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AN ELECTRICALLY CALIBRATED BOMB CALORIMETER

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After a review of the physical foundations of bomb calorimetry, a bomb calorimeter is described which can be heated electrically or by combustion. The evaporation of water is prevented by sealing the vessel completely. Other modifications in the normal technique are introduced after consideration of (*a*) the difference in temperature between the outer surface of the calorimeter and the thermometer immersed in it, (*b*) the effective 'boundary' of the calorimeter in electrical and combustion experiments, and (*c*) variation with temperature of the constants of the apparatus.

The heat of combustion of samples from a batch of thermochemical quality benzoic acid is found to be 26436 J/g under 'standard bomb conditions'. The standard error of the determination, a combination of errors in reproducibility of electrical and combustion experiments and in measurement of the corrections, is estimated to be 2·2 J/g.

CONTENTS

PAGE
1. THEORY OF BOMB CALORIMETER 554
  Departures from the ideal 554
    Control of stray heat 555
    Calibration 556
    Magnitudes 557
  Correction for heat transfer 558
    Heat of stirring and conduction to room 560
2. THE N.P.L. NO. 1 BOMB CALORIMETER 561
  Description 561
    Design calculations and tests 565
      Calorimeter stirring and temperature equilibrium 565
      Heat transfer 567
      Temperature observations and heat-transfer correction 571
      Variations in heat of stirring, conduction to room, and heat-transfer coefficient 572
  Experimental procedure 573
    Assembly for electrical calibration and combustion experiments 573
3. RESULTS 575
  Corrections 575
  Errors 577
  Comparison with other determinations 579
REFERENCES 580

The heats of formation of many chemicals can best be determined through burning them in oxygen in a bomb calorimeter. From the heat of combustion so measured, the heat of formation of the original chemical is derived by subtracting the heat of formation of the oxides in the products of combustion (such as water and carbon dioxide). In many cases the heat of formation is very much smaller than the heat of combustion, and this may need to be measured with high accuracy if the final answer is to be valid even within 1 %. The use of heats of formation in determining Gibbs free energy and hence the equilibrium of chemical reactions has been discussed, for example, by Rossini (1936).

The design of a calorimeter for measuring in absolute units the heats of combustion of chemicals was considered in detail by Dickinson (1915). There have been certain improvements in the original design (White 1928; Jessup & Green 1934), and there has been a careful discussion of the thermodynamical corrections (Washburn 1933), but the physical foundations of Dickinson's original work, though they have stood the test of many years' experience, deserve further consideration for at least two reasons. First, it may be possible to improve a little on the reproducibility of observations. Secondly, discussion is needed of certain systematic corrections, particularly those connected with the flow of heat between the calorimeter and its outer jacket. It seems desirable, therefore, to set out the theory from the beginning.

This paper falls into three sections: §1, Theory of the bomb calorimeter; §2, Design of the N.P.L. calorimeter; §3, Results of electrical calibration and the heat of combustion of benzoic acid of thermochemical purity.

1. Theory of bomb calorimeter

The ideal combustion calorimeter is a vessel (a thermodynamic 'system') whose heat content (enthalpy) can be raised either (1) by burning known masses of chemicals to form known quantities of combustion products, or (2) by converting a precisely measured amount of electrical energy into heat. The amount of heat entering the system must bear an accurately known relation to the change in one of its parameters. The pressure, volume, temperature or constitution of the system as a whole, or of any particular part of the system, will serve equally well as the parameter; but it must be strictly related to the total internal energy, and independent of the method by which the energy is changed. In most calorimeters, including the one described in §2, the chosen parameter is an approximation to the temperature of the system as a whole; and in this paper the parameter will be referred to as 'the temperature'. From a measurement of the change in temperature (1) when a known mass of chemical is burnt and (2) when a known quantity of electrical heat is generated, the heat of combustion per gramme of the chemical is calculated.

The temperatures on which the ideal determination depends need not be the temperatures of the entire calorimeter. Indeed, outlying parts of any practical bomb calorimeter are nearly always at different temperatures from the central parts. All that is required is for each temperature, as measured by a thermometer, to correspond in a known manner to a particular value of the total internal energy of the calorimeter. Nevertheless, since no heat enters or leaves an ideal calorimeter other than heat deliberately generated, it must eventually reach an equilibrium and be entirely uniform in temperature.

Departures from the ideal

It is difficult to set in logical order the departures from the ideal which have to be tolerated in practice. The following arrangement is perhaps most convenient, assuming that the final compromise will be the 'classical' bomb calorimeter with an isothermal outer jacket to be described in §2.

(1) As it is impracticable to keep the room and the observer always at the same temperature as the calorimeter, some heat must flow into or out of the calorimeter along the thermometer stem or leads, the leads to the heater and the leads for igniting the chemical.

(2) The temperature is therefore a function of time as well as of the heat deliberately generated.

(3) Complete thermal insulation of the calorimeter from its surroundings is impracticable for reasons additional to conduction along the leads. Ordinary lagging materials would change in temperature and absorb an uncertain amount (strongly dependent on time) of the calorimeter's heat. Vacuum jackets would have to be strictly vacuum-tight to avoid heat losses due to air being drawn past the calorimeter, and would introduce awkward complications of heat flow at the joints. An 'adiabatic' shield would prevent all heat flow if it could be kept always at the same temperatures as the outer surface of the calorimeter; but, during rapid heating especially, the outer surface of a calorimeter is not at the same temperature all over, and its temperatures are difficult to measure.

The 'classical' compromise is to surround the calorimeter with an 'isothermal' jacket, the inner surface of which is kept at a strictly constant temperature, with air of low humidity between jacket and calorimeter.

Control of stray heat

(4) Much heat now flows to or from the calorimeter, except when its temperature is close to that of the outer jacket.

(5) The flow of heat is so dependent on the temperature of the outer surface of the calorimeter that this temperature must be measured or kept as close as possible to the temperature within the calorimeter that is actually measured. (The second alternative is the 'classical' choice, but experiments described in §2 indicate that during the heating period some knowledge is required of the difference between the measured temperature and the average temperature of the outer surface.)

Approximate control of the outer-surface temperature is achieved by making the calorimeter mainly of a liquid and stirring the liquid as efficiently as possible without unnecessary generation of heat. An important effect of stirring, often regarded as the main consideration, is that the temperature of one thermometer can be taken as being the 'temperature of the calorimeter' to a close approximation for a large part of the time.

(6) The heat generated by stirring the liquid is considerable, perhaps 3 % of the total. Theoretical considerations show that correction for it is simple and exact provided that it is generated at a strictly uniform rate.

(7) The transfer of heat between the calorimeter and the outer jacket can be calculated, and the necessary correction made, provided that it is strictly proportional to the difference between two temperatures, one of which (the inner surface of the outer jacket) must be constant but need not be measured. The 'heat-transfer coefficient' must therefore be kept constant, independent of time and temperature during each individual experiment; it need not be the same in different experiments, though it usually is the same.

Transfer of heat by conduction along the solids in contact with the calorimeter can easily be kept proportional to the temperature difference. Transfer by radiation and by conduction through the air can be kept nearly proportional to the temperature difference provided this is not more than a few degrees. Transfer by convection in the air is liable to change in an unknown manner during an experiment; it must be kept to a minimum by making the air gap and the temperature gradient within it small. Transfer of heat by the evaporation and condensation of liquid from the outer jacket or calorimeter must be absolutely avoided.

Calibration

(8) The effective heat capacity of the calorimeter is determined when an electrical experiment is made, and a measured electrical heat input produces a measured rise in temperature of the thermometer. The true heat capacity, for which all parts of the calorimeter must undergo the same rise in temperature, need not be known. In a calculation of the heat of combustion the effective heat capacity from an electrical determination must be used. Thus the calorimeter used in the two experiments must be identical in effective heat capacity, and any unmeasurable differences in heat capacity, such as the relatively large differences that occur if some of the heat is used for evaporating a liquid and the vapour escapes from the calorimeter, must be avoided. The only quantities that need to be known in standard units are the heat capacities and rises in temperature of any parts of the calorimeter that are different in the two experiments, and these need not be known accurately if the corrections are small. The initial and final temperatures of the main thermometer need not be known on any particular scale, provided the thermometer readings are reproducible. Bomb calorimetry has been successfully carried out by measuring the mass of combustible and a standard heat input necessary to move a mercury column from a lower to an upper mark on a glass stem (Coops 1947).

A very important consequence of the fact that a calorimeter is a comparing instrument arises in dealing with systematic corrections. There are a number of quantities connected with practical calorimeters which cannot be known accurately, yet so long as these are unchanged between an electrical heating and a combustion, no systematic error results. On the other hand, a careful watch must be kept on quantities which may be slightly different in the two cases.

(9) One of the quantities which may in certain circumstances be left uninvestigated is the 'effective boundary' of the calorimeter. When the calorimeter vessel changes in temperature, the air around it and the solids touching it change also, and they remove some internal energy from the calorimeter proper. This introduces no error provided that the effective boundary is the same when the calorimeter is heated in either way.

The current leads to the electrical heater must of course pass across the interspace between the outer jacket and the calorimeter. If they are not particularly thick, they will rise in temperature when the heating current passes through them. Provided that their rise in temperature is no more than it would be during a heating by combustion, no harm is done; but if they rise too much in temperature the effective boundary of the calorimeter will be different in the two kinds of heating. This is a point which has received little attention in the literature.

To get full benefit from the advantages of using the calorimeter as a comparing instrument, the 'middle period', during which the heat is distributed to all parts should be of about the same duration whether the heating is electrical or by combustion.

