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THE HEATS OF COMBUSTION OF GRAPHITE, DIAMOND AND SOME NON-GRAPHITIC CARBONS

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CONTENTS

The heats of combustion of graphite and diamond have been redetermined in a high precision aneroid calorimeter. It is shown that the result obtained for graphite is consistent with all recently published figures with the exception of that reported by Prosen & Rossini (1944). The latter is significantly higher than any other. The heat of combustion of diamond is in good agreement with that found by Jessup (1938) when this is recalculated to modern thermodynamic standards. When the present results are combined with published data the best estimates for the two heats of combustion are shown to be:

$$\text{graphite} \quad -\Delta H^0_{298\cdot16} = 94042\cdot8 \pm 5\cdot9 \text{ cal/mole,}$$
$$\text{diamond} \quad -\Delta H^0_{298\cdot16} = 94490\cdot1 \pm 16\cdot7 \text{ cal/mole.}$$

The importance of preheating the graphite to 2700 °C shortly before combustion and of using material of small B.E.T. surface area are demonstrated.

Measurements were also carried out on samples of carbon black and high-temperature treated furan coke. The heat of combustion of the latter material was found to be greater than that of diamond.

1. INTRODUCTION

The heat of combustion of graphite is a key value in thermochemistry. In recent years it has also become of practical importance in the field of nuclear technology because of the extensive use made of graphite as a neutron moderator in nuclear reactors. Lattice defects are produced in the graphite crystal lattice as a result of neutron bombardment, most are spontaneously annealed, but there is a gradual accumulation of that small proportion which require a higher annealing temperature than the operating temperature of the reactor. If the graphite is subsequently heated to a higher temperature the remaining lattice defects become progressively annealed and heat is liberated, the net result being that the effective specific heat of the material is reduced (Simmonds 1965). It is therefore necessary to know the magnitude of this 'stored energy' in order to be able to predict the behaviour of a graphite moderated reactor when its temperature rises above the normal value. Small samples are consequently removed at intervals from the moderator and their stored energy content measured. The heat evolved can be measured directly at temperatures up to about 750 °C, but such measurements are difficult to make at higher temperatures so that the remaining stored energy, and the total stored energy, are normally obtained by measuring the increase in the heat of combustion of the graphite. In order to understand better the mechanism of defect formation and removal, stored energy measurements are also carried out on specimens of graphite that have been irradiated under different experimental conditions in high flux test reactors.

Nuclear grade graphite is made by carbonizing a mix of petroleum coke and coal tar pitch and then converting the amorphous carbon to 'artificial' graphite by heating it to 2800 °C. The product is highly crystalline with a low ash content. Its heat of combustion is normally measured in a conventional Bertholet type bomb calorimeter with benzoic acid used as a thermochemical standard (see, for example, Jackson & Cordall 1959). The elaborate cooling corrections necessary with such calorimeters could be considerably simplified if an aneroid calorimeter were used. In this the bomb is suspended in an evacuated jacket and acts as its own calorimeter. Meetham & Nicholls (1960) have discussed the general advantages of using calorimeters of this type; an additional advantage for stored energy work is that smaller weights of specimen are needed because of the lower thermal capacity of such calorimeters. Recently, an aneroid calorimeter was constructed in these laboratories for the accurate measurement of small amounts of stored energy in experimentally irradiated graphite. The precision obtained was 1 part in 10 000 and it was considered feasible to use this equipment to redetermine the heats of combustion of graphite, diamond and some non-graphitic carbons since an examination of the published literature indicated that some anomalies existed in the data.

2. Published values of the heats of combustion of carbon

The importance of obtaining an accurate value for the heat of combustion of graphite was recognized by many early workers and several determinations had been carried out before 1934 when the then published data were reviewed by Rossini (1934). His conclusions were that the existing data were quite unsatisfactory and that an accurate determination was urgently needed. It seemed at that time that there were different types of graphite, notably those designated as α and β graphite, with significantly different heats of combustion.

The first really accurate determinations of the heat of combustion of graphite were reported by Dewey & Harper (1938) and by Jessup (1938). Both natural and 'artificial' graphites were used, the latter being very similar to current nuclear grade graphite. The results obtained were reviewed by Rossini & Jessup (1938) who concluded that there was no statistically significant difference between the various figures so that the best estimate would be a mean weighted on the uncertainties of the various determinations.

A new value for the heat of combustion was published some years later by Prosen & Rossini (1944) and the available data again reviewed (Prosen, Jessup & Rossini 1944). It was shown in this review that the figures published in 1938 by Dewey & Harper and by Jessup were in error and required correction. When this had been done and the new results of Prosen & Rossini (1944) included, a new best estimate for the heat of combustion was calculated. This value, 94051·8 ± 10·8, the error being quoted as the uncertainty interval, was subsequently revised to 94054·0 cal/mole when the atomic weight of carbon was taken to be 12·011 (Stull 1961). The latter figure remains the currently accepted heat estimate for the heat of combustion of graphite.

Only two new results have been published since 1944. In 1952 Fraser & Prosen measured the stored energy content of a series of irradiated nuclear graphites and in a complementary investigation measured the heats of combustion of the unirradiated material and also some specimens of natural graphites. Values of 94066·0 and 94038·0 cal/mole respectively were found for the nuclear and natural graphites. They concluded that the difference between these two was not significant and that mean value of 94058·3 should be taken (Fraser & Prosen 1952). This was statistically indistinguishable from the current best value referred to above. More recently a value of 94042 cal/mole has been reported for spectroscopically pure artificial graphite by Lewis, Frisch & Margrave (1965). Unfortunately, these authors have calculated their error in a different manner from that normally employed so that it is not possible to include this value simply in an overall weighted mean.

The heat of combustion of diamond is important because it enables the heat of transition from graphite into diamond to be calculated. Only one value has been published in recent years, that of Jessup (1938) who in fact obtained two quite different sets of results from the two batches of material used. One set was rejected for experimental reasons and a mean value calculated from the other. It is this value recalculated in a similar manner to Jessup's original figure for graphite that provides the currently accepted best estimate for the heat of combustion of diamond, 94507·3 ± 20·3 cal/mole (Prosen *et al.* 1944). Of the data published before Jessup's only those of Roth and his coworkers are of more than historical interest (Roth & Wallasch 1913, 1915; Roth & Naeser 1925). These, when recalculated on the basis of modern values for the heat of combustion of benzoic acid and the atomic weight of carbon, are in reasonable agreement with those of Jessup. Nevertheless, the situation is rather unsatisfactory because Jessup was unable to give a complete explanation for the results obtained in the rejected set.

There have been no recent determinations of the heat of combustion of non-graphitic carbons and in view of the unsatisfactory nature of earlier experiments no worthwile figures can be quoted (Rossini 1934; Bichowsky & Rossini 1936).

3. Experimental

Aneroid calorimeter

The general design and arrangement of the aneroid calorimeter are shown in figures 1 and 2. Full engineering details of the construction will be published elsewhere (Lewis & Phillips 1966). In general the design follows that described by Meetham & Nicholls (1960).

The bomb, of 191 ml. capacity, is suspended from the lid of a vacuum jacket by a nylon rod which is attached to a swivelling connector underneath the lid, the lower end of the rod being screwed into a recess in the top of the body of the bomb. The vacuum jacket, which like the lid is made of copper, is mounted permanetly in a small constant temperature water bath through which water is circulated continuously from a large thermostat. An alternative overflow enables the water level in the bath to be lowered below the lid when it is necessary to remove this from the jacket. A steel safety shield is used to cover the bath during an experiment. This also prevents excessive evaporation of the water.

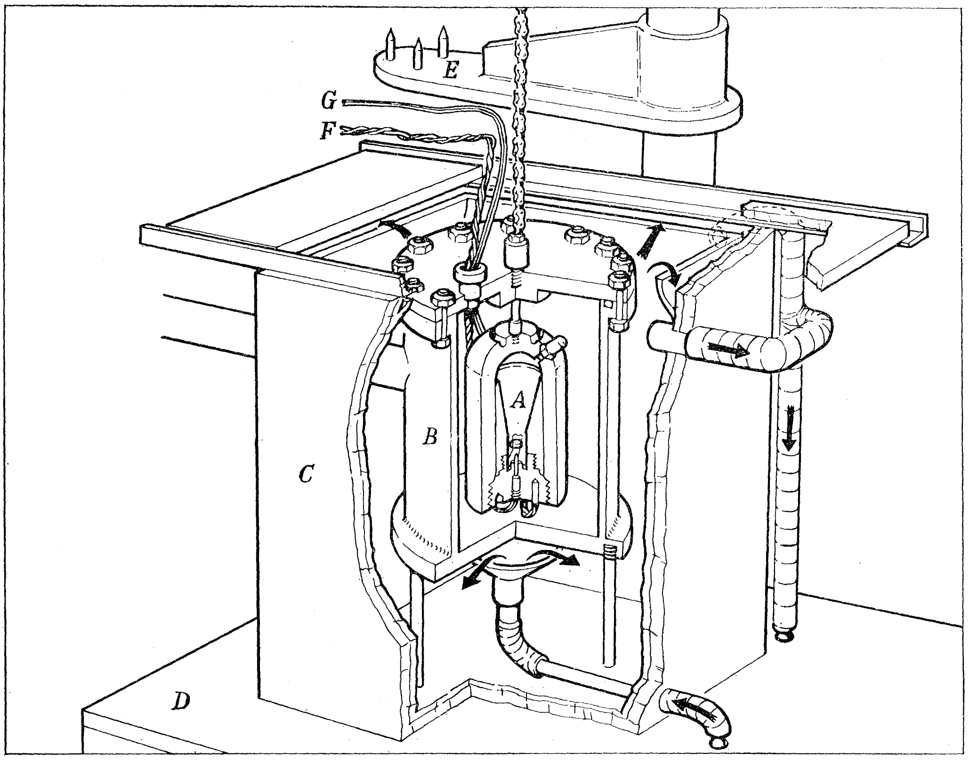

Figure 1. Schematic view of aneroid calorimeter. *A*, bomb; *B*, vacuum jacket; *C*, water bath; *D*, thermostat; *E*, support arm; *F*, resistance thermometer leads; *G*, firing leads.

