A Moving-Bomb Method for Combustion Calorimetry
of Organic Bromine Compounds

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For the purpose of developing a method for obtaining accurate heat of formation data for organic bromine compounds, a moving-bomb calorimeter for measuring heats of combustion at 25°C of solid and liquid samples has been constructed. The calorimetric system is calibrated by combustion of standard benzoic acid under certified bomb-calibrating conditions. However, in order to obtain well-defined, equilibrium final states in the bomb in combustion experiments with bromine compounds the bomb liquid must differ both in nature and amount from that specified for calibration experiments with benzoic acid. This may give rise to non-cancelling systematic errors. As a first step in defining errors, the reproducibility in calibration as well as combustion experiments has been studied. The paper describes in detail the apparatus, the procedure and the calculation of results, and reports data obtained in calibration experiments and in combustion experiments with paraffin oil and *p*-bromobenzoic acid.

Results from calibration experiments with benzoic acid and combustion experiments with paraffin oil demonstrated that the moving-bomb apparatus, the experimental procedure and the method of calculation of results, presented in this paper, were capable of giving results having a precision slightly better than 0.01 % which is comparable to that obtained with best available modern bomb-calorimetric techniques for compounds containing carbon, hydrogen and oxygen. Furthermore, the experiments with *p*-bromobenzoic acid showed that the various additional complications introduced into the procedure by the presence of a reasonable percentage of bromine in the sample did not affect the precision obtainable with the given apparatus and procedure.

Although the precision of the present method was found to be satisfactorily high, no conclusions could be drawn as to the accuracy of heat of combustion data obtained with this method. Experimental work designed to give information on this point has been done and will be reported in another paper.

T he available heat of formation data for organic bromine compounds are
few, and only a small number have an uncertainty interval * comparable

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* The terms *uncertainty interval, reproducibility, precision, accuracy* and related quantities used in this work have the same meaning as given in Ref.[1] The terms *reproducibility* and *precision* are used synonymously.

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to that of modern heat of formation data for other groups * of organic compounds **. Experimental data, from which heat of formation values with small uncertainty intervals can be calculated, have been reported on: (i) heats of bromination of certain alkenes [4,5] and cyclo-alkenes [5], (ii) heats of hydrobromination of cyclo-propane [6,7], propene [6,7] and the normal butenes [8], (iii) the heat of hydrogenation of vinyl bromide [9], and (iv) equilibrium constants for the system ethylene — hydrogen bromide — ethyl bromide [10]. Therefore, heat of formation values of low uncertainty are at present available for the following sixteen organic bromine compounds: bromoethane, bromoethene, 1-bromopropane, 2-bromopropane, 2-bromobutane, 1,2-dibromoethane, 1,2-dibromopropane, 1,2-dibromobutane, meso-2,3-dibromobutane, dl-2,3-dibromobutane, 2,3-dibromo-2-methylbutane, 1,2-dibromoheptane, 1,2-dibromocyclopentane, 1,2-dibromocyclohexane, 1,2-dibromocycloheptane, and 1,2-dibromocyclooctane. It is striking, however, that data are lacking for a number of organic bromine compounds of considerable interest to pure as well as to applied chemistry, including most of the lower monobromoalkanes, several of the lower dibromoalkanes, bromobenzene, the dibromobenzenes, benzyl bromide etc. Evidently, further work is required, aiming at the determination of experimental thermochemical data from which accurate heats of formation of organic bromine compounds can be calculated.

One of the heat of formation values referred to above was derived from experimental data obtained in a study of chemical equilibria, and the others could be calculated from data obtained by application of the methods of reaction calorimetry *** to various chemical reactions each involving one of the mentioned organic bromine compounds with other compounds of accurately known heats of formation. However, the experience of earlier experimental work on the thermochemistry of organic compounds suggests that neither equilibrium studies nor reaction calorimetry could compete in versatility and width of applicability with combustion calorimetry for obtaining experimental data leading to high-accuracy heat of formation values for organic bromine compounds. Therefore an accurate combustion-bomb calorimetric method for organic bromine compounds would certainly be capable of providing the majority of heat of formation data for such compounds. Heat of combustion work has been applied to organic bromine compounds in eight previous investigations [11-18]. None of the methods used in these can, however, be considered fully satisfactory for present-day requirements on accuracy.

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* "Group" should here be understood as "containing a certain combination of elements" such as C,H,O or C,H,O,N or C,H,O,Br or C,H,O,S.

** The uncertainties attached to the best available heat of formation data for groups of organic compounds vary according to the nature of the groups. As a rough generalization, however, it can be stated that modern thermochemical apparatus and technique [2,3] is capable of giving experimental results leading to standard heat of formation values having uncertainty intervals for the lower members of various homologous series in the range ± 0.1 to ± 0.6 kcal/mole.

*** Although no general agreement exists it has become practice among workers in thermochemistry to use the name reaction calorimetry only for the measurement of heats of reactions other than combustion in oxygen.

From, (i), the results obtained using the various combustion techniques for bromine compounds mentioned above, (ii), experience from recent applications of moving-bomb methods to organic sulfur compounds [23],[24], and (iii), results from recent systematic studies of certain details of various moving-bomb techniques [25],[26], it was evident that further development of the moving-bomb methods described in Refs.[15],[17],[18] should provide a combustion-bomb calorimetric method for organic bromine compounds capable of yielding data of comparable accuracy to those given by the best present-day methods for other groups of organic compounds [3].

Work on such a development has been in progress in this laboratory for some time. This paper describes the present status of development of apparatus and experimental technique, and reports results sufficient to indicate the precision of the method.

METHOD

The conventional substitution method was used, comprising two types of experiments: calibration experiments with benzoic acid and combustion experiments with bromine compound. In all experiments the temperature rise of the calorimeter was virtually the same.

The calorimetric system was calibrated by combustion of a standard sample of benzoic acid under certified bomb-calibrating conditions.

The bromine compound was burned in the platinum-lined bomb with paraffin oil of known heat of combustion as a burning aid. The amounts of sample and paraffin oil were so adjusted that virtually the same quantities of heat were released in the combustion experiments as in the calibration experiments. From 95 to 98 % of the bromine content of the sample was transformed to elemental bromine through the combustion process and the rest to hydrogen bromide. In these experiments the bomb contained an appropriate amount of arsenious oxide solution for reduction of the elemental bromine to bromide ion. Bomb and calorimeter vessel were so designed that during part of the reaction period of the calorimetric measurement a rotating motion could be imparted to the bomb to bring about proper agitation of the bomb contents. Hereby the elemental bromine was quantitatively reduced to bromide ion, the whole interior of the bomb was well rinsed by the final bomb solution and equilibrium between the liquid and the gaseous phase was attained. This established a homogeneous, stable and thermodynamically definable final liquid-gas system in the bomb. After completion of the calorimetric measurement the bomb liquid was quantitatively analyzed for the various constituents, in particular, arsenious oxide and nitric acid.

APPARATUS

The calorimetric system was of the stirred-liquid-calorimeter with constant-temperature-jacket type. The construction, and the influence of various constructional details on the performance of such calorimetric systems, have been discussed in considerable detail by several authors [27-33]. The adaptation of this type of calorimetric system for use with moving-bomb techniques has also been described in detail previously [23],[24]. Furthermore, certain experimental details of various moving-bomb techniques have also been treated in some detail previously [25],[26]. For these reasons and because several of the characteristics of the apparatus used in the present investigation are similar to those described in Refs.[23],[24], the description of the apparatus and the discussion of its functioning will be more thorough on certain selected points than on others.

Calorimetric assembly. The calorimetric assembly, shown diagrammatically in Fig. 1, consisted of the following main parts: combustion bomb B, calorimeter vessel $C_1 - C_{10}$ with moving mechanism $M_1 - M_{13}$ and other accessories, thermometer T, and jacket $J_1 - J_{25}$.
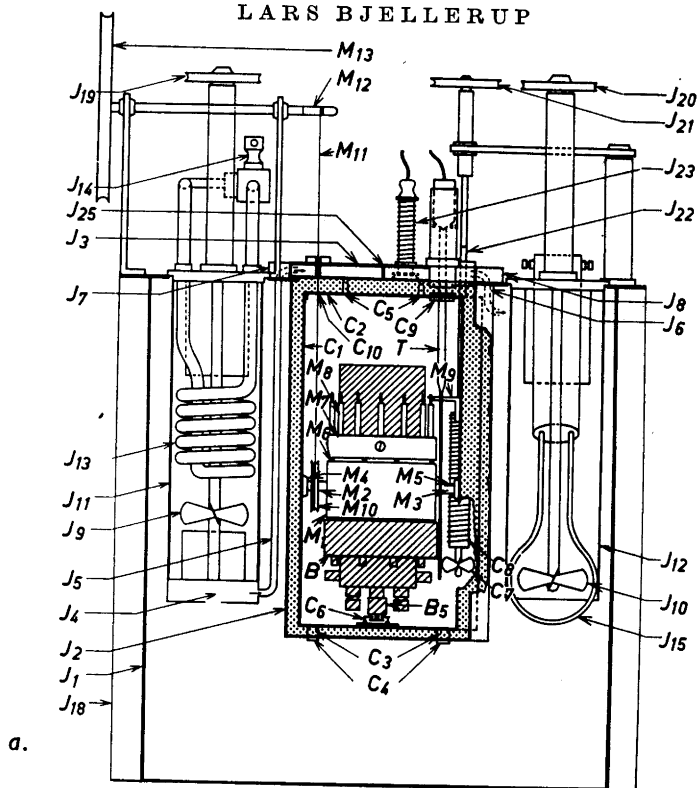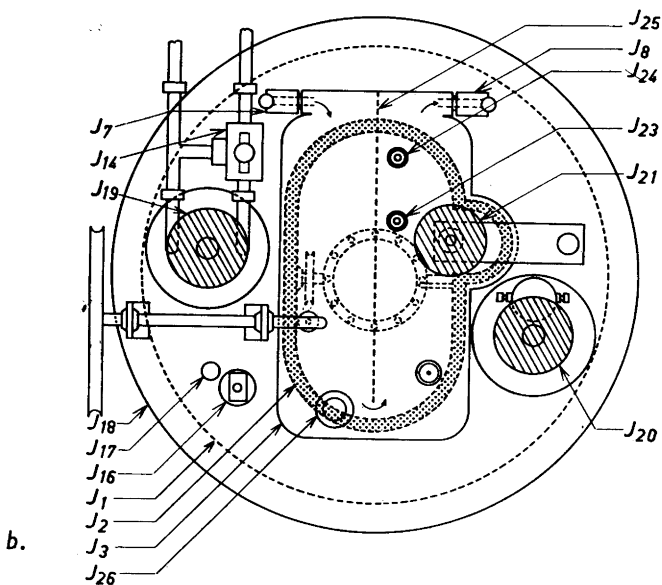
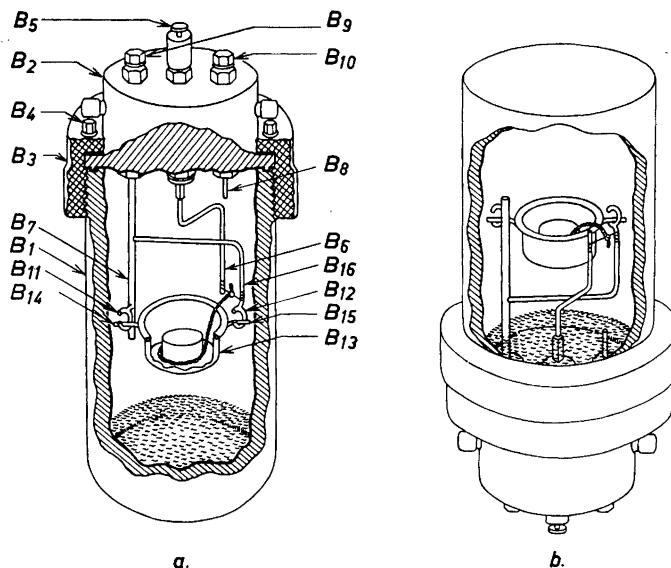**Fig. 1.** Assembled calorimetric system: a. Sectional view. b. Top view.

