COMBUSTION CALORIMETRY OF ORGANIC
BROMINE COMPOUNDS

By

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CHAPTER I

INTRODUCTION

The purpose of this research was to investigate the possibility of using ortho- and para-bromobenzoic acids as secondary reference compounds in the combustion calorimetry of organic bromine compounds. Waddington (39) has pointed out that the use of secondary reference compounds makes it possible to compare the results of different investigators and serves to control the chemical part of the investigation for a given class of compounds. It was suggested by the Standing Commission on Thermochemistry (28) in 1936 that ortho-bromobenzoic acid might be a suitable bromine compound for this purpose. para-Bromobenzoic acid was studied by Bjellerup (4) in his initial work on bromine compounds. It was decided to determine the heats of formation of the two compounds and to compare the utility of each.

Prior to the recent work of Bjellerup (4,5,6), eight investigations (2,10,25,26,27,34,35,37) had been conducted on the combustion calorimetry of bromine compounds. Most of this older work is of historical interest only, since generally it did not attain the accuracy expected in modern calorimetry. For a full discussion of prior work, see that of Bjellerup (8).

The heats of combustion of compounds containing only carbon, hydrogen, and oxygen can be determined with a precision of about 0.01% by use of static bomb calorimeters, but for most compounds that contain additional elements, the same degree of precision can be attained only by use of the moving bomb calorimeter. The first recorded attempt to use a moving bomb calorimeter is that of Popoff and Schirokich (27); their apparatus was a rocking bomb calorimeter devised to study halogen compounds. Since that time, improved rocking and rotating bomb calorimeters capable of the precision stated above have been developed, primarily at the University of Lund in Sweden and at the U. S. Bureau of Mines in Bartlesville, Oklahoma.

The principal advantage of the moving bomb calorimeter is the agitation of the solution in the bomb which brings about the rapid attainment of equilibrium between the gaseous and liquid phases and produces a homogeneous aqueous phase. In the case of bromine compounds, it is probably essential that such a calorimeter be used. It has been found that organic bromine compounds burn to form mixtures of hydrobromic acid and free bromine along with water and carbon dioxide. Such a mixture is difficult to define chemically. The reaction of free bromine with water is slow and thus not suitable for combustion calorimetry in which equilibrium must be attained rapidly. The reaction mixture may be converted to a well-defined system by adding reagents which reduce the free bromine to bromide ion, but which do not react during the rating periods with other species contained in the bomb, such as oxygen. Workers as early as Kablukov and Perelmann (25) applied this technique by using a solution of arsenic trioxide. Subsequent investigators continued to use arsenic trioxide when a reducing agent was applied (4,5,6,28,34). Comparatively large volumes of solution are required for reduction of appreciable amounts of free bromine since arsenic trioxide is not very soluble in water. With such large volumes, equilibrium cannot be attained rapidly in the final state when static bombs are used. On the other hand, in rotating bomb calorimeters, the free bromine is rapidly reduced by the arsenic trioxide, and the time necessary for gas-liquid equilibrium is minimized.

An additional part of this research was the development of a digital computer program which reduces combustion data for bromine and chlorine compounds to standard states. This program was written for a small memory computer, the IBM-650. The utility of computer calculations has been discussed by Waddington (40).

CHAPTER II

CHEMISTRY OF THE BOMB PROCESS

In the combustion calorimetry, the internal energy change of the idealized combustion reaction is the result which is calculated in the reduction to standard states. For bromine compounds, the idealized combustion reaction is represented by the equation

$$\begin{aligned} C_aH_bO_cBr_d(\underline{c} \text{ or } \underline{l}) &+ (a + b/4 - c/2)O_2(\underline{g}) \\ &\rightarrow aCO_2(\underline{g}) + b/2\ H_2O(\underline{l}) + d/2\ Br_2(\underline{l}), \end{aligned} \qquad (I)$$

where the reactants and products are in their standard states. In order to evaluate the internal energy change for this reaction, one must eliminate the energy effects associated with the side reactions and with the physical processes of thermal significance that occur during the combustion.

