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A New High Precision Calorimeter for the Measurement of Heats of Combustion: And the Heat of Combustion of Succinic Acid

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A NEW HIGH PRECISION CALORIMETER FOR THE MEASUREMENT OF HEATS OF COMBUSTION: AND THE HEAT OF COMBUSTION OF SUCCINIC ACID

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CONTENTS

The construction, calibration and use of a high-precision bomb calorimeter of the aneroid type are described. It consists of a stainless-steel combustion bomb as designed by Carlton-Sutton (1933) in a mantle of aluminium alloy, the temperature of which is measured by a platinum-resistance thermometer. A simple means of measuring the electrical ignition energy has been devised.

Because the time required for the attainment of a thermal steady state is greater for this type than for the conventional water calorimeter, the theory underlying methods of allowing for heat loss from the calorimeter to its surroundings has been critically re-examined, and the limitations of the commonly used Dickinson method (1914) have been clearly stated. For high precision to be attained, it proves to be particularly necessary that the conditions under which calibrations and measurements are performed shall be as similar as possible.

Working under optimum conditions, chosen after systematic trials, it is possible to reduce to 0·012 % the standard deviation of the values for the calibration constant, with benzoic acid as the standard substance.

The heat of combustion of succinic acid has been redetermined as

$$-\Delta U_R = 3020{\cdot}57 \pm 0{\cdot}43 \text{ cal/g (vac.).}$$

This agrees very well with the high-precision determination by Huffmann (1938) 3020·47 ± 0·43.

Succinic acid is suitable as a secondary standard for combustion calorimetry; and the best value is taken to be

$$3020{\cdot}5 \pm 0{\cdot}5 \text{ cal/g (vac.).}$$

Introduction

Recent developments in the technique of measuring heats of combustion of organic compounds make possible a precision error of only about 0·01 %. This is necessary for general chemical applications, inasmuch as these commonly require the determination of small

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differences between heats of formation of compounds; e.g. for *cis*- and *trans*-decalin, the difference is only 0·14 % of the quantity measured (Davies & Gilbert 1941). It probably represents a useful limit because of the difficulty of obtaining sufficiently pure substances.

For solid and liquid substances, the combustion reaction is usually carried out under controlled conditions with a high pressure of oxygen inside a stainless-steel bomb. The conventional type of high-precision calorimeter is based upon the design due to Dickinson (1914), in which the bomb is placed in a vessel containing efficiently stirred water, the temperature of which is measured with a platinum-resistance thermometer. It is usual in bomb calorimetry to surround the calorimeter with a constant-temperature environment. Adiabatic bomb calorimeters have been described (Hughes, Corruccini & Gilbert 1939), but are not commonly used. A different type of high-precision water calorimeter has been described by Coops, van Nes, Kentie & Dienske (1947) in which a specially designed Beckmann thermometer is used.

A simplification in design can be effected by replacing the water calorimeter by a metal block, this type being described as an aneroid calorimeter. A system in which the temperature of the bomb alone was measured was described by Féry (1912), but no results were reported so the accuracy of this system cannot be assessed. A high-precision aneroid calorimeter has been recently described by Magnus & Becker (1951). One of a different design is described below.

Three possible sources of error in the water calorimeter, namely, the estimation of the heat of stirring, the measurement of water into the calorimeter, and evaporation, are eliminated when an aneroid calorimeter is used. It appears from this work, however, that the time for heat equilibration is greater for the metallic calorimeter, so that for otherwise comparable conditions the correction for heat exchange is greater; but the system can nevertheless give very precise results. The theory of the calorimetric process, upon which is based the calculation of the heat exchanged between the calorimeter and its environment, is derived by considering an idealized system: a calorimeter at a uniform temperature suspended inside a constant temperature environment. Although the deviations of the aneroid calorimeter from the ideal system are much greater than are those for the water calorimeter, this need not be a disadvantage.

The real calorimeter can be most accurately defined as a system for which some function of temperature with time, $f(T, t)$, within certain limits, is related to the heat change involved, Q, thus,

$$Q = Kf(T, t),$$

where K is known as the calibration constant, this description being preferable to water equivalent or energy equivalent because its value depends upon the method used to calculate $f(T, t)$. It is usual in bomb calorimetry to compare the unknown heat of combustion of a substance with the known heat of combustion of benzoic acid. If the heat quantity employed in calibration is Q_1, associated with $f_1(T, t)$, and the unknown heat of combustion is Q_2, associated with $f_2(T, t)$, then

$$\frac{Q_1}{Q_2} = \frac{f_1(T, t)}{f_2(T, t)},$$

provided K is constant. In fact both Q and $f(T, t)$ consist of a number of terms, but in each there is one of predominating importance; in Q this is the heat of combustion of the substance Q', and in $f(T, t)$ it is the temperature rise T^*. The more accurate expression is therefore

$$\frac{Q_1}{Q_2} = \frac{Q'_1 + \Sigma q_1 + \Sigma \sigma_1 \pm \Sigma \rho_1}{Q'_2 + \Sigma q_2 + \Sigma \sigma_2 \pm \Sigma \rho_2} = \frac{T^*_1 + f'_1(T, t) + \Sigma \sigma^*_1 \pm \Sigma \rho^*_1}{T^*_2 + f'_2(T, t) + \Sigma \sigma^*_2 \pm \Sigma \rho^*_2},$$

where the $f'(T, t)$ represent the heat exchanged between the calorimeter and its environment (subsequently referred to as the cooling correction and denoted by ΔT), the q's represent additional heat terms such as the ignition energy and the heat of formation of any nitric acid produced, the σ terms represent two corresponding sets of systematic errors and the ρ terms the random errors in these several contributions. What is required is the accurate ratio Q'_1/Q'_2. Because of the complexity of the above expression it is necessary, in order to obtain the ratio, either that all the q terms and all the temperature terms of the right-hand side be known with high absolute accuracy, or that all these and Q'_1, Q'_2 be correspondingly identical. If the former were possible, the σ and ρ terms would be very small, while if the latter procedure be followed, the magnitudes of the systematic errors, σ, would be immaterial, but the ρ terms must still be kept within appropriate limits, e.g. a term contributing 1 % must be known with a precision of rather better than 1 % if an overall precision of 0·01 % is required in Q'_1/Q'_2. In practice it is not possible to make all the corresponding terms identical, but in our experience it is possible to realize sufficient reproducibility for systematic errors in Q'_1/Q'_2 to be negligible. If the σ terms are as much as 1 % in Q_1 and Q_2 severally, the ratio Q'_1/Q'_2, may depart by 1 % from unity before a systematic error of 0·01 % is produced in it.

Description of the apparatus

(1) *Calorimetric system*

The experimental aneroid calorimeter to be described has been developed around a Griffin–Sutton stainless-steel combustion bomb, which is fully described by Carlton-Sutton (1933). The material used for the calorimeter was the Noral alloy 50 S.W.P. (Northern Aluminium Co.). Its thermal conductivity is about 20 % less than that of pure aluminium, but its strength and hardness are about four times greater.

The calorimeter (figure 1) consists of four cylindrical blocks. The only thermal contact of importance between the bomb and the calorimeter is between the inside surface of the two central blocks and the cylindrical surface of the bomb. The minimum gap here which permitted easy assembly was 0·001 in. The four blocks are held together by three longitudinal brass bolts which are screwed down tightly so that the heat contacts may be as good and as reproducible as possible. Because the aluminium is so much softer than the stainless steel and small particles of dust tend to bind the surfaces together, it is necessary to lubricate the surfaces with a thin layer of oil to prevent sticking. This is done reproducibly for each experiment to maintain a constant heat capacity.

There are three adjustable conical brass supports affixed to the bottom block which fit into kinematic mountings in the air space. The brass plates of the latter are set into insulating blocks of Bakelite and guides are placed round them to facilitate the positioning of the calorimeter. On assembly, automatic connexions to the ignition circuit are made by phosphor-bronze strip spring contacts.

