36	.36
Platinum	9.6	.032	....	.31	.31
Gold	.3	.031	....	.01	.01
Mica	1.0	.208	....	.21	.21
Glass	2.0	.20	....	.40	.40
Nickel	14.8	.11	....	1.65	1.65
Hard rubber	....	....	....	.20	.20
Total	....	....	....	41.9	42.2

The two displacement buoys made to displace, respectively, the Williams and the Peters bombs are of copper and have the following constants:

TABLE 10

Volume, 700 cc; heat capacity, 6.3 g

Volume, 360 cc; heat capacity, 4.1 g

7. Heat Capacity of the Heating Coils.—The heat capacity of each of the heating coils used was computed from the weight of copper, mica, constantan, and solder, but as the specific heat of mica in particular was uncertain and rather large, a direct determination of the heat capacity of the two coils *K* and 7602 was undertaken. For this purpose the coils were successively supported within the calorimeter jacket surrounded by air only, with the leads connected as usual. A copper-constantan thermocouple with flat contact plates, insulated with thin mica strips, was arranged with one terminal on the inner surface of the jacket and the other on the surface of the coil. The cooling constant for the coil in this position was determined by two methods: First, by heating the coil several degrees above the temperature of the jacket, then allowing it to cool with no heat supplied, and plotting the observed temperature difference between coil and jacket against time; from these curves the cooling constant can be computed; second, by measuring the energy required to maintain a given constant difference of temperature between coil and jacket, from which the cooling constant is found directly. These two methods gave concordant results for each coil. The heat capacities were then determined by heating the coils electrically by successive steps of about 1°, while maintaining the jacket temperature nearly equal to the rising temperature of the coil. The total cooling corrections were thus made very small. Temperatures of the jacket were measured and those of the coils obtained from the same by differences as shown by the thermocouple.

The heat capacity of a portion of the air in the jacket evidently must be considered as included in the observed heat capacity of the coil. The assumption was made that heat was transmitted to the air equally by all the surface exposed within the jacket. On this assumption the amount to be subtracted from the observed heat capacity of the coils would bear to the heat capacity of all the air contained in the jacket the ratio of the total superficial area of the coil to that of the inner surface of the jacket plus that of the coil. Five determinations of the heat capacity of coil 7602 each gave 47.8 joules or 11.4 calories, an agreement entirely fortuitous, as the observations were not such as to give this precision. For coil K the results were less concordant, giving from 48.3 to 49.1 joules per degree, the mean being 48.7 joules or 11.6 calories.

8. Total Heat Capacity of the Calorimeter.—From the foregoing results the total heat capacity in 20° calories of the calorimetric system as used for heats of combustion may be calculated as follows:

TABLE 11

Temperature	15°	20°	25°	30°
Calorimeter with cover and thermometer	41.9	42.0	42.1	42.2
Bomb (6316_1)	275.0	275.8	276.2	276.4
Firing leads	.1	.1	.1	.1
Half cubic centimeter water	.5	.5	.5	.5
Oxygen, 30 atmospheres pressure	2.4	2.4	2.4	2.4
Ten drops oil	.2	.2	.2	.2
Charge of combustible	.4	.4	.4	.4
Crucible (6 gr. Pt.)	.2	.2	.2	.2
Standard mass of water at 20° and the equivalent heat capacity at other temperatures	3096.5	3094.0	3093.1	3092.9
Total	3417.2	3415.6	3415.1	3415.3

The relative heat capacities of water here given are from the calibration experiments in this investigation. The relative specific heat of water at 15° and 30°, as determined by different observers using different methods, differs by as much as 0.2 per cent, and the values here used, being determined under conditions peculiar to this calorimeter, would seem to be most nearly correct for use in determining the heat capacity of the calorimeter for use in combustion observations. These values are, however, a satisfactory mean between those found by other observers.

9. Adiabatic Method.—When energy is supplied to the calorimeter by a constant electric current in a coil of small heat capacity and small time lag the rise of temperature is very nearly linear, and by producing a similar rise of temperature in the jacket by the same means, observations, with very small cooling corrections, may be made as suggested by T. W. Richards. This method, therefore, seems to offer much greater advantages under these circumstances than when the rate of temperature rise changes greatly during the experiment.