As pointed out in the first chapter, organic bromine compounds burn to form mixtures of hydrobromic acid, free bromine, carbon dioxide, and water. Since water is present initially, the general combustion reaction may be represented by the equation

$$\begin{aligned} C_aH_bO_cBr_d(\underline{c} \text{ or } \underline{l}) &+ (a + b/4 - c/2 + y)O_2(\underline{g}) \\ &+ [d(n + 1/2) - b/2]H_2O(\underline{l}) \\ \rightarrow [y + \frac{d(1-x)}{4}]O_2(\underline{g}) &+ d(1-x)[HBr\cdot(n + x/2)/(1-x)H_2O(\underline{aq})] \\ &+ dx/2\ Br_2(\underline{g}), \end{aligned} \qquad (II)$$

where x is the fraction of bromine which forms free bromine and y is the number of moles of excess oxygen. The free bromine is reduced by means of arsenic trioxide to hydrobromic acid according to the following equation:

$$dx/2\ Br_2(\underline{g}) + dx/4\ As_2O_3(\underline{aq}) + dx/2\ H_2O(\underline{l}) \rightarrow dx/4\ As_2O_5(\underline{aq}) + dx\ HBr(\underline{aq}). \qquad (III)$$

Addition of reactions II and III gives

$$\begin{aligned} &C_aH_bO_cBr_d(\underline{c}\text{ or }\underline{l}) + (a + b/4 - c/2 + y)O_2(\underline{g}) \\ &\quad + [d(n + 1/2) - b/2]H_2O(\underline{l}) + dx/4\ As_2O_3(\underline{aq}) \\ &\rightarrow [y + \frac{d(1-x)}{4}]O_2(g) + aCO_2(\underline{g}) + d(HBr\cdot nH_2O) \\ &\quad + dx/4\ As_2O_5(\underline{aq}). \qquad (IV)\end{aligned}$$

The heats of the following reactions may be computed from the known molar values:

$$dx/4\ As_2O_5(\underline{aq}) \rightarrow dx/4\ As_2O_3(\underline{aq}) + dx/4\ O_2(\underline{g}); \qquad (V)$$

$$d(HBr\cdot nH_2O) + d/4\ O_2(\underline{g}) \rightarrow d(n + 1/2)H_2O(\underline{l}) + d/2\ Br_2(\underline{l}). \qquad (VI)$$

Side reactions that have small but appreciable thermal effects must be considered. Nitric acid is formed from the nitrogen present in commercial oxygen:

$$1/2\ N_2(\underline{g}) + 5/4\ O_2(\underline{g}) + 1/2\ H_2O(\underline{l}) \rightarrow HNO_3(\underline{aq}). \qquad (VII)$$

If the bomb contains platinum and/or gold, Bjellerup (4) has shown that one must consider the following reactions:

$$Au(\underline{c}) + 1/2\ O_2(\underline{g}) + 2HBr(\underline{aq}) \rightarrow HAuBr_2(\underline{aq}) + 1/2\ H_2O(\underline{l}); \qquad (VIII)$$

$$Pt(\underline{c}) + 1/2\ O_2(\underline{g}) + 4HBr(\underline{aq}) \rightarrow H_2PtBr_4(\underline{aq}) + H_2O(\underline{l}). \qquad (IX)$$

Sellers, Sunner, and Wadsö (33) have determined that the ionization reaction

$$H_3AsO_4(\underline{aq}) \rightarrow H^+(\underline{aq}) + H_2AsO_4^-(\underline{aq}) \qquad (X)$$

must also be considered.

The thermal effects of the physical processes which must be considered are treated extensively by Hubbard, Scott, and Waddington (24). In addition, a correction has been applied for the evolution of gases from the bomb solutions; this is discussed in Chapter IV.

From the directly observed data, one may determine the heat effects resulting collectively from the physical processes and from reactions IV, VII, VIII, IX, and X. By proper addition and subtraction of the calculated heat effects due to the physical processes and to reactions V, VI, VII, VIII, IX, and X from this collective value, one may determine the heat of reaction I as desired.