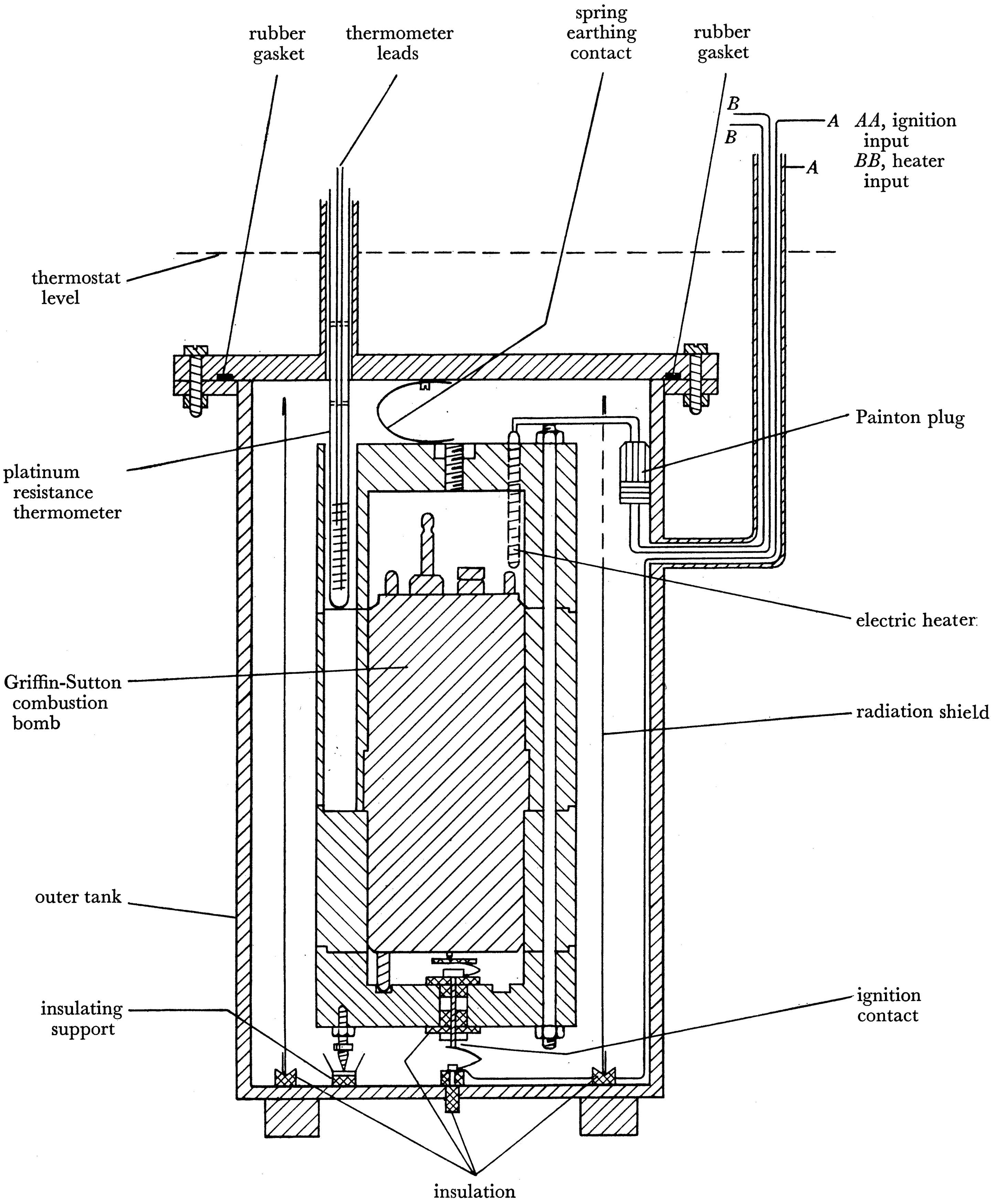

FIGURE 1. The calorimeter. The four sections of the aluminium mantle are shown enclosing the combustion bomb.

In the top block there are two heaters of resistance *ca.* 50 Ω made of 22 s.w.g. constantan wire wound on porcelain formers and sealed into thin glass tubes. The leads from these are attached to a Painton plug, chosen because of its small size, which can be fitted into a socket at the side of the air space. The heaters can be used in parallel, singly or in series. Because the rate of heat input is much greater than the rate of heat transference from the top block to the rest of the calorimeter, and because the thermometer is situated in the top block, when the heaters are switched off the temperature recorded falls until the heat has been uniformly distributed.

A hole into which the thermometer fits closely is drilled as near to the outer surface as possible. Because the heat generated in the bomb is more rapidly transferred to the two middle aluminium rings than to the other two, the shape of the temperature-time curve during the main period depends upon the position of the thermometer. The thermometer is used in the position shown because this gives what probably is a mean shape. The actual shape is unimportant; but it must be reproducible.

In spite of the complications which it introduces (Dickinson 1914; White 1918), a radiation shield is placed in the air space to reduce convection and the overall heat exchange. It is made of thin aluminium foil bent over at the edges to give it rigidity; and it rests on Bakelite supports at the bottom of the air space.

The brass tank forming the boundary of the air space has been made completely watertight. It can be raised so that the calorimeter may be assembled, and lowered so that the water thermostat completely surrounds it. The water thermostat is controlled to $\pm 0{\cdot}001^\circ$ C by the conventional type of toluene-mercury thermo-regulator, and is operated at 25° C.

The entire system is kept inside an air thermostat controlled at $21{\cdot}1 \pm 0{\cdot}05^\circ$ C by a modified form of the ether vapour regulator described by Green & Loring (1940).

(2) *Measurement of temperature*

A platinum-resistance thermometer of the Callendar type (Cambridge Instrument Co.) is used, with R_0 about 50 Ω. Although the most exact type of lead compensation is not possible with it, the leads are kept together in a metal shield and are not disturbed during an experiment, so it is sufficiently accurate for precision calorimetry. Resistance is not a linear function of temperature; but no account is taken of this as measurements are made under closely reproducible conditions. To reduce the increment in resistance due to the heating effect of the current through the thermometer coil to less than 1 % of the temperature rise, it was necessary to reduce this current to about $1{\cdot}8 \times 10^{-3}$ A.

The resistance of the thermometer is measured with a bridge based upon the one described by Westrum & Robinson (1949) and the circuit is given in figure 2. The resistance of the thermometer is exactly balanced by that of the measuring arm (R) between X and Y; when R_1 changes from 0 to 1000 Ω, R changes from *ca.* 55·85 to 56·35 Ω. R_1 is divided into units of 0·01 Ω, so the change in R can be measured to 1 part in 100 000. Variations of contact resistance in R_1 ($<0{\cdot}001$ Ω) have a negligible effect. R is, however, not a linear function of R_1, the deviation from linearity over the whole range being by a factor of about 2; hence the true resistances (R) must be calculated from the values of R_1.

The components of the bridge are immersed in transformer oil (Shell Diala Oil B) to reduce switch contact resistances and thermoelectric e.m.f.'s. The ratio arms and the shunted 57·4 Ω resistance (figure 2) were made of 34 s.w.g. manganin wire non-inductively wound on to brass tube formers which were previously covered with several coats of Silicone varnish (D.C. 996) which absorbs neither water nor oil and is an excellent insulator. Copper leads (16 s.w.g.) were silver-soldered to the manganin and the excess flux was carefully removed. They were insulated from the formers by mica sheets and held in place by Araldite resin (Aero Research Ltd), which forms such a rigid bond that the resistance wire is not disturbed if the leads are subsequently moved. The resistances were re-covered with Silicone varnish, annealed at 250° C for 6 h and allowed to cool slowly. The Silicone varnish remains plastic for sufficient time so that the strain in the wires is removed. The ratio arms have received identical treatments and have been made equal to 1 part in 10^6.