Fig. 2. Charged combustion bomb: a. In upright position. b. In inverted position.

Combustion bomb. The combustion bomb, shown in Fig. 2, was of a conventional three-part type consisting of body B_1, head B_2, and sleeve B_3. All three parts were made of stainless steel. The inner surface of the head, the bottom of the head and all internal fittings were lined with platinum of 0.20 mm thickness. A gas-tight seal between body and head was obtained through a gold gasket situated in a groove in the bottom of the flange of the head. The head was pressed against the body by the aid of eight set-screws B_4 in the sleeve and a chromium-plated, hard steel ring lying on top of the flange of the head below the set-screws. The design was very similar to that described in Ref.[34]

The head was equipped with a terminal B_5 for ignition, electrically insulated from the rest of the head, mainly through teflon washers, and ending with the platinum rod B_6. The head was also equipped with two platinum tubes, one B_7 for gas-inlet into the bomb and one B_8 for gas-outlet. The openings to the tubes could be closed by the two valves B_9 and B_{10} with gold packings.

To the gas-inlet tube were welded two open platinum rings B_{11} and B_{12} between which the platinum combustion crucible B_{13} could be suspended by the aid of a platinum ring having two short axles B_{14} and B_{15} as seen in Fig. 2. The design was similar to that described in Ref.[24] This device made it possible to charge the bomb in a conventional way, as described later, while it was in an ordinary upright position, place it in its suspension ring in the calorimeter vessel and then rotate the ring through 180 degrees about the axis M_2—M_3 so that the bomb could be temporarily fixed in an inverted position, as shown in Figs. 1 a and 2 b, while the crucible and its contents retained their original upright position. The charge was then ignited with the bomb in this position which directed the hot gases from the combustion blast towards the body of the bomb instead of towards the more sensitive head. When rotation of the bomb was started after completion of the combustion process the axles of the crucible suspension ring slipped out through the openings in the platinum rings B_{11} and B_{12} so that the crucible and suspension ring fell down into the bomb liquid and were thoroughly rinsed.

For ignition of the sample the two platinum rods B_6 and B_{16} were connected through a 0.05 mm platinum wire of approximately 10 mm length. One end of a fuse, consisting of a weighed piece of cotton string about 90 mm long, was attached to the mid-point of the thin platinum wire and the other end of the fuse was put in contact with the sample.

Application of a potential of 12 V to the ignition circuit caused such a rapid heating of the thin platinum wire to its melting point that only a small amount of energy (estimated to be less than 0.5 cal) was introduced into the calorimeter before the circuit was broken. During this process, however, the fuse was ignited and the fuse in turn ignited the sample. The variation in the electrical ignition energy from experiment to experiment was considered small enough to permit incorporation of this energy into the energy equivalent of the calorimeter. The internal volume of the bomb was 0.2670 liter.

Calorimeter vessel. The calorimeter vessel, consisting of can C_1 and lid C_2, had the shape shown in Fig. 1. The dotted space in Fig. 1 represents the air-gap between the calorimeter vessel and the constant-temperature-jacket. The distance between the outer surface of the calorimeter and the inner surface of the jacket was 10 mm at all points[32,p.168]. The can was supported on four cylindrical Bakelite pegs C_3 snugly fitting in four corresponding pits in the jacket well C_4. The three Lucite pegs C_5 in the calorimeter lid C_2 were just long enough to be slightly pressed against the under side of the jacket lid J_3 when this was placed in its closed position as shown in Fig. 1. Spring clip C_6, attached to the bottom of the can, could be lifted a few millimeters from the bottom and slid on to a knob on the electrical ignition terminal B_5. In this way, the bomb could be kept in the inverted position, shown in Fig. 1, during the fore period and the first part of the reaction period of the calorimetric experiments. Also, the spring clip served as an electrical lead to the ignition terminal.

The calorimeter lid was equipped with a calorimeter stirrer C_7, a 10 W calorimeter heater C_8, a rubber washer C_9 through which the thermometer T could be inserted and tightly positioned in the calorimeter, a small orifice C_{10} for the copper wire M_{11}, and two flat electrical contacts (not shown in the figure) leading to the heater C_8 and to the spring clip C_6, respectively.

Moving mechanism. The device used to effect appropriate agitation of the bomb contents during the reaction period consisted of the following parts shown in Fig. 1: the bomb supporting ring M_1 with axles M_2 and M_3 and bearings M_4 and M_5 attached to the wall of the calorimeter can; the flat ball bearing M_6; the bomb fastening ring M_7 with twelve evenly spaced rods M_8; the removable stud M_9 projecting from the wall of the calorimeter can; the pulley M_{10} on axle M_2 of the supporting ring; the 0.3 mm copper wire M_{11} wound on pulley M_{10}; the pulley M_{12} driven by a motor operating on pulley M_{13}.

Withdrawal of drive wire M_{11} from pulley M_{10} by rotation of pulley M_{12} gave the bomb a rotational motion about the horizontal axis M_2-M_3 perpendicular to the bomb axis. During this end-over-end rotation of the bomb, each passage through the inverted position shown in Fig. 1, brought one of the rods M_8 into contact with stud M_9, which pushed the rod, causing the bomb to rotate about the bomb axis (axial rotation) through one twelfth of a full revolution. Since the bomb in the inverted position was supported entirely by the ball bearing M_6, and did not fit too tightly in the supporting ring M_1, it was very easily axially rotated whilst in the inverted position. In all other positions during the end-over-end rotation, however, the bomb was more or less pressed directly against the supporting ring so that no axial rotation occurred with the bomb in these positions. Consequently, the moving mechanism, during the withdrawal of the drive wire, effected a compound rotation of the bomb about an axis perpendicular to the bomb axis and about the bomb axis at the same time. The speed of the axial rotation was one twelfth of the speed of the end-over-end rotation *.

In all experiments — calibration as well as combustion experiments — in the present work a length of 600.0 ± 0.5 cm of the 0.3 mm copper wire was wound around pulley M_{10} in 43 turns. The withdrawal of the wire was made at such a rate as to give the bomb an end-over-end rotation rate of 12 rpm and consequently an axial rotation rate of 1 rpm. Unwinding of all 43 turns of drive wire thus required a time of 215 sec. The agitation, due to this rotation, of the 30 ml of bomb solution used in all combustion experiments with bromine compounds, was found to be satisfactory for establishing a homogeneous and stable final liquid-gas system in the bomb.

The amount of frictional energy introduced into the calorimeter through the rotation was estimated, from a crude measurement of the force necessary to effect the rotation,

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* The author's thanks are due to Dr. S. Sunner, Thermochemistry Laboratory, University of Lund, for cooperation in the construction of the moving mechanism.

at approximately 2.5 cal per combustion experiment. The variation in this rotation energy from one experiment to another was difficult to assess but since the rotation was performed exactly in the same way in all experiments the rotation energy was considered constant and was incorporated into the energy equivalent of the calorimeter.

Thermometric system. The thermometric system consisted of a flat, 25 ohm platinum resistance thermometer T (Leeds & Northrup Co., Catalog No. 8160) positioned in calorimeter and jacket lid as shown in Fig. 1 and a type G-2 Mueller bridge (L. & N., Catalog No. 8069) in conjunction with a type HS reflecting galvanometer (L. & N., Catalog No. 2284-d) and a telescope equipped with a 1 000 mm scale which had been properly curved *. The distance between scale and galvanometer mirror was 93 cm in all directions. Using a thermometer current of about 4 mA and taking the last figure from galvanometer deflections the resistance could be read to the nearest 0.00001 ohm which was equivalent to 0.0001°C in the corresponding temperature value.

Jacket. The constant-temperature-jacket consisted of a water-filled, 43 l, cylindrical tank J_1 enclosing the calorimeter well J_2, which had a volume of about 10 l. The well was covered by a double-walled lid J_3, through which was circulated water from the jacket tank by the aid of a centrifugal pump J_4 and tubes J_5 and J_6 in hinges J_7 and J_8 as described in Ref.[24] The water in the tank was stirred by two 750 rpm propeller-stirrers J_9 and J_{10} operating in stirrer wells J_{11} and J_{12} (so that water was forced from bottom to top in well J_{11} and in the opposite direction in well J_{12}). Through a coil of copper tubing J_{13}, positioned around the stirrer shaft in well J_{11}, a constant flow of 21°C water was passed at a rate of 50 ml/min. J_{14} was a by-pass switch for the water flow. Around stirrer J_{10} was mounted a 22 W immersion heater J_{15}. The temperature of the jacket water was kept constant within a temperature interval of 0.003°C at about 25.22°C by balancing the constant cooling effect from coil J_{13} against an intermittent energy input from heater J_{15}. The heater was operated by a mercury-in-glass thermoregulator J_{16} (shown only in Fig. 1 b) *via* an electronic relay. The temperature of the jacket water was checked after each experiment by placing the resistance thermometer in hole J_{17} and reading it continuously for some minutes. J_{18} was a plastic sheet surrounding the jacket tank. J_{19}, J_{20} and J_{21} were pulleys for the two jacket stirrers and the calorimeter stirrer, respectively. J_{22} was a Lucite stud for coupling stirrer C_7 with pulley J_{21}. In the jacket lid were mounted two electrical terminals J_{23} and J_{24} which could be pushed down into the calorimeter well to make connection with the two flat contacts (*cf.* above) in the calorimeter lid leading to the heater and to the ignition spring clip [23, p. 21]. J_{25} was an interior wall in the jacket lid and J_{26} a glass window for inspection of the flow of water in the lid.