A considerable number of observations have been made by this method in the calorimeter No. 7602, which is fitted with an auxiliary stirrer and a heating coil capable of supplying enough energy to heat the jacket at the rate of 1° per minute. The method of taking these observations was similar to that already described except that the small cooling correction was computed from the mean difference in temperature between the calorimeter and the jacket, as observed by means of a thermocouple, the junctions of which were small flat plates, one resting on each of the surfaces and insulated from them by thin strips of mica. The total correction seldom exceeded 1 in 10 000.

In order to discover any systematic difference between the adiabatic and the ordinary method of observation the two methods were often applied alternately in the same series while raising the temperature by steps of 3° or 5° from 10° to 45°.

In the following series of results, dated March 18, 1913, taken from observations on a single filling of the calorimeter, the two methods, the ordinary and the adiabatic, were alternated, and corresponding results are marked a and o.

TABLE 12

Mean temperature	Joules per gram	Method
8°.5	14 290	a
11.5	14 273	o
14.9	[16] 14 257	a
18.0	14 245	o
20.9	14 240	a
24.0	14 238	o
26.9	14 238	a
29.9	14 239	o
32.9	14 239	a
35.9	14 240	o
38.9	14 242	a
42.0	14 245	o
44.9	14 254	a

[16] Not in agreement with other observations taken at this temperature; should be 14 252.

The two methods of observation appear from the second column to be in agreement to about 1 part in 15 000. Many other series of such determinations have failed to indicate any significant systematic difference between the results obtained by the two methods.

IX. COMBUSTION EXPERIMENTS

The three substances, sugar, benzoic acid, and naphthalene were chosen for the first series of experiments because of the fact that they have been widely used and are well adapted for use as standard substances for the calibration of bomb calorimeters. Their heats of combustion have been determined by a number of observers and for sugar and benzoic acid the results are in fair agreement, but for naphthalene the values found by different observers differ by nearly 0.7 per cent.

1. Bombs Used in the Experiments.—The two Peters bombs, the heat capacities of which have been determined, were used for most of the succeeding observations and most of these were with 6316_1. Observations with the Williams bomb showed no significant differences from those with the Peters bombs.

The two Peters bombs are entirely similar except that one is lined with platinum and the other with porcelain enamel. The material is steel for the body of the bomb and bronze for the cover. Details of construction are given in Fig. (9).

2. Materials Used for Combustion Experiments.—The sugar [17] used in these determinations was all from samples prepared by R. F. Jackson, of the Bureau of Standards, and contained less than 0.01 per cent of impurities, including water.

The benzoic acid for the 1910 series was from samples purified by G. E. Morey, of the chemical division of the Bureau of Standards. The original samples were from different sources and the samples used were purified in various ways. All the purified samples were, however, of such a degree of purity or at least of uniformity that various results appear entirely comparable for the different samples, showing no consistent differences greater than the errors of observation.

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[17] Bureau of Standards Circular No. 44, p. 83.

The naphthalene for the 1910 series also was prepared by Mr. Morey from samples obtained from different sources and the observations include a series made upon some samples as received, without further purification. The preparation of these materials is the subject of a separate report by Mr. Morey.

Difficulty is experienced in securing pure oxygen, which must be used at a pressure of from 30 to 45 atmospheres for filling the bombs. After considering this problem it was decided to prepare oxygen by the electrolytic process and compress it to a pressure of 100 atmospheres for use. With this object in view an electrolytic generator was designed and built. The generator consisted of a battery of nine cells connected in series and taking a current of about 20 amperes at 120 volts. For compressing the gas a two-stage compressor was designed and built, using mercury for the compressing pistons so that the oxygen during compression came in contact only with mercury and steel. Unfortunately the time required for building this apparatus was so long that it was impossible to have the pure oxygen for the present series of experiments and a supply was obtained commercially which contained only a small amount of nitrogen, amounting in different cylinders to from 0.3 per cent to 0.5 per cent. The remainder of a residue of about 2.5 per cent was found to be argon. The amount of nitric acid formed under like experimental conditions seems to be approximately proportional to the amount of nitrogen contained in the oxygen. The correction to be applied for the heat of formation of the HNO_3, as determined by titration, was usually about 1 part in 1000, so that the small amount of nitrogen present can hardly have had an appreciable effect on the results, beyond that accounted for by this correction.

3. Order of Procedure.—The required amount of water (total weight in air, of calorimeter and water = 3500 g), was weighed out in the calorimeter and the same placed in the jacket as for a heat capacity observation.