(10) Heat cannot be generated at the same point of a calorimeter by both methods of heating; nor can it be generated at the same rate. Hence the temperature of the outer surface of the calorimeter requires careful examination. During the middle period different parts of the outer surface will be at different temperatures, and their average will in general lag behind the temperature of any thermometer immersed in the liquid of the calorimeter. There is no reason to expect that the lag of the average outer surface temperature behind the thermometer will be the same in the two forms of heating. If they differ by as little as 1 s a correction should be made. Exploratory tests of the lags seem to be essential, for otherwise serious systematic errors are likely to be introduced.

The literature contains no reference to exploratory tests of this nature, and the electrical calibration of calorimeters where such tests have not been made must surely be open to some doubt.

Magnitudes

(11) The flame of the burning charge must not touch the wall of the bomb, because it would be cooled so much that combustion would be incomplete. This fact determines the minimum internal volume of the bomb, and its mass is then determined by its need to be strong enough to withstand the explosion if, by mischance, the charge should burn explosively. The size of the calorimeter is then made sufficient for the heat capacity of the liquid within it to be the major part of the total heat capacity of the calorimeter.

(12) The most desirable temperature rise during a heating is about 2° C. A smaller rise might not be measured accurately enough by the thermometer, or it might make the requirements of temperature control in the vicinity of the calorimeter too severe. With too large a rise the heat-transfer coefficient would not be sufficiently constant over the temperature range of an experiment.

(13) The mass of charge to be used is determined by its heat of combustion, the temperature rise, and the heat capacity of the calorimeter. It is usually about 1 g, and some ingenuity may be needed to weigh the charge with sufficient accuracy if, for instance, it is volatile or hygroscopic. The charge is ignited with a momentary electric current, whose energy should be kept to a minimum, and measured. If the charge is difficult to ignite, a small mass of readily ignited material may have to be included, and its heat of combustion must be known.

(14) The amount of electrical energy is fixed in the same way as the mass of the charge. The time for which a current is passed through the heater must permit an adequate number of observations to be made of the potential difference between the ends of the heater and the current through it. The initial steadying up of the current introduces a correction which must be kept small and be determined with adequate accuracy.

(15) To summarize, the 'classical' calorimeter differs from the ideal calorimeter chiefly because of (*a*) heat transferred between the calorimeter and its surroundings, (*b*) heat generated during stirring of the calorimeter liquid and (*c*) the time needed after a heating for the calorimeter to reach approximate equilibrium. The main problem of calorimetry is to correct for (*a*) during the time (*c*). When this has been solved, the minor corrections can be made.

Correction for heat transfer

There are several methods of correcting the temperature rise in a bomb calorimeter for the heat transferred between the calorimeter and the outer jacket. All are suitable for work of ordinary accuracy, but that of Dickinson (1915) and Jessup (1942*b*) is particularly suitable when slight departures from the ideal must be considered or when a critical examination has to be made of the differences in performance of a calorimeter when heated electrically and by combustion.

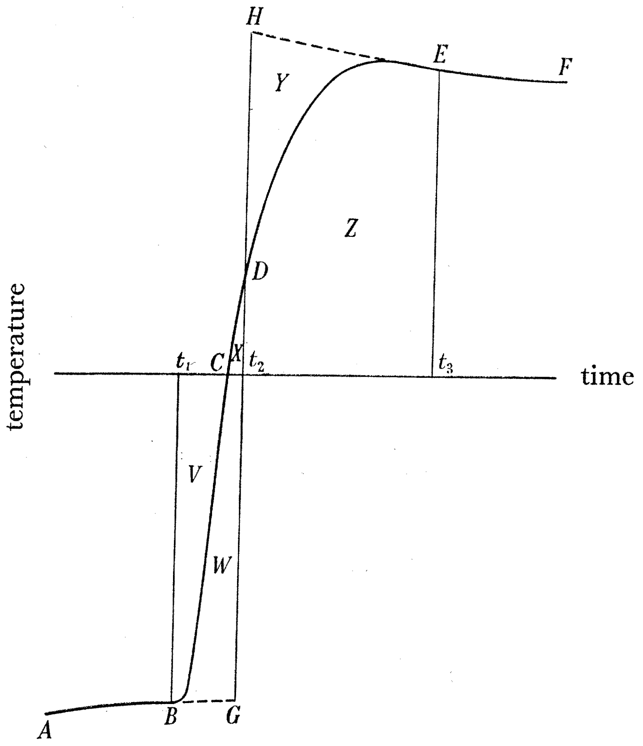


FIGURE 1. Temperature of outer surface of calorimeter.

Briefly, the method consists of extrapolating the initial and final temperature-time curves of the calorimeter to a time determined from the shape of the curve in the middle period. The proof seems to leave some doubt whether the method is exact, and until ideal requirements of the calorimeter can be precisely stated, it is difficult to discuss errors arising from the compromises which are made in reality.

The proof which follows appears to be rigorous. It applies in the first place to a calorimeter with no heat of stirring and no heat conduction to the room, assuming only that the heat-transfer coefficient is independent of time and temperature. It leads to a practical correction for heat transfer and an estimate of its casual error. Its extension to include a constant heat of stirring and conduction to the room is a simple matter. In practice, these are not strictly constant and the heat-transfer coefficient is not independent of temperature; consequent corrections are discussed in §2, after the description of the N.P.L. calorimeter.

In figure 1, let *ABCDEF* represent the average temperature over the outer surface of a calorimeter when it is heated either electrically or by a combustion and let $t_1 C t_2 t_3$ represent the constant temperature of the outer jacket. The period before the bomb charge is fired (or the heat switched on) at *B* is usually called the initial period; the period corresponding to *BCDE* is the middle period; and that corresponding to *EF* is the final period. *E* is any point on the curve after which the curve converges exponentially towards the time axis.

The parts *AB* and *EF* of the curves can be taken to represent either the surface temperature or the temperature of the calorimeter as a whole, because in the initial and final periods any well-designed calorimeter is very nearly in thermal equilibrium. If Newton's law holds exactly, the curves *AB* and *EF* are exponentials with the same differential equation

$$\mathrm{d}T/\mathrm{d}t = -k(T-T_0), \tag{1}$$

where k is the heat-transfer coefficient (divided by the heat capacity of the calorimeter) and T_0 is the temperature of the outer jacket.

The section *BCDE* of the curve represents the average temperature over the outer surface only. Experiments have shown that the curves for temperatures at other positions in a calorimeter of good design would be similar in shape to *BCDE*, but could be displaced by up to 20 s to the right or left of *BCDE*. For measurements of the highest accuracy, the position of the curve *BCDE* must be known within an error of about 1 s or 0·01° C. It must be emphasized, however, that during the middle period information is not needed about any part of the calorimeter other than the outer surface; the 'temperature of the calorimeter' in this period is indefinite and unobservable, in spite of its frequent mention in the literature.

If *B* and *E* are any convenient points on the initial and final exponential curve, the quantity Q_h of heat from the main heat supply will be given by

$$Q_h/c = (\text{ordinates } Bt_1 + t_3E) + Q_k/c, \tag{2}$$

where c is the heat capacity of the calorimeter and Q_k (having regard to sign) is the heat transferred from the calorimeter to its outer jacket in the interval t_1t_3. By Newton's law,

$$Q_k = ck\int_{t_1}^{t_3}(T-T_0)\,\mathrm{d}t;$$

that is, in figure 1, $$Q_k = ck(-V+X+Z),$$

where V, X, Z are areas under the curve, taken positively.

For some instant, t_2, in the interval t_1t_3, let an ordinate Gt_2DH be drawn, cutting the extensions of the initial and final exponential curves at G and H. We note that the areas

$$-V+X+Z = -[t_1t_2GB]+[t_2t_3EH]+W-Y+X.$$

We now choose t_2 as the instant when $W-Y+X=0$. It follows that

$$Q_k = -ck[t_1t_2GB]+ck[t_2t_3EH].$$

The expression $-ck[t_1t_2GB]$ is the heat that would be transferred from the calorimeter during the interval t_1t_2 if it began at the temperature corresponding to B and no heat were generated within it. But the curve BG records the change of temperature which the calorimeter would undergo in such circumstances. Hence

$$-ck[t_1t_2GB] = c(\text{ordinates } Gt_2 - Bt_1).$$

Similarly $$ck[t_2 t_3 GB] = c(\text{ordinates } t_2H - t_3E).$$

Therefore $$\begin{aligned} Q_k/c &= (\text{ordinates } Gt_2 - Bt_1) + (\text{ordinates } t_2H - t_3B) \\ &= (\text{ordinates } Gt_2 + t_2H) - (\text{ordinates } Bt_1 + t_3E), \end{aligned}$$

and, substituting in (2), $$\begin{aligned} Q_h/c &= (\text{ordinates } Gt_2 + t_2H) \\ &= \text{ordinate } GH. \end{aligned}$$

Thus the temperature rise, Q_h/c, due to the main heat supply, can be evaluated as follows: First, by using figure 1, find a time t_2 for which the areas $(W+X)$ and Y are equal. Secondly, determine the temperatures that would be reached by extrapolating the initial and final exponential curves to the instant t_2. The difference between these temperatures is the required temperature rise, Q_h/c.

If heat could be put into the calorimeter instantaneously at time t_2, and be perfectly distributed at once, the temperature of the calorimeter (and its outer surface) would follow the curve *ABGDHEF*. There are logical advantages in a method of correcting for heat transfer which has such a simple physical explanation. A more practical advantage is that the method enables a numerical extrapolation to be made, giving weight to all the observations along the initial and final exponential curves, and leading to an evaluation of the casual errors of the extrapolated temperatures.