The whole apparatus was kept in a thermostated room at a temperature of 23.0±0.2°C.

EXPERIMENTAL PROCEDURE

Calibration experiments

The calorimetric system was calibrated by combustion of NBS standard benzoic acid, under the conditions given in the NBS certificate [35]. The recommendations, also given in the certificate, for certain details of the procedure were followed except for the method of igniting the sample. The ignition was effected with the device described above (p. 1515) using the procedure given below for the heat of combustion experiments. In all other details (including for example rotation of the bomb) the procedure of the calibration experiments was, wherever possible, the same as that for the combustion experiments. From what will be said later it will be evident that the most important difference in procedure between calibration and combustion experiments was in the nature and amount of the liquid placed in the bomb before the experi-

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* Thermometer and bridge had both been calibrated at the National Bureau of Standards, Washington, D. C.

ments. In the calibration experiments 0.810 ml (corresponding to 3 g per liter of bomb volume) of water was introduced into the bomb but in the combustion experiments with the bromine compound 30.05 ml of an arsenious oxide solution (corresponding to 112 g of water per liter of bomb volume) were placed in the bomb. The corresponding effect on the results obtained will be discussed later.

Heat of combustion experiments

Preparation and assembly of the initial system. A portion of the p-bromobenzoic acid sample was made into a pellet having a mass corresponding to an amount of 6.0 mg-atoms of bromine. The pellet was lightly polished with a soft brush to remove any loose fragments of substance from its surface. It was then placed in the pre-weighed platinum combustion crucible and the whole was weighed to the nearest 0.00001 g. Paraffin oil of known composition and heat of combustion was added to the pellet in the crucible in such an amount that the temperature rise obtained in the combustion experiment would be, within 1 %, the same as that obtained in the calibration experiments. The weight of paraffin oil added was obtained by weighing crucible with contents to the nearest 0.00001 g. The cotton string fuse was weighed and attached to the mid-point of the thin platinum ignition wire. The crucible with its contents was placed in the crucible support in the bomb head and the free end of the fuse was immersed in the oil in the crucible. In the bottom of the bomb body was placed 30.05 ml of 0.0627_9 M arsenious oxide (As_2O_3) solution and the bomb was assembled. The gas-inlet opening of the bomb was connected to a cylinder of oxygen containing 0.3 % of nitrogen as an impurity but no combustible impurities. To remove the air from the bomb the latter was flushed with oxygen for 3 min at a rate of flow of 800 ml/min (at 23°C and 1 atm). The gas-outlet valve was closed and the bomb filled with oxygen to a final pressure of 30.0 $\pm$ 0.05 atm at 25°C. The filling required a time of about 12 min. The bomb was tested for leaks by immersion in water for 2 min. The outer surface of the calorimeter can and lid and the inner side of the well were polished with chamois leather and the copper wire of the moving mechanism was wound around pulley M_{10} (Fig. 1). Fastening ring M_7 was placed on the bottom of the calorimeter can under the supporting ring M_1. Ball bearing M_6 was placed in its groove on the fastening ring and the bomb was lowered into the supporting ring, ball bearing and fastening ring. The fastening ring with the ball bearing was pressed against the supporting ring and locked in position by two set-screws in the fastening ring. Stud M_9 was put in place and the bomb was carefully rotated through 180° about axis M_2—M_3 and fastened in the inverted position, shown in Fig. 1, by spring clip C_6. Water, of 24.1°C temperature, was then added to the can until can and contents balanced, within 0.05 g, a counterpoise which remained unchanged throughout the work *. The mass of water added was about 5 000 g. Immedi-

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* Thus the mass of water in the calorimeter can varied from experiment to experiment with the total mass of contents introduced into the bomb, all other masses in the calorimetric system being kept constant. The variations thus introduced into the energy equivalent of the calorimetric system were accounted for in the calculations of the experiments.

ately after weighing, the calorimeter can with contents was placed in the jacket, and the calorimeter lid was pressed into place after the drive wire had been fed through orifice C_{10} (Fig. 1). The wire was then fed through the corresponding orifice in the jacket lid and the latter was put in place over the well. The end of the drive wire was fastened to pulley M_{12} (Fig. 1) and the calorimeter stirrer was connected with pulley J_{21}. The resistance thermometer was put in place in the calorimeter and the calorimeter stirrer was started.

Calorimetric observations. The calorimeter was heated to a temperature of 24.057°C and left to reach thermal equilibrium. After about 20 min, when equilibrium had been established, the temperature of the calorimeter had reached the value 24.087°C. At this temperature, which in all experiments was taken as starting point for the calorimetric observations, the resistance-*versus*-time readings of the fore period were begun. The fore period had a duration of 20 min and the thermometer resistance was read every 2 min at the times 0, 2, 4, ..., 18 min. During these readings the bridge current was adjusted to give a bridge sensitivity corresponding to a galvanometer deflection of 1.0 mm of scale length per 0.0001 ohm of change in the bridge setting. After the 18th min reading the bridge sensitivity was reduced to give a galvanometer deflection of 400 mm. of scale length per 0.1000 ohm of change in the bridge setting * and the bridge was set at a preselected reading corresponding to about two thirds of the total temperature rise of the calorimeter during the reaction period **. At time 20 min the charge was ignited and the reaction period began. During the first 3 min of the reaction period, when the temperature rose very rapidly, resistances were read from the galvanometer deflections without changing the bridge setting from the preselected value mentioned above. For convenience the resistance was not observed at certain selected times, but instead the time was recorded on a chronograph when passing through certain selected resistance values. These values were so chosen as to give time-temperature data at small enough intervals to permit calculation of the energy exchange between calorimeter and surroundings with sufficient accuracy, *cf.* Ref.[32] and below. The intervals were in order, in °C, 0.004 (approx.), 0.05, 0.05, 0.1, 0.1, 0.1, 0.1, 0.1, 0.1, 0.05, 0.05, 0.025, 0.025, 0.0125. Immediately before time 23 min, when the temperature rise was becoming slow again, the bridge sensitivity was reset at the value it had during the fore period, and the rest of the calorimeteric observations were done by reading the resistance — operating the bridge in the conventional way — at selected times. From time 23 min to time 25 min the resistance was read every half minute and each minute from 25 min to 36 min. Thermal equilibrium had always reestablished not later than at time 36 min and therefore the reaction period was always taken to be 16 min long. During the after period, which began at time 36 min and had a duration of 20 min, the resistance was read every 2 min at the times 38, 40, ..., 56 min. Finally the jacket temperature was measured with the calorimeter thermometer.

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* A change in resistance of 0.1000 ohm corresponded in this interval to a temperature change of 0.9950°C.

** The temperature rise obtained in all experiments in this work was 0.88 ± 0.01°C.

Chemical analysis of the final system. After disassembly of the apparatus the bomb gases were slowly let out and the liquid phase in the bomb was quantitatively transferred to a volumetric flask and diluted to 250 ml. In order to determine the chemical composition at the end of the reaction period of the liquid phase in the bomb, aliquot portions of the diluted bomb solution were withdrawn and used for determination of the concentrations of the following components: (i) nitric acid, (ii) bromoaurous acid, (iii) bromoplatinous acid, (iv) arsenious oxide, and (v) hydrobromic acid.

(i) Nitric acid was determined colorimetrically by a diphenylamine method [36] as follows. A 2 ml sample of the diluted bomb solution was mixed with 10 ml of conc. sulphuric acid in a glass-stoppered flask and the mixture was allowed to cool to room temperature. 1 ml of a diphenylamine solution was then added, consisting of 200 mg of diphenylamine dissolved in a mixture of 26 ml of water and conc. sulphuric acid to a volume of 250 ml. After a selected standard time-interval (usually 15 min) the absorbance of the solution was measured with a photoelectric colorimeter using a red filter. The nitric acid concentration was then read from a reference curve obtained with nitrate standards containing the same amounts of arsenious oxide, arsenic oxide and hydrobromic acid as the samples. The amount of nitric acid formed in each combustion experiment was about 0.1 mmole.

(ii) Bromoaurous acid was determined colorimetrically on a 2 ml sample by a rhodanine method [37,38]. The amount of bromoaurous acid formed in each combustion experiment was found to be about 0.005 mmole.

(iii) Bromoplatinous acid was determined on a 2 ml sample by oxidation with bromine to bromoplatinic acid which latter was determined colorimetrically by an iodide method [38,39]. The amount of bromoplatinous acid formed in each combustion experiment was found to be about 0.0015 mmole.

(iv) Arsenious oxide was determined by titration with potassium permanganate [40] using the following procedure. To a 50 ml sample of the diluted bomb solution was added 10 ml of 3 M sodium hydroxide, 15 ml of 6 M hydrochloric acid and one drop of 0.002 M potassium iodide. The mixture was titrated with 0.1 N potassium permanganate solution using a platinum electrode for indication of the end point, at which a change in potential of about 250 mV was obtained for an addition of 0.005 ml of the permanganate solution. The amount of hydrobromic acid present in the sample was found not to interfere with the determination of the arsenious oxide.

(v) Hydrobromic acid was determined by potentiometric titration of a 20 ml sample (to which had been added 30 ml of water and 6 ml of 5 M nitric acid) with 0.04 M silver nitrate solution. The amounts of arsenious oxide and arsenic oxide present in the sample were found not to interfere with the determination of hydrobromic acid.

CALCULATION OF RESULTS

The corrected temperature rise

The difference between the temperature of the calorimeter at the end of the reaction period (*i.e.* at time 36 min) t_f and the temperature of the calori-

meter at the beginning of the reaction period (*i.e.* at time 20 min) t_i constitutes "the observed temperature rise" of the calorimeter $t_f - t_i$. This quantity is conveniently considered as the sum of two terms Δt and Δt_{ex}, where Δt is "the corrected temperature rise", *i.e.* the temperature rise of the calorimeter during the reaction period due to the heat of the actual bomb process, and Δt_{ex} is "the heat exchange correction", *i.e.* the temperature rise of the calorimeter during the reaction period due to energy exchange between calorimeter and environment. The value of Δt, needed in the further calculations, was obtained from eqn. 1.

$$\Delta t = t_f - t_i - \Delta t_{ex} \tag{1}$$

Values of all three quantities on the right in this equation were calculated from the temperature-time $(t - \tau)$ observations of the calorimetric experiment in the following way *.