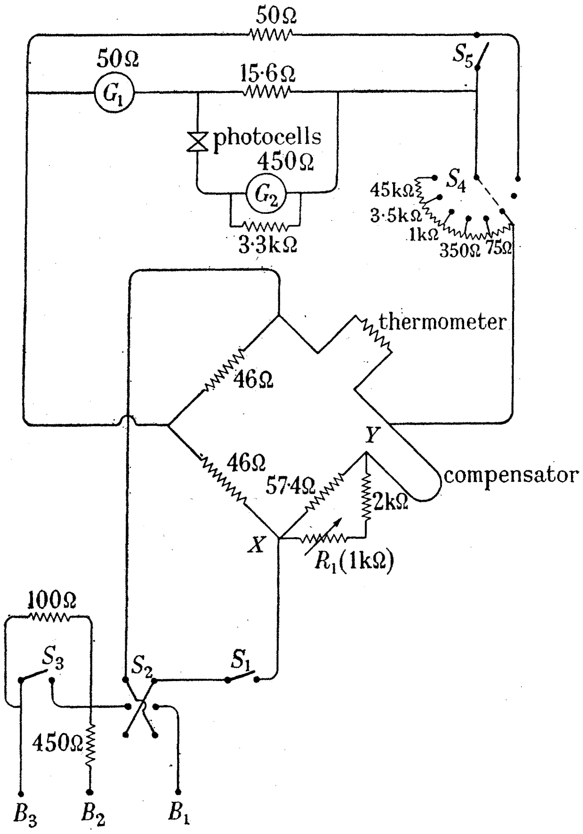

FIGURE 2. The bridge circuit. A 2 V cell is connected either to B_1, B_2 or to B_1, B_3. The former connexion gives a bridge current one-tenth of the maximum. The latter connexion gives either maximum or one-third maximum current as S_3 is closed or opened. S_1, on-off switch; S_2, reversing switch; S_4, multi-point switch to control the sensitivity of the galvanometer amplifier; S_5, second sensitivity control switch; G_1, primary galvanometer; G_2, secondary (indicating) galvanometer.

The variable arm consists of six decade dials, one of which provides the 2000 Ω series resistance. The 100, 10, 1·0 and 0·1 step decades are Muirhead and Co.'s type 5A. The 0·01 Ω step decade was constructed according to the principles described by Mueller (1913) and the resistances of this dial were made by the method described by Sturtevant (1945).

The direction of current through the bridge can be reversed and its maximum value can be reduced by factors of 3 and 10, the latter being used for calorimetric measurements. The voltage source is a 2 V accumulator.

The output voltage to be detected for the smallest change of resistance of the measuring arm is $3{\cdot}5 \times 10^{-3}$ V, and it is therefore necessary to amplify the deflexion of the galvanometer by means of an amplifier based upon the design described by Preston (1946) except that series feedback is used as described by MacDonald (1947). The galvanometers are somewhat overdamped because this helps to reduce random fluctuations.

The resistances of the bridge were calibrated against those of a Smith's difference bridge (Cambridge Instrument Co.). It was demonstrated that a $0{\cdot}4\,\Omega$ change provided by the Smith's bridge could be measured to a precision of 1 part in 100000, and it remained constant to this degree over a period of 2 months.

The sensitivity of the detector is such that approximately 10000 mm deflexion of the secondary galvanometer correspond to 1°C; i.e. the limit of sensitivity is *ca.* 10^{-5}° C, but random fluctuations due to electromagnetic pick-up in the low-resistance bridge circuit correspond to *ca.* 2×10^{-5}° C. This is not serious, as a large number of readings are taken to establish temperature-time curves and the initial and final temperatures are taken from these.

DETERMINATION OF AUXILIARY QUANTITIES

(1) *Ignition energy*

Solid substances are burned in the form of compressed pellets which are ignited by means of a narrow strip of filter-paper (*ca.* 0·003 g) placed in intimate contact. The filter-paper is ignited by the electrical heating effect in a 10 cm length of 44 s.w.g. platinum wire, wrapped round the paper and attached to the appropriate terminals of the bomb.

The heat of combustion of the filter paper (Whatman no. 1) was determined with the Griffin–Sutton water calorimeter (Carlton-Sutton 1933) to be 4118 ± 10 cal/g. The heat of combustion of the filter-paper fuse is about 0·4 % of the total heat. It is weighed sufficiently accurately for each experiment for random errors to be unimportant unless it is not uniform in composition.

The electrical energy supplied for the ignition is variable, especially as the filament is fused by the heat of combustion of the filter-paper; hence it must be measured for each experiment. The voltage source is a low-impedance 8 V transformer, so that to a first approximation, the voltage across the filament is independent of the current (a 1 % drop occurs during the ignition). To obtain the energy dissipated as $V\int I\,\mathrm{d}t$, is is necessary to derive the current integral by measuring the voltage integral across a small resistance (*ca.* $0{\cdot}1\,\Omega$), in series with the filament. The integrating circuit is shown in figure 3. The low-voltage input is amplified by a twin-triode cascade amplifier of gain 600, with a cathode-follower stage to supply the necessary power output. The amplified a.c. voltage is then rectified so that the voltage across the $0{\cdot}1\,\mu$F smoothing condenser is equal to the double-amplitude peak voltage of the amplifier output. This charges the $11\,\mu$F condenser through the 1 MΩ charging resistor, and the voltage across this condenser is measured by a valve-voltmeter circuit. The charging voltage must at all times be large compared with the voltage across the condenser so that it is sensibly equal to the amplifier output. The time constant for the charging process is about one-tenth of that for discharging through the 10 MΩ grid resistor of the valve voltmeter. This makes readings simple to take as the meter deflexion is virtually stationary after an ignition.

A linear calibration curve of electrical energy against deflexion is obtained for inputs of up to 6 s duration, and this is the part of the curve used. The random error in this measurement is less than ±3 %.

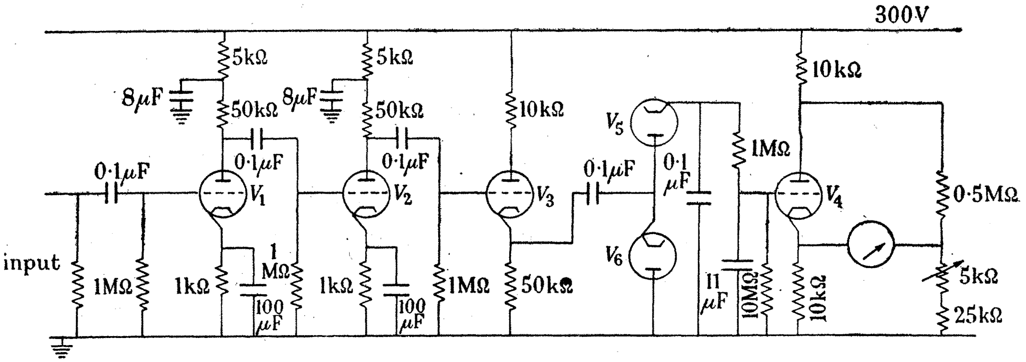

FIGURE 3. The ignition current integrating circuit. V_1–V_2, V_3–V_4, 6SN7; V_5, V_6, EA50.

The electrical ignition energy varies from *ca.* 0·6 to 1·6 cal, a variation of 0·03 % of the total heat quantity. The inclusion of this measurement improves the standard deviation of the calibration experiments with benzoic acid from 0·018 to 0·012 %. Previous workers have either devised a system in which the ignition wire is not fused so that an approximately constant amount of electrical energy can be supplied, or they have assumed that this quantity is constant. The measurement of this energy quantity is important, especially as the modern tendency is to reduce the total heat quantity.

(2) *Completeness of combustion*

It is necessary to test the gases after a combustion for carbon monoxide to ascertain whether combustion is complete. From the heat of combustion of carbon monoxide (Rossini 1939) it is calculated that,

$$1\text{ ml. CO} \rightarrow 1\text{ ml. CO}_2\ (25^\circ\text{ C, 1 atm}) \quad \Delta H = -0{\cdot}33\text{ cal.}$$

For a heat quantity of 3000 cal to be determined to 1 part in 30000, there must be less than 0·3 ml. of carbon monoxide in the gases after a combustion. In this case the test to be used must have a sensitivity of about 0·0038 %. The method used is that due to Winkler (1935). The gases to be tested are stored in a 1 l. flask over 1 ml. of a specially prepared palladous chloride solution for 24 h, 5 ml. of acid ammonium molybdate solution are added, and the liquid is observed in a ½ in. diameter tube and compared with a blank test. The presence of a blue colour indicates the presence of carbon monoxide.

The sensitivity of the test was examined and Winkler's results were confirmed. With our conditions, the limit of sensitivity is 0·001 % by volume. If carbon monoxide is detected in the gases after a combustion, the combustion value is rejected (see Coops *et al.* 1947).