The bomb is made in three parts, a base on which the sample crucible is mounted and in which is sealed the platinum resistance measuring thermometer, the body, and a radiation shield which is screwed into the base and helps to speed up temperature equilibriation by absorbing thermal radiation from the flame and conducting the heat directly to the base. This shield is unscrewed after each run to enable the crucible to be removed and replaced. The base and body are screwed tightly together to give a good metal to metal contact, a trapped rubber O-ring seal being used to produce a gas-tight joint. All parts of the bomb are made from a high tensile strength copper-tellurium alloy (0·05 % Te) which has substantially the same thermal conductivity as pure copper. In order to prevent any corrosion all internal surfaces are goldplated and have an additional thin film of rhodium deposited on top. The external surfaces of the bomb and the internal surfaces of the vacuum jacket are kept highly polished to minimize radiation losses. Two Schrader-type valves are located on the top of the body, two being used in order to facilitate purging of the bomb gases. When the bomb is being filled or emptied gas connectors each containing a Schrader valve depresser are screwed on to the valves, that on the inlet valve being connected to the oxygen supply, that on the outlet being connected either to the atmosphere or else to a sample vessel. After the bomb has been filled the connectors are removed, rubber sealed caps screwed in their place, and the bomb tested for leaks by being completely immersed in a bath of industrial alcohol. If any bubbles are seen after 15 min the run is discarded. A similar test is carried out immediately after each combustion.

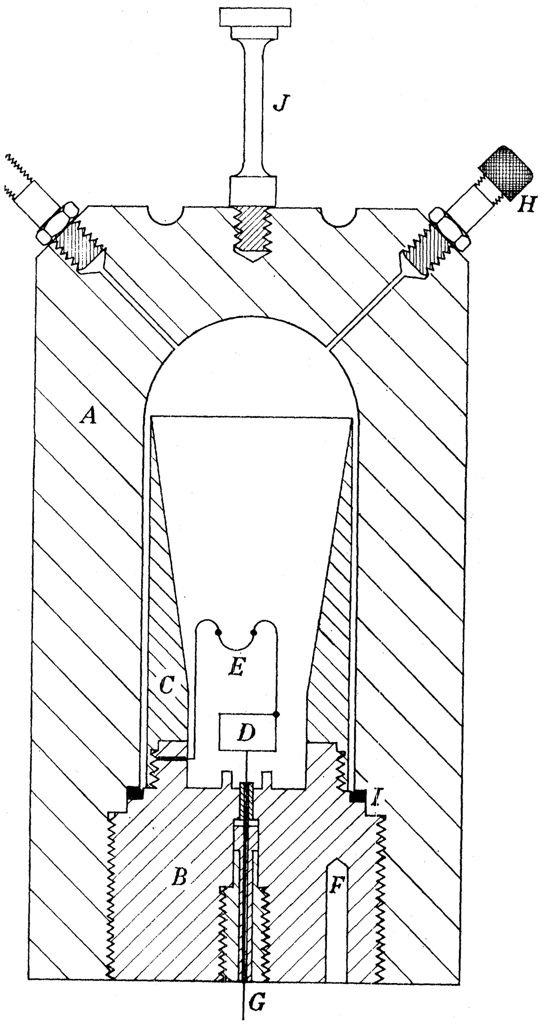

Figure 2. Cross section of bomb. *A*, main body; *B*, base; *C*, flame shield; *D*, crucible; *E*, platinum fuse; *F*, resistance thermometer pocket; *G*, insulating sleeve; *H*, Schrader valve; *I*, O ring seal; *J*, nylon rod. (Half size.)

A small platinum resistance thermometer of the potential lead type is sealed into a recess in the base with Wood's metal. This thermometer which was supplied by Messrs Tinsley, is made to the design of Barber (1933). It consists of a nominal 25 Ω platinum resistance mounted inside a helium filled platinum sheath sealed by a soft glass pinch through which the four platinum leads are taken. As these leads are very fragile their ends are firmly tied to the seal by a glass fibre binder cemented with Araldite resin and the four connecting leads which are of 35 s.w.g. enamelled copper, tied and soldered to the loops thus formed. The other ends of the connecting leads are soldered to 14 s.w.g. copper connectors embedded in an Araldite plug which is inserted through an O-ring seal in the lid of the vacuum jacket. The connecting leads are all 56 cm long and are strapped together with cotton to ensure that each has the same temperature gradient.

Two electrical firing leads are connected to the base of the bomb; both of these consists of 14 strands of 36 s.w.g. tinned copper sheathed in p.v.c. One lead is connected to the base itself and the other to the end of the 18 s.w.g. platinum wire which forms the crucible cradle and which passes through a composite gas-tight insulating sleeve located in the base. These two leads which are also soldered to copper connectors in the Araldite plug, are made shorter, 51 cm, than the resistance leads so that they and not the latter receive any accidental strain that might arise if the lid is inadvertently moved with respect to the base. Appropriate connexions are made from the outer side of the Araldite plug to a 6·3 V firing circuit and to a resistance bridge. A screened four-core cable is used for the external leads to the bridge, the total resistance of the four separate leads being equal within 1 %. The external portions of the connectors are protected from the water in the bath by the Araldite plug.

A platinum fuse wire of 0·1 mm diameter and about 1 cm long is connected across the crucible between the top of the cradle and a terminal post permanently attached to the base. A short length of cotton is tied to the wire so that it hangs down into the crucible and touches a small benzoic acid initiator pellet which is used to ensure ignition of the graphite specimen. When the platinum fuse is fired the cotton ignites and this in turn sets alight the benzoic acid pellet. The fuse ruptures at each firing and a fresh piece is welded in place with a gas torch at the beginning of each determination.

The base of the bomb cannot be unscrewed from the body because of the leads permanently connected between it and the lid. Consequently the body is screwed on and off the base instead, the swivelling connexion in the lid enabling this to be done. The lid is attached to a counterpoised lifting chain which facilitates assembly and prevents possible strains coming on to the connecting leads. Two counterweights are used which automatically allow for the reduction in weight when the bomb is lifted clear of the vacuum jacket and the base and shield detached. When the bomb is being assembled or dismantled the base is supported rigidly on an arm that can be swivelled horizontally into position underneath it. This arm has three lugs which fit into corresponding sockets in the base and prevents this turning when the body is rotated.

The vacuum jacket lid is bolted on to the jacket over a rubber O-ring seal. An oil diffusion pump guarded by a liquid nitrogen trap and backed by a gas ballast pump is used to evacuate the jacket. At the start of each experiment the jacket is evacuated by the ballast pump alone for about 2 h to remove residual traces of alcohol from the leak testing procedure. A final pressure of less than 10^{-5} torr is normally obtained; a higher pressure indicates a leak and the experiment is consequently abandoned. The pressure is measured with a Philips cold cathode ionization gauge.

The oxygen used to fill the bomb is purified of any combustible vapours by being passed first over copper oxide at 500 °C and then over soda-asbestos. The purified gas is stored under pressure in a reservoir which is connected as required to the inlet Schrader valve by means of a flexible coupling and a valve connector. A pressure gauge and a controlling needle valve in the filling line enable the pressure in the bomb to be adjusted to 30 atm gauge pressure with an accuracy of ±2 Lb./in.^{2}. After each combustion the residual gases are analysed for carbon monoxide so that a correction can be applied to the calculated heat evolved. A sample of the gases is collected under pressure in a $\frac{1}{2}$ l. sampling vessel which is attached to the outlet valve and this vessel then connected to an infrared gas analyser calibrated for CO. A trap is inserted between the vessel and the analyser to remove CO_2, which would otherwise interfere with the CO determination. This sampling procedure is necessary because the gas analyser is located in another laboratory. The oxygen used in the bomb contains sufficient nitrogen for traces of nitric acid to be formed during combustion so that 1 ml. of distilled water is pipetted into a recess in the base of bomb and after combustion this, and any condensate on the sides of the radiation shield and body, are washed into a flask and titrated.

The temperature of the water in the bath, which is measured by a Beckman thermometer of 1 degC scale, varies slightly from run to run within the maximum range $25 \pm 0{\cdot}1$ °C but during any combustion remains constant to $\pm 0{\cdot}002$ degC. Heat losses from the thermostat to the surround are less than the heat gained by pumping so that a cooling coil is immersed in the thermostat through which water at 22 °C is circulated from a second thermostat located outside the room. Temperature control is achieved in a conventional manner by the use of a heater controlled by a mercury toluene regulator used in conjunction with an electronic relay.