Heat of stirring and conduction to room

Whatever the physical meaning of k and T_0 in equation (1), the method of evaluating the temperature rise GH will be the same, since the construction is purely geometrical. It can easily be shown that the proof and the method are the same if the calorimeter is gaining heat (from the stirrers) at a rate sJ/s and losing heat by conduction to the room (along the thermometer stem, etc.) at a rate rJ/s, provided that $(s-r)/c = a+bT$, where a and b are constant. Equation (1) becomes

$$\begin{aligned} \mathrm{d}T/\mathrm{d}t &= -k(T-T_0) + a + bT \\ &= -k_c(T-T_c), \end{aligned}$$

where $$k_c = k-b \quad \text{and} \quad T_c = (kT_0+a)/(k-b).$$

This is not different in form from (1) and no alteration in the method of evaluating GH is involved; k_c may be called the 'apparent heat-transfer coefficient' and T_c is the 'convergence temperature', since after infinite time $T = T_c$.

In practice, to a first approximation s is independent of T and r is linearly dependent on T. The assumption that $(s-r)/c = a+bT$ is therefore likely to be very nearly true. Any departures from this assumption, involving terms in higher powers of T, must be investigated experimentally and the error in the temperature rise calculated in relation to an actual experiment.

Constancy of k_c and T_c. The assumptions on which the above proof was made must now be formally revised. Instead of $k = $ const. and $T_0 = $ const. it is necessary that $k_c = $ const. and $T_c = $ const. The implication is that a, b, k and T_0 should all be constant. In a well-designed calorimeter they must be nearly constant, and the corrections involved, if not negligible, must be known accurately enough for their errors to be negligible.

2. The N.P.L. no. 1 bomb calorimeter

Description

Object. A bomb calorimeter, of the 'classical' type described in § 1 has been constructed at the N.P.L. for two purposes. It is needed for determinations of the heat of combustion of pure organic materials to an accuracy commensurate with the purity of the materials, about 99·9 %; the first results, for pyridine, α-, β- and γ-picoline and 2:5- and 2:6-lutidine, have already been published (Cox, Challoner & Meetham 1954). Secondly, it was required for testing standard calorimetric substances, to be used in determining the heat capacities of secondary bomb calorimeters. Details will now be given of the calorimeter and its use for evaluating the heat of combustion of a sample of thermochemically pure benzoic acid (B.D.H. batch no. 692782).

Bomb. The same bomb, of capacity 0·277 l., was used throughout the present work. The bomb and lid were machined from a fully softened bar of stainless steel (composition C, 0·06 %; Si, 0·60 %; Mn, 0·60 %; Cr, 18·90 %; Ni, 11·15 %; Mo, 3·32 %; Nb, 0·84 %). The locking ring was of aluminium bronze and was screwed by hand to press a tongue in the lid into a rubber O-ring in a square groove in the bomb.

The insulated firing post of the bomb was of stainless steel. The insulation and gas seal was provided by a tapered fibre bush protected under the lid by a mica washer. A small amount of fibre was exposed to the gases of the bomb, but was shielded from the direct radiation of the flame and suffered no observable change during an experiment. The firing leads of platinum were attached by clamps to the firing post and to a parallel post in metallic contact with the bomb. The latter post also supported a steel ring in which rested a platinum crucible 2·5 cm in diameter and 1·5 cm in depth.

The benzoic acid in the crucible was in contact with 7 mm of platinum wire, 0·1 mm in diameter, supported by platinum wires 0·5 mm in diameter attached to the firing posts. To ignite the charge a 6 V wet battery was connected to the leads; measurements with a Duddell oscillograph indicated that the fine platinum wire fused in 0·008 s, and that 0·5 to 0·6 J of electrical energy was generated. The products of combustion of organic materials in the bomb had to be analyzed. To facilitate filling and analysis a stainless-steel tube reached from a valve within the lid to the bottom of the bomb. A second opening through the lid was also closed by a valve during an experiment, and afterwards pure oxygen could be blown through the bomb to wash out the last traces of combustion products into the analytical train.

The electrical heater was of slightly flattened manganin wire, approximately 2 m long and 10 Ω in resistance, wound on a mica sheet. It was enclosed between two mica sheets in a flat copper sheath 4 by 8 cm by 0·2 cm thick, with copper leads of 22 s.w.g. widening to 18 s.w.g. within a copper tube. Both tube and sheath were filled with a Silicone oil. The upper end of the tube protruded 0·4 cm through the calorimeter lid, to which it was clamped by a nut, and sealed with a rubber washer. Each heater lead of 18 s.w.g. copper was screwed in a brass connector about 2 cm from the point where it emerged from the copper tube into the air space above the calorimeter lid. Each brass connector was soldered to a copper strip 0·4 by 0·1 by 15 cm, in a silk sheath. The other ends of the strips were soldered to heavy copper leads from the battery, and were provided with terminals for potential leads. A correction was applied for the small part of the potential drop which corresponded to heat not entering the calorimeter.

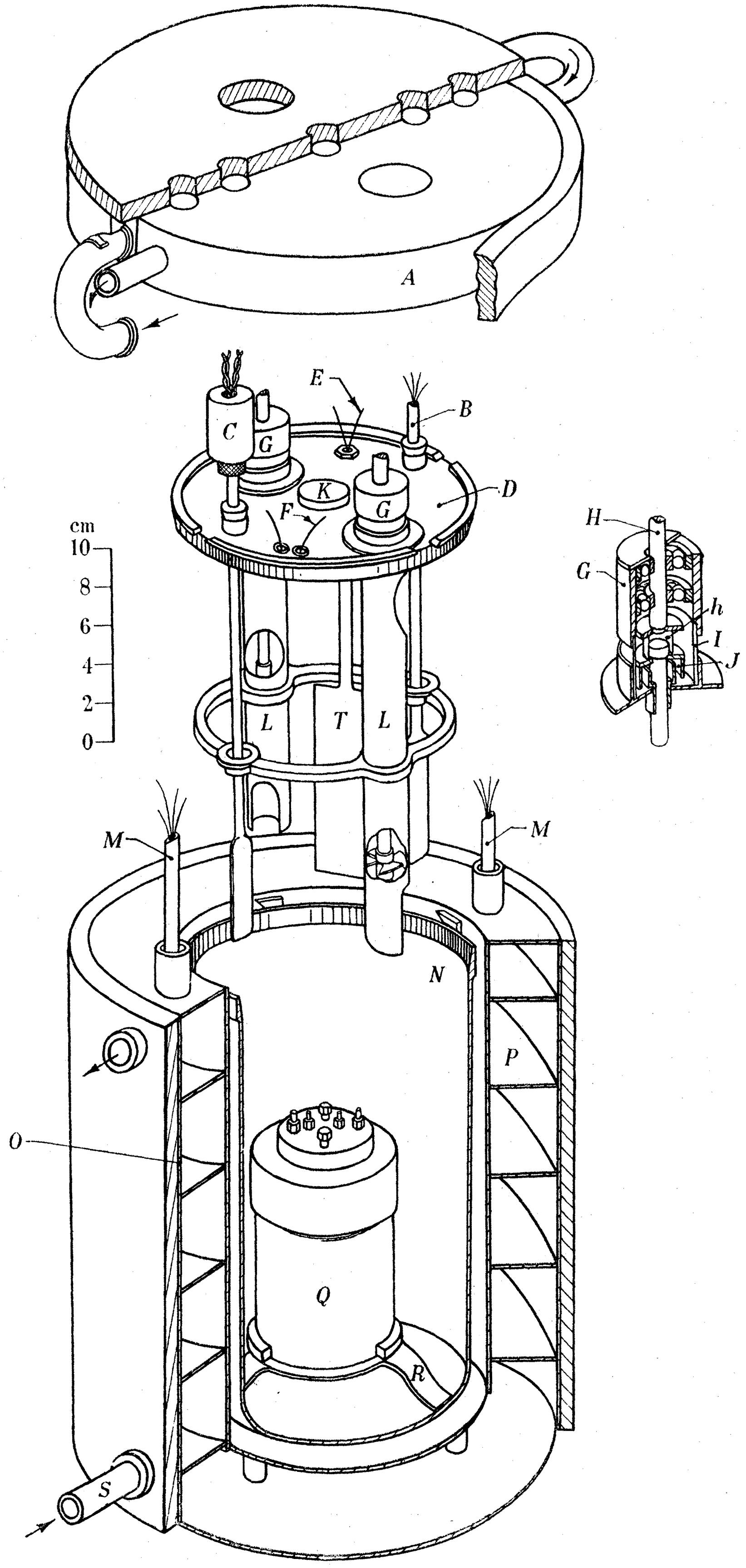
The heater current was from a 60 V, 200 Ah wet battery with a 5 Ω resistance in series. The total electrical energy was measured with the help of two Vernier potentiometers, the time being determined by an electronic count of the N.P.L. standard millisecond waves.

The calorimeter is shown in figure 2. It was designed (1) to reach a uniform temperature quickly after a heat input of 34500 J, (2) to exchange heat with its surroundings as slowly and consistently as practicable, and (3) to be air-tight and thus avoid errors resulting from the evaporation of water. It was in two parts, a 'vessel', containing a removable tripod for the bomb; and a 'lid', to which the stirrers and heater were attached, and through which passed the thermometers, the heater leads, and the firing leads for the bomb.