Experimental method

(1) *Determination of the heat quantity*

The solid substance is compressed into cylindrical pellets and the weights of these adjusted by scraping so that reproducible heat quantities are obtained. The pellets are weighed to about 3×10^{-6} g into the silica crucible from a stoppered weighing bottle and the weights are corrected to vacuum. The filter-paper fuse is also weighed to the same sensitivity.

A cylindrical platinum shield with a cover is placed over the crucible, as this seems to assist complete combustion. The bomb is then assembled and 1 ml. of water placed inside. The air inside the bomb is swept out by twice filling to 15 atm with oxygen and releasing the pressure. The bomb is then filled to a pressure of 30 atm. Ordinary cylinder oxygen is used, and no differences in the final results have been detected when using oxygen from different cylinders, so that if a combustible impurity is present, it would seem to be reproducible in quantity. The electrical ignition energy is measured at the moment of combustion by the method described above.

After a combustion, the residual gases from the bomb are tested for carbon monoxide as described above. The bomb is then washed out with a small volume of distilled water (*ca.* 10 ml.) and the washings titrated for nitric acid with N/20-sodium hydroxide solution using bromophenol blue as indicator. The heat of formation is taken from Coops *et al.* (1947) as 13·97 kcal/mol at constant volume at 25° C. This acid-base titration is in dilute solution and requires an acid end-point because the solution is saturated with carbon dioxide. The end-point is therefore not sharp and is taken as near as possible to a standard colour.

The carbon residue in the crucible is determined as the difference in weight of the crucible after it has been dried over potassium hydroxide and after heating to red heat in air. The heat of combustion of carbon is taken to be 8080 cal/g (Coops *et al.* 1947). This correction is usually about 0·3 % of the total heat; and it is the least satisfactory part of the heat quantity determination because the change in weight is ascribed only to the carbon residue.

(2) *Determination of the temperature rise*

Temperatures are derived as resistances of the platinum thermometer which are calculated from the bridge readings, and are expressed in ohms. The approximate quantities in degrees Centigrade are also quoted so that these can be compared with those obtained by other workers.

When the calorimeter has been assembled, heat is put in so that the desired starting temperature can be reached quickly. It is then necessary to leave the calorimeter for at least as long as the main period (60 min) so that this heat is properly distributed. The temperature measurements are as usual divided into those of the fore-period, main-period and after-period.

The times for bridge readings from 220·0 to 250·0 Ω (corresponding to an interval of *ca.* 0·1° C) at 1·0 Ω intervals, constitutes the fore-period. The procedure adopted is to set the bridge at a known value and record the time at which the galvanometer spot passes the scale zero. Times are measured to a precision of 0·2 s using a calibrated stop-watch.

The direction of current through the bridge is reversed for each successive reading to eliminate errors due to the drifting of the true zero (i.e. the position of the galvanometer spot when the bridge is exactly balanced) with respect to the scale zero, such drifting being caused by variations of thermo-e.m.f.'s. When the bridge reading reaches 250·0 Ω, the ignition key is depressed and the meter deflexion of the current integrator is recorded. This completes the fore-period readings which take about 24 min.

Bridge readings during the main-period are recorded at 50·0 Ω intervals for the sharply rising portion up to 1000 Ω. The sensitivity of the galvanometer amplifier is reduced to $\frac{1}{10}$ and current reversal used for successive readings. The first interval is about 50 s and the remaining ones are about 12 s. The maximum temperature, *ca.* 1060 to 1070 Ω, is reached about 13 min after the ignition (this corresponds to a temperature rise of *ca.* 1·8° C).

The temperature now begins to fall, and readings are taken at 1·0 Ω intervals until about 50 min after ignition, when the rate of cooling approaches that predicted by Newton's law. The readings of the after-period are now taken at 0·5 Ω intervals, usually from 1050·0 to 1025·5 Ω (i.e. a temperature interval of about 0·05° C occurring in about 70 min), using the same procedure as for the fore-period.

The total time for the temperature measurements is usually between 130 and 160 min.

CALCULATION OF THE HEAT EXCHANGED BETWEEN THE CALORIMETER AND ITS ENVIRONMENT

In this work the Dickinson method (1914) is used to calculate this exchange heat. It is necessary to investigate the assumptions and limitations of this procedure especially for the aneroid calorimeter, although the following treatment can be extended to include the water calorimeter by taking account of the heat of stirring.

It is assumed that the calorimeter has a uniform surface temperature (T_v) and that it is separated by a gap from a thermostat (at T_w) which completely surrounds it. It is also assumed that the heat transfer across this gap obeys Newton's law; so, if Q_E is this exchange heat,

$$\mathrm{d}Q_E = W\,\mathrm{d}T_v = -k(T_v - T_w)\,\mathrm{d}t, \tag{1}$$

where W is the heat capacity of the calorimeter and k is a constant.

The temperature-time curve for the process is shown in figure 4. The heat of combustion, Q_B, is liberated instantaneously at time t_b, but the transfer of this heat to the calorimeter takes a finite period of time, $t_e - t_b$, during which heat is exchanged between the calorimeter and the thermostat. Then

$$W(T_e - T_b) = Q_B + Q_E.$$

By putting $k/W = G$,

$$Q_B = W\left[(T_e - T_b) + G\int_{t_b}^{t_e}(T_v - T_w)\,\mathrm{d}t\right]. \tag{2}$$

The quantity inside the brackets is known as the 'corrected temperature rise', and the second term within the brackets is known as the cooling correction, ΔT.

When $Q_B = 0$, i.e. $t < t_b$ or $t > t_e$, and if $\mathrm{d}T_v/\mathrm{d}t$ be termed g, it follows from equation (1) that

$$g = -G(T_v - T_w). \tag{3}$$

G can be determined from pairs of corresponding values of g and T_v, i.e. for g_1 at T_1 and g_2 at T_2, since

$$G = \frac{g_1 - g_2}{T_2 - T_1}. \tag{4}$$

A constant value of G can only be obtained when $Q_B = 0$, i.e. only from the slope values after t_e; and this provides the most satisfactory basis for selecting the minimum length of the main period. T_w can be obtained from the relation

$$T_w = T_1 + g_1/G. \tag{5}$$

ΔT may be determined by an integration method involving the evaluation of $\int_{t_b}^{t_e} T_v \, dt$. Procedures for this with special reference to bomb calorimetry are admirably described by Coops *et al.* (1947).

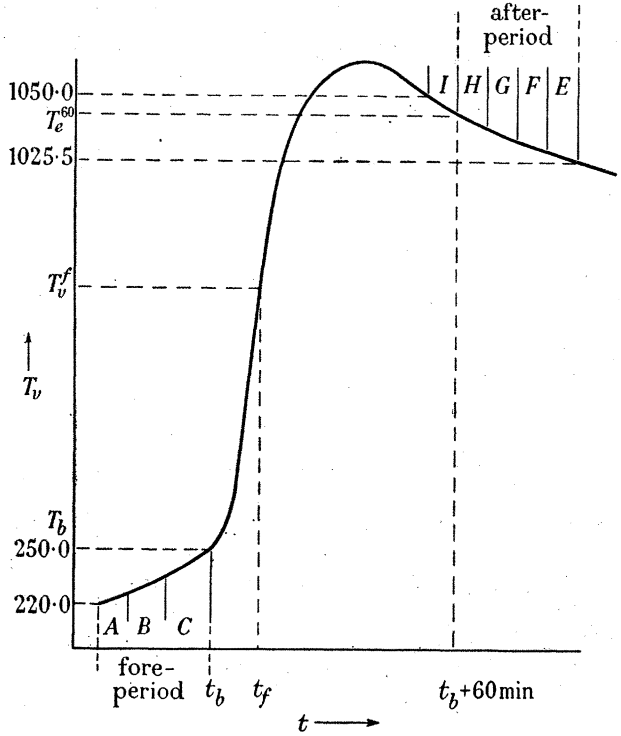

Figure 4. A typical temperature-time curve. The numerical ordinates are typical bridge readings.

Extrapolation methods can also be used to evaluate ΔT, the most common one being that due to Dickinson. The treatment is essentially as follows.