The resistance bridge is a Tinsley 6 decade instrument (type 4162-B/10) built to Smith's third method with each step of the last decade corresponding to $10^{-4}\,\Omega$. The off-balance current of the bridge is amplified by a Tinsley galvanometer photocell amplifier (type 5214) which gives a 1 cm deflexion on bridge current reversal for each step change in the lowest decade and thus enables differences of $10^{-5}\,\Omega$ to be measured precisely corresponding to temperature changes of 10^{-4} degC. This bridge has been calibrated at the National Physical Laboratory and is rechecked regularly against an N.P.L. calibrated standard resistance. There is a very slight discrepancy between the bridge and the resistance at 25 °C which disappears at 24·3 °C. Although this is not important it was decided for convenience to operate the bridge at 24·3 °C and not at 25 °C as originally intended. Thermostatic control of the temperature of the oil bath in which the resistance coils are immersed was found to be unsatisfactory because small local variations in the bath temperature arising from the operation of the control mechanism gave rise to spurious currents in the bridge. The simple procedure was therefore adopted of circulating oil continuously through the bridge, an equilibrium temperature being reached when the heat dissipated by the circulating pump balances the heat loss to the surround. By maintaining the room temperature at 23·3 °C the oil bath can be kept at $24{\cdot}3 \pm 0{\cdot}1$ °C indefinitely. During any experiment random variations in the stability of the bridge correspond to temperature fluctuations of the order of 3×10^{-5} degC the major source of these variations being due to instrument 'noise'. A current of only 1 mA is needed for the resistance thermometer so that self-heating effects were negligible.

Heat is evolved by the specimen, by the benzoic acid initiator pellet, by the cotton fuse and by the electrically heated fuse wire. The weights of the benzoic acid pellet and the cotton fuse are known so that the heat released by these can be calculated. It is not possible to predict the energy dissipated by the fuse since the length of this varies slightly from run to run. An energy integrator is therefore placed in the firing circuit between the power supply and the connecting leads (Lewis & Phillips 1966). In this the varying potential developed across a 0·1 Ω resistance by the firing current is tapped off by a transformer, rectified, amplified by two transistors and applied to a 100 mF condenser. The potential built up on the condenser is indicated on a sensitive voltmeter. Although the recorded voltage dies away once the fuse ruptures the time constant is long enough for the maximum indicated voltage to be read with sufficient accuracy. Full scale deflexion corresponds to 8·4 J. The integrator was initially calibrated by firing a suitable fuse inside a specially built copper block calorimeter. The rise in temperature of the block was measured by a platinum resistance thermometer embedded in it and the energy dissipated compared with the voltage indicated. In order to be able to re-calibrate the integrator at regular intervals a 62 Ω resistance is connected into the circuit so that it can be switched in place of the fuse in a dummy firing. This resistance, dissipates 0·84 J/s when the firing voltage is applied and enables the rate of rise of voltage to be checked. The two methods of calibration agree to within 5 % and as the energy released is only about 3 J this is completely acceptable.

Materials used

The materials used were natural graphite, artificial graphite, diamond, carbon black and furan coke. Two different types of natural graphite were examined, a finely powdered commercial material supplied by Kropfmuhl A. G., Germany and single crystals from the Ticonderoga mine, New York State. The latter were received embedded in calcite and after being picked out by hand were purified by successive digestions in HCl and HF-H_2SO_4 mixtures. This treatment reduced the impurity level from about 3 % to less than 200 p/M; X-ray analysis showed that no crystallographic damage had occurred. The Kropfmuhl graphite was relatively pure and received no chemical treatment. As received it contained about 30 % of the rhombohedral structure but this was reduced to about 10 % by the heat treatment which was given to all specimens with the exception of diamond. This heat treatment consisted of heating the samples to 2700 °C in an atmosphere of pure argon. The samples were allowed to cool to room temperature in argon and then quickly transferred to a desiccator. This preheating was carried out to remove surface contamination, to reduce the hydrogen content (to about 5 p/M) and to reduce further the ash content.

Three different types of artificial graphite were used, a spectroscopically pure graphite (National Carbon grade AGKSP), British reactor grade graphite (pile grade A), and a graphite specially manufactured at A.E.R.E. Harwell (Artifact 628, which contained 35 % of 'Dixie-therm M' carbon black in addition to the usual petroleum coke and coal tar pitch). Only a few measurements were carried out on this last material which was included in the programme to enable the effect of the presence of a non-graphitizable carbon black to be ascertained. Some measurements were carried out on the carbon black on its own. Because such blacks normally contain a high proportion of hydrogen a small batch that had been preheated to a temperature of only 2000 °C was also examined. This had a much higher hydrogen content than that preheated to 2700 °C. The furan coke was made by polymerizing furfuryl alcohol, carbonizing the polymer and heating the carbonized material to 2700 °C. It was examined because it is non-graphitic and has a highly cross-linked structure.

The diamonds were small gem stones each of which had been optically examined to ensure that flaws and inclusions were absent. They were supplied by the courtesy of the South African Diamond Bureau.

All materials except diamond were analysed, the results of typical analyses being given in table 1. Insufficient material was available to carry out chemical analysis on the diamonds but the results obtained with similar quality gem stones (Raal 1957) are included in table 1. The major constituents in the ash obtained from the carbons were silica and calcium oxide.

Calorimetric grade benzoic acid supplied by British Drug Houses Ltd was used to calibrate the bomb calorimeter and also to initiate the ignition of the carbon samples. The material used was batch no. 760161, which was certified as having been tested at the National Chemical Laboratory, Teddington, giving a heat of combustion of 26439·0 ± 6·2 J/g under standard bomb conditions, the quoted error being twice the standard error of the mean. As the sample tested was inevitably a small one this value is not significantly different from the best estimate for the heat of combustion of pure benzoic acid calculated by one of us to be 26434·4 ± 1·2 J/g (Hawtin 1966). This latter figure, which corresponds to an intrinsic gain in internal energy of 26414·1 J/g, was used in all calculations.

Experimental procedure

All the carbon specimens, but especially the single crystals of graphite and the diamond, proved difficult to ignite and burnt much more slowly than the benzoic acid standard. A series of preliminary combustions was therefore carried out in a specially constructed observation bomb in order to determine the best conditions to be adopted in the final measurements. The observation bomb had windows located above and to the side of the sample crucible. Particular attention was paid to the nature and duration of the flame to the amount of residue and to whether any sooty deposits were formed. It was found necessary to use a small igniter pellet of benzoic acid to initiate burning of the specimens. With the graphite single crystals and the diamond a 100 mg pellet of benzoic acid was used with about 300 mg of sample. In all other cases a 50 mg pellet was used with about 350 mg of the material. These quantities were calculated to raise the temperature of the aneroid bomb by a convenient 2 degC. Under these conditions much less than 1 % of the sample remained unburnt and little CO was formed. The combustion periods ranged from about 75 s for most materials to about 190 s for the graphite single crystals and the diamond. As the effect of surface area was to be investigated the artificial graphites, the furan coke, and the diamonds were not powdered to facilitate combustion but were broken into pieces of about 2 mm across. In order to avoid loss from the crucible during combustion it was necessary to lightly compress both the Kropfmuhl graphite powder and the carbon black into pellets which were then broken into three or four pieces.

The benzoic acid burnt readily and rapidly and attempts were made to prolong the burning time of the pellets used in calibrating the bomb in order to lessen the difference between the middle periods obtained with benzoic acid and with graphite, etc. It was found that the only successful way of doing this was to make a single pellet of the material

TABLE 1. APPARENT HEATS OF COMBUSTION OF CARBON

carbon combusted	number of samples burnt	ash content (p/M)	apparent heat of combustion $(-\Delta H_c^\circ)$ (J/g)	standard deviation (J/g)	standard error (J/g)	overall uncertainty (J/g)	corresponding values in cal/mole: apparent heat of combustion (cal/mole)	corresponding values in cal/mole: overall uncertainty (cal/mole)
spectroscopic graphite (National Carbon AGKSP)	25	< 6 (taken as nil)	32758·3	8·63	1·76	4·14	94039·0	11·9
Kropfmuhl natural graphite	10	40	32737·8	9·01	3·00	6·39	93980·3	18·3
Ticonderoga natural graphite	16	100	32757·3	11·03	2·85	6·10	94036·1	17·5
British pile grade A	11	220	32768·9	6·31	2·00	4·55	94069·7	13·1
furan coke	7	290	32950·3	17·13	6·99	14·16	94590·2	40·6
diamond	5	15	32911·0	10·03	5·02	10·27	94477·4	29·5
spectroscopic graphite (National Carbon AGKSP) (150 °C preheat)	4	< 6 (taken as nil)	32771·4	3·53	2·04	4·62	94077·3	13·3
carbon black (2700 °C preheat)	2	200	32811·4	—	—	—	94191·6	—
carbon black (2000 °C preheat)	2	200	32890·8	—	—	—	94419·6	—
artifact 628	2	200	32798·7	—	—	—	94155·2	—

and to burn this in a close fitting platinum crucible. About 480 mg was required to raise the temperature of the aneroid bomb 2 degC. Pellets of this weight were made each being about 13 mm in diameter and 3 mm thick. In a crucible 10 mm deep the burning time was approximately 15 s. Attempts to lengthen the burning period further by, for example, mixing an inert ceramic oxide powder with the benzoic acid were unsuccessful as incomplete combustions always resulted. The effect on the middle period of this difference in combustion times will be described below.

All materials were stored in desiccators and weighed quickly in the crucible. All weighings were made to ±2 μg and corrected to vacuum. The crucible was placed in the bomb which was then assembled, filled with oxygen, and leak tested. Before the bomb was placed in the jacket its temperature was adjusted to a suitable point just below 23 °C by blowing either hot or cold air on it. This procedure reduced the length of the initial period to a convenient value. The bomb was finally placed in position and the jacket evacuated to a pressure of 10^{-5} torr. Temperature measurements, with the platinum resistance thermometer, were begun when the jacket pressure had reached this figure. An arbitrary zero time was chosen when the bomb had warmed up to 23 °C and temperature readings were then taken every minute up to and including the 14th minute. The sample was ignited on the 15th minute with the galvanometer protected against the sudden temperature change by a 10 kΩ series resistance. Normally, temperature measurements were resumed on the 60th minute and recorded every minute up to the 90th. During these periods the temperature changes were linear within the accuracy of the experiment. The period between the 15th and the 60th minute was arbitrarily defined as the middle period. Because of the difficulty of following the rapid temperature changes during this period, especially during the first 10 min after ignition, readings were only taken during a comparitively few combustions. The temperature of the water bath was checked every 3 min during the experiment.