The calorimeter vessel was of brass 0·16 cm thick, rhodium-plated and highly polished. The stirrer vanes rotated at a constant speed of 1300 rev/min in tubes of 2·5 cm diameter. Where the stirrer shafts passed through the outer shell they were broken by connectors of copper-nickel, 1 cm in diameter and 0·05 cm in wall thickness. Each connector possessed a brass skirt, rotating in a space of capacity 3 cm^3, half filled with a thin Silicone oil. The oil seals permitted the calorimeter to be made air-tight and allowed the materials within it to expand by 2 cm^3 without the escape of air. A third oil seal, attached to the centre of the lid, added 3 cm^3 to the capacity for expansion, and this was found to be adequate for determinations in which the calorimeter rose in temperature from 22 to 25° C. The upper bearings of the stirrer shafts did not form part of the calorimeter proper, but their brass housings were attached to the lid of the calorimeter by glass tubes of 2·5 cm external diameter, 0·1 cm wall thickness, and 1·5 cm clear height. Thus the 'effective boundary' of the calorimeter intersected the glass tubes and the copper-nickel connectors of the stirrer shafts.

The copper leads to the electrical heater were precisely located in the air-space above the lid of the calorimeter, so that the 'effective boundary' of the calorimeter where it intersected these leads was reproduced from experiment to experiment. The firing leads for the bomb were less important, being of thinner copper, but they were treated in the same way. All four leads were in position for every experiment.

Care was taken that there was no avoidable alteration in mass of the materials used in the calorimeter. Before each experiment the lid assembly, not including the thermometers, heater leads or firing leads, was dried and weighed to the nearest 0·01 g. Any difference in mass from a standard value was ascribed to an excess or shortage of oil in the oil seals, and was corrected for accordingly. The calorimeter, with rubber bungs in the two thermometer holes of the lid, was filled with water to a total of 10340 g. Any small differences in mass after correction for atmospheric density, and the effect of the mass of the charge and the oxygen in the bomb, were also allowed for. The principal thermometer, a platinum resistance of small lag, has been described elsewhere (Gittings 1951). Its resistance of about 29 Ω was read to 0·00001 Ω with a 7-dial Smith no. 3 bridge (Smith 1912), using a constant current of 0·8 mA. The bridge was kept in a room controlled at 22° C, and a steady stream of air at 22° C and 42 % relative humidity (controlled by a saturated solution of potassium carbonate) was blown through it. A check on the main coils was made



A	Outer jacket half-lids with peripheral insulation of expanded rubber and upper insulation of cork. Tubing admits circulating water to labyrinth.
B	Fifteen copper and fifteen constantan leads from multiple-junction thermometer.
C	Four copper leads from platinum resistance thermometer.
D	Lid, tightly fitting to vessel *N*.
E	Two copper leads to manganin heater.
F	Two copper firing leads.
G	Brass housings of stirrer bearings.
H	Top of stirrer shaft coupled to constant speed motor. At *h*, the shaft is thermally interrupted by a copper-nickel connector, 0·05 cm in wall thickness.
I	Glass tube, 0·1 cm in wall thickness.
J	Brass skirt, rotating in 1·5 cm^3 of thin oil.
K	Additional oil seal containing 5 cm^3 of thin oil.
L	Stirrer tubes. Vanes draw water into bottom of tube and throw it out through holes at side and top.
M	Glass stems of multiple-junction thermometers immersed in water of outer jacket.
N	Brass calorimeter vessel 0·16 cm thick, rhodium-plated and highly polished outside.
O	Double-walled brass outer jacket, rhodium-plated and highly polished on surfaces facing calorimeter. Surrounded by aluminium foil and air insulation.
P	Helical space in outer jacket for water circulation.
Q	Bomb, fully softened stainless steel body and lid with aluminium bronze locking ring. The lid carries two firing lead connexions and two unions for inlet and exhaust of gas with two hard-chromed stainless steel valves.
R	Brass tripod supporting bomb.
S	Water inlet to outer jacket.
T	Manganin wire heater.

FIGURE 2. N.P.L. no. 1 bomb calorimeter.

by measuring a standard 29 Ω resistance in an oil bath of known temperature before and after each experiment. The out-of-balance current of the bridge was amplified by a galvanometer amplifier with a controllable feed-back and was indicated by a mirror galvanometer of period 0·25 s (Preston 1946). A galvanometer scale graduated in tenths of an inch was used, and by adjusting the feed-back it was possible to arrange that 0·1 in deflexion corresponded to 0·0001 Ω.

In this form the bridge proved to be highly suitable for making measurements of moving temperatures at specified times, during the initial and final periods of an experiment. For the middle period, when changes of temperature were rapid, the sensitivity was reduced by a factor 10.

The second thermometer comprised fifteen copper/constantan junctions in a silver sheath, the cold junctions being immersed in pure melting ice. Its sensitivity was approximately 600 μV/° C and the e.m.f. was measured with a Diesselhorst potentiometer to the nearest 0·1 μV. This thermometer was for use in measurements of less than the highest accuracy.

The outer jacket (figure 2) was divided for convenience of assembly into three separate vessels, the main part and two half-lids, all of brass, rhodium-plated and polished on the inward-facing surfaces. Water from a 40 l. reservoir was steadily pumped through the outer jacket from the bottom, spirally up the sides and through a labyrinth in the lid, the channels everywhere being about 2·5 cm square in section. When the calorimeter was between 1° C colder and 1° C warmer than the outer jacket, the entire inward-facing surface of the latter was found to be uniform in temperature within the reproducibility of the thermocouples used, i.e. within 0·02° C.

A thermometer, of fifteen copper/constantan junctions, was immersed in the outer jacket with its bulb at about the mean level of the bomb. The temperature of the thermometer was allowed to rise 0·01° C during the heating period in six experiments, and the calorimeter was found to gain an extra 0·0006° C, reasonably in agreement with calculation. In precise experiments, therefore, the temperature of the water in the 40 l. reservoir was adjusted with a heater or by the occasional addition of about 1 g of ice, to maintain the temperature of the thermometer steady within ±0·001° C.

The calorimeter stood on three ivory pegs in the outer jacket, and except near the irregularities in the lid, the air gap was everywhere 1 cm. This is about the maximum distance for which convection should introduce no serious error (White 1928). (Evidence is submitted in tables 2 and 6 which suggests that convection did play some part in heat transfer, but the resulting errors can be calculated and are found to be small.) The outer jacket was earthed; the calorimeter was electrically insulated with a resistance of at least 10 MΩ.

The outer jacket surrounded the calorimeter completely except for three holes 1·3 cm in diameter and two holes 2·8 cm in diameter in the lid. Two small holes were used for thermometer stems, the gaps being packed with cotton-wool. The third small hole contained two heater leads and cotton-wool. The two large holes contained the bearing housings of the stirrers, tightly fitting, with an insulating layer of transparent adhesive tape. Thermocouples in the stirrer housings indicated that when 34 500 J were put into the calorimeter, only about 2 J were absorbed by the stirrer housings. Thus the thermal contact between the housings and the outer jacket was adequate, when the calorimeter was used as a comparing instrument.

It was also important to have good thermal contact between the heater leads and the outer jacket. This was achieved by flattening the leads, insulating them in sleeves of artificial silk and gripping them between the lid and the main part of the outer jacket, the area of contact being about 1·2 cm^2 for each lead. Tests with thermocouples showed that satisfactory thermal contact had been achieved.

Design calculations and tests

The calorimeter was found to have a heat capacity of about 17250 J/° C. (This figure is not comparable with that of Cox *et al.* (1954) because of a change in water content.) It differed from an ideal calorimeter in five main ways:

(1) When heat was put in, temperature equilibrium was not reached instantaneously.

(2) Heat was transferred to and from the surroundings.

(3) The 'boundary' of the calorimeter was indefinite; when heat was put in, materials near the boundary rose less in temperature than the main part of the calorimeter.

(4) The quantities a, b, k, T_0 were not strictly constant.

(5) When the calorimeter was heated, some parts at once began to rise in temperature but others lagged behind. Thus, during the period $t_1 t_3$ in figure 1, the symbol T did not necessarily have the same meaning on both sides of the heat-flow equation

$$\mathrm{d}T/\mathrm{d}t = -k_c(T - T_c).$$

The departures from the ideal were acceptable only if the consequent uncertainties in the determinations were small. Calculations and tests were necessary to ensure that this was indeed the case. First, the time needed for temperature equilibrium to be reached, the 'middle period', $t_1 t_3$ in figure 1, was about 10 min. In this interval, were the conditions governing heat transfer (T, a, b, k, T_0) sufficiently accurately known? Secondly, was the temperature T_0 of the outer jacket sufficiently constant for the duration of an experiment, particularly in the initial period compared with the final period? Thirdly, was the dependence of a, b and k on the temperature T of the calorimeter small enough to be corrected for without undue error? Fourthly, was the 'boundary' nearly enough the same in an electrical calibration as in a combustion experiment?

The corrections needed as a result of the differences from an ideal calorimeter were evaluated sufficiently well for practical purposes, though the error in one of them was as large as the reproducibility error of the heat measurements. The evaluations were made as follows.

Calorimeter stirring and temperature equilibrium

The speed of the stirrers was such that they generated 0·31 J/s within the calorimeter, raising its temperature by about 0·001° C/min. In experiments with the stirrers and bomb in a transparent vessel the same shape as the metal calorimeter, and with oak dust in the water, no dead space could be found and it seemed likely that any heat generated inside the calorimeter would be uniformly distributed within a reasonable time. However, in view of the importance of point (5) above, and of §1, paragraph (14), an investigation was made of the temperature lags at different positions on the outer surface, with respect to the thermometer in the water.