If rates of heat transfer in the calorimeter are proportional to temperature differences, the rise of T_v after the instant of combustion will follow an inverted exponential course, and if there were no heat exchange, the $T_v : t$ curve would be as shown in figure 5 and

$$T_v = T_e - (T_e - T_b)\, e^{-t/r},$$

where r is a parameter for the system. A retardation time of a seconds is included to account for various lags so that

$$T_v = T_e - (T_e - T_b)\, e^{-(t-a)/r}. \tag{6}$$

A time t_f is defined so that

$$-g_b(t_f-t_b)-g_e(t_e-t_f) = G\int_{t_b}^{t_e}(T_v-T_w)\,\mathrm{d}t.$$

Substituting from (3) for g_b and g_e; and from (6) for T_v, it follows that

$$t_f = t_b+\int_{t_b}^{t_e}\mathrm{e}^{-(t-a)/r}\,\mathrm{d}t.$$

Measuring time from the instant of combustion, so that $t_b = 0$, and taking the main-period sufficiently long for $\mathrm{e}^{-t_e/r}\rightarrow 0$, it follows that

$$t_f = r\,\mathrm{e}^{a/r}\overset{\frown}{=}a+r.$$

Then at t_f, $$T_v^f = T_e-(T_e-T_b)\,\mathrm{e}^{-1}.$$

According to this result, the intercept on the ordinate at 63 % of the temperature rise, obtained by extrapolating with slopes g_b and g_e, is equal to the corrected temperature rise. t_f is usually taken at 60 % of the rise to allow for non-instantaneous combustion.

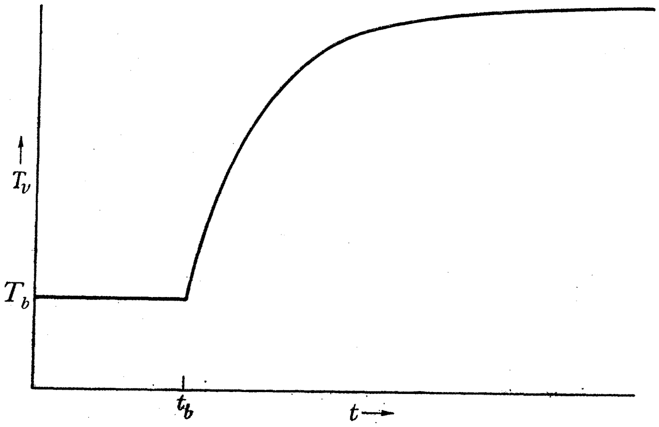

FIGURE 5. The simple theoretical temperature-time curve.

In the foregoing theory, t_f should be constant. This implies that (T_e-T_b) must be unique; but it is not possible to define a single unambiguous value for T_e. Also, equation (6) is of the wrong form as it is incompatible with a main-period of the generally observed shape as shown in figure 4. It is of interest, therefore, to derive a more exact equation for the complete $T_v:t$ curve and then to examine the consequences of the simple extrapolation procedure described above.

The form of the curve for the temperature rise when there is no heat exchange with the surroundings, as shown in figure 5, can be expressed by

$$T_v = A(1-\mathrm{e}^{-bt}).$$

which becomes equation (6) if $A = T_e$, $T_b = 0$ and $\mathrm{e}^{-bt} = \mathrm{e}^{-(t-a)/r}$. In this case

$$\frac{\mathrm{d}T_v}{\mathrm{d}t} = Ab\,\mathrm{e}^{-bt}.$$

The rate of temperature change due to heat exchange with the surroundings is given by

$$\frac{\mathrm{d}T_v}{\mathrm{d}t} = -G(T_v-T_w).$$

Hence the overall rate of temperature change is given by

$$\frac{\mathrm{d}T_v}{\mathrm{d}t} = Ab\,\mathrm{e}^{-bt} - G(T_v - T_w).$$

This differential equation may be solved to give

$$(T_v - T_w)\,(b-G) + Ab\,\mathrm{e}^{-bt} = \mathrm{e}^{-Gt}\,[Ab - T_w(b-G)], \tag{7}$$

thus giving the relation between T_v and t over the complete curve after the moment of combustion.

It is now possible to derive an equation for the tangent to the after-period curve at some particular time t_1. For the after-period, e^{-bt} is effectively zero. The following equation of the form $y = mx + c$ is for the tangent to the after-period curve at time t_1:

$$y = \frac{-G\,\mathrm{e}^{-Gt_1}[Ab - T_w(b-G)]}{b-G}\,x + \left\{\frac{\mathrm{e}^{-Gt_1}[Ab - T_w(b-G)]\,[1+Gt_1] + T_w(b-G)}{(b-G)}\right\}. \tag{8}$$

The second term on the right-hand side is the intercept on the y-axis, which decreases as t_1 is increased. Consequently, if we assume that the time for 60 % of the temperature rise is not markedly dependent upon T_e (i.e. the main-period curve rises sharply), then the corrected temperature rise will be lower the later the time at which the final temperature is taken. This effect is shown in an exaggerated fashion in figure 6.

Next, the effect of varying thermostat temperature can be considered. For two cases where all the conditions except the thermostat temperature are identical, e.g. the heat quantity (directly related to A) and the cooling constants (G) are the same for both, if the influence of the different fore-period slope, which is in practice a small effect, be ignored, then from equation (8) the point of intersection of the two tangents to the after-periods at time t_1 may be calculated. The expression for this point of intersection reduces to

$$t_{\text{intersection}} = \frac{(1+Gt_1) - \mathrm{e}^{Gt_1}}{G}.$$

The value is negative and is independent of the rate of rise of the main-period. Thus, the lower the thermostat temperature, the lower is the corrected temperature rise; and this relative lowering is greater, the later the time at which the final temperature is taken. The effect of thermostat temperature upon the corrected temperature rise is shown in figure 7. These consequences of the extrapolation procedure have been experimentally demonstrated, but as the system on which the foregoing treatment is based is obviously over-simplified, no quantitative agreement between the experimental curves and those predicted from the above has been sought.

Thus, any method of computing the cooling correction which involves linear extrapolation of the fore- and after-periods must be used with great care. The defects are the more important in the present work because of the long extrapolation of the after-period slope which is required. Nevertheless, the Dickinson method is so simple that it is preferred when comparable conditions between calibrations and measurements are used; for, as explained in the introduction, a large error in the cooling correction is tolerable if the conditions are closely similar. The cooling correction is about 1 % of the total; so that if conditions are kept reproducible to 1 %, it could contain a constant error of 100 % of its amount before a systematic error of 0·01 % is caused in the calculated value of the heat of combustion.

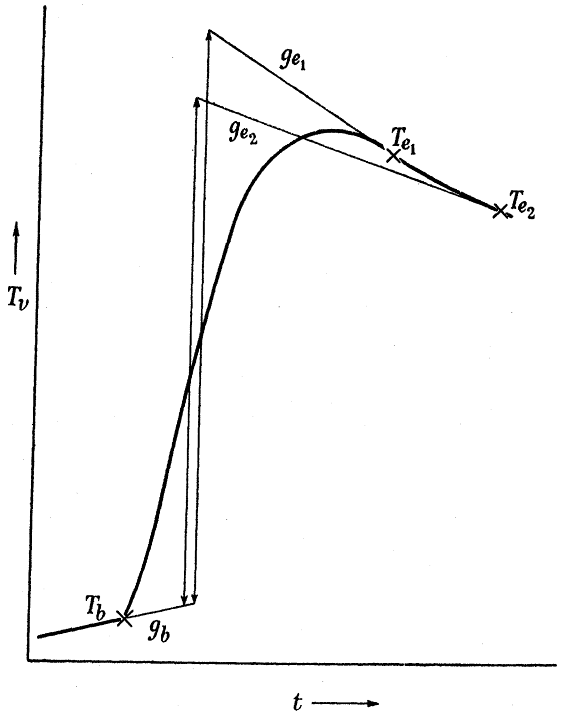

FIGURE 6. The dependence of corrected temperature on T_e.