At the end of a combustion, air was admitted to the jacket and the bomb removed and again leak-tested. A sample of the bomb gas was taken for CO analysis and the remainder vented to the atmosphere. The bomb was dismantled and the crucible removed, dried over a hot plate, cooled in a desiccator and weighed. It was then heated to a red heat over a burner, cooled and again weighed. This procedure gave the weight of unburnt carbon and the weight of ash remaining in the crucible. No significant amounts of ash were ever found, either with benzoic acid or with the carbon samples. The interior of the bomb was always free from sooty or other deposits and filtration of the bomb gases showed that there was no suspended particulate matter present. However, duplicate samples of all materials, except benzoic acid and diamond, were burnt off slowly in air in a muffle furnace and significant although small amounts of ash were then obtained (table 1), the values being in accord with the figures calculated from spectroscopic analysis. It was concluded that under the violent combustion conditions obtaining in the bomb finely divided ash was carried out of the crucible and deposited as an invisible layer inside the bomb. This hypothesis was confirmed when irradiated graphite was examined in a subsequent series of experiments. After each combustion the bulk of the radioactivity, from the ash, was found deposited on the flame shield and on the base of the bomb. The ash values used in calculating the results were the mean values obtained from the slow combustions of a number of samples identical to those burnt in the bomb. As the impurity levels were very low no errors arose because of possible variations between individual samples. The weight of unburnt carbon was always much in excess of the ash and it was assumed in making the calculations that the residue had an impurity level identical to that of the original material. In other words all the ash from the burnt portion of the sample had left the crucible.

4. Calculation of the results

In principle the calculation follows the procedures adopted by Coops, Jessup & van Nes (1956) and by Prosen (1956). The calorimeter system is defined as consisting of the bomb with its platinum resistance thermometer and attached electrical leads, the standard mass of water placed in the bomb, the platinum crucible, and that amount of oxygen which fills the bomb at 30 atm pressure and 23 °C. In each experiment the temperature of the system is raised very nearly 2 degC and the energy equivalent is defined as the quantity of energy expended divided by the actual temperature rise. If no alterations are made to the system between calibration measurements with benzoic acid and combustion experiments with graphite, etc., the only correction that need be applied to the energy equivalent is the heat capacity of the sample burnt.

In theory the heat evolved (Q) in an experiment is simply determined by producing a standard temperature rise in the system by combustion of the proper mass of benzoic acid in a series of calibration experiments and then reproducing this temperature rise as closely as possible by the combustion of the substance under investigation. In practice it is impossible to reproduce the temperature rise and other conditions exactly and the energy equivalent is calculated from the corrected temperature rise and the mass of benzoic acid burnt. From this the heat evolved in a combustion experiment is determined from the corrected temperature rise obtained from that experiment.

Notation

c_i	constant in the linear regression of θ against t during the initial period	(degC)
c_f	constant in the linear regression of θ against t during the final period	(degC)
g_b	$\mathrm{d}\theta/\mathrm{d}t$ at the time of firing	(degC/min)
g_e	$\mathrm{d}\theta/\mathrm{d}t$ at the start of the final period	(degC/min)
g_i	gradient of the linear regression of θ against t during the initial period	(degC/min)
g_f	gradient of the linear regression of θ against t during the final period	(degC/min)
k	Newton's law coefficient	(min^{-1})
m_B	mass of benzoic acid starter	(g)
m_C	mass of ash-free carbon consumed	(g)
m_S	mass of benzoic acid used in calibration	(g)
q_c	heat release from cotton	(J)
q_i	heat release from electrical ignition	(J)
q_n	heat release from nitric acid formation	(J)
q_w	Washburn correction	(J)
q_{CO_2}	extra heat to allow for CO formation	(J)

Q	heat supplied to bomb	(J)
Q^0	heat release under thermodynamic standard conditions	(J)
t	any time	(min)
t_b	time of firing	(min)
t_e	start of final period	(min)
t_x	Dickinson extrapolated time	(min)
Δt	delay time	(min)
$\Delta\theta$	corrected temperature rise	(degC)
$\delta(\Delta\theta)$	correction to observed temperature rise	(degC)
$-\Delta E_{B(\theta)}$	heat of combustion of benzoic acid under actual bomb conditions	(J/g)
ΔE^0_B	intrinsic gain in internal energy on combustion of benzoic acid	(J/g)
ΔE^0_{C}	intrinsic gain in internal energy on combustion of carbon	(J/g)
$-\Delta H^0_{\mathrm{C}}$	heat of combustion of carbon	(J/g)
ϵ	true energy equivalent of bomb	(J/degC)
ϵ_i	energy equivalent of initial system	(J/degC)
$\epsilon_{\mathrm{s.i.}}$	standard energy equivalent of initial system	(J/degC)
$\epsilon_{\mathrm{c.i.}}$	allowance for variable contents in bomb	(J/degC)
θ	any temperature	(degC)
θ_b	temperature at time of firing	(degC)
θ_e	temperature at start of final period	(degC)
θ_i	mean temperature of initial period	(degC)
θ_f	mean temperature of final period	(degC)
θ_∞	final temperature of bomb after infinite time	(degC)

Observed and corrected temperature rise

If the temperature of the bomb at the instant of firing is θ_b and at the start of the final period is θ_e the observed temperature rise is given by

$$\Delta\theta_{\mathrm{obs.}} = \theta_e - \theta_b;$$

θ_b is obtained by extrapolation of the temperature-time curve measured during the initial period before firing.

This temperature rise is not, however, the correct value to use in the calculations since for the duration of the middle period (that is the time between the time of firing and the start of the final period) the calorimeter will have been exchanging heat with its surroundings. This heat exchange is calculated from the observed temperatures and times on the assumption that the system obeys Newton's law of cooling. The total rate of temperature rise is given for an aneroid calorimeter by

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

where k is the 'cooling constant' of the calorimeter, θ_j is the jacket temperature and θ the temperature of the external surface of the bomb.

For an aneroid calorimeter $\theta_j = \theta_\infty$ where θ_∞ is the temperature that would be attained by the calorimeter after an infinite time. Values for θ_∞ and k can be calculated from the data of the initial and final periods since if g_i and g_f are values of $\mathrm{d}\theta/\mathrm{d}t$ at the mean temperatures θ_i and θ_f of the initial and final periods it follows that

$$k = \frac{g_i - g_f}{\theta_f - \theta_i}, \tag{2}$$

$$\theta_\infty = \frac{g_i \theta_f - g_f \theta_i}{g_i - g_f}. \tag{3}$$

In practice the variations of temperature with time in the initial and final periods are linear, within the limits of the experimental accuracy. Values of g_i, g_f, θ_i and θ_f can therefore be found objectively by carrying out linear regressions on the temperature time readings of the initial and final periods.

The classical method due to Dickinson (1915) for obtaining the corrected temperature rise consists in finding a time (t_x) such that

$$-g_b(t_x - t_b) - g_e(t_e - t_x) = k\int_{t_b}^{t_e} (\theta - \theta_\infty)\,\mathrm{d}t = \delta(\Delta\theta), \tag{4}$$

where g_b, g_e are the gradients of the temperature time curves at the time of firing (t_b) and at the start of the final period (t_e). When a linear regression is carried out on these data,

$$g_b = g_i,$$

$$g_e = g_f.$$

As yet no analytical form has been found for the evaluation of the integral in equation (4) and consequently it must be evaluated numerically from the experimental temperature readings of the middle period. The corrected temperature rise ($\Delta\theta$) is then given by

$$\Delta\theta = \theta_e - \theta_b + \delta(\Delta\theta). \tag{5}$$

Now the application of a linear regression to the data of the initial and final period implies that they may be represented by an equation of the type

$$\theta = gt + c. \tag{6}$$

For purely practical reasons it was found more convenient to express the extrapolated time (t_x) in terms of a delay time (Δt) defined as

$$\Delta t = t_x - t_b. \tag{7}$$

Hence substitution in equation (5) for θ_e, θ_b and $\delta(\Delta\theta)$ from equations (6) and (7) yields $\Delta\theta$ as

$$\Delta\theta = (g_f - g_i)\,(t_b + \Delta t) + (c_f - c_i). \tag{8}$$

Determination of the energy equivalent with benzoic acid

If a quantity of energy, Q, is added to a fixed calorimeter system in which the corrected temperature rise is $\Delta\theta$ then the energy equivalent (ϵ) is given by

$$\epsilon = Q/\Delta\theta. \tag{9}$$

When the heat is supplied by combustion and other allied reactions the situation is modified from that described by equation (9) and the energy equivalent must be expressed under some fixed system parameters. Thus the energy equivalent of the fixed initial system (ϵ_i), which is not necessarily the same as the fixed final system, is given by

$$\epsilon_i = \frac{Q_{(\theta_b+\Delta\theta)}}{\Delta\theta}, \tag{10}$$

where the use of the suffix θ to Q implies that Q_θ is the quantity of heat which would have been evolved by the system if the reactions had taken place at the constant temperature θ. In an actual bomb where m_S grams of benzoic acid are burnt $Q_{(\theta_b+\Delta\theta)}$ is given by

$$Q_{(\theta_b+\Delta\theta)} = m_S(-\Delta E_{B(\theta_b+\Delta\theta)})+q_i+q_c+q_n, \tag{11}$$

where $-\Delta E_{B(\theta_b+\Delta\theta)}$ is the heat of combustion of benzoic acid at temperature $(\theta_b+\Delta\theta)$ and under the actual bomb conditions. It is calculated from the heat of combustion under thermodynamic standard conditions $(-\Delta E^0_B)$ by the application of a suitable 'Washburn' correction (Prosen 1956). q_i is the electrical energy required to ignite the fuse, q_c is the heat evolved from the burning cotton fuse, and q_n is the heat evolved from the production of nitric acid.