CHAPTER III

EXPERIMENTAL

Apparatus

The calorimeter used in this research was that of the U. S. Bureau of Mines in Bartlesville, Oklahoma, with laboratory designation BMR-2. The description of "a typical apparatus" may be found in the first volume of "Experimental Thermochemistry" (38). The primary difference between the apparatus used and that described in the reference given above is that rotation was effected by a direct-drive mechanism (20). With this mechanism, the time of rotation is not limited as it was in the wire method used earlier. The automatic stopping provision was not used, but rather rotation was continued, once started, for the duration of each experiment; in this way equilibrium and homogeneity in the final state were assured, and any erratic behavior of the rotating mechanism could be observed in the final rating period (19).

The bomb used was a tantalum-lined bomb, devised by Smith (36), with laboratory designation TA-2. The only platinum parts employed in the bomb were the crucible and its supporting ring. These were readily removable and a check on the loss of platinum due to corrosion could be made by weighing. It has been shown that tantalum is inert to halogens and thus the corrosion of the bomb lining need not be considered (23).

The time and temperature observations were made respectively by use of a chronograph and a 25-ohm platinum resistance thermometer in conjunction with a Leeds and Northrup G-2 Mueller-type bridge.

Materials

The materials used for calibration of the calorimeter were benzoic and succinic acids. The benzoic acid was the National Bureau of Standards standard sample 39h with a certificate value for the heat of combustion of 26.434 ± 0.003 abs kj g^{-1} (6317.9 ± 0.7 cal g^{-1}). When the reduction to standard states was applied for the conditions specified in the certificate, the $\Delta E_c^o/M$ value was 6313.0 ± 0.7 cal g^{-1}. The succinic acid was a sample prepared by Good et al. (20), which has been found to have a heat of combustion, $\Delta E_c^o/M$, of 3019.8 ± 0.4 cal g^{-1} (18).

The ortho- and para-bromobenzoic acids were obtained from Pierce Chemical Company, Rockford, Illinois. The ortho-bromobenzoic acid was recrystallized from benzene. The para-bromobenzoic acid was recrystallized from ethanol. The recrystallized materials had sharp melting points corresponding to the literature values (22).

The dried materials from the recrystallizations were zone-refined by means of the apparatus described by Good et al. (20). Each compound was deliberately contaminated with 0.01% by weight of a commercial dye and then placed in a large tube which was temporarily sealed to the heavy-walled tubing of the zone refining apparatus. After sealing this system to a vacuum line, the pressure above the materials was maintained at less than 0.1 micron for about two hours. The system then was filled with a dry helium atmosphere and the compound was melted into the heavy-walled tubing by means of an air-bath heater. The large tube used for melting the material into the heavy-walled tubing then was removed, and the receiver was sealed in its place. The assembled tubing and receiver,