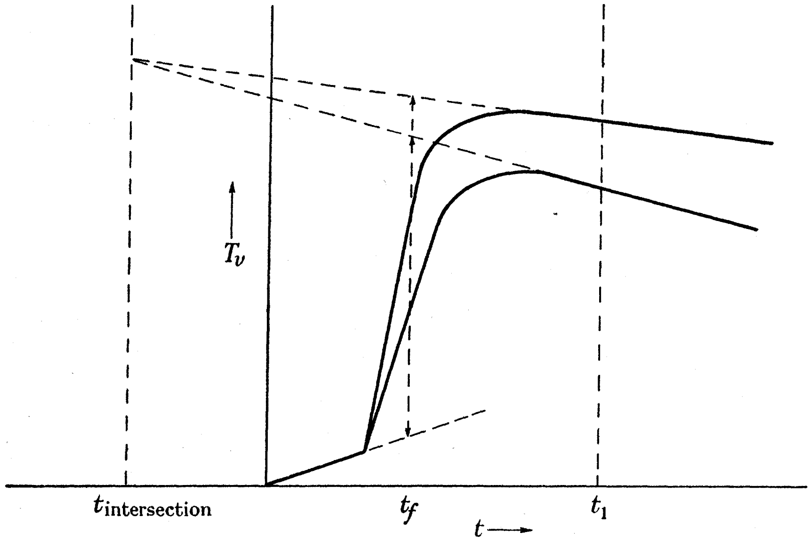

FIGURE 7. The dependence of corrected temperature on thermostat temperature.

In practice, the fore- and after-periods are divided into subperiods as shown in figure 4. The slope of bridge reading with time is determined for each subperiod graphically. Two lines are obtained corresponding to the two directions of current through the bridge and the mean is taken. The slope of thermometer resistance with time is derived from that of bridge reading with time by an expression which takes account of the non-linear relationship.

The mean of the three fore-period slopes, g_1, is taken to be the value at the mean thermometer resistance of the fore-period, T_1. With these values a cooling constant, G, is calculated for each of the after-period subperiod slopes, i.e. for each g_2, T_2, using the relation

$$G = \frac{g_1 - g_2}{T_2 - T_1}.$$

A constant value of G is expected only when the heat of the bomb process has been completely distributed in the calorimeter. It has been found in experiments so far that this does not occur until about 60 min after ignition. Hence the main period is chosen to be exactly 60 min long which is greater than the usual value for a water calorimeter (*ca.* 10 to 20 min), probably because of the many long conductance paths along which temperature must be equilibrated. The mean value of G obtained from the after-period slopes is used in calculating the thermostat temperature T_w by the relation

$$T_w = T_1 + g_1/G.$$

The initial temperature T_b, at the time of ignition t_b, is read off from the last fore-period curve and the final temperature T_e from the after-period curve. The calibration and accuracy tests have been done using two final temperatures, one 60 min after ignition, T^{60}, and one 80 min after ignition, T^{80}. The time, t_f, at which the temperature rise is 60% of $(T_e - T_b)$ is read off from the main-period curve. The value of $(t_f - t_b)$ varies from about 125 to 140 s, whereas according to the Dickinson theory it should be constant. This variation has three causes: (*a*) the heat contacts inside the calorimeter will not be exactly reproducible, (*b*) the time of ignition is a vague concept and will not correspond exactly with the time the ignition key is depressed, and (*c*) pellets will not always burn at the same rate. The inadequacy of this theory for the present calorimeter is also shown by the fact that according to it, the main period should be approximately $9(t_f - t_b)$. Actually, it is $27(t_f - t_b)$.

All the observations of the fore- and after-periods are then combined in calculating the correct slopes g_b and g_e at T_b and T_e by using a rearrangement of the expression for T_w, thus:

$$g_b = G(T_w - T_b), \quad g_e = G(T_w - T_e).$$

The cooling correction is calculated by the Dickinson method, so that

$$\Delta T = -g_e(t_e - t_f) - g_b(t_f - t_b),$$

and the corrected temperature rise $= (T_e - T_b) + \Delta T$.

Calibration of the apparatus

The apparatus was calibrated with benzoic acid. The most recent value for the isothermal heat of combustion at 25° C under the standard conditions proposed by Washburn (1933), namely, 30 atm of oxygen, 3 g of benzoic acid and 3 g of water per litre of bomb space, is that determined by Jessup (1942, 1946). This value is 26429·4 ± 2·6 J (int.)/g (vac.) or 6317·84 cal/g (vac.) as 1 thermochemical calorie = 4·1833 J (int.) (*Selected values* 1952). The conditions used in this work are: 30 atm of oxygen, 0·5 g of benzoic acid, 1·0 g of water and a bomb volume of 266 ml. When the correction factor given by Jessup & Green (1934) is applied, the isothermal heat of combustion is 6317·67 cal/g (vac.). For calibration purposes, the required non-isothermal heat of combustion is calculated by subtracting the isothermal correction for the bomb process (Washburn 1933), where in this case the temperature changes from 23·455 to 25·244° C. The heat of combustion of benzoic acid under these conditions is 6317·10 cal/g (vac.).

TABLE 1*a*. CALIBRATION OF THE APPARATUS WITH BENZOIC ACID

		heat quantity											
no.	weight of b.a. (g, vac)	b.a.	f.p.	C	HNO_3	e.i.e.	total	corr. rise (60)	K^{60}	Δ	corr. rise (80)	K^{80}	Δ
14	0·500192	3159·76	12·52	0·73	0·22	1·05	3172·82	0·367701	8628·80	0·21	0·367363	8636·74	0·81
15	0·499244	3153·77	11·98	0·81	0·22	1·18	3166·34	0·366951	8628·78	0·19	0·366511	8639·14	3·21
17	0·499230	3153·69	12·52	0·89	0·22	1·45	3166·99	0·366983	8629·80	1·21	0·366686	8636·79	0·86
18	0·499203	3153·52	12·37	0·61	0·94	0·94	3167·16	0·367101	8627·49	1·10	0·366794	8634·71	1·22
19	0·500068	3158·98	12·45	0·45	0·51	0·85	3172·34	0·367721	8627·03	1·56	0·367421	8634·07	1·86
20	0·499570	3155·83	12·40	0·63	2·97	0·95	3171·52	0·367567	8628·41	0·18	0·367260	8635·63	0·30
21	0·500015	3158·64	12·29	0·71	0·94	0·93	3172·09	0·367542	8630·55	1·96	0·367268	8636·99	1·06
22	0·500303	3160·46	11·91	0·37	0·87	0·47	3173·34	0·367766	8628·69	0·10	0·367475	8635·53	0·40
23	0·499780	3157·16	12·32	1·41	0·15	0·94	3169·16	0·367237	8629·74	1·15	0·366919	8637·22	1·29
24	0·498308	3147·86	12·61	1·47	0·73	0·59	3160·32	0·366251	8628·84	0·25	0·365944	8638·08	0·15
25	0·497868	3145·08	12·48	0·33	0·36	0·44	3158·03	0·366034	8627·70	0·89	0·365770	8633·92	2·01
26	0·501260	3166·51	12·24	0·65	0·58	1·75	3180·43	0·368645	8627·35	1·24	0·368352	8634·21	1·72
27	0·498580	3149·58	12·58	0·83	0·22	0·83	3162·38	0·366446	8629·87	1·28	0·366127	8637·39	1·46
28	0·500619	3162·46	12·60	0·44	0·65	0·40	3175·67	0·368097	8627·26	1·33	0·367787	8634·54	1·39
								mean	8628·59		mean	8635·93	

TABLE 1*b*. SECOND CALIBRATION OF THE APPARATUS WITH BENZOIC ACID

		heat quantity											
no.	weight of b.a. (g, vac.)	b.a.	f.p.	C	HNO_3	e.i.e.	total	corr. rise (60)	K^{60}	Δ	corr. rise (80)	K^{80}	Δ
81	0·498429	3148·63	12·43	1·28	0·51	0·75	3161·04	0·366338	8628·75	0·40	0·366034	8635·92	0·69
86	0·496401	3135·81	12·62	0·83	0·73	0·83	3149·16	0·364918	8629·77	0·62	0·364609	8637·09	0·48
91	0·499846	3157·58	12·56	0·94	0·44	0·19	3169·83	0·367386	8628·06	1·09	0·367062	8635·68	0·93
92	0·496692	3137·65	12·37	1·43	0·44	0·22	3149·25	0·364918	8630·02	0·87	0·364592	8637·74	1·13
								mean	8629·15		mean	8636·61	

Symbols not defined in the text:

b.a. = benzoic acid.
f.p. = filter paper.
C = carbon.
HNO_3 = nitric acid.
e.i.e. = electrical ignition energy.