When graphite, etc., is burnt the energy equivalent (ϵ_i) is no longer applicable to the calorimeter since the combustible material has a different heat capacity from the benzoic acid used in calibration runs. It is convenient therefore to define a new energy equivalent ($\epsilon_{\text{s.i.}}$) which is that for the standard calorimetric system containing only those substances common to all experiments (i.e. oxygen, water, cotton and platinum fuse). Thus

$$\epsilon_{\text{s.i.}} = \epsilon_i - \epsilon_{\text{c.i.}}, \tag{12}$$

where $\epsilon_{\text{c.i.}}$ is a correction term calculated in this case from the specific heat of the benzoic acid and the mass used.

Determination of a heat of combustion

The total heat evolved in the bomb during a combustion run is given by

$$Q = (\epsilon_{\text{s.i.}}+\epsilon_{\text{c.i.}})\,\Delta\theta, \tag{13}$$

where $\epsilon_{\text{c.i.}}$ is calculated from the masses of combustible materials placed in the bomb and their appropriate specific heats.

The corresponding heat release under thermodynamic standard conditions (Q^0) is

$$Q^0 = Q - q_w, \tag{14}$$

where q_w is a thermodynamic heat correction calculated according to the method of Prosen (1956). It is only possible to apply the thermodynamic correction in this simple way because in the present experiments the experimental reference temperature $(\theta_b+\Delta\theta)$ was in fact 25 °C which is also the thermodynamic reference temperature. The gain in internal energy of the carbon on combustion calculated on an ash free basis is given by

$$-\Delta E^0_{\text{C}} = (Q^0 - m_B(-\Delta E^0_B) - q_i - q_c + q_{\text{CO}_2})/m_{\text{C}}, \tag{15}$$

where m_B is the mass of benzoic acid starter, (ΔE^0_B), q_i and q_c have the meanings already assigned to them, q_{CO_2} is the extra quantity of heat that would have been evolved if the small quantity of CO formed had burnt to CO_2, m_{C} is the weight of ash free carbon burnt in the bomb. There is no nitric acid correction term (q_n) in this equation since it is experimentally found to be zero.

The heat of combustion of the carbon at constant pressure is then found from the relation

$$(-\Delta H^0_{\mathrm{C}}) = (-\Delta E^0_{\mathrm{C}}) + P\Delta V. \tag{16}$$

The modern Washburn correction described by Prosen (1956) corrects the gases to unit fugacity (or the real gas at zero pressure). It is therefore only necessary to calculate the $P\Delta V$ term for the solids and liquids in the bomb (Prosen 1965, private communication). Corrections have only to be applied to the gases if the chemical reaction involves a volume change.

Numerical calculations

The numerical calculations arising from the foregoing theory are repetitive and tedious. In order to facilitate these calculations a series of FORTRAN (S2) programs for the I.B.M. 7030 (STRETCH) computer were written. The mechanics of the operation of these programs will be described elsewhere (Hawtin, Gardner & Huber 1966).

5. EXPERIMENTAL RESULTS

Errors

The error terms in this paper are defined in a manner which is entirely consistent with normal statistical and thermochemical usage (Rossini 1956). The more important definitions are summarized in appendix 3.

Delay times

As explained in the preceding section heat losses from the calorimeter were allowed for in terms of a delay time. These delay times were determined for the benzoic acid calibrations and the carbon combustions in a series of experiments. Values of 0·024 ± 0·039 min and 0·253 ± 0·028 min respectively were obtained. For an overall accuracy of 1 part in 10000 in the final result the delay times for the calibration and the combustion experiments must be known to better than ±0·16 min. The standard errors of the determinations quoted above are considerably less than this figure. In view of this and of the experimental difficulty in their determination the delay times were not determined in every experiment and the calculations were carried out assuming the mean values quoted above. Statistical examination of the results showed that there was no significant variation in the delay times for the various carbons and the overall mean value of 0·253 min was used in all the calculations.

The heat transfer coefficient of the calorimeter (ϵk) calculated from the energy equivalent of the bomb and the Newton's law coefficient, was found to be 1·97 J degC^{-1} min^{-1} and this corresponded to a Newton law coefficient of 0·00031 min^{-1}.

Standard energy equivalent of the bomb

The calculations of the standard energy equivalent ($\epsilon_{\mathrm{s.i.}}$) were made with an assumed intrinsic gain in internal energy on combustion for benzoic acid (ΔE^0_{B}) of −26414·1 J/g with a corresponding standard error of ±0·6 J/g (Hawtin 1966). The value of $\epsilon_{\mathrm{s.i.}}$ was determined as the mean of 20 calibration runs and was numerically equal to 6345·25 J/degC with a standard deviation of 0·67 J/degC and a corresponding standard error of the mean of ±0·15 J/degC.

Heats of combustion of carbon

The heats of combustion of the various carbons were calculated as previously described and the values obtained are summarized in table 1. In deriving the values for the heat of combustion ($-\Delta H^0_C$) quoted in the table a value of +1 J/mole was assumed for $P\Delta V$ and the atomic weight of carbon was taken as 12·011. The values of the standard deviation of the sample and the standard error of the mean were calculated in the normal manner. The overall uncertainty was estimated as suggested by Rossini (1956), as twice the overall standard error of the mean.

6. Discussion

The classical method for the determination of the heat of combustion of a carbon involves the accurate determination of the CO_2 formed from the reaction in the bomb. This method, first employed with acceptable accuracy by workers at the National Bureau of Standards in Washington, has been brought to a very high degree of precision (Jessup 1938; Prosen & Rossini 1944). The method is, however, time consuming and requires considerable experimental expertise. The procedure used in the present studies is in principle very much simpler, although allowance for the ash content of the graphite is a major problem. Experimentally it proved impossible to determine the weight of ash present in the sample burnt, and in calculating the results it was necessary to assume that any residue present in the crucible after combustion had the same composition as the original carbon. As explained above experiments with irradiated graphite have shown that this is a reasonable assumption. It is further necessary to assume that the ash content of the sample is the same as the mean of a series of ash determinations found by slow combustions of similar graphites. An overall accuracy of 1 in 10000 requires a knowledge of the ash content to better than 100 p/M. For low impurity graphites of the type used in these studies this requirement is in fact fulfilled since 100 p/M is considerably greater than the observed scatter on the ash contents. When the results were calculated on this basis values for the apparent heats of combustion were obtained as listed in table 1.

This method of correcting for the presence of impurities in the graphite by subtracting the weight of ash is not necessarily sound because the assumption is made that the impurities are originally present in the graphite in the same form as they are found in the ash, namely as oxides. As the materials used were preheated to 2700 °C it is more correct to assume that the impurities are present as carbides which oxidize during the combustion process. Thus not only will the weight of ash differ from the original impurity content but, in addition, heat will be evolved by the oxidation of the carbides. In order to obtain the highest accuracy it is necessary therefore to calculate for these two effects. Fortunately, calcium and silicon form the largest part of the impurity content (Lewis & Phillips 1966) and it is sufficient to calculate the correction for these two elements only. This has been done (appendix 1) and the results shown in a graphical form in figure 3. When the corresponding corrections are applied to the results in table 1 values for the true heat of combustion as quoted in table 2 are obtained. Determination of the amount of CO_2 produced rather than weight of carbon burnt circumvents these difficulties only if the impurities are inert. If the impurities are in fact present as carbides due allowance for the heat of formation of the oxides must still be made. The correction to be applied in this case is also shown in figure 3. Rossini & Jessup

(1938) concluded that, with the exception of Ceylon graphite, the samples examined at the National Bureau of Standards did in fact contain inert impurities. However, the latest information from the Bureau on the heats of combustion of natural (spectrographically pure) graphite and artificial (reactor) graphite (Fraser & Prosen 1952) suggests that the impurities are not in fact inert in reactor graphite. The recalculated figures (appendix 2) yield 94040·1 cal/mole for the heat of combustion of natural graphite and 94068·0 cal/mole for artificial graphite. Examination of the uncertainties in these results by the Student *t* test shows that the probability of so large a difference arising by chance is only 8 %. The ash content of the reactor graphite used in this study is not known but if an arbitrary figure of 600 p/M is taken (see, for example, Currie, Hamister & McPherson 1956) then on applying a correction due to this ash content the value reported by Fraser & Prosen for the heat of combustion of reactor graphite is reduced to 94048·4 cal/mole. This value for the ash content is of necessity very tentative and to counterbalance this the assigned uncertainty level for this heat of combustion has been arbitrarily increased by 6 to 26 cal/mole.

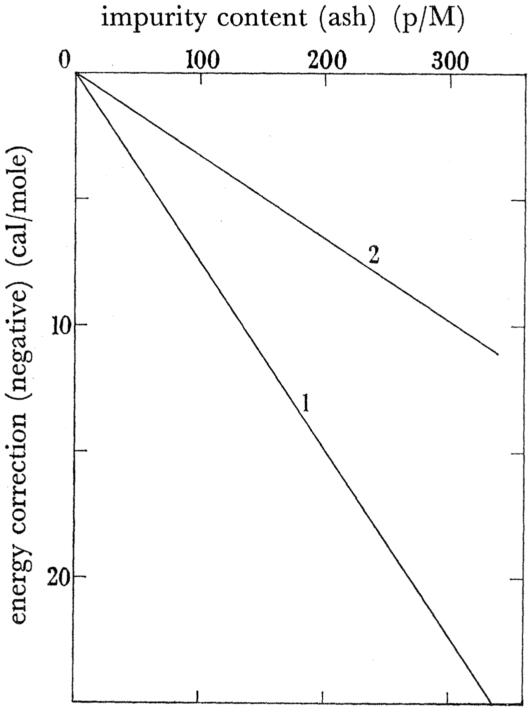

FIGURE 3. Energy correction for chemically active impurities in the carbon. Weight burnt determined by (1) weight loss; (2) CO_2 formed.