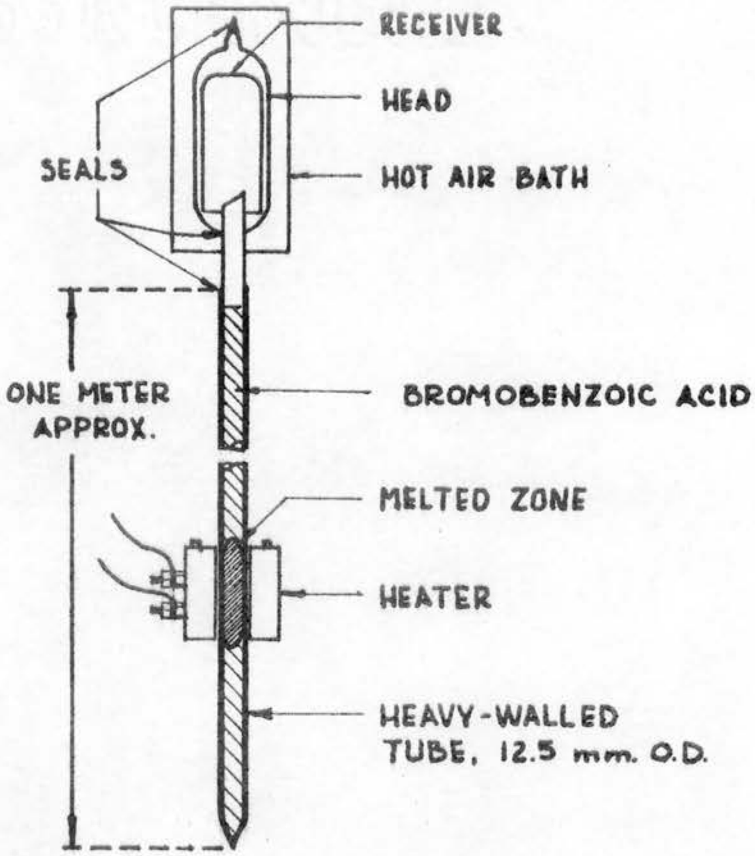

Figure 1. Zone Purification Apparatus

shown in Figure 1, were maintained at a pressure of less than 0.1 micron for two hours and then filled with dry helium. With para-bromobenzoic acid, the dye impurity was consolidated in the lower portion of the tube after thirteen heater passes. This compound did not sublime. For the ortho isomer, seven heater passes were required to remove the dye impurity. A noticeable amount of the ortho isomer sublimed into the receiver, and an air-bath heater was applied to the receiver in order to melt the material back into the tube. The upper one-half of the material in the tubing was retained in each case for use in the calorimetric experiments.

The neutralization equivalents of the materials were determined. The bromine content of the materials was determined by potentiometric titration of the solutions obtained by burning the materials in the bomb in the presence of arsenic trioxide solutions. The results are as follows:

	ortho-Bromobenzoic Acid	para-Bromobenzoic Acid
% theoretical neutralization equivalent	100.0_6	99.9_3
% theoretical bromide	99.9_3	99.8_4

Both compounds gave negative spot tests for anhydride (16).

The combustible fuse material was unmercerized cotton thread with an empirical formula of $CH_{1.774}O_{0.887}$ whose heat of combustion, $\Delta E_c^{o}/M$, was 4050 cal g^{-1} (14). The fuse wire used for igniting the thread was a platinum wire, 0.002-inch in diameter with a resistance of 0.50 ohm cm^{-1}.

Combustible materials were removed from the commercial oxygen by passing it over a bed of copper oxide at 650°C and then through a series of absorption tubes packed with chemicals in the following order:

magnesium perchlorate, Ascarite, magnesium perchlorate, and phosphorus pentoxide.

The iodine solution used for titrating bomb solutions was prepared from reagent grade iodine and potassium iodide and was standardized against arsenic trioxide, National Bureau of Standards standard sample 83a, under conditions similar to those for the bomb solutions.

The comparison experiment solution was prepared with reagent grade arsenic trioxide and arsenic pentoxide and with a non-oxidizing, constant-boiling sample of chemical grade hydrobromic acid.

The combustion experiment solution was prepared with reagent grade arsenic trioxide.

All of the above solutions were stored in a dark place after preparation to prevent photolysis.

Calorimetric Procedures

The calorimetric experiments were of three types: calibration experiments, comparison experiments, and combustion experiments. These experiments were basically the same, the only differences being in the amounts and kinds of combustible materials and in the quantity and composition of solution placed in the bomb.

In the combustion experiments, about 1.054 g of bromobenzoic acid was burned with 25 ml of 0.6336 M arsenic trioxide solution in the bomb. This amount of material produced about a one-degree temperature rise.

The calibration experiments were designed so that the temperature rise would be essentially the same as that obtained in the combustion experiments. These experiments were conducted, as nearly as practicable, under the conditions specified by the National Bureau of Standards certificate for benzoic acid but subject to the temperature-rise limitation specified above. The solution used in these experiments was one milliliter of water. These experiments were done merely as a check on the comparison experiments.

The comparison experiments were special calibration experiments designed to cancel some errors which might occur in reducing the data for bromine compounds to their standard states (19,40). These experiments were set up in such a manner that the temperature rise was virtually the same as that for the combustion experiments, and also so that the final state of the bomb was essentially the same as that in the combustion experiments. A combination of benzoic and succinic acid was used to produce the proper temperature rise and proper amount of carbon dioxide. A solution slightly over 25 ml in volume which was 0.209 M in hydrobromic acid, 0.01172 M in arsenic trioxide, and 0.0517 M in arsenic pentoxide was placed in the bomb to produce the required final solution composition. This method of calibration tends to cancel errors which might result from lack of accurate information concerning the final state of the bomb.

The operations which will be described next were executed in the same order and in as nearly the same amount of time as possible for both combustion and comparison experiments to cancel such errors as those resulting from evaporation from the calorimeter vessel and the calculation of the corrected temperature rise.