A sample of the combustible of about the desired amount was compressed into a briquette and weighed in the platinum crucible in which it was to be burned. The amount used varied from 0.6 g to over 2 g, depending upon the material. After weighing, the crucible was placed in the bomb, the cover screwed in place, and the inlet coupled to the oxygen filling system. First the bomb was exhausted to a few centimeters pressure by means of the laboratory vacuum system, then it was filled with oxygen from the supply cylinder to a pressure of two or three atmospheres and exhausted again. This process removed practically all of the nitrogen originally in the bomb and left it ready for filling to a pressure of about 30 atmospheres for naphthalene combustions or sometimes a higher pressure for sugar and benzoic acid combustions.

After filling to the required pressure, the bomb was removed to the calorimeter, the electrical connections made, and the calorimeter cover and jacket cover put in place, as prevously described. The temperature rise was known approximately from the amount of substance to be burned, and the jacket temperature was so adjusted that the final temperature of the calorimeter would be not over a few tenths of a degree, preferably three tenths (see p. 239), above it. Oil was used to retard evaporation from the calorimeter as in the heat capacity observations. The remainder of the observation was carried out as in the case of electric heating except that a second observer was not required. The method of computing the cooling correction, described on page 233, leaves only a single observation to be made during the rapid temperature rise.

4. Form of Observation and Computation Sheet.—Observations were made and computations carried out on specially prepared sheets similar to those used for the heat-capacity observations described above. The following sheet is taken from the records on the combustion of benzoic acid.

TABLE 13

Department of Commerce
BUREAU OF STANDARDS
Washington

COMBUSTION RECORD

				RESISTANCE	TIME	DIF.	OBS.	COILS
T_R	1-52-28							
T_M	1-53-31			27.3308	1-44-42	14		20.
DT	1-03=63″			9	56	14		5.
r	$.0^5788$ corrected			10	45-10	13		2.
rDT	.00050			11	23	14		.2
R	27.33450			12	37			.1
R_1 corr.	.33500							
		dR	.0037 ω	27.3341	1-51-39	11		
		dT	466″	42	50	13		
		r	$.0^579_4$	43	52-03	13		
		Mean R	27.333	44	16	12		
		dR	.0004 ω	45	28			
		dT	426″					
		r_2	$.0^694$	Fired	52-47			
		Mean R	27.606					
FIRE	1-52-47	Calor.	7602	27.47	53-29			
Substance B Acid		Bomb	6316r					
1913 Sample		Wt.	3500.0					
Wt.	7.9896	Corr.	— .3	27.605	1-55-11			
Cru.	6.5185	Tare	— 409.3	58	48			
Net	1.4711	Vac.	+ 3.4	59	56-15			20.
		Mass	3093.7	59	57-10			5.
O. Pres.	30 Atm.	In place of Standard Mass of 3094.0.		58	58-34			2.
Wire	2 cm.			57	2-00-42			.5
Tit.	4.0 c.c.							.1
Remarks	Correction		3412.4	54	05-40			
=10.8 Cal.		Excess Mass	— .3					No coil corrections are significant.
		Equiv.	3412.1					
T_R	1-58-34							
T_M	1-53-31							
DT	5-03=303″							
r	$.0^695$							
rDT	.00029							
R_2	27.60580							
R_2 corr.	27.60609							
R_1	27.33500							
DR	.27109							
K	10.0690	OUTER BATH						
DT	2°.7296	THERM.						
		Time	Temp.	Room.				
EDT	9313.6	1-43	24°.05	20°.3				
Corr.	10.8	2-06	24°.05	20°.3				
Cal.	9302.8							
Cal. per gram	6323.8							

5. Corrections.—Aside from the calorimetric corrections already discussed under Section VIII, combustion observations require corrections tabulated on page 242 for heat capacity of the combustible, the oxygen and a small amount of water placed within the bomb to saturate the oxygen, for the heat liberated in the formation of secondary products such as nitric acid, when nitrogen is present in the oxygen, and for the energy supplied in combustion of the ignition or fuse wire used to fire the combustible.

The electric fuse used for igniting the charge in the calorimeter may be either of platinum or iron, but since iron wire burns instead of only melting, it is much more certain to ignite such substances as are easily fused, and for this reason is more commonly used, in spite of the fact that a correction must be applied for the heat supplied by its combustion. The wire generally used weighed 132 mg per meter and the correction for heat liberated in its combustion is 2.25 calories per centimeter, as the heat of formation of iron oxide is about 1600 calories per gram of iron. From 1 to 3 cm were used according to the substance to be ignited. Naphthalene ignited readily with 1 cm while sugar required 3 cm of wire.