Four main types of graphite have been burnt in the present studies and the results obtained are listed in table 2. A statistical examination of these results using a modified *t* test (Paradine & Rivett 1964) shows that the results obtained for Kropfmuhl graphite are significantly lower than those obtained with spectrographically pure graphite, British reactor graphite and Ticonderoga natural graphite and for this reason they are excluded from further consideration at this stage.

A major problem in comparing the results obtained by different workers in this field of thermochemistry is the different units in which the results are expressed. A further difficulty

TABLE 2. HEATS OF COMBUSTION CORRECTED FOR IMPURITY CONTENT

carbon combusted	apparent heat of combustion (table 1) (J/g)	apparent heat of combustion (table 1) (cal/mole)	ash content (p/M)	ash correction (J/g)	ash correction (cal/mole)	true heat of combustion (J/g)	true heat of combustion (cal/mole)
spectroscopic graphite (National Carbon AGKSP)	32758·3	94039·0	nil	nil	nil	32758·3	94039·0
Kropfmuhl natural graphite	32737·8	93980·3	40	−1·0	−3·0	32736·8	93977·3*
Ticonderoga natural graphite	32757·3	94036·1	100	−2·6	−7·5	32754·7	94028·6
British pile grade A	32768·9	94069·7	220	−5·7	−16·3	32763·2	94053·4
furan coke	32950·3	94590·2	290	−7·5	−21·4	32942·8	94568·8
diamond	32911·0	94477·4	15	not applicable		32911·0	94477·4
spectroscopic graphite (National Carbon AGKSP) (150 °C preheat)	32771·4	94077·3	nil	nil	nil	32771·4	94077·3
carbon black (2700 °C preheat)	32811·4	94191·6	200	−5·2	−14·8	32806·2	94176·8
carbon black (2000 °C preheat)	32890·8	94419·6	200	−5·2	−14·8	32885·6	94404·8
artifact 628	32798·7	94155·2	200	−5·2	−14·8	32793·5	94140·4

* Uncorrected for rhombohedral content.

arises in the widespread corrections that have subsequently been published in the literature. In appendix 2 calculations are described to bring all the data published since 1938 on to the currently accepted 'correct' thermochemical basis employing an atomic weight of 12·011 for carbon. The results are summarized in table 3 which lists the early data obtained at the National Bureau of Standards in the years 1938–44 and in table 4 which lists data obtained subsequently and not therefore previously considered in the determination of the 'best' heat of combustion of graphite. The value of the heat of combustion of Kropfmuhl graphite found in the present work is excluded from table 4 on the statistical grounds given above.

TABLE 3. HEAT OF COMBUSTION FOR GRAPHITE DATA PUBLISHED BETWEEN THE YEARS 1938 AND 1944 (RECALCULATED BY PRESENT AUTHORS)

source	type of graphite	number of determinations	heat of combustion $-\Delta H^0_{298\cdot16}$ (cal/mole)	assigned overall uncertainty (cal/mole)
Dewey & Harper (1938)	artificial 1	4	94067	—
	artificial 2	4	94033	—
	Ticonderoga	4	94050	—
	Buckingham	4	94059	—
	Baffin Island	4	94062	—
	mean		94054	±24
Jessup (1938)	Ceylon	4	94420	—
	Ceylon	4	94041·0	—
	Ceylon	4	94024·2	—
	Buckingham	3	94020·9	—
	artificial 1	6	94054·2	—
	artificial 2	3	94051·5	—
	mean		94040·6	±13·1
Prosen & Rossini (1944)	Buckingham	5	94062·3	—
	Buckingham	4	94068·0	—
	artificial	5	940745	—
	artificial	3	940781	—
	mean		94070·0	±13·1

In every case any ash present is assumed to be inert.

TABLE 4. RECENT DETERMINATIONS OF THE HEAT OF COMBUSTION OF CARBON (RECALCULATED WHERE NECESSARY BY PRESENT AUTHORS)

source	type of graphite	ash content (p/M)	number of determinations	heat of combustion $-\Delta H^0_{298\cdot16}$ (cal/mole)	assigned overall uncertainty (cal/mole)
Fraser & Prosen (1952)	natural	nil	6	94040·1	26·7
	artificial	600 (assumed*)	6	94048·4	26·1
Lewis *et al.* (1965)	SP2	nil	13	94042·0	22·5*
present work	Ticonderoga	100	16	94028	17·5
	AGKSP	nil	25	94039·0	11·9
	PGA	220	11	94053·4	13·1

* Estimated by present writers.

Examination of the data in tables 3 and 4 shows that the results obtained by Prosen & Rossini (1944) are significantly high. If these are excluded a 'best' estimate for the heat of combustion of graphite may be derived from the remainder by weighting each determination inversely as the square of its assigned uncertainty. This yields a value for the heat of combustion of graphite of 94042·8 ± 5·8 cal/mole, which is virtually identical with the weighted mean figure of 94039·7 ± 9·8 found for spectrographically pure graphite. For this reason since this type of graphite is unaffected by problems of ash content it would appear reasonable to adopt it as the standard form of graphite.

The heat of combustion of diamond ($-\Delta H^0_{298\cdot 16} = 94477\cdot 4 \pm 29\cdot 5$ cal/mole) is in accord with the recalculated results of Jessup (Prosen *et al.* 1944) who showed that the heat of combustion of diamond was related to graphite by the equation

$$-\Delta H^0_{298\cdot 16}\,(\text{diamond}) = (1\cdot 004820 \pm 0\cdot 000216)\,(-\Delta H^0_{298\cdot 16}\,(\text{graphite}))$$

on the basis of this equation and the best estimate of the heat of combustion of graphite calculated above Jessup's work yields

$$-\Delta H^0_{298\cdot 16}\,(\text{diamond}) = 94496\cdot 1 \pm 20\cdot 3\ \text{cal/mole}.$$

These two estimates are identical within the limits of their assigned uncertainties and it follows that the best estimate of this heat is given by a weighted mean of the two values

$$-\Delta H^0_{298\cdot 16}\,(\text{diamond}) = 94490\cdot 1 \pm 16\cdot 7\ \text{cal/mole}.$$

The heat of transition for the reaction

$$\text{C}(s, \text{graphite}) \rightarrow \text{C}(s, \text{diamond})$$

is then given by

$$\Delta H^0_{298\cdot 16} = 447\cdot 3 \pm 17\cdot 6\ \text{cal/mole}.$$

It is essential to preheat the carbon (other than diamond) to at least 2700 °C as a pretreatment before combustion. If this is not done the heats of combustion obtained are significantly higher than those observed after the pretreatment. Thus the results in table 2 show that for

$$\text{C}(\text{AGKSP}, s, 150\,^\circ\text{C pretreatment}) \rightarrow \text{C}(\text{AGKSP}, s, 2700\,^\circ\text{C pretreatment}),$$

$$\Delta H^0_{298\cdot 16} = -38\cdot 3 \pm 17\cdot 9\ \text{cal/mole}$$

and for

$$\text{C}(\text{black}, s, 200\,^\circ\text{C pretreatment}) \rightarrow \text{C}(\text{black}, s, 2700\,^\circ\text{C pretreatment}),$$

$$\Delta H^0_{298\cdot 16} = -328\ \text{cal/mole}.$$

It was originally thought that these differences were due to hydrogen removal from the surface but chemical analysis of similar specimens failed to reveal the presence of significant quantities of hydrogen. In a recent report, for example, Rappeneau, Fillatre & Yvars (1963) have shown that heat treatment of certain carbon blacks to temperatures in the region of 2700 °C considerably reduces the disorder of the black and they conclude that this is indicative of a graphitization process in the black. The graphitization process is, however, extremely imperfect and the average crystallite size of about 130 Å is only a third that of British reactor graphite. Since the reduction in the disorder within the carbon black is only partially complete the heat of combustion of the treated specimen would be expected to be lower than the untreated specimens but higher than the corresponding true graphites. This is in fact the case. This conclusion is further supported at least qualitatively by the finding that artifact 628 which is a synthetic carbon consisting of part graphite and part carbon black has a heat of combustion lower than the black and higher than graphite. The method of manufacture of AGKSP graphite has not been revealed; X-ray analysis shows that it is of a similar type of structure to British reactor grade graphite, but it may well contain a small quantity of poorly graphitized material which would account for its high heat of combustion before thermal treatment to 2700 °C.

The value obtained for the heat of combustion of furan coke (94568·8 ± 60·6 cal/mole) is statistically higher than the value found from diamond in the same calorimeter system (94477·4 ± 29·5 cal/mole). This is important since furan coke is a highly crosslinked carbon which is not graphitized at 2700 °C. The high value obtained for its heat of combustion thus indicates most clearly the importance of crystalline disorder in determining the heat of combustion of a carbon.