In a series of tests, the temperature rise of the surface of the calorimeter during heating periods both by combustion and electrical methods was studied with the help of thermocouples and 10 m of 40 s.w.g. enamelled copper wire used as a resistance thermometer. The copper wire was wound spirally round the cylindrical sides of the calorimeter. The soldered junctions of the thermocouples were flattened to approximately 0·1 mm thick by 0·5 by 3 mm, and were held in metallic contact with the lid and the base of the calorimeter in eleven different places, by strips of aluminium foil; 10 cm of the leads were held to the approximately isothermal metal surface by adhesive tape at each end. Readings were found to be the same when a couple was attached under the lid immediately beneath a couple on the lid. There was also close agreement between the copper resistance thermometer and thermocouples attached to the cylindrical surface. The temperatures were measured with potentiometers by two observers at 10 s intervals during a heating period, to determine the average lag of each temperature behind the platinum thermometer whose resistance was measured by a third observer. It was found that lags between the various thermometers could be as much as 20 s; for example, a region of the surface near the top of the heater rose in temperature early in electrical experiments, whereas the rise in temperature of the flat part of the lid was late. From the area enclosed between each heating curve and the curve for the platinum resistance thermometer a lag in seconds was calculated. From considerations of the rate of radiation and conduction across the air gap, the conduction through solids in the interspace, the heat transfer from the cylindrical sides, the base, the flat part of the lid and the stirrer housings should be approximately in the ratio 6:1:1:1. Appropriate 'weights' were assigned to the average lags of the corresponding parts of the outer surface, and the overall average lag was calculated. The results are summarized in table 1, together with estimates of the errors based on the reproducibility of observations.

Table 1. Lag of outer surface of calorimeter, behind platinum resistance thermometer

	lag in tenths of a second (standard error in brackets)				
method of heating	sides	base	lid flat	housings	weighted mean
benzoic acid	55 (7)	120 (19)	207 (10)	38 (12)	77 (10)
electrical (normal rate)	−44 (1)	28 (15)	97 (13)	−46 (7)	−21 (7)

For the purpose of heat transfer in the middle period, table 1 shows that the lag of the outer surface behind the platinum thermometer was 7·7 s in a combustion experiment and −2·1 s in an electrical heating at the normal rate. These estimates were used in applying the correction for heat transfer during the calorimetric determinations, for which the copper resistance wire and the thermocouples were removed. Without the correction in applying the electrically determined heat capacity to a combustion experiment there would have been a systematic error of about 16 J in 34500 J.

Under the heading of 'Lags', the problem of temperature equilibrium in a bomb calorimeter was discussed by Jaeger & Steinwehr (1906), Dickinson (1915, pp. 207, 208, 222) and White (1928, pp. 70, 86, 88); but there are no references to the outer surface of the calorimeter. White found that the lag of the thermometer (i.e. of its mercury meniscus or its galvanometer) behind the temperature which the calorimeter would have if it were in equilibrium, had no effect on the calorimetry provided the lag coefficient and heat-transfer coefficient are constant throughout an experiment. He took the view that 'when a calorimeter is calibrated it is calibrated, lag effects and all', but this view is not tenable in the light of results such as those in table 1.

Believing that he was examining a lag of convection currents in the interspace, Dickinson placed a differential platinum thermometer in the interspace and measured the temperature gradient across it. He found the differential thermometer lagged 2·5 s behind the thermometer in the calorimeter during a heating period. Whether heat was transferred by convection currents or not, the specific heat of air and its thermal conductivity are such that the air near the differential thermometer must have very nearly reached its equilibrium temperature within 0·05 s. Hence the lag that Dickinson observed was approximately the lag behind the calorimeter thermometer of the region of the calorimeter surface nearest the differential thermometer wire. The position of the stirrer was such that the differential thermometer would almost certainly have shown quite different lags if it had been moved to other regions in the interspace. Also, if his calorimeter had been heated by a combustion during these tests, instead of electrically, still other lags are likely to have been observed. Dickinson estimated that the effect of a 2·5 s error in the time of all observations in the heating period would be to introduce an error of under 1/10000, but he thought the source of error was a lag of convection currents in the interspace, and that this was 'somewhat analogous to the lag of calorimetric thermometers which itself produced no error in the results'.

Heat transfer

In general during a bomb calorimeter experiment, heat is transferred between the calorimeter vessel and its outer jacket. For the net amount of heat transferred to be negligible (say, less than 1 J), it would be necessary to maintain the inner surface of the outer jacket within 0·001° C of the outer surface of the calorimeter throughout the experiment. In the middle period when heat is being generated within the calorimeter, the outer surface itself cannot be even nearly uniform in temperature, and the adiabatic condition must be regarded as unattainable. Instead, it is necessary to maintain the outer jacket as nearly as possible at a constant temperature, and to correct for the heat transfer. In the present work the outer jacket was kept within 0·001° of 24° C, and the room within 0·1° of 22° C.

Heat transfer to and from a calorimeter may take place in six ways: (1) by evaporation and condensation of water; (2) by radiation; (3) by conduction and convection between the calorimeter and the outer jacket; (4) by conduction between the calorimeter and the outside air; (5) by heating the air, and other materials having a finite heat capacity, in the space between the calorimeter and its outer jacket (the 'effective boundary' of the calorimeter has already been mentioned); and (6) by a transfer of heat from leads which have been heated by an electric current.

(1) *Evaporation.* Previous experimenters, e.g. White (1910), Dickinson (1915) and Jessup (1934, p. 475), found evidence of evaporation from calorimeters that were imperfectly

sealed. During the present series of experiments a balance was available which proved capable of weighing 10 kg within 1 or 2 mg, and it was practicable to make determinations of evaporation by direct weighing, with the calorimeter sealed in different ways. The calorimeter was assembled with bomb and water, but with rubber stoppers in the thermometer holes. The only opening through the lid was a hole of diameter 1 cm, and this was sealed as well as possible with a plug of soft wax. When the calorimeter was kept at 22° C it lost 0·7 mg/h by evaporation into the room whose relative humidity was 50 %. The calorimeter was then weighed, heated from 22 to 25° C, cooled, and reweighed. Each heating cycle produced a loss in weight of approximately 3 mg in addition to the steady loss of 0·7 mg/h. During a normal determination, the loss in weight would therefore have been 4 mg, corresponding to a loss of 10 J by evaporation of water.

TABLE 2. HEAT TRANSFER BETWEEN CALORIMETER AND OUTER JACKET

conductor	total effective cross-section (cm^2)	effective length (cm)	conductivity (mW/cm °C)	heat transfer (W/° C)
air:				
direct	1634	1	0·241	0·394
via heater leads	7·6	0·7	0·241	0·001
3 ivory supports	1·3	0·7	5·4	0·010
stirrer housings:				
2 glass oil-traps	1·6	1	10	0·016
2 Cu-Ni connectors	0·33	1	226	0·075
leads to heater:				
2 thick Cu leads	(0·084)	(11·2)	—	—
2 Cu wires, 18 s.w.g.	(0·023)	(2·0)	—	—
total, as 18 s.w.g.	0·023	5·1	3840	0·017
2 ignition leads	0·023	9	3840	0·010
total heat transfer by conduction				0·523
estimated heat transfer by radiation				0·039
total, by calculation				0·562
observed total heat-transfer coefficient, *ck*				0·866

The oil-sealing arrangements that have already been described were therefore adopted. The change in mass in a period of 48 h, including two heating cycles, was now found to be less than 2 mg, i.e. within the limit of weighing.

(2) *Radiation.* The area of the rhodium-plated outer surface of the calorimeter was 1634 cm^2, and its emissivity was 0·076. By Stefan's and Kirchhoff's laws the heat transfer, when the calorimeter was at 23° C and the outer jacket at 24° C, was 0·0386 J/s. It will be seen in table 2 that this represents under 5 % of the total heat transfer. With normal precautions to prevent variations in emissivity of the surfaces during an experiment, the heat transfer by radiation could be taken as proportional to the difference in temperature between the calorimeter and the outer jacket, i.e. as obeying Newton's law.

(3) *Conduction between calorimeter and outer jacket.* Table 2 gives details of the materials in thermal contact with both the calorimeter and the outer jacket, and their individual contribution to the heat transfer when the difference in temperature was 1° C. The total, when added to the estimated heat transfer by radiation, was only 65 % of the observed value. It would seem probable that, although the rate of heat transfer is a minimum

when the surfaces are separated by about 1 cm (White 1928), the convective heat transfer is still considerable. Other evidence of convection is given in connexion with table 6, below, where also its effect on accuracy is considered.

(4) *Conduction from the calorimeter to the room.* The air of the room was controlled at 22° C, the outer jacket at 24° C, and the calorimeter varied from 23 to 25° C. Table 3 gives details of the materials which connected the calorimeter with the air of the room without making intermediate thermal contact with the outer jacket. The estimates of heat transfer along these materials are only approximate, because it was not certain where the heat flowed from them to the air of the room or how much heat, if any, passed between them and the outer jacket. To ensure that the estimates are on the high side, the shortest possible effective length has been assumed in each case and heat flow to or from the outer jacket has been ignored.

TABLE 3. HEAT TRANSFER FROM CALORIMETER TO AIR OF ROOM

(Estimates on the high side)

conductor	total effective cross-section (cm^2)	effective length (cm)	conductivity (mW/cm °C)	heat transfer (W/°C)
multiple thermocouples:				
glass stem	0·33	6·5	10	0·0005
15 Cu wires, 48 s.w.g.	0·0002	6·5	3840	0·0001
15 eureka wires, 38 s.w.g.	0·0027	6·5	25	0·0001
air and insulation	—	—	—	negligible
platinum thermometer:				
glass stem	0·19	6·5	10	0·0003
4 Pt wires (½ mm)	0·0079	6·5	700	0·0008
2 twin-bore silica tubes	0·068	6·5	14	0·0002
			total	0·0020

It follows from table 3 that, when the calorimeter was at 25° C, approximately 0·006 J/s escaped along the thermometer stems, compared with 0·002 J/s when the calorimeter was at 23° C. These rates are not negligible, but it was shown in §1 that the method of correcting for heat transfer allows for a linear dependence on temperature of $s-r$, where s is the heat of stirring and r the rate of heat loss by conduction to the room.