The mass of the combustibles and of the platinum placed in the bomb were determined on a microbalance as follows: (i) weigh the fuse of cotton thread 7 cm in length; (ii) weigh the platinum crucible; (iii) weigh the combination of the platinum crucible, cotton fuse and the pellet of sample to be burned; (iv) weigh the same combination as in iii plus the auxiliary material (only for comparison experiments); and (v) weigh the platinum supporting ring. The masses determined were corrected for air buoyancy.

Following the weighings, the bomb was assembled. A platinum fuse wire, 80 mm in length, was attached to the electrical contacts provided on the bomb head, and a small coil was made at the point where the thread was to be tied. The platinum supporting ring and the crucible with the sample and cotton fuse were positioned in the mountings provided on the bomb lid, and the cotton fuse was tied to the fuse wire by means of tweezers.

The solution required for the specific experiment was pipetted into the bomb; a thin film of beef tallow was placed on the bomb lip; and the assembled bomb lid was secured on the bomb. The bomb was flushed for ten minutes with oxygen at a flow rate of 400 ml per minute to remove the air contained in the bomb. The bomb valves were then closed, and the bomb was charged with oxygen to a pressure of 30.00 ± 0.05 atmospheres.

While the bomb was charged with oxygen, deionized water was placed in the calorimeter can and its temperature was adjusted to 1.5 degrees below the starting temperature. The water and the calorimeter can then were balanced against a tare to within 0.05 g. High-pressure air was blown into the calorimeter well, and the calorimeter can was wiped with tissue to insure that no water would be in the air space between the jacket and the can. The can was then placed in the calorimeter, and the electrical connections were soldered in position. The sealed bomb was positioned in the calorimeter can, and its cover was put in place. The electrodes then were attached. At this point, the bomb lid was at the bottom, and this position was retained until rotation was started. In this manner, the sensitive bomb lid was protected by the solution contained in the bomb and the hot combustible gases were directed away from it.

The heater circuit and ignition circuit were checked. The controlled-temperature calorimeter-well lids were closed, and the platinum resistance thermometer was positioned in the calorimeter can. The water in the calorimeter can was heated to a predetermined temperature just below 24°C by means of a heater coil which is a permanent part of the calorimetric system. The jacket temperature was read, and after the calorimeter had reached a uniform temperature drift, the time-temperature obsrvations for the initial rating period were recorded for eight equal temperature intervals of about 0.003 degree. The sample then was ignited, and the ignition energy was recorded by a calibrated current integrater. During the period when the temperature rose rapidly, time-temperature observations were recorded for preselected resistances at intervals varying from five to no longer than fifteen seconds. The rotation was started at the mid-point time (see Appendix A). After the calorimeter reached a uniform temperature drift, about twelve minutes after ignition, time-temperature observations were recorded at intervals of two minutes for a sixteen-minute final rating period. The temperature of the jacket was read by means of the platinum resistance thermometer to make sure that the jacket temperature had not changed by more than 0.001°C.

The bomb was discharged through the gas ports which had strips of filter paper inserted in them to catch solution coming from these ports. (Periodic checks were made to determine if complete reduction of free bromine had occured by passing the combustion gases through starchiodide solution.) The bomb was opened and carefully inspected for carbon or soot which would indicate incomplete combustion. The solution in the bomb was transferred to a 500-ml beaker by carefully pouring the bulk of the solution and then rinsing the internal parts of the entire bomb including the gas ports as well as the filter paper with distilled water.

The platinum materials were fired over a grid-top burner in preparation for another experiment. The bomb and rotating mechanism were dried with high-pressure air; the calorimeter can was drained; and the circuit leads were detached. The large rotation bearing was oiled with one drop of light-weight oil.

Analytical Procedures

The bomb solution with rinsings (about 250 ml total volume) was made basic with sodium bicarbonate solution and then was titrated with standard iodine solution to determine unoxidized arsenic trioxide. The entire solution was transferred to a 500-ml volumetric flask and diluted to volume with distilled water. The concentration of the iodine solution used for these titrations did not change during the time required for conducting the experiments. The concentrations of the arsenic trioxide in the starting solutions was checked throughout the entire course of the experiments and did not change.