The mean temperatures t_I and t_{II} (in ohms **) and the rates of temperature rise $R_I = \left(\dfrac{dt}{d\tau}\right)_I$ and $R_{II} = \left(\dfrac{dt}{d\tau}\right)_{II}$ (in ohm/min) of the calorimeter during the fore and after periods, respectively, were computed from the ten resistance readings of each period using eqns. 2—5.

$$t_I = \frac{1}{10} \ (t_0 + t_2 + \ldots + t_{18}) \tag{2}$$

$$t_{II} = \frac{1}{10} \ (t_{38} + t_{40} + \ldots + t_{56}) \tag{3}$$

$$R_I = \frac{1}{330} \ [9(t_{18} - t_0) + 7(t_{16} - t_2) + \ldots + (t_{10} - t_8)] \tag{4}$$

$$R_{II} = \frac{1}{330} \ [9(t_{56} - t_{38}) + 7(t_{54} - t_{40}) + \ldots + (t_{48} - t_{46})] \tag{5}$$

The obtained values for t_I, t_{II}, R_I and R_{II} were inserted in eqns. 6 and 7 to give values for t_i and t_f.

$$t_i = t_I + 11 \ R_I \tag{6}$$

$$t_f = t_{II} - 11 \ R_{II} \tag{7}$$

The value of Δt_{ex} was calculated from eqn. 8 ***

$$\Delta t_{ex} = [R_{II} + K(t_{II} - \frac{1}{\tau_f - \tau_i} \int_{\tau_i}^{\tau_f} t \, d\tau)](\tau_f - \tau_i) \tag{8}$$

where K is the leakage modulus of the calorimeter system (in ohm/min ohm), τ is the time at which the temperature of the calorimeter is t, τ_i is the time

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* The computation of "the heat exchange correction" has been discussed by several authors, see for example Refs. 2 (p. 743), 27 (p. 228), 28 (p. 37), 32, 33, 41—44, 45 (p. 94), 46 (p.136).

** Throughout the calculations for obtaining the value of Δt all temperature values were expressed in resistance (in ohms) of the given resistance thermometer, as measured with the given bridge.

*** This equation is identical with "the improved form of the Regnault-Pfaundler formula" given in Ref. 28 (p. 41, eqn. 13) and Ref. 2 (p. 746, eqn. 18).

at which the reaction period begins and τ_f the time where it ends. The term containing the integral should be physically interpreted as the mean temperature of the calorimeter during the reaction period. In all experiments τ_i and τ_f were 20 min and 36 min, respectively, the value of K was calculated from eqn. 9

$$K = -\frac{R_{II}-R_I}{t_{II}-t_I} \qquad (9)$$

and the value of the integral was obtained from the temperature-time data of the reaction period by numerical integration using the trapezium method.

It should be mentioned that a necessary condition for using eqn. 8 in the computation of Δt_{ex} is that, within the temperature interval of the calorimetric observations, the rate of temperature rise of the calorimeter, due to energy exchange with the environment, should be a linear function of the calorimeter temperature, which could be represented for example by the following relation

$$R = \frac{dt}{d\tau} = K(t_j-t) + w \qquad (10)$$

where t_j is the constant temperature of the jacket and w is the rate of temperature rise of the calorimeter, due to constant energy leakage from the environment to the calorimeter mainly through the stirring of the calorimeter water. The present apparatus was checked in respect of this requirement by measuring, as given in Refs.[32,47], R for various calorimeter temperatures t while the temperature of the jacket t_j was kept constant. The results are given in Table 1.

The energy equivalent of the calorimetric system

The energy equivalent of the calorimetric system varied with nature and amount of the contents introduced into the bomb. In addition, the experimental procedure used in this work required the amount of water in the calorimeter vessel to vary, as described on p. 1518, with the total mass of contents in the bomb, so that the total mass of bomb-contents plus water remained constant. For convenience in calculation of the results from calibration as well as heat of combustion experiments, the energy equivalent of the calorimetric system was divided into three parts: (i) the energy equivalent of a "standard calorimetric system" consisting of the whole system as assembled for a fictive experiment with no contents in the bomb $\varepsilon°(Calor.)$*, (ii) the energy equivalent of an amount of water equal in mass to the contents of the bomb $C_P(H_2O)m^i(Cont.)$, where $C_P(H_2O)$ is the heat capacity of liquid water at temperature t_i and $m^i(Cont.)$ is the total mass of the contents of the bomb, and (iii) the energy equivalent of the contents of the bomb $\varepsilon(Cont.)$ **. The last quantity was different in the initial and final states of the experiment, i.e. the states in the bomb at the beginning and at the end of the reaction

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* The notation used in this section is the same as that in Ref.[48]
** With "contents of the bomb" was understood all removable matter in the interior of the bomb, including the platinum combustion crucible and its suspension ring.

period. These two energy equivalents are denoted by ε^i(Cont.) and ε^f(Cont.), respectively. Let $-\Delta E_{\text{I.B.P.}}$ be "the heat of the isothermal bomb process", $i.e.$ the amount of heat released in the actual bomb process if it occurred isothermally at a selected temperature t_h, let $\Delta E_{\text{ign.}}$ be the amount of electrical energy introduced into the calorimetric system to ignite the sample, and let $\Delta E_{\text{rot.}}$ be the amount of energy introduced into the calorimetric system by the rotation of the bomb in the reaction period: then the following relation holds

$$-\Delta E_{\text{I.B.P.}} + \Delta E_{\text{ign.}} + \Delta E_{\text{rot.}} =$$
$$\ulcorner\varepsilon°(\text{Calor.})-C_{\text{p}}(\text{H}_2\text{O})m^i(\text{Cont.}) + \varepsilon^i(\text{Cont.})](t_h-t_i) + [\varepsilon°(\text{Calor.})-$$
$$C_{\text{p}}(\text{H}_2\text{O})m_i(\text{Cont.}) + \varepsilon^f(\text{Cont.})](t_f-\Delta t_{\text{ex}}-t_h) =$$
$$[\varepsilon°(\text{Calor.})-C_{\text{p}}(\text{H}_2\text{O})m^i(\text{Cont.})](t_f-\Delta t_{\text{ex}}-t_i) + \varepsilon^i(\text{Cont.})(t_h-t_i) +$$
$$+ \varepsilon^f(\text{Cont.})(t_f-\Delta t_{\text{ex}}-t_h) \tag{11}$$

In the present work t_h was taken as 25°C and all experiments were so arranged as to give $t_f-\Delta t_{\text{ex}}$ a value which was virtually 25.0°C. Without significant loss in accuracy the relation

$$t_h = t_f-\Delta t_{\text{ex}}$$

could therefore be inserted in eqn. 11 which together with eqn. 1 gave the following relation

$$-\Delta E_{\text{I.B.P.}} + \Delta E_{\text{ign.}} + \Delta E_{\text{rot.}} =$$
$$[\varepsilon°(\text{Calor.}) - C_{\text{p}}(\text{H}_2\text{O})m^i(\text{Cont.}) + \varepsilon^i(\text{Cont.})] \Delta t \tag{12}$$

which could be rearranged to give eqn. 13

$$\varepsilon°(\text{Calor.})-(\Delta E_{\text{ign.}}/\Delta t)-(\Delta E_{\text{rot.}}/\Delta t) =$$
$$-\Delta E_{\text{I.B.P.}}/\Delta t + C_{\text{p}}(\text{H}_2\text{O})m^i(\text{Cont.}) - \varepsilon^i(\text{Cont.}) \tag{13}$$

In all calibration and heat of combustion experiments the quantities $\Delta E_{\text{ign.}}$, $\Delta E_{\text{rot.}}$ and Δt differed from certain fixed values by amounts small enough to permit considering the quantities $\Delta E_{\text{ign.}}/\Delta t$ and $\Delta E_{\text{rot.}}/\Delta t$ in eqn. 13 as being constant throughout the work and incorporating them into the constant value of $\varepsilon°$(Calor.). For simplicity this was done by removing the two terms from eqn. 13 which thereby changed to:

$$\varepsilon°(\text{Calor.}) = -\Delta E_{\text{I.B.P.}}/\Delta\text{t} + C_{\text{p}}(\text{H}_2\text{O})m^i(\text{Cont.}) - \varepsilon^i(\text{Cont.}) \tag{14}$$

The values of m^i(Cont.) and ε^i(Cont.) in eqn. 14 could be computed, as given in detail in Ref.[48], from data obtained in each calibration experiment. The value of the term $-\Delta E_{\text{I.B.P.}}$ could also be computed from the data obtained in a calibration experiment by use of the relation

$$-\Delta E_{\text{I.B.P.}} = -m'\Delta Ec/M(\text{Benzoic acid})-\Delta E(\text{HNO}_3)-m'''\Delta Ec/M(\text{Fuse}) \tag{15}$$
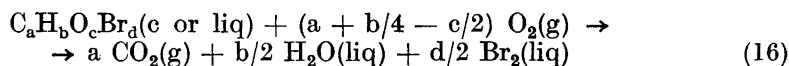
where m' is the mass of benzoic acid burned, $-\Delta Ec/M$(Benzoic acid) is the quantity of heat evolved by combustion at t_h°C of one unit of mass of the standard benzoic acid under the actual bomb conditions of the calibration experiment, $-\Delta E(\text{HNO}_3)$ is the small quantity of heat evolved during the

combustion process by the formation from water, oxygen and nitrogen (present as impurity in the oxygen) of a certain amount of nitric acid, m''' is the mass of fuse burned to ignite the benzoic acid sample, and $-\Delta Ec/M$(Fuse) is the heat of combustion of the fuse under the actual bomb conditions of the calibration experiment.

From the data obtained in each calibration experiment a value of $\varepsilon°$(Calor.) could thus be computed by the aid of eqn. 14. A set of calibration experiments was made in all of which the initial contents of the bomb were within practical limits the same. Therefore the values of m^i(Cont.) and ε^i(Cont.) were within required limits the same for all experiments in the set. Therefore the values of $-\Delta E_{\text{I.B.P.}}/\Delta t$ computed from the individual experiments were averaged before eqn. 14 was used for calculation of the $\varepsilon°$(Calor.) value of the calorimetric system, cf. Table 2.