A small amount of nitric acid is formed from the nitrogen contained in the oxygen. The amount is nearly proportional to the heat liberated in the combustion and to the percentage of nitrogen present, and was determined by titration after each combustion. The heat of formation of HNO_3 from $N+O+H_2O$ is about 230 calories per gram of acid. The correction for this nitric acid amounts to 1.45 calories per cubic centimeter of the one-tenth normal NaOH solution used for titration. This correction is applied to the total calories (i. e., heat capacity × temperature rise).

Apparently in all previous investigations the amount of heat supplied by the electric current during the very short time before the wire melts has been considered negligible. This seemed to be hardly justified and a supplementary experiment was made to determine the magnitude of this quantity. A small copper cylinder was hollowed out and fitted with a copper sleeve in such a way that by running in insulated terminals at the ends, a 1, 2, or 3 cm length of the iron fuse wire could be mounted within this closed copper box and fired in the same way as when mounted in the calorimeter. In order to guard against partial combustion of the iron by the small amount of oxygen contained in the copper "calorimeter" the openings were made tight with wax, after forcing carbon dioxide through the inclosed space to drive out the air. This copper "calorimeter" was about 12 mm in diameter, 30 mm long, and had a water equivalent of 3 g. In order to measure the rise in temperature of this small mass of copper a fine constantan wire was soldered at one end to it and at the other end to a solid bar of copper of similar dimensions and the circuit was closed through a galvanometer by means of copper leads. This arrangement gave a sensitive calorimetric device which was calibrated by replacing the iron wire by a platinum wire and supplying energy by means of an electric current while measuring the current and voltage by means of a milliammeter and a voltmeter. The calibration gave a deflection of 2.45 cm on the galvanometer scale for 1 joule supplied to the "calorimeter." Experiments with the iron wire melted out by the current from two storage cells in series for each 2 cm of length, and no external resistance, gave for the energy supplied to melt the wire, 0.5 calorie per cm of wire. This correction for a length of 3 cm of wire is not quite negligible.

A number of combustions were made with different amounts of oxygen present in the different bombs, and it was found that when the amount of oxygen was much less than two and one-half times that required to unite with the combustible charge, there were often evidences of incomplete combustion as indicated by a reduction in the total heat liberated as well as by the occasional presence of a slight amount of soot, and by the odor of the products of combustion.

When the amount of oxygen was increased to three times that required to unite with the charge no indications of incomplete combustion were observed, except in rare instances, and no further changes in the observed heat of combustion were noted with further increases in the amount of oxygen employed.

A further check on the completeness of combustion is afforded by the fact that analyses of the products failed to show the presence of carbon monoxide.

X. RESULTS OF COMBUSTION EXPERIMENTS

Observation of the heats of combustion of the three substances sugar, benzoic acid, and naphthalene, as well as of the heat capacity of the bomb, have been carried out intermittently for more than three years by the author, and of late by other observers as well, for study and certification of standard samples of the above materials.

The mass of data collected to date is so great that only a comparatively brief summary of it can be given. The number of combustions amounts to some hundreds. In general, a single observation very seldom departs from the general mean of corresponding observations by much more than 1 part in 1000. Some of the earlier work in the earlier form of calorimeter did not show quite so good agreement.

1. Naphthalene.—A series of 17 observations in February, 1910, on five different samples gave 9617 calories per gram weight in air against brass weights with a mean variation of 3.4 calories and a maximum difference from the mean of 11 calories.

A series of 101 observations was made between March and November, 1910, upon four lots obtained from three different dealers, the quality ranging from "highest purity" to "crude flakes." Samples from these various lots were prepared as follows: (1) Unpurified, (2) purified by crystallizing from alcohol, (3) by subliming this sample once, and (4) by recrystallizing from a mixture of liquids having the same heat of combustion as naphthalene. (See Mr. Morey's report.) Tests were made on the original material and on the three prepared samples. The results of this series of observations are tabulated below.

TABLE 14

Heats of Combustion of Various Samples of Naphthalene

	Lot 1. Kahlbaum highest purity	Lot 2. Merck crude flakes	Lot 3. Merck best	Lot 4. Eimer & Amend best imported
Sample 1	9618.7—4 obs.	9617.1—4 obs.	9620.6—3 obs.	9615.8—3 obs.
Sample 2	9620.1—4 obs.	9618.2—4 obs.	....	....
Sample 3	9621.3—4 obs.	9619.4—20 obs.	9615.8—4 obs.	9620.1—12 obs.
Sample 4	9623.7—4 obs.	9620.1—5 obs.	9622.0—4 obs.	....