(5) *The heat capacity of air and other materials in the interspace between the calorimeter and the outer jacket.* When, during an experiment, the calorimeter was heated from 23 to 25° C, the average temperature of the air in the interspace between it and the outer jacket may be assumed to have risen by 1° C. The brass and copper-nickel connectors, by which the stirrer shafts (at the calorimeter temperature) were connected to the motor shafts (at the outer-jacket temperature), also rose by an average of approximately 1° C. The rise in temperature of the electrical leads in the interspace was measured with thermocouples in trial experiments. An estimate of the total heat absorbed by these materials is given in table 4. In addition, some heat must have been absorbed by the thermometer leads and stems outside the calorimeter, but this was neither measured nor calculated.

It was calculated that, because of heat flowing across the brass wall of the calorimeter, the temperature of the brass rose by an average of 0·00005° C less than the calorimeter water; and that the total of 16·1 J in table 4 was therefore too high by about 0·04 J which was negligible.

Table 4. Heat absorbed by materials in the interspace

(When temperature of calorimeter rose by 2° C)

material	total mass (g)	average temp. rise (°C)	specific heat (J/g °C)	heat absorbed (J)
air	1·92	1·0	1·03	2·0
3 ivory supports	1·73	1·0	0·4	0·7
stirrers:				
2 glass tubes	4·64	1·0	0·84	3·9
2 Cu-Ni connectors	2·90	1·0	0·41	1·2
leads to heater:				
2 Cu strips	7·70	0·5	0·38	1·5
2 Cu wires, 18 s.w.g.	0·30	1·2	0·38	0·2
2 brass connectors	3·74	0·8	0·37	1·1
2 ignition leads	2·1	1·0	0·38	0·8
insulation:				
silk, 0·4 g; phenolic resin, 2·0 g; polyvinyl chloride, 1·0 g	3·4	1·0	1·4	4·7
			total	16·1

(6) *Electrical heating of the leads.* In normal electrical determinations of the heat capacity of the calorimeter, a current of 3·8 A was passed for 240 s not only through the heater, but through the two copper strips, the two brass connectors, and the two 18 s.w.g. copper heater leads. The heat generated in the interspace, calculated from the observed resistances including the contact resistances at the brass connectors, is given in table 5.

Table 5. Heat generated and absorbed in interspace

(3·8 A for 240 s)

leads to heater	heat generated (J)	heat absorbed (J)		
		outer jacket	calorimeter	interspace
2 Cu strips	3·6	0·6	—	3·0
2 Cu wires, 18 s.w.g.	1·7	—	0·85	0·85
2 brass connectors	1·05	—	—	1·05
			total	4·9

Of the 6·35 J generated a part was absorbed in the calorimeter and another part in the outer jacket. Estimates of these amounts, and of the unabsorbed residue, which must evidently be absorbed in the interspace, are given in table 5. For the copper strips the estimates were based on temperature measurements with thermocouples. Of the heat generated in the 4 cm of 18 s.w.g. copper, half was assumed to enter the calorimeter.

During an electrical heating, according to table 5, 4·9 J of heat from the leads was absorbed in the materials of the interspace above the lid of the calorimeter. This was reasonable since, from table 4, the total heat absorbed by these materials (including 0·2 J by the air) was found to be 8·5 J; and the remaining 3·6 J would be supplied from the calorimeter.

In a combustion the entire 8·5 J must have been supplied from the calorimeter. Corrections were therefore applied to the potential measurements during the heating period to include the 4·9 J, and also the other 0·85 J from the 18 s.w.g. copper, as part of the heat put into the calorimeter. (The fact that the potential leads were attached outside the outer jacket was also taken into account.) In the published descriptions of other electrically calibrated calorimeters, it is not as a rule clear whether any check of the heating in the interspace has been made.

Temperature observations and heat-transfer correction

Each experiment lasted 60 min, the initial, middle and final periods being 17·5, 10 and 32·5 min. Temperatures were read at each half-minute by pre-setting the bridge, reversing the current 1 s before the time of observation, and correcting the bridge setting mentally if the galvanometer did not return to the same position 1 s after the time of observation.

The gain of heat by the calorimeter in the initial period of an experiment, and the loss of heat in the final period, necessitated no correction. The two periods were necessary only to permit extrapolations of the temperature-time curves to the instant t_2 in figure 1. The correction for heat transfer in the middle period was made by calculating t_2 graphically and then extrapolating the temperature-time curves by a numerical method.

The time t_2 was calculated by graphical integration from the observed curve corresponding to $BCDE$ in figure 1, with resistances taking the place of temperatures. The observed resistances were those of the platinum thermometer immersed in the water, and they were corrected, in effect, to represent the average temperature of the outer surface of the calorimeter.

The resistance observations in the initial and final periods were averaged in groups of five and the bridge corrections applied to each average, giving a value of R every 2·5 min. An approximate estimate was now made of R_c, the resistance corresponding to the convergence temperature T_c. With the help of 6-figure tables, $\log_{10}|R-R_c|$ was written down for each R. By the method of orthogonal polynomials the best quadratics were fitted to the seven values in the initial period and to the thirteen values in the final period. (The object of fitting curves of higher than the first degree was to make the determination independent of R_c, whose evaluation was needed only to make the arithmetic easier.) The extrapolated values at time t_2 of $\log_{10}|R_i-R_c|$ and $\log_{10}|R_f-R_c|$ were found, and from them the 'initial' and 'final' resistances R_i and R_f. From the thermometer calibration (R_f-R_i) was converted to (T_f-T_i) in degrees Celsius (although an arbitrary scale would have served). It was possible to estimate the standard errors of R_i and R_f and, from them, the standard error of (T_f-T_i) considered as a statistic derived from the full set of 100 observations. This was done on six occasions and the standard errors on rises of about 2° C were 8, 8 and 10×10^{-5} °C for electrical determinations, and 13, 9 and 17×10^{-5} °C for combustions of benzoic acid. These errors, in conjunction with any error in determining t_2, determined the accuracy to which it was worth while making individual temperature measurements. It was a real advantage for the Smith no. 3 bridge to possess a seventh dial, reading the thermometer resistance to 0·00001 Ω (equivalent to about 0·0001° C). The above temperature errors were about 1 in 20000, compared with standard deviations of about 1 in 10000 in a series of repeated measurements of heat (see § 3). Evidently the thermometry must have made an appreciable contribution to the casual error of observations.

Variations in heat of stirring, conduction to room, and heat-transfer coefficient

In §1 it was shown that the above correction is valid for heat transfer and heat of stirring, if the change in temperature due to such heat effects throughout the middle period can be put into the form

$$\mathrm{d}T/\mathrm{d}t = -k_c(T-T_c),$$

where k_c and T_c are constant during any particular experiment. This requires that the heat of stirring s and the conduction to room r should be expressible in the form

$$(s-r)/c = a+bT,$$

where a and b are constant; and that the heat-transfer coefficient k and the outer-jacket temperature T_0 should be constant. Reasonable constancy of T_0 was achieved, but tests were required to find how well the other conditions were satisfied.

To test whether the heat of stirring and the heat-transfer coefficient were constant at different temperatures, two series of experiments were made. In the first series, the temperature of the outer jacket was controlled in turn at approximately 23, 23·5, 24, 24·5 and 25° C; the calorimeter was brought to a temperature about 0·01° C below that of the outer jacket and allowed to rise through a total of about 0·02° C while being stirred. The mean rate of temperature rise was then dependent only on the heat of stirring and the heat transfer from the calorimeter to the room. Throughout the second series of experiments the temperature of the outer jacket was controlled at 24° C, while the calorimeter was brought in turn to approximately 23, 23·5, 24·5 and 25° C and its rate of temperature change measured over periods of about 20 min at each step. From the results of the two series of experiments, and the heat conduction to the room calculated in table 3, table 6 was constructed.

TABLE 6. HEAT OF STIRRING (s); CONDUCTION TO ROOM (r); AND HEAT TRANSFER COEFFICIENT (ck)

temp. (°C)	r (J/s)	s (J/s)	$s-r$ (J/s)	ck (J/s°C)	$60k$ (°C/min°C)
23	0·002	0·322	0·320	0·866	0·00302
23·5	0·003	0·319	0·316	0·864	0·00301
24	0·004	0·316	0·312	—	—
24·5	0·005	0·313	0·308	0·823	0·00289
25	0·006	0·310	0·304	0·846	0·00295

In table 6 the values of $(s-r)$ are taken from the best straight line through the values that were observed in the first of the above series of experiments. The standard deviation of the observed points from this line was 0·003 J/s, and there is little doubt that the heat of stirring depended to a small degree on the temperature of the calorimeter, though the measurements were not accurate enough to indicate whether s depended on second or higher powers of T. The stirrers were driven at constant speed and, in view of the fact that the viscosity (non-turbulent) of water decreases by 4·6 % between 23 and 25° C, the decrease of s by 3·6 % in table 6 is not surprising.

A small error arises because in the expression $(s-r)/c = a+bT$ the symbol T represents the temperature of the water in the calorimeter, whereas in the expression

$$\mathrm{d}T/\mathrm{d}t = -k_c(T-T_c)$$

it represents the temperature of the outer surface of the calorimeter. If the outer surface lags 10 s behind the water, the error from this cause is less than 0·2 J in 34 500 J.