The heat of combustion of the sample

The most useful thermodynamic quantity that can be calculated from the experimental data obtained in a combustion experiment with an organic bromine compound is the standard heat of combustion of the compound, $-\Delta Ec°$(Compound), at the reference temperature, t_{h}, of the combustion experiment. This is the change in energy associated with the "idealized combustion reaction" represented by eqn. 16, in which all reactants and products are in their thermodynamic standard reference states [49]:
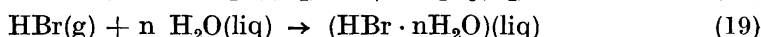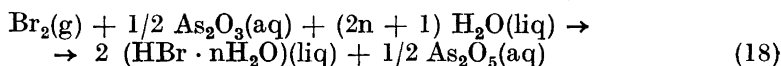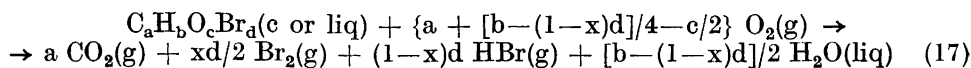
$$C_aH_bO_cBr_d(c \text{ or } liq) + (a + b/4 - c/2)\ O_2(g) \rightarrow$$
$$\rightarrow a\ CO_2(g) + b/2\ H_2O(liq) + d/2\ Br_2(liq) \qquad (16)$$

The various steps in which the value of $-\Delta Ec°$(Compound) is computed from the experimental data will be treated in this section.
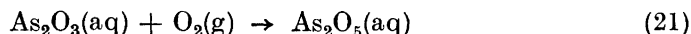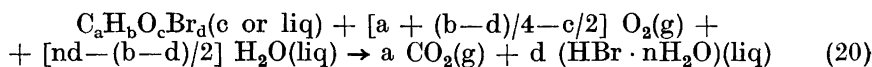
The heat of the isothermal bomb process, $-\Delta E_{\text{I.B.P.}}$, was calculated, using eqn. 14, directly from the experimental data obtained in a heat of combustion experiment and the $\varepsilon°$(Calor.) value determined in the calibration experiments. To assign the measured heat-quantity to the corresponding amount of chemical reaction, it was only necessary to define the initial and final states of the bomb contents with an accuracy equivalent to the precision in the calorimetric data. This required a chemical analysis of the final system as described previously (p. 1520). The description of the initial and final states is treated in full detail in Ref.[48] The chemical change of the contents of the bomb from the initial to the final state in the bomb process, which is usually called "the chemistry of the bomb process", is conveniently described through a set of arbitrary reactions consistent with the actual initial and final states. The various reactions are selected so that the associated energy changes shall be known with appropriate accuracy.

The chemistry of the bomb process. Through the present and previous work the chemistry of the bomb process in combustion experiments with organic bromine compounds is well established. The combustion of an organic bromine compound in a bomb in oxygen at 30 atm pressure results in the following transformations of the elements in the sample: the carbon is quantitatively transformed to carbon dioxide, part of the hydrogen is transformed to hydrogen
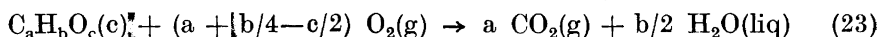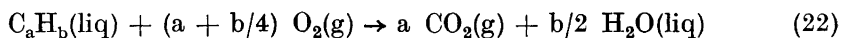
bromide and the rest to water, and part of the bromine is transformed to hydrogen bromide and the rest to elemental bromine. This part of the bomb process is conveniently represented by eqn. 17. Of the products formed in reaction 17 the elemental bromine is quantitatively reduced to hydrobromic acid by the arsenious oxide solution, as represented in eqn. 18, while the hydrogen bromide and the water are absorbed by the bomb solution forming hydrobromic acid as given in eqn. 19:

$$C_aH_bO_cBr_d(c \text{ or liq}) + \{a + [b-(1-x)d]/4-c/2\} \ O_2(g) \rightarrow$$
$$\rightarrow a \ CO_2(g) + xd/2 \ Br_2(g) + (1-x)d \ HBr(g) + [b-(1-x)d]/2 \ H_2O(liq) \quad (17)$$

$$Br_2(g) + 1/2 \ As_2O_3(aq) + (2n + 1) \ H_2O(liq) \rightarrow$$
$$\rightarrow 2 \ (HBr \cdot nH_2O)(liq) + 1/2 \ As_2O_5(aq) \quad (18)$$

$$HBr(g) + n \ H_2O(liq) \rightarrow (HBr \cdot nH_2O)(liq) \quad (19)$$

The actual bomb process can thus be described as the sum of eqn. 17, $xd/2$ times eqn. 18 and $(1-x)d$ times eqn. 19. For calculation purposes it is, however, useful to represent the actual bomb process not by the more realistic eqns. 17—19 but instead by the hypothetical eqns. 20 and 21:

$$C_aH_bO_cBr_d(c \text{ or liq}) + [a + (b-d)/4-c/2] \ O_2(g) +$$
$$+ [nd-(b-d)/2] \ H_2O(liq) \rightarrow a \ CO_2(g) + d \ (HBr \cdot nH_2O)(liq) \quad (20)$$

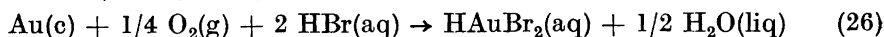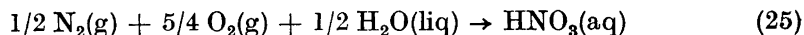$$As_2O_3(aq) + O_2(g) \rightarrow As_2O_5(aq) \quad (21)$$

It is seen that the sum of eqn. 20 and $xd/4$ times eqn. 21 is identical with the aforementioned sum of eqn. 17, $xd/2$ times eqn. 18 and $(1-x)d$ times eqn. 19. The bomb process was therefore considered to comprise one reaction in which all of the bromine compound reacted according to eqn. 20 and another reaction in which the amount of arsenious oxide consumed during the process reacted according to eqn. 21. Further reactions during the bomb process were the combustion of the auxiliary oil and of the fuse, respectively, according to the following equations:

$$C_aH_b(liq) + (a + b/4) \ O_2(g) \rightarrow a \ CO_2(g) + b/2 \ H_2O(liq) \quad (22)$$

$$C_aH_bO_c(c) + (a + [b/4-c/2) \ O_2(g) \rightarrow a \ CO_2(g) + b/2 \ H_2O(liq) \quad (23)$$

Since a significant part of the gaseous carbon dioxide formed in reactions 20, 22 and 23 was dissolved in the bomb liquid the reaction given in eqn. 24 also contributed to the bomb process.

$$CO_2(g) \rightarrow CO_2(aq) \quad (24)$$

Finally, to account for the small amounts of nitric acid, bromoaurous acid and bromoplatinous acid present in the final bomb solution, side reactions according to eqns. 25—27 were also assumed to occur in the bomb process.

$$1/2 \ N_2(g) + 5/4 \ O_2(g) + 1/2 \ H_2O(liq) \rightarrow HNO_3(aq) \quad (25)$$

$$Au(c) + 1/4 \ O_2(g) + 2 \ HBr(aq) \rightarrow HAuBr_2(aq) + 1/2 \ H_2O(liq) \quad (26)$$

$$Pt(c) + 1/2 \ O_2(g) + 4 \ HBr(aq) \rightarrow H_2PtBr_4(aq) + H_2O(liq) \quad (27)$$

From this is evident that the isothermal bomb process could conveniently be described as the sum of the main combustion reaction 20 and the auxiliary combustion reactions 21—27.

The heat effect, $-\Delta E$(Compound), associated with the main combustion reaction 20 can be called the "heat of the combustion of the sample in the bomb process". This quantity was obtained from the observed "heat of the isothermal bomb process", $-\Delta E_{\text{I.B.P.}}$, by subtraction of the heat effects $-\Delta E$(As), $-\Delta E$(Oil), $-\Delta E$(Fuse), $-\Delta E$(CO$_2$), $-\Delta E$(HNO$_3$), $-\Delta E$(Au), and $-\Delta E$(Pt), these being the heats associated with the actual amounts of reaction according to eqns. 21—27, respectively. For computation of the latter quantities it was necessary to know (i) the amounts of reaction and (ii) the molar heats of reaction for the various auxiliary combustion reactions.

The amounts of reaction in the bomb process. The amounts of reactions 20, 22, and 23 were computed from composition and mass of the bromine compound, the paraffin oil, and the fuse, respectively, that were placed in the bomb. The amount of reaction 21 was determined from the amount of arsenious oxide consumed in the bomb process, obtained from the analytical determinations of arsenious oxide in the initial and final bomb solutions. The amount of reaction 24 was determined as given in Ref.[48] The amounts of reactions 25—27, finally, were obtained from the experimentally determined amounts of nitric acid, bromoaurous acid and bromoplatinous acid in the final bomb solution.

Heats of reaction for the auxiliary combustion reactions. The values used for the molar heats of reaction for the various auxiliary combustion reactions are summarized below. The data were either obtained directly as results from experimental thermochemical work or computed from data given in Ref.[49]

$-\Delta E$ (reaction 21) $= (77.4 \pm 0.1) \times 10^3$ cal/mole at 25°C, Ref.[50]

$-\Delta E°$(reaction 22) $= -\Delta Ec°/M$(Oil) $= 10\ 980.5 \pm 1.2$ cal/g at 25°C, this work

$-\Delta E°$(reaction 23) $= -\Delta Ec°/M$(Fuse) $= 3\ 971 \pm 4$ cal/g at 25°C, this work

$-\Delta E$ (reaction 24) $= (3.89 \pm 0.14) \times 10^3$ cal/mole at 25°C, Ref.[48]

$-\Delta E°$(reaction 25) $= 14.176 \times 10^3$ cal/mole at 25°C, Ref.[49]

$-\Delta E°$(reaction 26) $= 8 \times 10^3$ cal/mole at 25°C, Ref.[49] *

$-\Delta E°$(reaction 27) $= 43.4 \times 10^3$ cal/mole at 25°C, Ref.[49] **

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* Since no value has been found for the standard heat of formation of HAuBr$_2$(aq) a guess, from related data given in Ref. [49] of -32 kcal/mole was used for this quantity in calculating $-\Delta E°$(reaction 26). As will be seen in the following the error resulting from use of this uncertain value for $-\Delta E°$(reaction 26) will be small.

** In calculating this heat of reaction the value -91.0 kcal/mole was used for the standard heat of formation of H$_2$PtBr$_4$(aq) at 25°C.