Symbols defined in the text:

K = calibration constant (cal/ohm)
Δ = deviation of *K* from the mean.

Note. Heat quantities are expressed in thermochemically defined calories, and temperature rises in ohms.

When quantities greater than 0·5 g of benzoic acid were burned in the Griffin–Sutton bomb, small amounts of carbon were deposited on the bomb walls, presumably owing to the flame reaction zone hitting these walls. To prevent this it was necessary to depart from the Washburn conditions.

British Drug Houses thermochemical standard benzoic acid has been used. Erratic results were obtained at first until the fused lumps of acid were finely ground before pelleting to promote more even burning. The results of this calibration are shown in table 1. The weights of benzoic acid used have been corrected to vacuum.

K^{60} is the calibration constant obtained by dividing the total heat quantity in calories by the corrected temperature rise for T_e^{60} in ohms. The result may be expressed

$$K^{60} = 8628{\cdot}59 \pm 0{\cdot}59\ (\pm 0{\cdot}007\ \%),$$

where the precision error given is calculated by the method proposed by Rossini (1939) and is the double standard error of the mean. The standard deviation of these results, $\sigma = 0{\cdot}012\%$. Similarly,

$$K^{80} = 8635{\cdot}93 \pm 0{\cdot}82\,(\pm 0{\cdot}01\,\%)$$

and $\sigma = 0{\cdot}018\,\%$. A larger precision error is expected for K^{80} because of the larger cooling correction.

K^{80} is greater than K^{60} because of the defect of the extrapolation procedure illustrated in figure 6 and explained above.

The close reproducibility of the conditions is apparent from table 1. The total variation in heat quantity is only 0·75 %, and the various contributions are fairly constant except for the large nitric acid correction in no. 20. The results given in table 1 (*b*) were obtained 5 months after those given in table 1 (*a*); and the good agreement shows the stability of the apparatus. The details of the calculation of the corrected temperature rises are not given. In these experiments, T_b was virtually constant, the variation in temperature rise being taken up in T_e. The variation of the cooling constant, G, was only $\pm 0{\cdot}8\,\%$, this being within the limits proposed by White (1918) for precision calorimetry. $t_f - t_b$ varied between 135 and 144 s for the reasons given above.

Because of the relative novelty of this calorimetric system, it was considered desirable to carry out some series of experiments with varying conditions to see within what limits this calibration constant was applicable.

Variation of the calibration constant with the size of the cooling correction

In the first series of tests the size of the cooling correction was varied by using a different thermostat temperature for each experiment. The results are given in table 2. The variation is shown in figure 8, assuming a linear relationship and excluding no. 29, shown by a dashed circle, because of a dubious carbon determination. Double standard deviation circles are drawn using the standard deviation of the original calibration.

Table 2

no.	weight of b.a. (g. vac.)	heat quantity						T_w	$\%\Delta T^{60}$	corr. rise (60)	K^{60}	$\%\Delta T^{80}$	corr. rise (80)	K^{80}
		b.a.	f.p.	C	HNO_3	e.i.e.	total							
cal.	—	—	—	—	—	—	—	—	1·13	—	8628·59	1·60	—	8635·93
32	0·498782	3150·86	12·75	0·45	0·44	0·69	3164·29	56·1110	2·65	0·366721	8628·60	3·52	0·366162	8641·78
7	0·501600	3168·66	11·91	1·45	4·34	1·00	3184·46	56·0568	4·41	0·369014	8629·64	5·79	0·368151	8649·87
31	0·498885	3151·51	12·67	0·73	0·22	0·56	3164·23	56·0060	5·88	0·366475	8634·23	7·68	0·365355	8660·70
30	0·496563	3136·84	12·53	0·23	0·15	0·57	3149·86	55·9512	7·66	0·364872	8632·78	9·96	0·363456	8666·41
33	0·499214	3153·58	12·29	0·86	0·29	0·70	3166·00	55·9013	9·42	0·366347	8642·08	12·30	0·364600	8683·49
29	0·493749	3119·06	12·37	3·02	0·36	0·68	3129·45	55·8988	9·49	0·362552	8631·73	12·38	0·360750	8674·84

ΔT = cooling correction (ohms). T_w = thermostat temperature (ohms).

The curves demonstrate the defects of the extrapolation procedure illustrated in figure 7 and explained above, i.e. the curves have positive slopes and that for K^{80} is greater than that for K^{60}. (*a*) and (*b*) denote the ranges of variation of the percentage cooling correction for the original calibration. The variation of K^{60} over the range (*a*) is *ca.* 0·001 %; and that of K^{80} over the range (*b*) is *ca.* 0·004 %. Such variations are negligible. Also, the fact that nearly all the circles, which show precision errors, cross the lines indicates that this error is not greatly increased by increasing the size of the cooling correction. Thus this latter only makes a small contribution to the total precision error which comes mainly from the heat quantity determination.

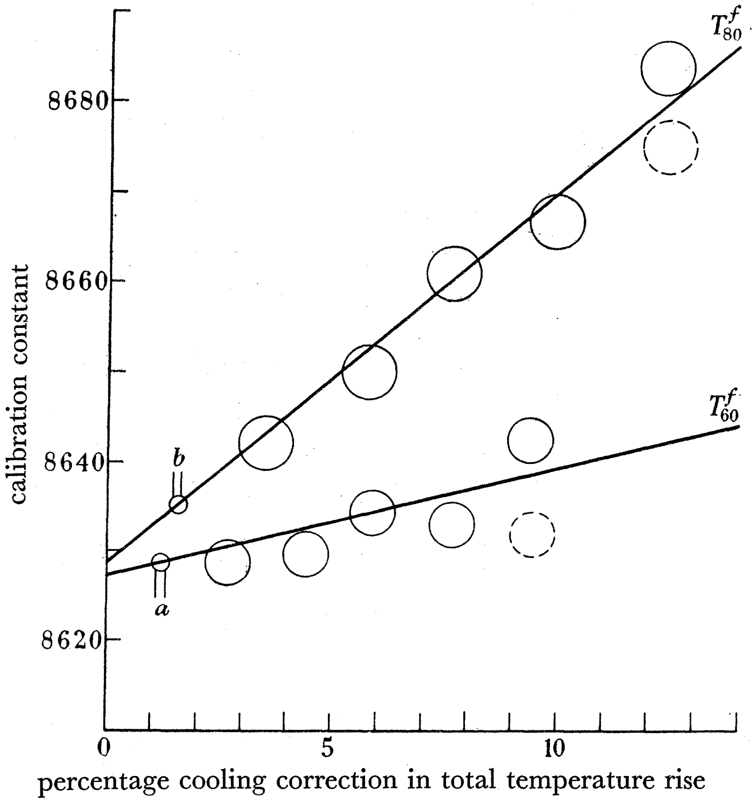

FIGURE 8. The variation of the calibration constant with the percentage cooling correction.

Variation of the calibration constant with heat quantity

In the second series the total heat quantity was varied. The thermostat temperature and the final temperature were kept as constant as possible; so the cooling corrections were of similar amount for each experiment. The appropriate heat of combustion of benzoic acid for each sample weight was calculated in the manner indicated above. The results are given in table 3.

Unfortunately, carbon monoxide was detected after the combustions with the 0·3, 0·2 and 0·1 g quantities. The lower the weight of benzoic acid, the greater the carbon residue and the less the amount of nitric acid formed, indicating that the temperature reached in the crucible was insufficient to promote complete combustion.

The results for the 0·4 and 0·6 g quantities are very close to the original calibration value, although the heat is being varied by ±20 %. Consequently, there will be no variation under the original calibration conditions where the heat quantity was varied by only ±0·38 %.

The difference between K^{60} and K^{80} increases as the temperature rise decreases because the error introduced by linear extrapolation is a constant one.

The values of K^{60} for the 0·2 and 0·1 g quantities are low by about 0·25 %, whereas incomplete combustion tends to increase K. This indicates a systematic error in temperature measurement which is also indicated by the linear dependence of the G values on the temperature differences. The variation is unlikely to be caused by convection because the rates of temperature change are proportional to the temperature difference between the calorimeter and thermostat up to 1·3° C difference. In the fore-period of the calibration experiments, when this temperature difference is 1·55° C, there may be convection, but it appears to be reproducible.