As mentioned above the results obtained with Kropfmuhl graphite are very much lower than with any other carbon. Kropfmuhl graphite is a finely divided powder which in the untreated state contains high percentages of rhombohedral graphite (up to 40 %), this percentage is reduced to about 10 % after thermal annealing at 2700 °C. Boehm & Coughlin (1964) have shown that the heat liberated by rhombohedral graphite on its transition to hexagonal graphite is 140 ± 40 cal/mole so that the 'true' heat of combustion of hexagonal Kropfmuhl graphite should be reduced by an amount corresponding to the presence of 10 % of rhombohedral graphite. Thus, $-\Delta H^0_{298\cdot16}$ becomes 93963·3 ± 18·7 cal/mole. The rhombohedral variety is introduced into the normal hexagonal graphite during the grinding process so that a finely ground material should have a higher heat of combustion than the parent specimen. It is interesting to note therefore that the value of the heat of combustion of Ticonderoga graphite found by Dewey & Harper (1938), who ground their graphite to a fine powder, is higher than that found in the present investigation. However, in view of the assigned uncertainties the significance of this particular observation is not high. Even if the rhombohedral content of a finely ground up graphite is removed by a subsequent high temperature treatment it would still be reasonable to expect the higher surface area material to have a higher energy content. However, it has also been shown that the fresh surface produced by grinding readily chemisorbs oxygen (see, for example, Fedorov, Zarifyants & Kiselev 1963) and as the presence of this surface oxide would reduce the heat of combustion, the net result is that a finely ground graphite has a lower and not a higher heat of combustion than that of low surface area materials.

Figure 4 is a graph of the observed heat of combustion of graphite plotted against its B.E.T. surface area. The vertical and horizontal lines drawn on this curve represent the experimental uncertainties in determining the heats of combustion and the surface areas. The gradient of the dotted line corresponds to a rate of change in the heat of combustion of $1\cdot6\,\mathrm{cal\,mole^{-1}\,m^{-2}}$ of B.E.T. surface. Typically the graphites used have a B.E.T. surface area of approximately $0\cdot4\,\mathrm{m^2/g}$ ($4\cdot8\,\mathrm{m^2/mole}$); if therefore the heat of combustion of graphite varies at the rate of $1\cdot6\,\mathrm{cal\,mole^{-1}\,m^{-2}}$ of surface it follows that for an overall accuracy of ±1 part in 10000 it is essential that the surface area should not depart from this figure by more than $\pm 0\cdot4\,\mathrm{m^2/g}$.

The following requirements are therefore necessary for any graphite used in the determination of its standard heat of combustion

1. The graphite shall be crystalline with average crystallite diameter not less than 400 to 500 Å (i.e. not smaller than the crystallites in British pile grade graphite).

2. The graphite sample shall be given a pretreatment by heating it to 2700 °C in an inert gas.
3. The graphite shall not be ground.
4. The graphite shall have a surface area not greater than 0·8 m^2/g.

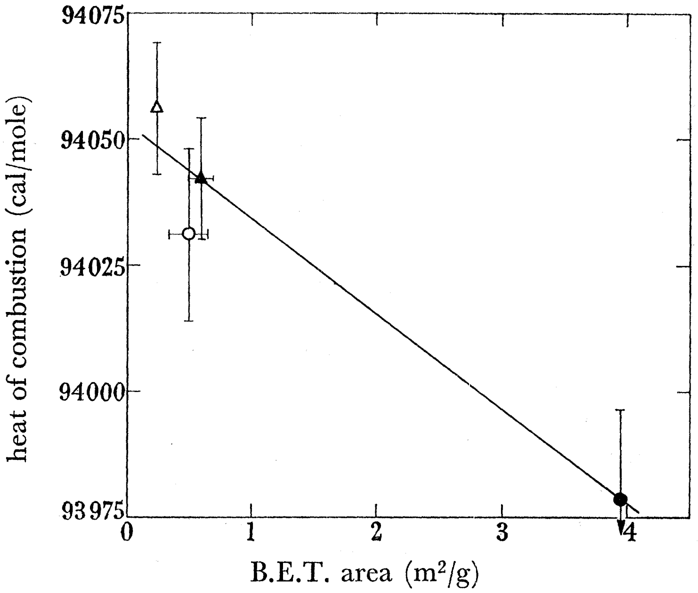

FIGURE 4. Dependence of the heat of combustion of graphite on the B.E.T. surface area. △, Pile grade A; ▲, AGKSP; ○, Ticonderoga; ●, Kropfmuhl (corrected for rhombohedral content).

7. CONCLUSIONS

The standard heat of combustion of various graphites and carbons have been determined and the results obtained are as follows:

	$-\Delta H^0_{298\cdot16}$ (cal/mole)
National Carbon AGKSP	94039·0 ± 11·9
Ticonderoga natural graphite	94028·6 ± 17·5
Kropfmuhl (hexagonal form)	93963·3 ± 18·7
British pile grade A	94053·4 ± 13·1
furan coke	94568·8 ± 40·6
diamond	94477·4 ± 29·5

The low value obtained with Kropfmuhl graphite is thought to be due to surface adsorption of oxygen and the high value obtained with furan coke to carbon cross linkages.

The above results for AGKSP, Ticonderoga and pile grade A graphites when combined with selected previously published data yield the following best estimate for the heat of combustion of graphite ($-\Delta H^0$)

$$-\Delta H^0_{298\cdot16} = 94\,042\cdot8 \pm 5\cdot9 \text{ cal/mole.}$$

Similarly, the best estimate for the heat of combustion of diamond is

$$-\Delta H^0_{298\cdot16} = 94\,490\cdot1 \pm 16\cdot7 \text{ cal/mole.}$$

The heat of transition from graphite to diamond thus becomes

$$\Delta H^0_{298\cdot16} = 447\cdot3 \pm 17\cdot6 \text{ cal/mole.}$$

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Appendix 1. The effect of ash content on the heat of combustion

The graphites burnt in the present experiments were preheated to 2700 °C in an inert atmosphere, and under these conditions, any solid impurities are present as carbides. The ash correction described in the main text is, however, made on the assumption that the impurities are present as inert oxides. Analysis of the ash of a typical 'artificial' graphite shows that it consists mainly of silica and calcium oxide in approximately equal amounts by weight. During the thermal pretreatment these elements are converted into carbides which in turn, during the combustion, undergo exothermic reactions:

$$\text{(i)}\quad \mathrm{SiC+2O_2 = SiO_2+CO_2} \qquad (-\Delta H_f^0 = 269{\cdot}1\,\text{kcal/mole or } 9578\,\text{cal/g Si});$$

$$\text{(ii)}\quad \mathrm{CaC_2+2\tfrac{1}{2}O_2 = CaO+2CO_2} \qquad (-\Delta H_f^0 = 325{\cdot}0\,\text{kcal/mole or } 8109\,\text{cal/g Ca}).$$

If the concentrations of silicon and calcium impurities are both x mg/g carbon then on combustion, by stoichiometry, $2{\cdot}14x$ mg of silica and $1{\cdot}40x$ mg of calcium oxide will be produced for every gram of carbon. Impurity contents are normally quoted as ash content, in this case because the other constituents can be neglected, the weight of ash will be $3{\cdot}54x$ mg.

The effect of the impurity content on the heat liberated per gram of graphite burnt can be demonstrated by considering the behaviour of a graphite which has an ash content of, say, 300 p/M, that is 1 g produces 0·3 mg of ash. Equating this with the above figure of $3{\cdot}54x$ mg gives x as 0·085. Thus the silicon and calcium content of the original graphite is 0·085 mg/g and consequently the SiC and $\mathrm{CaC_2}$ contents are 0·121 and 0·136 mg/g respectively. The amount of carbon which burns as graphite is depleted by the amounts combined as carbides and these are 0·036 mg/g as SiC and 0·051 mg/g as $\mathrm{CaC_2}$, leaving 0·999743 g/g of 'free' carbon.

If the heat of combustion of graphite is 94042 cal/mole then the heat liberated by the combustion of 1 g of this, 300 p/M graphite, is given by

$$\begin{aligned} \text{heat of combustion of } 0{\cdot}999743\,\text{g C} &= 7827{\cdot}65\,\text{cal},\\ 0{\cdot}121\,\text{mg SiC} &= 0{\cdot}69\,\text{cal},\\ 0{\cdot}136\,\text{mg CaC}_2 &= 0{\cdot}81\,\text{cal},\\ \text{total heat released} &= 7829{\cdot}15\,\text{cal}. \end{aligned}$$

This heat release is of course the observed heat release when 1 g of the impure carbon is burnt. Now the apparent heat of combustion is derived from this figure by the method described in the main text by assuming that the impurity content is inert and is of the same weight as the ash content, that is it merely reduces the amount of carbon burnt. Thus the apparent heats of combustion given in table 2 were calculated from the relation

$$\text{heat of combustion/g ash free graphite} = \frac{\text{observed heat release/g sample}}{1-\text{ash content/g sample}}.$$

In the hypothetical case considered above

$$\text{heat of combustion} = \frac{7829{\cdot}15}{1-0{\cdot}0003} = 7831{\cdot}50\,\text{cal/g} = 94064\,\text{cal/mole}.$$

It can be seen that the apparent heat of combustion calculated by the earlier method is 22 cal/mole larger than the true value for a graphite containing 300 p/M of ash. A proportionately smaller or greater error will be obtained if the calculations are repeated for ash contents other than 300 p/M (figure 3). The heats of combustion listed in table 2 were found from the apparent heats in table 1 by applying the appropriate correction found from figure 3.

It is important to stress the fact previously made in the Discussion that the calculations described above only apply to active impurities in the graphite when the heat of combustion is determined by the weight loss technique. When the impurities are inert and present as oxides the simple ash correction described in the main text is all that is necessary. In the present experiments the impurities were always in the active state due to the high temperature pretreatment of the samples.