This table includes all the observations made with bomb 6316_1, on the given samples. A few observations with the "Williams" bomb gave results lower by about 3 parts in 10 000. These latter are not given the same weight as those with bomb 6316_1, since only a small number of observations had been made on the heat capacity of the "Williams" bomb.

While these results indicate in each lot of material a slight increase in the heat of combustion with progressive purification, the maximum difference between any two of the values is less than 1 part in 1000. The mean deviation of the original individual observations from the general mean, taken without regard to the samples, is less than 3.0 calories, i. e., only perhaps 50 per cent more than would be expected from a series of observations with a single sample. This indicates that naphthalene as obtained on the market differs in general by less that 1 part in 1000 in heat of combustion from the purest material.

All the observations up to this point were made in the earlier calorimeter No. 6583.

A series of six observations made in April, 1912, with calorimeter 7602 on a sample of naphthalene prepared for standard samples, gave 9618.8 with a mean deviation of 1.9 and a maximum deviation of 3.5.

A series of 12 observations made in August, 1912, with calorimeter No. 7602, using an entirely new determination of the heat capacity of the calorimeter and a newly prepared sample of naphthalene gave 9623.6 with a mean deviation of 2.1 calories and a maximum deviation of 4.2 calories.

The weighted mean of the foregoing results for the heat of combustion of naphthalene is 9622 ± 2 calories (20°) per gram, weighed in air.

2. Benzoic Acid.—A series of 14 observations made with calorimeter No. 6583 in February, 1910, on four samples purified by several methods from a single lot of material, gave 6328 calories, with a mean deviation of 4.5 and a maximum deviation of 10. The observations on different samples showed no systematic difference, hence all are averaged together. A series of five observations made in April, 1912, with calorimeter 7602, gave 6331 calories with a mean deviation of 3.0 and a maximum deviation of 5.1.

A series of 11 observations made in September, 1912, on a newly prepared sample, gave 6330 ± 1.8 calories (mean deviation).

A series of nine observations in May, 1913, on a newly prepared sample gave 6329 ± 1.4 calories (mean deviation).

The weighted mean of the foregoing results for the heat of combustion of benzoic acid is 6329 ± 2 calories (20°) per gram, weighed in air.

3. Sucrose or Cane Sugar.—A series of 12 observations made in February, 1910, with calorimeter No. 6583, gave 3951 calories with a mean deviation of 3 and a maximum deviation of 6 calories.

A series of 14 observations made in September, 1912, with calorimeter No. 7602, gave 3948 ± 1.1 calories.

The weighted mean of the foregoing results for the heat of combustion of pure sucrose is 3949 ± 2 calories (20°) per gram, weighed in air.

4. Review.—The following table of comparative results, in so far as the available data will permit, is given in terms of 15° calories instead of 20° calories and for the substances as weighed in air against brass weights. Wrede gives the following figures for specific gravities: Naphthalene 1.145, benzoic acid 1.34, and sucrose 1.58. The results of Fischer and Wrede and of Wrede are expressed in kilo-joules and for weights in vacuo. The former reduced their results to calories by means of the ratio 4.177 for the calorie to the joule, a figure which differs by more than 2 parts in 1000 from that deduced from observations in this investigation (p. 237). The results of both Fischer and Wrede and of Wrede, however, have been reduced to 15° calories by Roth for the Landolt and Börnstein tables, by the use of the ratio 4.189, and as this figure seems much more nearly the correct one, the results quoted below for these authors are those as recomputed by Roth.

TABLE 15

Résumé of Previous Results

Authority	Naptha-lene	Benzoic acid	Sucrose	Date
Stohmann, Rodatz, Hertzberg	....	6315	....	1887
Berthellot, Vieille	....	....	3962	1887
Berthellot, Luginin	....	6322	....	1888
Berthellot, Recoura	....	6345	....	1888
Stohmann, Kleber, Langbein	9628 9619	6322	....	1889
Stohmann, Langbein	....	....	3955	1892
Atwater and Snell	....	....	3959	1903
Fischer and Wrede	9641	....	....	1904
Fries	....	6334	....	1907
		6318	....	1910
Fischer and Wrede	....	6325	3952	1909
Wrede	9633	6323	3952	1910
Roth	9643	....	....	1910
Leroux	9631	....	....	1910
Dickinson	[18] 9612	[18] 6323	[18] 3945	1910 1912

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[18] Here reduced to a basis of 15° calories (by division by 0.999) for comparison with the other results which are expressed in these units.