A probable explanation of this systematic error is an interaction between the thermostat and thermometer temperatures, arising because the thermometer coil is not immersed very far in the aluminium block. The magnitude of such an interaction cannot be calculated, but it does not appear to be detrimental to obtaining accurate results.

TABLE 3. VARIATION OF CALIBRATION CONSTANT WITH HEAT QUANTITY

		heat quantity										
no.	weight of b.a. (g. vac)	b.a.	f.p.	C	HNO_3	e.i.e.	total	$10^5 G$	corr. rise (60)	K^{60}	Corr. rise (80)	K^{80}
34	0·400966	2532·94	12·28	0·51	0·15	0·80	2545·66	3·837	0·295100	8626·43	0·294769	8636·12
35*	0·301829	1906·67	12·42	1·05	0·22	0·69	1918·95	3·692	0·222234	8634·82	0·221941	8646·22
36*	0·201007	1269·78	12·58	2·15	0·00	0·49	1280·70	3·500	0·148587	8619·19	0·148300	8635·87
37*	0·099547	628·84	12·31	1·71	0·00	0·81	640·25	3·364	0·074278	8619·65	0·074020	8649·69
38	0·600578	3793·92	12·82	0·71	0·29	0·71	3807·03	4·159	0·441188	8629·04	0·440835	8635·95
cal.	0·5	—	—	—	—	—	3170	4·0	—	8628·59	—	8635·93

* Carbon monoxide detected. cal. = mean values for calibration. G = cooling constant (s^{-1}).

HEAT OF COMBUSTION OF SUCCINIC ACID

The desirability of secondary standards in combustion calorimetry has been discussed at length by Verkade & Coops (1924). Keffler (1934) found that succinic acid possessed satisfactory properties for this purpose. In 1936 it was proposed as a secondary standard by the Commission Permanente de Thermochimie de la Union Internationale de Chimie, and a preliminary value given for its heat of combustion. Although its heat of combustion has been measured on several occasions, no final value has yet been accepted.

Succinic acid has, however, two possible disadvantages. For high-precision calorimetry, it is not desirable to use a substance which is crystallized from water and which cannot be dried by either fusion or sublimation. Nevertheless, the excellent agreement (see below) between the high-precision calorimetric measurements where the drying conditions are varied shows that it can be dried sufficiently by heating. Also it has a low heat of combustion per gram, and there is some difficulty in achieving complete combustion, but this was overcome by igniting the pellet at two points.

The results now obtained could be used either to demonstrate further the absence of systematic errors in the calorimetric method or to redetermine the heat of combustion of succinic acid. We consider that the former task has been completed and choose therefore to do the latter.

The succinic acid used was a sample of B.D.H. Analar material recrystallized four times from distilled water and dried by heating in air to 130° C for 6 h followed by 110° C for 18 h

The results are shown in table 4. The weights were corrected to vacuum; the density of succinic acid is 1·562 g/ml. (Huffman 1938), 30 atm of oxygen were used, 1 ml. of water was placed in the bomb, and the platinum cover and shield were placed over the crucible. The total heat quantity given is that obtained by multiplying the corrected temperature rise for T_e^{60} by K^{60}. The $-\Delta U_B$ values are the isothermal values of the heat of combustion of succinic acid in cal/g (vac.) under the conditions given above, the isothermal correction for the process being 0·54 cal. The values $-\Delta U_B^{60}$ and $-\Delta U_B^{80}$ correspond to K^{60} and K^{80} respectively. These results may be expressed

$$-\Delta U_B^{60} = 3024{\cdot}33 \pm 0{\cdot}23 \text{ cal/g (vac.) } (\pm 0{\cdot}008\,\%),$$

$$-AU_B^{80} = 3024{\cdot}27 \pm 0{\cdot}26 \text{ cal/g (vac.) } (\pm 0{\cdot}009\,\%).$$

The difference between $-\Delta U_B^{60}$ and $-\Delta U_B^{80}$ is not significant, and this is a justification for using the Dickinson method with a fixed-length main-period.

TABLE 4. THE HEAT OF COMBUSTION OF SUCCINIC ACID

no.	weight of s.a. (g. vac.)	heat quantity total	f.p.	C	HNO_3	e.i.e.	$-\Delta U_B^{60}$	Δ	$-\Delta U_B^{80}$	Δ
39	1·045065	3172·21	12·26	1·33	0·36	0·71	3024·45	0·12	3024·50	0·23
40	1·045006	3172·87	12·33	0·82	0·51	0·90	3024·37	0·04	3024·38	0·11
41	1·044798	3172·86	12·51	0·76	0·58	0·78	3024·79	0·46	3024·80	0·53
42	1·044054	3169·15	12·34	1·09	0·29	0·56	3024·36	0·03	3024·31	0·04
44	1·046391	3176·20	12·31	1·00	0·22	1·07	3023·86	0·47	3023·81	0·46
45*	1·043052	3163·92	12·03	1·03	0·15	0·46	(3022·72)	—	(3022·74)	—
46	1·044130	3168·61	12·55	1·49	0·07	0·81	3023·77	0·56	3023·81	0·46
47	1·043956	3170·39	12·29	0·70	0·58	1·10	3024·71	0·38	3024·62	0·35
48	1·044456	3170·11	12·30	1·74	0·22	1·33	3024·10	0·23	3023·92	0·35
49	1·044133	3170·38	12·70	1·19	0·36	1·05	3024·52	0·19	3024·29	0·02
							mean 3024·33		mean 3024·27	

43, failure of carbon determination.
$-\Delta U_B$ = heat of combustion.

* Carbon monoxide detected.
Δ = deviation of ΔU_B from the mean.

To obtain the energy change for the combustion reaction at 1 atm pressure and for the substances involved in their standard states, i.e. $-\Delta U_R$, the Washburn corrections are applied (Washburn 1933). Then

$$-\Delta U_R^{60} = 3020{\cdot}57 \pm 0{\cdot}43 \text{ cal/g (vac) } (\pm 0{\cdot}014\,\%).$$

The error quoted here is the total precision error which includes the calibration error and the uncertainty in the value for benzoic acid.

Comparison with previous measurements

A list of the determinations of the heat of combustion of succinic acid is given below in chronological order:

authors		$-\Delta U_R$(cal/g)
Longuinine	1888	3012
Stohmann, Kleber & Langbein	1889	3021 ± 5*
Longuinine	1891	3002
Verkade, Hartmann & Coops	1924	3020·9 ± 2·0
Beckers	1931	3021·17 ± 1·3*
Keffler	1934	3019·77 ± 1·0
Roth & Becker	1937	3020·47 ± 0·56
Huffman	1938	3020·47 ± 0·43
this work	1953	3020·57 ± 0·43

Huffman corrected the values of Beckers, Keffler, and Roth & Becker for the non-standard conditions used in calibration. These and Huffman's own results have been corrected for the change in the accepted value of the heat of combustion of benzoic acid. The earlier measurements could not be corrected accurately because the experimental conditions were not defined. They were therefore multiplied by $-\Delta U_B$ (Keffler)/$-\Delta U_R$ (corrected) to place them on a common basis. The errors have either been calculated by the usual method (Rossini 1936) or estimated(*).

The values obtained after 1924 are in remarkably good agreement. The only high-precision measurements are the last two and the difference between these is not significant.

Succinic acid therefore appears to be a good secondary standard for high-precision combustion calorimetry. From Huffman's result and that obtained here, the best value is considered to be

$$-\Delta U_R = 3020{\cdot}50 \pm 0{\cdot}50\,\text{cal/g (vac)}.$$

The molecular weight of succinic acid is 118·087 whence,

$$-\Delta U_R = 356{\cdot}69 \pm 0{\cdot}06\,\text{kcal/mole},$$
$$-\Delta H_R = 356{\cdot}39 \pm 0{\cdot}06\,\text{kcal/mole}.$$

These are the appropriate isothermal values at 25° C and may be corrected to other temperatures using

$$\frac{\mathrm{d}(-\Delta U_R)}{\mathrm{d}T} = -27\,\text{cal/mole. deg.}$$

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