A similar but smaller correction is necessary for active impurities when the carbon dioxide evolution technique as employed at the National Bureau of Standards is used. No correction for impurity content is necessary with this latter technique when the impurities are inert.

APPENDIX 2. RECALCULATION OF PUBLISHED HEAT OF COMBUSTION DATA TO THE CURRENTLY ACCEPTED THERMOCHEMICAL STANDARD CONDITIONS

Introduction

All data on the heats of combustion of carbon published up to and including 1944 were expressed as N.B.S. international joules (int. j). This unit has subsequently become obsolete and has been replaced by the modern absolute joule (J). These units are converted to calories by the relations:

$$\begin{aligned} 1\ \text{thermochemical calorie} &= 4{\cdot}1833\ \text{int. j} \\ &= 4{\cdot}1840\ \text{J}. \end{aligned}$$

Data of Dewey & Harper (1938)

Dewey & Harper published their data as the heat content change without external work ($-\Delta U_{298{\cdot}16}$). From this $-\Delta H_{298{\cdot}16}$ is obtained by the addition of the external work term ($P\Delta V$) which was calculated by Jessup (1938) to be +11 int. j/mole and has been recalculated by one of us to be 12 int. j/mole. Hence

$$-\Delta H_{298{\cdot}16} = -\Delta U_{298{\cdot}16} + 12\ \text{int. j/mole}.$$

This may be reduced to the heat of combustion under thermodynamic standard conditions ($-\Delta H^0_{298{\cdot}16}$) by the subtraction of 33 int. j/mole (Rossini & Jessup 1938),

$$-\Delta H^0_{298{\cdot}16} = -\Delta H_{298{\cdot}16} - 33.$$

The heat of combustion for benzoic acid used by Dewey & Harper to calibrate their bomb was subsequently shown to be in error (Prosen *et al.* 1944) and this error necessitates a correction of +0·0336 % to their heats of combustion. Thus

$$-\Delta H^0_{298{\cdot}16}(\text{revised}) = 1{\cdot}000336(-\Delta H^0_{298{\cdot}16}).$$

Finally, the atomic weight of carbon was revised in 1961 to 12·011 which requires a further correction such that

$$-\Delta H^0_{298{\cdot}16}(\text{correct}) = -1{\cdot}0000227\Delta H^0_{298{\cdot}16}(\text{revised})\ \text{int. j/mole}.$$

Combination of the above correction terms and conversion of the resulting figure in international joules/mole to calories/mole yields

$$-\Delta H^0_{298\cdot 16} = 0\cdot 2391325(-\Delta U_{298\cdot 16}-21)\ \text{cal/mole},$$

where $-\Delta U_{298\cdot 16}$ represents Dewey & Harper's published figure in int. j/mole.

Data of Jessup (1938)

These are presented as a heats of combustion under his specified conditions $(-\Delta H_{298\cdot 16})$. The values included an allowance of +11 int. j/mole for $P\Delta V$. The addition of 1 int. j/mole brings them into line with the current estimate for the external work term. The heats of combustion are converted into standard heats of combustion by the subtraction of 33 int. j/mole. Thus

$$-\Delta H^0_{298\cdot 16} = (-\Delta H_{298\cdot 16}+1-33)\ \text{int. j/mole}.$$

Some of the data used by Jessup were subsequently shown to be incorrect (Prosen *et al.* 1944) and their correction required an addition of 0·0071 % to the published results. Finally, conversion of the results to cal/mole and due allowance for the changed atomic weight of carbon yields the overall correction formula as:

$$-\Delta H^0_{298\cdot 16} = 0\cdot 2390681(-\Delta H_{298\cdot 16}-32),$$

where $-\Delta H_{298\cdot 16}$ is Jessup's published figure in int. j/mole.

Data of Prosen & Rossini (1944)

These data are presented as the heat of combustion under thermodynamic standard conditions $(-\Delta H^0_{298\cdot 16})$. The calculation of the value of $\Delta H^0_{298\cdot 16}$ included an allowance of +1 int. j/mole for $P\Delta V$. This is all that is necessary in this case since by 1944 the National Bureau had altered the basis of their calculation of the Washburn correction from unit pressure to unit fugacity (Prosen 1965). Allowance for the correct atomic weight of carbon and conversion to cal/mole yields

$$-\Delta H^0_{298\cdot 16}(\text{correct}) = 0\cdot 2390511(-\Delta H^0_{298\cdot 16})\ \text{cal/mole},$$

where $-\Delta H^0_{298\cdot 16}$ is the value for the heat of combustion of carbon in int. j/mole published by Prosen & Rossini.

Data of Fraser & Prosen (1962)

The data of Fraser & Prosen were expressed as absolute joules/mole. Since the recommended atomic weight of carbon has been altered subsequent to the publication of their data these must be corrected as described above for the results of Prosen & Rossini. In addition as described in the main body of the report Fraser & Prosen assumed when oxidizing artificial graphite, that any impurities present were inactive. On the basis of the current work this seems an unreasonable assumption and in recalculating their results for artificial graphite it is assumed that their material contained 600 p/M of 'active' impurities so that the value found requires a correction of −19·6 cal mole. Thus the corrected values become for natural graphite

$$-\Delta H^0_{298\cdot 16}(\text{correct}) = 0\cdot 2390111(-\Delta H^0_{298\cdot 16})\ \text{cal/mole}$$

and for artificial graphite

$$-\Delta H^0_{298\cdot 16}(\text{correct}) = 0\cdot 2390111(-\Delta H^0_{298\cdot 16})-19\cdot 6\ \text{cal/mole}.$$

APPENDIX 3. STATISTICAL TERMS EMPLOYED IN THIS PAPER

The present paper employs a number of statistical terms in the examination of the errors in the experimental data. The data reduction and the methods of presentation used are in accord with published specific recommendations to the field of thermochemistry (Rossini 1956). Unfortunately not all workers adhere strictly to these recommendations and in view of this it is convenient to summarize the various statistical terms commonly used in the analysis of data.

Mean and standard deviation of a single sample of size n

In the theory of errors a sample of n equally reliable values is considered as a sample of n drawn at random from an infinitely large parent population. The mean of the sample (m) is then taken as the arithmetic mean defined by

$$m = \left(\sum_{i=1}^{n} x_i\right) \Big/ n \tag{i}$$

and the standard deviation of the sample (S) which is a measure of the spread of values (x_i) in the sample is given by

$$S = \sqrt{\left(\frac{\sum_{i=1}^{n} (m - x_i)^2}{n}\right)}. \tag{ii}$$

Estimation of the mean and standard deviation of the parent population from the statistics of a single sample

Best (defined as the most probable) estimates are assigned to the parameters of the parent population from the statistics of a single sample by the application of statistical theory on the assumption that errors in the individual measurements are normally distributed.

Because the number of observations (n) taken is of necessity, finite the mean of the sample m is only an approximation to the true mean of the parent population (μ). The standard deviation of the parent (σ) is not normally known and must be estimated from the data of the sample. An unbiased estimate of σ (often given the symbol S') is obtained from the relation

$$S' = \sqrt{\left(\frac{nS^2}{n-1}\right)}. \tag{iii}$$

Standard error of the mean

The standard deviation (σ_m) of the distribution of the means of all possible samples of size n drawn from the parent population is called the standard error of the mean (or often the standard error). It is readily obtained from the relation (Paradine & Rivett 1964)

$$\sigma_m = \frac{\sigma}{\sqrt{n}}. \tag{iv}$$

Unfortunately it is seldom known in the practical case and must be estimated through equation (iii) yielding a best estimate for the standard error (S'_m) as

$$S'_m = \sqrt{\frac{S^2}{n-1}}. \tag{v}$$

The importance of the standard error of the mean lies in its use for calculating the probability P of the occurrence of an error u in m greater than some chosen value E and as such it forms the basis of Student's t test.

Combination of mean values of differing precision to form an overall mean and standard error

Separately obtained mean values, if they are in reasonable accord with one another, may be combined by weighting them inversely as the squares of their standard errors (Rossini 1956) whence their weighted mean becomes

$$\overline{m} = \sum_{1}^{N} \frac{m_i}{(\sigma_m^2)_i} \Big/ \sum_{1}^{N} \frac{1}{(\sigma_m^2)_i} \qquad \text{(vi)}$$

and their corresponding overall standard error

$$\sigma_m = 1 \Big/ \left(\sum_{1}^{N} \frac{1}{(\sigma_m^2)_i} \right)^{\frac{1}{2}}. \qquad \text{(vii)}$$

Whether or not the original values were in reasonable accord is difficult to determine objectively. A practical method sometimes used is to compare the estimate of σ_m prepared through equation (vii) with the estimate given by

$$\sigma_m = \sqrt{\left[\sum_{1}^{N} \frac{1}{(\sigma_m^2)_i} (m_i - \overline{m}) \Big/ (N-1) \sum_{1}^{N} \frac{1}{(\sigma_m^2)_i} \right]}. \qquad \text{(viii)}$$

If the ratio of the two estimates lies in the range $\frac{1}{2}$ to 2 it is commonly assumed that the original values were in reasonable accord one with another.

Assigned overall uncertainty or uncertainty interval

The application of the above formulae to the field of thermochemistry requires the introduction of a new error term, the uncertainty interval (Rossini 1956). This term and its synonym assigned overall uncertainty are used interchangeably in the thermochemical literature. It is defined as twice the overall standard error found by summing the individual standard errors according to the relationship in equation (vii). In the determinations of the heat of combustion of carbon these constituent errors are the standard error of the carbon combustions, the standard error of the benzoic acid calibrations, and the standard error in the determination of the heat of combustion of benzoic acid. This latter term was estimated from data published from a number of sources (Hawtin 1966).