For rigorous calculation of the "heat of the combustion of the sample in the bomb process", $-\Delta E$(Compound), according to the scheme outlined above, the given auxiliary heat of reaction data should all be applicable to actual conditions of the bomb process instead of being standard heats of reaction as some of them are. This apparent inconsistency is explained and eliminated through the mode of calculation used for the reduction of the obtained heat of combustion in the bomb process to the standard heat of combustion [48].

Reduction to standard heat of combustion. Through the various steps of the calculation described above a value was obtained for the heat of the combustion of the sample in the bomb process, $-\Delta E$(Compound), at the temperature $t_h = 25°C$. This value referred to reaction according to eqn. 20, with reactants and products in their actual states in the bomb process. The thermodynamically more useful standard heat of combustion, $-\Delta Ec°$(Compound), according to eqn. 16 was finally computed from the obtained $-\Delta E$(Compound) value by application of the Washburn reduction as given in Ref.[48] The various terms of this reduction were conveniently expressed as the sum of two quantities: (i) $-\Delta E$(HBr), the amount of heat associated with oxidation of the hydrobromic acid, formed in reaction 20, to elemental bromine according to eqn. 28

$$(HBr \cdot nH_2O)(liq) + 1/4\ O_2(g) \rightarrow (n + 1/2)\ H_2O(liq) + 1/2\ Br_2(liq) \quad (28)$$
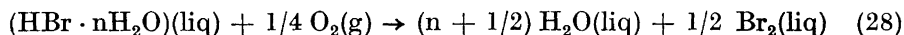
and, (ii) $-\Delta E_\Sigma$, the amount of heat corresponding to "the remaining Washburn corrections" (see Ref.[48]). The amount of reaction for reaction 28 was computed from the mass and composition of the combustion sample, and the molar heats of reaction for various values of n were calculated from data in Ref.[49] (*cf.* Ref.[48]).

All the various heat quantities discussed above were combined in the over-all eqn. 29 to give the resulting value for $-\Delta Ec°/M$(Compound), the standard heat of combustion per gram of compound according to eqn. 16.

$$-\Delta Ec°/M(\text{Compound}) = \frac{1}{m'}\left\{-\Delta E_{\text{I.B.P.}} - [-\Delta E(\text{As}) - E\Delta(\text{Oil}) - \Delta E(\text{Fuse}) -\right.$$
$$\left.-\Delta E(CO_2) - \Delta E(HNO_3) - \Delta E(Au) - \Delta E(Pt)] - \Delta E(HBr) - \Delta E_\Sigma\right) \quad (29)$$

In eqn. 29, m' denotes the mass of the bromine compound placed in the bomb and all other symbols have been defined previously.

Final over-all precision. The estimation of the final over-all precision in the $-\Delta Ec°/M$(Compound) values obtained, will be discussed in a later paper [51].

RESULTS

The energy exchange between calorimeter and environment

The calorimetric system was checked for linearity in the relation between calorimeter temperature and rate of energy exchange between calorimeter and environment by the method given on p. 1522. The results given in Table 1 were obtained from a series of measurements of the rate of temperature rise of the calorimeter at various calorimeter temperatures, while the temperature

of the jacket was kept constant at 25.495 $\pm$ 0.001°C *. In the various columns of the table are listed: (i) t, the average temperature of the calorimeter during the time interval in which the corresponding rate of temperature rise was measured; (ii) $(dt/d\tau)_{obs.}$, the observed rate of temperature rise; (iii) $(dt/d\tau)_{calc.}$, the rate of temperature rise calculated from the equation

$$dt/d\tau = [13.67_8 \ (25.4950 - t) + 1.00_6] \cdot 10^{-4}$$

which is a "least squares" fit of eqn. 10 to the measured values of t and $(dt/d\tau)_{obs.}$; and (iv) $(dt/d\tau)_{obs.} - (dt/d\tau)_{calc.}$, the difference between the observed and the calculated rate of temperature rise.

Table 1. Results from the checking of the calorimetric system for linearity in the relation between calorimeter temperature and rate of energy exchange between calorimeter and environment.

$t°$	$(dt/d\tau)_{obs.}$ 10^{-4}deg/min	$(dt/d\tau)_{calc.}$ 10^{-4}deg/min	$(dt/d\tau)_{obs.} - (dt/d\tau)_{calc.}$ 10^{-4}deg/min
24.2218	18.37	18.42	-0.05
24.2476	18.13	18.07	$+0.06$
24.6224	13.02	12.94	$+0.08$
24.8056	10.36	10.44	-0.08
24.8175	10.18	10.27	-0.09
24.9856	8.03	7.97	$+0.06$
25.2201	4.79	4.77	$+0.02$

Since the uncertainty in the measured $(dt/d\tau)_{obs.}$-values in the first column of Table 1 was about $\pm$ 0.04 $\times$ 10^{-4} deg/min it was evident from the values listed in the last column that the agreement between observed and calculated $dt/d\tau$-values was satisfactory and that therefore the calorimetric system was unctioning so as to permit calculation of the energy exchange between calorimeter and environment by eqn. 8.

Calibration experiments

The experimental procedure used in the calibration experiments and the method of calculation of results have already been described, p. 1517 and 1522.

The benzoic acid was National Bureau of Standards standard sample 39 g [35] and the fuse was a cotton string having a percentage composition corresponding to the empirical formula $CH_{1.85}O_{0.91}$.

For reduction of weight in air to mass and calculation of the energy equivalent of the initial contents of the bomb, the following values at 25°C of density, ϱ, and specific heat, c_P, were used: for benzoic acid, $\varrho = 1.320$ g/ml [35,52], $c_P = 0.287$ cal/g deg [53]; for fuse, $\varrho = 1.5$ g/ml [45 (p. 81)], $c_P = 0.4$ cal/g deg [45 (p. 93)].

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* It should be observed that all other calorimetric experiments in the present work were performed with the jacket having a temperature of 25.22°C, *cf.* p. 1517.

The results obtained are presented in Table 2. The heading of the table gives the experimental conditions which were common to all the calibration experiments, and in the various columns are listed the data obtained for the individual experiments. The symbols denote:

t_h	the reference temperature to which the calorimetric experiments are ascribed
t_i	the initial temperature of the actual bomb process
P^i(gas.)	the initial pressure, at t_h, of the gaseous phase in the bomb
V(Bomb)	the volume of the bomb
V^i(H_2O tot.)	the volume of water introduced into the bomb
m(Pt)	the mass of removable platinum parts in the bomb (crucible and suspension ring)
m^i(Cont.)	the mass of the initial contents of the bomb (see p. 1522)
$-\Delta E c/M$(Benzoic	acid NBS 39 g) heat of combustion (per gram mass) of standard benzoic acid NBS 39 g under the actual bomb conditions
$-\Delta E c/M$(Fuse)	heat of combustion (per gram) of the fuse under the actual bomb conditions
ε°(Calor.)	the energy equivalent of the standard calorimetric system (see p. 1522)
ε^i(Cont.)	the energy equivalent of the initial contents of the bomb (see p. 1523)
m'	the mass of benzoic acid burned
m'''	the mass of fuse burned
Δt	the corrected temperature rise (see p. 1520)
$-\Delta E$(HNO_3)	the heat evolved through the formation of the nitric acid
$-\Delta E_{I.B.P.}$	the heat of the isothermal bomb process (see p. 1523)

The value given in Table 2 for the heat of combustion of the standard benzoic acid under the actual bomb conditions of the calibration experiments, $-\Delta E c/M$(Benzoic acid NBS 39g), was computed from the certified value [35] (cf. Refs.[54,55,52]) of 26.4338 ± 0.0026 abs. kj/g mass (6317.83 ± 0.62 cal/g mass) under certificate conditions by multiplication with a factor obtained as given in the certificate [35], cf. Refs.[43] (p. 37), [54] (p. 261). The actual conditions adhered to certificate conditions so closely that the required factor did not differ from unity to any significant extent. The value given in Table 2 for the heat of combustion of the fuse under the actual bomb conditions, $-\Delta E c/M$(Fuse), is in fact the standard heat of combustion of the fuse, $-\Delta E c^\circ/M$(Fuse), obtained from heat of combustion experiments with the fuse. The error introduced into the results of the calibration experiments by this approximation was not significant.

Heat of combustion experiments

Two sets of combustion experiments were performed, one with the sample of paraffin oil used as auxiliary material in the combustion experiments with the bromine compound, and one with a sample of p-bromobenzoic acid. The

Table 2. Results of calibration experiments.

$t_h = 25°C$ V(Bomb) = 0.2670 liter m^i(Cont.) = 20.745 g ε^i(Cont.) = 3.198 cal/deg

$t_i = 24.1°C$ $V^i(H_2O$ tot.) = 0.810 ml $-\Delta Ec/M$(Benzoic acid NBS 39 g) = 6 317.83 ± 0.62 cal/g [a]

P^i (gas.) = 30.0 atm m(Pt) = 8.528 g $-\Delta Ec/M$(Fuse) = 3 971 ± 4 cal/g [a]

| m' | m''' | Δt | $-\Delta E(HNO_3)$ | $-\Delta E_{I.B.P.} / \Delta t$ |
g	g	deg	cal	cal/deg
0.79944	0.00535	0.87412	1.00	5 803.52
0.79986	0.00502	0.87431	1.65	5 804.53
0.80154	0.00583	0.87660	1.10	5 804.52
0.80168	0.00562	0.87687	1.00	5 802.68
0.80117	0.00480	0.87555	0.70	5 803.69
0.80103	0.00561	0.87573	0.70	5 805.16
			Mean	5 804.02
			Standard deviation of mean	± 0.36

$\varepsilon°$(Calor.) = 5 821.54 ± 0.36 cal/deg

[a] At 25°C under the actual bomb conditions; see text for further comments.

experimental procedure used in the heat of combustion experiments and the method of calculation of results have been described previously, p.1518 and 1524. It should, however, be noted that since no reducing agent was required in the combustion experiments with the paraffin oil, the initial bomb liquid used in the paraffin oil experiments was the same as that used in the calibration experiments, *i.e.* 0.810 ml of water.