A comparison of the above results shows very satisfactory agreement with the later observers on the heat of combustion of benzoic acid but a much less satisfactory agreement for the other substances.

As to the results for naphthalene, the early result of Berthellot's investigations (not given in the table) was 9692, a figure manifestly too high, in the light of later observations. Although Wrede's recorded observations were quite concordant, he particularly notes the fact that he does not consider them very reliable, as he found large variations which he attributes to differences in the structure of the substance depending upon its treatment. The experience of the author has been entirely different from this. As has been noted, samples of naphthalene from widely different sources and of widely different degrees of purity have been examined. Nearly all the observations have been made with samples compressed into briquets but some have been made with blocks cut from the fused material. A number of observations were made with a sample which had been exposed to bright skylight for several months until it showed a decided brown cast on the surface. Briquets were even made up containing as much as possible of the brown surface layer. The amounts of combustible, the pressure of oxygen, and the shape of combustion crucible were changed over the widest practicable range, but no variations were found comparable with the difference between Wrede's results and the present ones.

The results on sucrose also are somewhat lower than those of other observers. The only apparent explanation for this difference is found in the fact that the present observations are corrected for the heat generated in the firing wire before it is ignited. This correction does not seem to have been made by other observers, and while it could hardly be large enough to account entirely for the differences which exist, its real magnitude can not be estimated from the data published. The effect of this correction on the results for sucrose is greater than on those for benzoic acid, on account of the smaller heat of combustion of the former, and it is more important if a greater length of fuse wire is used with the sucrose charges, as is sometimes done because of the lower inflammability of sucrose.

In view of the agreement among different observers, it would seem that benzoic acid is preferable to either naphthalene or sucrose for the accurate standardization of bomb calorimeters.

XI. SUMMARY

A critical examination of such sources of error in calorimetric measurements as occur in the use of the combustion bomb shows that most of these errors can be avoided or reduced to a negligible quantity by care in the design, construction, and use of the calorimeter.

The cooling corrections for a calorimeter designed in accordance with the conclusions reached can be made by a very simple procedure and with an accuracy corresponding to perhaps 1 part in 10 000 of the total amount of heat measured.

A method of electrical calibration was used, which enables the results of combustion observations to be expressed directly in calories almost independently of the electric units, or if the heat capacity of the electric heating element used in the calibration is known, to be used to check serious errors in either the calorimetric system or the electrical calibrating system.

Observations have been made with two different calorimeters built especially for the purpose and each calibrated by the above method several times independently. Both calibrations and combustions cover a period of more than three years, during which time hundreds of observations have been made with different electrical equipment, and samples of material obtained from different sources and purified at different times and in different ways.

Determinations of the heat of combustion of naphthalene gave **9622** ± 2 calories (20°) per gram weighed in air, with a maximum deviation from the mean of about 5 in 10 000 for groups of observations upon the same samples and about the same maximum deviation of different groups of observations from the mean of all, regardless of the sample.

Determinations of the heat of combustion of benzoic acid gave **6329** ± 1 calorie (20°) per gram weighed in air, with a maximum deviation of about 1 in 1000 for the earlier experiments and 5 in 10 000 for the later ones. Observations taken on samples, some by no means pure, from different sources, show a maximum deviation of 15 in 10 000 and a mean deviation of 7 in 10 000.

Determinations of the heat of combustion of sucrose, fewer in number, gave **3949** ± 2 calories (20°) per gram weighed in air. The later observations show a maximum deviation of a little less than 1 in 1000 and a mean deviation of about 3 in 10 000, though the earlier ones show a maximum deviation of 15 in 10 000.

It appears that, of the three materials included in this investigation, benzoic acid is the most desirable as a combustion standard, as indicated by the agreement between the results of different observers. Naphthalene has been found very reliable and convenient, although it requires care in handling, since a gram briquet will lose more than 1 mg per hour by sublimation. An accuracy of 3 parts in 10 000 is attainable.

Sucrose seems not to be so well adapted for use as a combustion standard as is benzoic acid because of its lower heat of combustion, its frequent failure to ignite, and the lower precision of the results obtained.

XII. BIBLIOGRAPHY

The references which might be cited if the general subject of calorimetry were included are so numerous and the field which would be covered is so far outside the scope of this paper that no attempt has been made to introduce an exhaustive bibliography.

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