The amount of nitric acid formed was determined by Devarda's method of Kjeldahl analysis on a 100 ml aliquot of the diluted bomb solution. Blanks were run using starting solutions.

Two checks were made for the reaction of platinum. One method was to determine the weight loss of the crucible and its supporting ring. It was observed that the mean weight loss per experiment was the same in the comparison and combustion experiments thus indicating that the loss was due to mechanical abrasion. The other method was an adaptation of a standard colorimetric method of analysis for platinum (32). When trace quantities of Pt(III) chloride are added to As_2O_3-As_2O_5-HBr solutions and allowed to stand forty minutes, a colored iodide complex (λ_{max} = 490 millimicrons) is formed in the basic solutions after the iodine titrations. The absorption by the complex obeys Beer's Law, and the color due to quantities of platinum of thermal significance can be discerned visually. Since no such color was observed in the bomb solutions, it was deduced that no significant amount of platinum reacted.

It was determined by independent combustion experiments that no thermally significant amount of gold reacted with bromine in the bomb used.

CHAPTER IV

CALCULATIONS AND RESULTS

Units of Measurement

The data reported are in terms of the 1961 atomic weights (12) and fundamental constants. This basis required a revision of the molar values of the heats of formation of carbon dioxide and water as well as the values of the gas constant. The original values were taken from references (30) and (31). The calculated values for the heats of formation of carbon dioxide and water were -94.0517 kcal mole^{-1} and -68.3149 kcal mole^{-1}, respectively. The values of the gas constant used were 0.0820509 l. atm mole^{-1} deg^{-1} and 1.98710 cal mole^{-1} deg^{-1}. The defined values of 0°C = 273.15°K and 1 calorie = 4.1840 absolute joules were used.

A set of weights calibrated by the National Bureau of Standards were used for calibrating the laboratory weights used. The 25-ohm platinum resistance thermometer was calibrated by the National Bureau of Standards, and the G-2 Mueller-type bridge was calibrated by Smith (36) against a National Bureau of Standards certified resistor.

Reduction to Standard States

The change in internal energy for the idealized combustion reaction (reaction I of Chapter II) was calculated by use of the computer program according to the computation form shown in Appendix B. The corrected temperature rise was determined by the mid-point time method shown in Appendix A. Two corrections were included which had not been applied in the earlier methods for reduction to standard states. One was the recent improvement by Sellers et al. (33) in treating the heat effect resulting from the ionization of arsenic acid. The other was a correction for the dependence of the solubility of gases upon temperature; the development of this correction is shown below.

The heat effects associated with the exchange of oxygen and carbon dioxide between the gaseous and aqueous phase accompanying temperature change are not significant when the solution volume is one milliliter, but they can be appreciable with the volume of solution used for compounds containing elements other than carbon, hydrogen, and oxygen. It should be noted that corrections similar to these should be made for any species contained in the bomb which is transferred from one phase to the other as a result of a change in temperature. For bromine and chlorine compounds, one only needs to be concerned with the effects associated with water, carbon dioxide, and oxygen. The correction for the transfer of water is treated in the method of Hubbard et al. (24) by use of a term B which does not depend upon the nature of the solution. This is a convenient procedure; accordingly, the correction terms for the transfer of oxygen and carbon dioxide are developed in a similar manner.

For this derivation, let n be the number of moles of a gaseous species dissolved, ΔE^* The molar internal energy of solution of the gaseous species in the aqueous phase, P the partial pressure of the particular gaseous species; furthermore, let the symbols without subscripts and the symbols with zero subscripts correspond respectively to any temperature of interest and to the reference temperature. The total change in internal energy for n moles of a gaseous species dissolving is

$$\Delta E = n\,\Delta E^*.$$

Differentiating with respect to temperature

$$\frac{d\,\Delta E}{dT} = n\frac{d\,\Delta E^*}{dT} + n\,\Delta E^*\frac{d\ln(n)}{dT} = n\left[\frac{d\,\Delta E^*}{dT} + \frac{1}{R}\left\{\frac{\Delta E^*}{T}\right\}^2\right],$$