Paraffin oil USBM-P3a. The oil was a sample of redistilled mineral oil obtained from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines, Bartlesville, Oklahoma, under the laboratory designation Paraffin oil USBM-P3a. The oil was found to have a percentage composition corresponding to the empirical formula $CH_{1.89}$ and a density, ϱ, of 0.8755_0 g/ml at 20.00°C and 0.8723_5 g/ml at 25.00°C. For use in calculation of the energy equivalent of the initial contents of the bomb and in reduction to standard states the following values at 25°C of specific heat, c_P, and energy of compression, $(\partial E/\partial P)_T$, were used: $c_P = 0.53$ cal/deg [45 (p. 93)], $(\partial E/\partial P)_T = -0.0060$ cal/g atm. The latter value was calculated from the density values given above using the approximate relation $(\partial E/\partial P)_T = -T(\partial V/\partial T)_P$ as discussed in Ref.[56 (p. 542—43)].

The results obtained in the combustion experiments with the paraffin oil are presented in Table 3. The denotation of the symbols is the same as in Table 2. The following additional symbols are used:

$-\Delta E c^\circ/M$(Fuse)	the standard heat of combustion (per gram) of the fuse
ε(Calor.)	the energy equivalent of the actual calorimetric system minus the contents of the bomb (see p. 1522); this quantity is related to ε°(Calor.) through the equation ε(Calor.) $= \varepsilon^\circ$(Calor.) $- c_P(H_2O)m^i$(Cont.)
$-\Delta E_\Sigma/m''$	the heat to be evolved, per gram of paraffin oil burned, through the reactions constituting the sum of the remaining Washburn corrections (p. 1527)
$-\Delta E(CO_2)/m''$	the heat evolved, per gram of paraffin oil burned, from the dissolution of carbon dioxide in the final bomb solution
m''	the mass of paraffin oil burned
$-\Delta E_B/M$	the heat of combustion per gram of the compound in the isothermal bomb process at the temperature t_h (see Ref.[48])
$-\Delta E c^\circ/M$	the standard heat of combustion per gram of compound at the temperature t_h; as discussed in Ref.[48] the following relation holds: $-\Delta E c^\circ/M = -\Delta E_B/M - \Delta E_\Sigma/m''$

p-*Bromobenzoic acid.* The p-bromobenzoic acid used in the combustion experiments was a highly purified sample *.

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* The principal aim with the combustion experiments in the present work was to investigate the precision obtainable with the described bomb-calorimetric method and not to determine an accurate value for the heat of combustion of the sample used in the combustion experiments. For this reason it was necessary to have access to a suitable organic bromine compound sample of fairly high purity, but the detailed description of the purification process and of the determination of the purity of the sample was not of primary interest. It is intended to report on these details in a later paper dealing with the heats of combustion and formation of p-bromobenzoic acid and with the possible use of this compound as a test substance for bomb combustions of organic bromine compounds.

Table 3. Results of combustion experiments on paraffin oil USBM-P3a.

$t_h = 25.0°C$	$V(Bomb) = 0.2670$ liter	$\varepsilon°(Calor.) = 5\ 821.54 ± 0.36$ cal/deg	$\varepsilon(Calor.) = 5\ 801.16$ cal/deg
$t_i = 24.1°C$	$V^i(H_2O\ tot.) = 0.810$ ml		$\varepsilon^i(Cont.) = 3.21$ cal/deg
$P^i(gas.) = 30.0$ atm	$m(Pt) = 8.528$ g	$-\Delta Ec°/M(Fuse) = 3\ 971 ± 4$ cal/g	$-\Delta E_\Sigma/m'' - \Delta E(CO_2)/m'' = -3.4$ cal/g

| m'' | m''' | Δt | $-\Delta E(HNO_3)$ | $-\Delta E_B/M$ |
g	g	deg	cal	cal/g
0.46138	0.00508	0.87687	0.70	10 986.2
0.46100	0.00525	0.87590	0.80	10 981.3
0.46186	0.00567	0.87788	0.65	10 982.5
0.46122	0.00534	0.87694	2.05	10 985.7
			Mean	10 983.9
			Standard deviation of mean	± 1.2

$$-\Delta Ec°/M = 10\ 980.5 ± 1.2\ cal/g$$

For use in reducing weight in air to mass in the calculation of the energy equivalent of the initial contents of the bomb and in the reduction to standard states, the following values at 25°C of density, specific heat and energy of compression were used: $\varrho = 1.889$ g/ml, $c_\text{p} = 0.18$ cal/deg g, $(\partial E/\partial P)_T = -0.0029$ cal/g atm. These values were obtained as follows: the density value was calculated from the value $\varrho^{20} = 1.894$, given in Ref.[57], using a value for the temperature coefficient of the density of 0.00054 g/ml deg, which is the average of the two values given for benzoic acid in Ref.[52]; the specific heat value was obtained from the value given earlier in this paper for benzoic acid, by assuming the molar heat capacities for benzoic acid and p-bromobenzoic acid to be approximately the same; and the energy of compression value given above is that obtained for benzoic acid from data given in Ref.[52]

The results obtained in the combustion experiments with the p-bromobenzoic acid sample are presented in Table 4. The denotation of symbols is the same as in Tables 2 and 3 except for m', which see below. The following additional symbols denote:

$V^i(\text{soln.})$	the volume of arsenious oxide solution introduced into the bomb
$C^i(\text{soln.})$	the concentration of As_2O_3 in the initial bomb solution
$-\Delta Ec°/M(\text{Oil})$	the standard heat of combustion per gram of the auxiliary paraffin oil at the temperature t_h
m'	the mass of p-bromobenzoic acid burned
$n^f(As_2O_5)$	the number of moles of As_2O_5 in the final solution
$-\Delta E(CO_2)$	the heat evolved from the dissolution of carbon dioxide in the final bomb solution
$-\Delta E(\text{Au})$	the heat evolved through the formation of the bromoaurous acid
$-\Delta E(\text{Pt})$	the heat evolved through the formation of the bromoplatinous acid
$-\Delta E(\text{HBr})$	the heat to be evolved through oxidation to elemental bromine of the hydrobromic acid in the final solution
$-\Delta E_\Sigma$	the heat to be evolved through the reactions constituting the sum of the remaining Washburn corrections (see p. 1527)

DISCUSSION OF METHOD AND RESULTS

The precision of the method

The over-all precision [1] (p. 430) of heat of combustion data obtained with the present method will be discussed in a later paper [51]. The immediate precision [1] (p. 430) of the results from the calibration and from the combustion experiments presented above can, however, be used for comparison of the precision of the present technique with that of other bomb-calorimetric techniques.

As is seen from Table 2 the precision obtained in the calibration experiments with benzoic acid was 0.006 % in terms of standard deviation of the mean of the six experimental values. This figure is comparable to the best

Table 4. Results of combustion experiments on p-bromobenzoic acid.

$t_h = 25.0°$ C V(Bomb) = 0.2670 liter $\varepsilon°$(Calor.) = 5 821.54 ± 0.36 cal/g m(Pt) = 8.529 g

$t_i = 24.1°$C V^i(soln.) = 0.03005 liter $-\Delta Ec°/M$(Oil) = 10 980.5 ± 1.2 cal/g ε(Calor.) = 5 772.09 cal/deg

P^i(gas.) = 30.0 atm C^i(soln.) = 0.06279 mole As₂O₃/liter $-\Delta Ec°/M$(Fuse) = 3 971 ± 4 cal/g ε^i(Cont.) = 32.09 cal/deg

m' g	m'' g	m''' g	Δt deg	$n^f(As_2O_6)$ mole	$-\Delta E(CO_2)$ cal	$-\Delta E(HNO_3)$ cal	$-\Delta E(Au)$ cal	$-\Delta E(Pt)$ cal	$-\Delta E(HBr)$ cal	$-\Delta E_\Sigma$ cal	$-\Delta Ec°/M$ cal/g
1.19492	0.05444	0.00568	0.88022	0.001444	14.71	2.00	0.04	0.08	31.34	−1.99	3 673.37
1.20108	0.04585	0.00568	0.86800	0.001473	14.56	0.70	0.04	0.06	31.50	−2.03	3 673.45
1.20034	0.04690	0.00518	0.86899	0.001451	14.59	1.35	0.05	0.10	31.48	−2.03	3 673.35
1.19825	0.05258	0.00553	0.87899	0.001462	14.70	1.00	0.04	0.06	31.43	−2.01	3 674.50
1.20048	0.05637	0.00573	0.88758	0.001468	14.82	1.35	0.04	0.05	31.49	−2.00	3 673.16
1.20161	0.04606	0.00549	0.86873	0.001470	14.59	0.65	0.04	0.04	31.52	−2.03	3 674.31
1.20115	0.05425	0.00535	0.88377	0.001465	14.77	0.75	0.04	0.06	31.50	−2.01	3 674.06

Mean 3 673.74

Standard deviation of mean ± 0.20

precision obtained in calibration experiments with other present-day combustion calorimetric systems of static-bomb as well as moving-bomb type. The combustion experiments with paraffin oil, presented in Table 3, were performed under the same experimental conditions as the calibration experiments. The precision obtained was 0.011 %, from a set of only four individual experiments (see table). In a later series of combustion experiments on paraffin oil [51] with the same apparatus the standard deviation of the mean of six experimental values was found to be 0.008 %. Although slightly high these figures are also satisfactory in comparison with results from other modern bomb-calorimetric work. Thus the results obtained in the experiments with benzoic acid and paraffin oil demonstrated that the reproducibility obtainable with the apparatus and technique was satisfactory. More specifically, the assumption made earlier in this paper was confirmed that for certain energy quantities, such as the ignition energy $\Delta E_{ign.}$ and the bomb-rotation energy $\Delta E_{rot.}$, the variation in value from one calorimetric experiment to another was small enough to accept them as constant in all the calorimetric experiments. Tables 2 and 3 also prove that the apparatus and technique gave satisfactory precision in the temperature—time measurements and in the calculation of heat exchange corrections Δt_{ex}.

The precision obtained in the heat of combustion experiments with p-bromobenzoic acid, presented in Table 4, was 0.005 % in terms of standard deviation of the mean of seven experimental values. This high precision was virtually the same as that obtained in the calibration experiments with benzoic acid, which showed that neither did the presence of bromine in the compound affect the reproducibility of the combustion process of a pelleted sample, nor was the reproducibility affected by the presence of a large amount of bomb liquid or by the additional uncertainty in the determination of the amount of heat associated with the oxidation of arsenious oxide to arsenic oxide.

The various experiments of the present work thus have shown that the precision of heat of combustion results obtained with the described moving-bomb method for organic bromine compounds is comparable to the precision obtained with the best modern combustion calorimetric systems for other groups of organic compounds.