The values of the heat transfer coefficient (ck) in table 6 were computed from the observed rates of temperature change in the second series of experiments described above, together with the smoothed values of ($s-r$) in the table. They indicate either that the method of observation involved a standard deviation of individual determinations of about 0·02 J/s °C, or that ck varied by about this amount under the influence of temperature change. The measurement of k is known to be difficult. Results reported by Jessup (1934, table 2), for example, indicate that his k was at least 7 % higher at the higher temperatures (in one experiment, over 30 %); he attributed this to variable evaporation of water from the calorimeter when its temperature exceeded that of the outer jacket.

Apart from irregular changes in k from one experiment to another, it is evident that if evaporation from the calorimeter occurs in the final period of an experiment the systematic increase in k, considering it as a function of temperature, may be very large. A small increase in k with increasing temperature can be expected in any case, owing to the temperature coefficient of the thermal conductivity of the air in the interspace and to the difference between Newton's law and Stefan's fourth-power law; theoretically k should be about 0·3 % higher at 25 than at 23° C. Finally, if there is any convective heat transfer, k may go through a minimum value when the calorimeter and its outer jacket are nearly at the same temperature.

The variation of k with temperature in table 6, in spite of its inaccuracy, suggests that there was a minimum value of k and that there may also have been some linear dependence on temperature, though the latter appears to have been in the opposite sense from that expected.

Values of k consistent with table 6 were applied to the curves, corresponding to BCD in figure 1, that were observed both in electrical determinations and combustion experiments. The effect was to make the time t_2 0·007 min later in an electrical determination and 0·015 min earlier in a combustion experiment. A correction was therefore applied to the electrically determined heat capacity of the calorimeter, reducing it by 1·1 J/° C, before using it for the heat of combustion of benzoic acid.

Experimental procedure

In the preparation for an electrical calibration or the combustion of benzoic acid an identical procedure was adopted because, after an electrical calibration, it was usual to recool the system to its starting temperatures and carry out a combustion experiment without dismantling the calorimeter. In the following brief description of the preparation, the quantities needed for thermodynamical corrections are printed in italics.

Assembly for electrical calibration and combustion experiments

The components of the bomb and calorimeter were dried. A platinum firing wire was weighed and attached to the electrode posts of the bomb. A platinum crucible was weighed, charged with benzoic acid, and reweighed. A hair hygrometer in the balance case was read, and a barometer was read and corrected for the effect of temperature on the density of the mercury column. The mass of the benzoic acid was calculated (*about* 1·3 g).

The crucible was mounted in the bomb (*capacity about* 0·29 l.) in which 1 g *of distilled water* was placed before sealing.

A cylinder of hydrocarbon-free oxygen was connected to the bomb, which was charged to 5 atm and discharged; this process was carried out five times for the removal of atmospheric nitrogen. (It was estimated and confirmed by experiment that the resulting loss of water from the bomb was only about 0·05 g.) The bomb was finally charged to 450 Lb/in.^{2} at 22° C, equivalent to 30·9 atm at 25° C. To test for leaks the bomb was immersed in water for 30 min.

The calorimeter lid was weighed to the nearest 0·01 g. The bomb was placed in the calorimeter, and this was charged with distilled water that had been freed from dissolved gases by boiling at reduced pressure. The lid was placed in position, its joint being sealed with a trace of vacuum grease, after the firing leads had been connected. The calorimeter was set on the balance pan. Water was added through a thermometer hole until the weight was close to 10 340 g, the thermometer holes were sealed with rubber stoppers of known mass, and the calorimeter was weighed to the nearest 0·01 g. A hygrometer in the balance case and a barometer were read, and the weighing was corrected to specified atmospheric conditions (760 mm Hg, 0% relative humidity, and 22° C).

The calorimeter was lowered into the outer jacket, the thermometers were put in place, and the firing leads and heater leads were connected. The lid of the outer jacket and its cork-lined cover and expanded rubber side-insulation were put on, and the outer jacket thermometers were put in place. The motors were connected to the stirrers. Dewar vessels containing a mixture of granulated pure ice and distilled water were provided for the cold junctions of the multiple thermojunction thermometers.

The temperature of the room was controlled at $22 \pm 0{\cdot}1°$ C for at least 12 h. The calorimeter stirrers and the water circulating pump of the outer jacket were switched on. The temperature of the outer jacket water was adjusted until the thermometers in the outer jacket were steady at $24{\cdot}000 \pm 0{\cdot}001°$ C. Twenty minutes before the experiment was due to start the temperature of the calorimeter was raised by means of its heater to 22·8° C.

The resistance bridge was used to measure a standard resistance of about 29 Ω and the temperatures of both the bridge and the standard resistance were read. The platinum thermometer was connected to the bridge.

Electrical determination. From the start of the experiment the battery of 60 V was discharged through a ballast resistance and a stabilizing resistance equal to the heater. For the first 20 min the resistance of the thermometer was measured to the highest accuracy within 1 s of each half minute. The heater timer was pre-set.

At time 20 min 10 s the heater was switched on in place of the stabilizing resistance, and was switched off at 24 min 10 s. Every 10 s during this period the current supplied and the potential across the heater were read with potentiometers whose residual e.m.f.'s and calibrations had been checked within 0·2 μV. The half-minute temperature readings continued, at one-tenth of full sensitivity, until time 30 min, when full sensitivity was resumed. At time 62 min 30 s the temperature readings were stopped, and the bridge was checked with the standard resistance.

Benzoic acid combustion. A 6 V battery was connected through a tapping key, a low resistance shunt, and thick copper cables to the firing leads. The potential terminals of the shunt were connected to a Grassot fluxmeter, so calibrated that it could measure the electrical energy used to fuse the firing wire. The procedure was similar to that in an electrical determination, except that at time 20 min the firing key was closed and the deflexion of the fluxmeter was noted.

3. Results

The N.P.L. no. 1 calorimeter, described in §2, was used for determining the heat of combustion of samples of 'thermochemical standard' benzoic acid, B.D.H. batch no. 692782. The samples were in the form of pellets, each about 0·8 cm in diameter and weighing about 0·19 g. Seven pellets of total mass 1·3 g would lie flat in a crucible of diameter 2·5 cm. The samples represented a large stock of benzoic acid, purified and mixed in one batch, which had been all pelleted in one run. Sample jars were filled at the beginning and end, and at four equal intervals during the pelleting run.

Between 25 March and 24 May 1954, eight electrical determinations were made of the effective heat capacity of the calorimeter, including 1·3 g of benzoic acid and the full amount of oxygen; and fifteen experiments were performed in which benzoic acid was burnt. One of the latter was rejected because of a suspected error in weighing the benzoic acid. The results of the remainder, corrected to the standard condition of the calorimeter, are tabulated in tables 7 and 8.

The standard deviation of the population of individual determinations was about 10 in 100000 for the electrical experiments and 17 in 100000 for the combustions. These values include the error in measuring the rise in temperature, which was 4 in 100000 in the electrical experiments and 7 in 100000 in the combustions. The standard errors of the means were obtained by dividing by the square root of the number of observations. These casual errors were not the only important errors in a determination of the heat of combustion of benzoic acid, and the overall error of the determination is discussed in a later paragraph.

Corrections

In arriving at the values in the right-hand columns of tables 7 and 8 corrections were applied as follows:

Electrical (*table* 7). Calibrations as a function of temperature of the standard cells, 0·01 current shunt passing 3·8 A, 10000:10 voltage divider potentiometers; residuals of the potentiometers; passage of current through the potential leads; heat generated in the current leads in the interspace; changes in resistance of the heater circuit in the first 10 s after switching on. (The correction in the measurement of time was negligible.)

Combustion (*table* 8). Lag of outer surface, cf. electrical experiments; effective heat-transfer coefficient, cf. electrical experiments; calibration of the balance weights; buoyancy correction using 1·32 g/cm^3 as the density of benzoic acid at 25° C; electrical heat of ignition; heat of formation of nitric acid from traces of nitrogen in the combustion oxygen.

Electrical and combustion experiments. Corrections for differences from the adopted standard masses of calorimeter lid, benzoic acid, firing leads, platinum crucible and assembled calorimeter; bridge calibration; thermometer calibration; corrections for heat-transfer coefficient and heat of stirring, assuming them constant.

One more correction, which may be considered in two parts, is necessary if the benzoic acid is to be burnt in different circumstances. The first part arises because during a combustion there is a change in materials which form part of the calorimeter. The calorimeter can conveniently be divided into (*A*) the materials which change during a combustion (1·3 g of benzoic acid and 2·6 g of oxygen) and (*B*) all the rest, including 1 g of water in the bomb and about 9 g of excess oxygen. The electrically observed heat capacity was $c = c_A + c_B$, where c_A can be calculated as 3·2 J/° C.