or

$$\frac{d\,\Delta E}{dT}/n_o = \frac{n}{n_o}\left[\frac{d\,\Delta E^*}{dT} + \frac{1}{R}\left\{\frac{\Delta E^*}{T}\right\}^2\right],$$

but from the treatment of Hubbard et al. (21), $\frac{d\,\Delta E}{dT}/n_o$ is equivalent to B for the vaporization correction, and

$$\frac{n}{n_o} = \frac{K^*P}{K_o^*P_o} \doteq 1 \qquad \text{for} \quad T = 2 \text{ or } 3^oC$$

thus

$$B = \left[\frac{d\,\Delta E^*}{dT} + \frac{1}{R}\left\{\frac{\Delta E^*}{T}\right\}^2\right].$$

The terms for carbon dioxide and oxygen were symbolized $B(CO_2)$ and $B(O_2)$, and their use shown in Appendix B (items 75 and 76).

The auxiliary data [the density, ρ; the specific heat, c_p; and the pressure coefficient for the internal energy, $(\partial E/\partial P)_T$] for the combustible materials used for reduction of weights to <u>in vacuo</u> and for corrections to standard states are shown below; the values in parenthesis were estimated from compounds of similar structure.

	ρ g ml^{-1}	c_p cal deg^{-1}	$(\partial E/\partial P)_T$ cal atm^{-1} g^{-1}
Benzoic acid	1.320	0.0289	-0.0028
Succinic acid	1.564	0.287	(-0.0028)
p-Bromobenzoic acid	1.894	(0.18)	(-0.0028)
o-Bromobenzoic acid	1.929	(0.18)	(-0.0028)
Fuse	1.5	0.4	(-0.007)

The values indicated for the following factors were constant for all experiments:

Reference temperature, t_h = 25.000°C;
Initial temperature, t_i = 24.000°C;
Initial pressure of oxygen, P^i(gas) = 30.00 atm;
Bomb volume, V(bomb) = 3.412 l.;
Mass of platinum, m(Pt) = 12.75 g.

Results

The results of the calibration and comparison experiments are listed in Tables I and II respectively. The results of the combustion experiments for ortho-bromobenzoic acid and para-bromobenzoic acid are listed in Tables III and IV. In these tables, the symbols and abbreviations are those used in the tabulations of Hubbard et al. (29) with two exceptions. One is the term, ΔE_{cor} to standard states, which is the sum of items 81-85 inclusively, 87-89 inclusively, 93 and 94 of the computation form in Appendix C. The other is the term, $\mathcal{E}(\text{cont})(\Delta t_c)^*$, which is $[\mathcal{E}^i(\text{cont})(t_i - t_h) + \mathcal{E}^f(\text{cont})(25 - t_f + \Delta t_{cor})]$ according to the notation of the reference just cited.

The derived results of Table V include the molar values for ΔE_c°, the standard internal energy change of the idealized bomb reaction, ΔH_c^o, the standard enthalpy change of the same reaction, and ΔHf^o, the standard enthalpy change for the formation of the crystalline compounds from their elements in their standard states.

TABLE I

APPLIED HEAT EQUIVALENT BY CALIBRATION EXPERIMENTS[a]

m'(Benzoic Acid), g	0.63372	0.62961
m'''(Fuse), g	0.00117	0.00105
Δt_c, deg	1.00139	0.99489
m'$\Delta E_c^o/M$ (Benzoic Acid), cal	-4000.68	-3974.73
m'''$\Delta E_c^o/M$ (Fuse), cal	-4.74	-4.25
$-\Delta E_{dec}(HNO_3)$, cal	-0.14	-0.10
$-\Delta E$, cor. to std. states[b], cal	-2.92	-2.90
$-\Delta E_{ign}$, cal	-0.53	-0.57
$\mathcal{E}$(cont)$(\Delta t_c)^{*c}$, cal	4.22	4.19
$\mathcal{E}_{app}$(calor)$(-\Delta t\ )$, cal	4004.79	3978.36
$\mathcal{E}_{app}$(calor), cal deg^{-1}	3999.23	3998.79
Mean, $\mathcal{E}_{app}$(calor), cal deg^{-1}	3999.01	

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[a] 1.00 ml of water was added to the bomb.