The accuracy of the method

Although the precision obtainable with the present method has been found to be high, the presence of undetected systematic errors might render the accuracy of obtained heat of combustion data much lower than actually would be attainable with this high precision. Therefore the accuracy of the method has to be investigated, and there are several possible ways of doing this. Since the principal use for heat of combustion data is to derive corresponding heats of formation, a suitable approach would be to compare, for certain selected bromine compounds, heats of formation calculated both from heat of combustion data and from calorimetric data on heats of reactions other than combustion. Such a comparison has been made and the results will be reported in a later paper [51]. It will, however, be appropriate to include in the

present discussion of method and results an examination of certain details of the technique which could possibly cause systematic errors.

The calorimetric part of the measurement

The energy exchange between calorimeter and environment. It was experimentally demonstrated earlier that the functioning of the present calorimetric system allowed calculation of the energy exchange between calorimeter and environment during the reaction period of an experiment by eqn. 8 given on p. 1521. A necessary prerequisite for this is, however, that equilibrium has been reestablished in the bomb before the after period starts. The question about attainment of equilibrium in the bomb will be discussed later in this paper.

The energies of ignition and of rotation of the bomb. It was evident from the discussion on p. 1523 that, as long as both calibration and combustion experiments were so arranged that the obtained Δt-values were virtually the same in all experiments, it was only the *variation* in the energies of ignition and of rotation from one set of experiments to another that might give rise to systematic errors. As has already been pointed out, such variations would also affect the precision in the various sets of measurements. Since this precision, however, was found to be as high as could be expected, the variations in the two mentioned quantities could not be significant.

The heats of reaction for the auxiliary combustion reactions. Any uncertainties in the molar heat of reaction values for the auxiliary combustion reactions 21—27, given on p. 1525, will give rise to corresponding systematic errors in obtained heat of combustion values. As is seen from Table 4 the quantities $-\Delta E(HNO_3)$, $-\Delta E(Au)$ and $-\Delta E(Pt)$ associated with the actual amounts of reactions 25—27 are small enough to permit large uncertainties in the corresponding molar heats of reaction *. Therefore, although the molar heat of reaction 26 has a high degree of uncertainty (p. 1526), the systematic errors from reactions 25—27 are probably small enough to be neglected. The variation in value of the quantity $-\Delta E(Fuse)$ in calibration as well as combustion experiments is small enough to give with the uncertainty in the $-\Delta E°$ (reaction 23)-value satisfactory cancellation of errors from this quantity and therefore this error in the obtained heat of combustion values is also small enough to be neglected. The systematic errors associated with the uncertainties in the molar heats of reaction 21, 22 and 24 are, however, significant. These errors will be treated more fully in a later paper [51] dealing with the evaluation of the final over-all precision in the obtained heats of combustion. It may be pointed out that all these three molar heats of reaction were obtained, as specified on p. 1526, from recent experimental work directly in connection with the work presented in this paper.

Chemical part of the measurement

Homogeneity and equilibrium in the final state in the bomb. It has already been stressed that, as the method requires a large volume of bomb liquid, it is

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* Since the quantity $-\Delta E(HNO_3)$ appears in calibration as well as combustion experiments the error from this quantity is partly cancelled through the procedure of the given method.

imperative that homogeneity in the final liquid phase and equilibrium between the gaseous and the liquid phase in the bomb should be achieved before the after period of a measurement has started. The presence of a large volume of bomb liquid and the mode and duration of the rotation of the bomb in the present work brought about a thorough rinsing of the whole interior surface of the bomb, except for certain parts of the platinum rod B_6 (Fig. 2), and the gas-inlet tube B_7. Homogeneity of the liquid phase was therefore rapidly obtained.

Considering equilibration of the bomb gases with the bomb solution, it was found (see below) that, at the end of the reaction period, no hydrogen bromide or elemental bromine could be detected in the gaseous phase and therefore these components must have been quantitatively transferred to the bomb solution during the reaction period. The carbon dioxide was a third component, the equilibration of which between the gaseous and the liquid phase was of primary importance for the present method. Recently, the influence of various experimental factors on the rate of absorption of carbon dioxide in the final bomb liquid and the time required for reaching equilibrium between the gaseous and the liquid phase has been experimentally studied for different moving-bomb techniques [26]. Since the results of this investigation were utilized in designing the moving mechanism used in the present work, it can be confidently assumed that in all experiments the distribution of carbon dioxide between the gaseous and the liquid phase in the bomb was complete within the reaction period.

Chemistry of the bomb process. The accuracy of the heat of combustion data can only compare with the over-all precision of the experimental results if the nature and amount of the various chemical reactions 21—27, constituting the bomb process, are known to a corresponding degree of accuracy.

The amounts of reactions 20, 22, and 23 were obtained, as described earlier, from the composition and mass of the bromine compound, the paraffin oil, and the fuse, respectively. A possible check on the completeness of the sum of these three reactions would be by an experimental determination of the total amount of carbon dioxide present in the bomb after the combustion. Due to the large amount of bomb liquid such a determination would be experimentally very difficult, and no such measurement has been attempted.

A check on the completeness of the transformation of the bromine in the combustion sample to hydrogen bromide according to eqn. 20 would be the analytical determination of the amount of bromide ion in the final bomb liquid *. This was done in the experiments presented in Table 4 by potentiometric titration of aliquot 20 ml samples of the diluted bomb solutions with silver nitrate solution and calculation of the total amount of hydrogen bromide present in the final bomb liquid. It was necessary to correct for the small amounts of hydrogen bromide consumed in reactions 26 and 27 and therefore present in the final bomb liquid as $HAuBr_2$ and H_2PtBr_4, respectively. From

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* That no detectable amounts of bromine, in the form of hydrogen bromide or elemental bromine, were present in the final gas phase was demonstrated in separate combustion experiments by discharging the bomb gases, at the end of the reaction period, through a sodium hydroxide solution and analyzing the solution for bromide ion.

available stability constants [58] for these compounds it was estimated * that by the silver nitrate titration approximately one of the bromines in $HAuBr_2$ and none of the bromines in H_2PtBr_4 were titrated as bromide ion. Taking account of this in the calculation of the total amount of bromine present in the final bomb liquid the following figures were obtained for the recovery of the amount of bromine introduced into the bomb with the combustion sample: 99.3, 99.4, 99.6, 99.0, 99.5, 99.7, 99.8, and 99.8 %, respectively. Because of the uncertainties in the analytical method the deviation of these figures from the theoretical value 100.0 could not be considered significant and therefore the figures could be taken as an indication of the absence of gross "chemical" errors in this part of the method.

The actual oxidation state of the dissolved gold and platinum in the bomb liquid was difficult to assess. Combination of available data on oxidation potentials [59] with the concentrations of the various constituents in the final bomb solution implied that the gold should be present as Au(0) and the platinum as Pt(II). It was, however, experimentally found that the precipitation of metallic gold from the bomb solution was very slow and therefore it could be assumed that the oxidation state of the entire amount of gold, which had been dissolved during the combustion process was — at the end of the reaction period — Au(I) and that the precipitation of gold during the after period was completely negligible.

If arsenious oxide solution is not affected by gaseous oxygen under bomb conditions the amount of reaction 21 should be equivalent with the amount of elemental bromine formed in the actual combustion reaction 17. It is a principal requirement that no reaction between the arsenious oxide solution and the oxygen in the bomb should take place in either the initial or the final period of the calorimetric experiment. This question will be discussed next.

Stability of the arsenious oxide solution. For possible use as a reductant in combustion experiments with organic compounds containing chlorine the former I.U.C. Standing Commission for Thermochemistry discussed [60] three different reducing agents: arsenious oxide, hydrazine monohydrochloride and formic acid. Of these compounds only arsenious oxide has been further studied [61]. Instead of the monohydrochloride, hydrazine dihydrochloride has also been studied for such purposes [62]. A comparison has recently been made [63] of arsenious oxide and hydrazine dihydrochloride for use in static-bomb combustion calorimetry of organic chlorine compounds. Arsenious oxide was used as reductant in the introductory moving-bomb work on organic bromine compounds in this laboratory [17,18] and since a closer study (see below) showed that an arsenious oxide solution of the composition used in the present work was completely stable under the experimental bomb conditions of the present technique, this substance was chosen as a reductant for the further work.

The stability of the arsenious oxide solution and the accuracy of the analytical procedure were tested by treating 30.01 ml samples of the arsenious oxide solution in the following ways: (1) The sample was diluted in a volumetric flask to 250.0 ml, (2) The sample was placed in the bomb body and the bomb

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was closed. It was shaken for a minute and then opened. The contents were carefully transferred to a volumetric flask by repeated rinsing with water and diluted to 250.0 ml, (3) The sample was placed in the bomb which was then closed and filled with oxygen to a pressure of 30 atm. After 24 h the oxygen was discharged and the liquid contents were transferred to a volumetric flask and diluted as above, (4) The sample was placed in the bomb and used for a combustion experiment with benzoic acid or paraffin oil. After the experiment the bomb liquid was transferred as above to a volumetric flask and diluted to 250.0 ml. Numerous experiments of this type were performed. From all the solutions obtained under items 1 to 4 aliquot samples of 50 ml were withdrawn and titrated with potassium permanganate solution according to the method described above (p. 1520). The volume of permanganate solution consumed was in all the experiments 15.05 ml within $\pm$ 0.1 % *. These results indicated that, within the precision of the analytical method, no oxidation of the arsenious oxide solution occurred during combustion experiments with compounds containing only carbon, hydrogen and oxygen. Therefore it could be confidently assumed that the stability of the reductant during the initial and final period of an experiment was satisfactory.

Amount of reaction. From what has been said above on the analytical determinations of the amounts of carbon dioxide and hydrogen bromide present in the final state in the bomb it was evident that the only feasible way of determining the amount of reaction for the main combustion reaction 20 was from the mass and composition of the organic bromine compound placed in the bomb. This makes the question of the purity of the combustion sample most important.

Purity of the sample. The use of the above method for determination of the amount of reaction 20 requires that the impurities in the combustion sample are known in nature and amount or, preferably, that the purity of the sample is high enough to give no significant contribution to the uncertainty of the over-all method. In the latter case the absence of inert impurities, such as water, is especially important.

Application of the principle of comparative measurements to the present method

The application of the method of comparative measurements to combustion-bomb calorimetric studies of organic sulfur, chlorine and bromine compounds, respectively, has been discussed recently by various authors [64–66]. Three different methods, which should be adaptable for use in studies of bromine compounds, were mentioned in Ref.[66] The technique described above constitutes a fourth possible method. On account of the nature of this work the discussion of the present technique from the method-of-comparative-measurements point of view will, however, be deferred to a later paper.

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* For two solutions from combustion experiments with benzoic acid a slightly lower result was obtained.

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