TABLE 7. RESULTS OF ELECTRICAL CALIBRATIONS

date (1954)	°C rise	J/°C
25 March	1·97461	17252·2
30	1·99760	17247·6
2 April	1·99550	17251·1
6	1·98567	17253·5
9	1·99099	17250·5
13	1·99186	17252·7
22	1·98481	17251·2
21 May	1·98841	17250·7
heat capacity of calorimeter in electrical experiments		17251·2
corrections for use in combustion experiments:		
different effective heat-transfer coefficient		−1·1
different lag of outer surface		−7·9
heat capacity of calorimeter in combustion experiments		17242·2
S.D. of single determination		1·7
S.E. of mean		0·6

TABLE 8. APPARENT HEAT OF COMBUSTION OF BENZOIC ACID WITHOUT THERMODYNAMIC CORRECTIONS

(Heat capacity of calorimeter in standard condition taken as 17242·2 J/° C)

date (1954)	jar no.	mass	°C rise	J/g
8 April	1	1·29424	1·98495	26435·4
12	3	1·30434	2·00027	26434·4
21	3	1·29820	1·99132	26437·0
26	4	1·32941	2·04004	26444·1
28	5	1·33079	2·04194	26443·7
29	5	1·29778	1·99131	26444·2
10 May	6	1·31151	2·01160	26443·5
11	6	1·28458	1·96994	26440·6
12	1	1·31728	2·01972	26434·9
13	1	1·30900	2·00701	26435·9
14	2	1·36946	2·09951	26433·0
17	2	1·36404	2·09210	26444·2
20	2	1·36834	2·09814	26436·4
24	2	1·36041	2·08652	26443·4
			mean	26439·3
			S.D.	4·2
			S.E. of mean	1·1

When benzoic acid was burnt, the heat generated was taken up by (*A′*) the products of combustion and (*B*) the rest of the system. The ratio of the quantities of heat under (*A′*) and (*B*) cannot be the same in all calorimeter systems, but no error occurs if every bomb reaction begins and ends at 25° C. The following process is imagined: (*a*) the calorimeter system is taken from 25° C to the firing temperature T_i by removing heat $(25 - T_i)\,(c_A + c_B)$, (*b*) the benzoic acid is burnt, and (*c*) the system is taken from the new temperature T_f to 25° C by removing heat $(T_f-25)\ (c_{A'}+c_B)$. The total heat removed must be independent of the details of the calorimeter system. In rearranging terms, it equals $c_B(T_f-T_i)+c_A(25-T_i)+c_{A'}(T_f-25)$. Since c_A and $c_{A'}$ are small compared with c_B, and since at the N.P.L. T_f was approximately 25° C, the expression may be written

$$c_B(T_f-T_i)+c_A(T_f-T_i)+c_{A'}(25-25) = (c_B+c_A)\ (T_f-T_i).$$

Hence the heat of combustion found by using the electrically observed heat capacity, c_A+c_B, was the correct heat of combustion 'at 25° C'.

Besides fixing the temperature at which the combustion must be considered to take place, it is necessary to specify the pressure in the bomb and the masses of materials used compared with the cubic capacity of the bomb. Otherwise there would be uncertainty concerning the internal energy of the residual oxygen, the water vapour, the carbon dioxide, the liquid water and the gases in solution (Washburn 1933). Washburn calculated formulae for the energy necessary to convert all gaseous and dissolved oxygen and carbon dioxide to the pure gaseous substance at 1 atm and 25° C, and all water vapour and liquid to the pure liquid at 1 atm and 25° C, i.e. to convert them to what he called the standard states. Many thermochemical data are now expressed in terms of such standard states, but it is preferable to regard the samples of benzoic acid, not as a pure chemical, but as a standard calorimetric substance, and to express its heat of combustion in conditions similar to those normally occurring in practice. Jessup (1942 *a*), adapting a suggestion of Washburn (1933), used the following 'standard bomb conditions':

(1) The temperature of the calorimeter before and after the experiment (T) is 25° C (as discussed in the previous paragraph).

(2) The pressure before combustion (p) is 30 atm at 25° C.

(3) The number of grammes of benzoic acid burnt (m_B) is three times the number of litres enclosed by the bomb (v).

(4) The number of grammes of water placed in the bomb before combustion (m_W) is three times the number of litres enclosed by the bomb.

To allow for the difference between conditions (2), (3) and (4) and the N.P.L. conditions, it was necessary to subtract 2·9 J/g from the observed heat of combustion of benzoic acid. Hence the heat of combustion of the sample of benzoic acid under 'standard bomb conditions' was 26436·4 J/g.

Jessup (1942 *a*) gave a formula for calculating the heat of combustion under other conditions, from which the following has been derived:

Heat of combustion of the benzoic acid under conditions different from (1), (2), (3) and (4) equals (joules per gramme)

$$26436{\cdot}4+0{\cdot}5(p-30)+1{\cdot}1(m_B/v-3)+0{\cdot}8(m_w/v-3)-1{\cdot}2(T-25).$$

Errors

The causes from which errors may originate can be summarized thus:

(1) Random variations in the overall performance of the calorimeter during electrical determinations, evident as reproducibility errors when the results of a series of electrical determinations are compared.

(2) Random variations in the overall performance of the calorimeter during combustion experiments, evident as reproducibility errors in the same way as in (1).

(3) Random errors in knowing the corrections and in assuming them to be unchanged between one experiment and another.

(4) Systematic errors.

Systematic errors would arise from a failure to grasp all the differences between the N.P.L. calorimeter and the ideal calorimeter. For such differences as have already been discussed, systematic corrections have been applied; the corrections are equally likely to be too large or too small, and must be considered under (3). Nothing is at present known about any remaining systematic differences.

Errors of types (1) and (2) are estimated at the foot of table 7 and table 8. They include casual errors in the corrections that were determined independently in every experiment; that is, errors in weighing, graphical integration, curve fitting and extrapolation, and in the electrical heat of ignition. They also include errors in estimating the heat of formation of nitric acid, so far as these were truly random. The heat of formation of nitric acid was not more than 10 J in experiments in which 34 500 J was generated. It was assumed that all the nitric acid was formed in the ten minutes after the charge was ignited, and on this reasonable assumption the errors would be expected to be random.

Errors of type (3) require consideration. They arise in making corrections which are systematic in the sense that a value of the correction is determined once and for all, and is then applied to every experiment of its kind. An effort was made to ensure that the error in the estimate of each systematic correction was suitably small and equally likely to be positive as negative. It was intended to combine these type (3) errors with types (1) and (2) and evaluate an overall standard error of the determination.

The calibrations of electrical components and balance weights were accurately known and led to no appreciable error. In electrical determinations, the heat generated in the current leads in the interspace was about 6 J, of which it was estimated that 0·6 J was absorbed by the outer jacket. Only the 0·6 J appears in any correction; this quantity was determined with thermocouples, but no experimental estimate of the standard error was made as it seemed likely to be less than 0·3 J, i.e. less than 1 in 100 000. The changes in resistance of the heater circuit were quite similar in a series of tests. The correction for them amounted to 2 in 100 000, and the standard error, including the difficulty of balancing a potentiometer only a few seconds after switching on, may be estimated as 1 in 100 000.

The correction of the heat of combustion to 'standard bomb conditions' was calculated from the dimensions and temperatures of the calorimeter system, and its error is negligible. The two remaining systematic corrections were made in table 7. The first arose from the slight dependence on temperature of the heat-transfer coefficient *ck*, and was 1·1 J/° C or 6 in 100 000 of the heat capacity of the calorimeter. To judge from the measurements of *ck* at different temperatures used in preparing table 6, the combined standard error should not exceed 2 in 100 000. The second correction in table 7 was caused by the lag of the outer surface of the calorimeter behind the thermometer in the middle period. Its standard error, the root of the sum of the squares of the errors given in brackets on the right of table 1, is 1·2 s, equivalent to 5·7 in 100 000.

The casual errors of all kinds are collected and combined in table 9. It will be seen that the combined standard error was therefore 8·3 in 100000, corresponding to a standard error of 2·2 J/g in the heat of combustion of benzoic acid.

TABLE 9. STANDARD ERROR OF THE DETERMINATION OF THE HEAT OF COMBUSTION OF BENZOIC ACID

	parts per 100000
(1) reproducibility of electrical determinations	3·5
(2) reproducibility of combustion experiments	4·2
(3) heat in interspace	1·0
change in heater on switching on	1·0
variability of *ck*	2·0
lag of outer surface	5·7
root of sum of squares; combined standard error	8·3

Comparison with other determinations

The benzoic acid burnt in the present investigation was taken in the form of samples from a 15 kg batch. Another sample from the same batch was examined by the freezing-point technique by the Chemical Research Laboratory, Teddington. The apparatus used was described by Herington & Handley (1950), but the helices were made of pure silver wire instead of the stainless steel normally employed. This method of analysis will not detect the presence of impurities insoluble in molten benzoic acid, e.g. the presence of quartz powder, filter paper or metals, and the method does not apply to types of impurities which form solid solutions with benzoic acid. The concentration of liquid-soluble, solid-insoluble impurity was determined by using phthalic anhydride as added impurity by the method of Schwab & Wichers (1944). The following values were found:

moles % purity	99·977 (standard error 0·012),
i.e. mole fraction of impurity	0·00023 (standard error 0·00012).

If the object of the investigation had been to determine the heat of formation of pure benzoic acid a still purer material could have been prepared for the purpose. Nevertheless, the purity was already sufficiently high for it to be worth while comparing the results of this investigation with those of other workers using other batches of benzoic acid. Jessup (1942*a*) gave a list of determinations, corrected to the same standard bomb state as has been used above. When converted from international joules per gramme to (absolute) joules per gramme, the results read:

	J/g
Fischer & Wrede (1909)	26441
Wrede (1910)	26432
Dickinson (1915)	26439
Roth, Doepke & Banse (1928)	26410
Jaeger & Steinwehr (1928)	26423
Jessup & Green (1934)	26431
Prosen & Rossini (see Jessup 1942*a*)	26435
Jessup (1942*a*)	26434
Coops & van Nes (1955)	26437
Coops & Adriaanse (1955)	26435
this investigation	26436

The two values published in 1942 were lower by 1 J/g than the figures quoted above, but have since been amended by the authors. No definite conclusion can be drawn from the comparisons, but they would not contradict the claim, for the most recent determinations, that samples of benzoic acid prepared in different laboratories and measured in different calorimeters give reproducible results. The last five heats of combustion, indeed, differ by little more than the standard errors of the individual determinations.

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