[b] This item is the collection of several terms defined as the sum of 81-85 inclusively, 87-89 inclusively, and 93-94 inclusively, from the computation form in Appendix C.

[c] This item is the collective term defined as $\mathcal{E}^i(\text{cont})(t_i - t_h) + \mathcal{E}^f(\text{cont})(25 - t_f + \Delta t_{cor})$.

TABLE II

APPLIED HEAT EQUIVALENT BY COMPARISON EXPERIMENTS

m'(Benzoic Acid), g	0.56967	0.56896	0.56955	0.56948	0.56959	0.56974	0.56964
m"(Succinic Acid), g	0.11966	0.11900	0.11959	0.11967	0.11970	0.11944	0.11961
m'''(Fuse), g	0.00096	0.00104	0.00117	0.00119	0.00112	0.00094	0.00110
Δt_c, deg	0.98675	0.98519	0.98655	0.98672	0.98666	0.98663	0.98677
$n^f(As_2O_3)$, mole	0.0002828	0.0002835	0.0002830	0.0002833	0.0002812	0.0002818	0.0002818
$m'\Delta E_c^o/M$ (Benzoic Acid), cal	-3596.33	-3591.85	-3595.57	-3595.13	-3595.83	-3596.77	-3596.14
$m''\Delta E_c^o/M$ (Succinic Acid), cal	-361.35	-359.36	-361.14	-361.38	-361.47	-360.68	-361.20
$m'''\Delta E_c^o/M$ (Fuse), cal	-3.89	-4.21	-4.74	-4.82	-4.54	-3.81	-4.46
$-\Delta E^f_{dec}(HNO_3)$, cal	-0.21	-0.18	-0.21	-0.19	-0.19	-0.19	-0.19
$-\Delta E$, cor. to std. states[b], cal	-9.80	-9.78	-9.80	-9.80	-9.80	-9.80	-9.80
$-\Delta E_{ign}$, cal	-0.61	-0.55	-0.40	-0.47	-0.49	-0.40	-0.47
$-\Delta E_{decomp}(As_2O_5)$, cal	-0.82	-0.77	-0.81	-0.78	-0.94	-0.90	-0.90
$\mathcal{E}_{app}(cont)(\Delta t_c)^{*c}$, cal	27.01	26.97	27.01	27.01	27.01	27.01	27.01
$\mathcal{E}_{app}(calor)(-\Delta t_c)$, cal	-3945.99	-3939.73	-3945.66	-3945.56	-3946.25	-3945.55	-3946.14
$\mathcal{E}_{app}(calor)$, cal deg^{-1}	3998.98	3998.94	3999.44	3998.66	3999.60	3999.01	3999.05

Mean and standard deviation of the mean for $\mathcal{E}_{app}(calor)$, cal deg^{-1} 3999.09 ± 0.12

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[a] 25.034 ml of 0.2093 M HBr, 0.01172 M As_2O_3 and 0.05170 M As_2O_5 was added to the bomb.

[b] See footnote b, Table I.

[c] See footnote c, Table I.

TABLE III

ENERGY OF IDEALIZED COMBUSTION REACTION FOR p-BROMOBENZOIC ACID[a]

$m'(p\text{-}C_7H_5O_2Br)$, g	1.05354	1.05369	1.05350	1.05364	1.05346	1.05374	1.05324	1.05418
$m'''(\text{Fuse})$, g	0.00097	0.00112	0.00109	0.00116	0.00109	0.00103	0.00110	0.00094
Δt_c, deg	0.98255	0.98276	0.98226	0.98261	0.98234	0.98263	0.98234	0.98310
$n^f(As_2O_3)$, mole	0.0002919	0.0002919	0.0002919	0.0002934	0.0002934	0.0002931	0.0002919	0.0002929
$\mathcal{E}_{app}(\text{calor})(-\Delta t_c)$, cal	-3929.29	-3930.17	-3928.14	-3929.53	-3928.46	-3929.61	-3928.46	-3931.51
$\mathcal{E}(\text{cont})(-\Delta t_c)^{*}$[b], cal	-27.49	-27.49	-27.48	-27.49	-27.48	-27.49	-27.48	-27.50
ΔE_{ign}, cal	0.53	0.55	0.51	0.59	0.55	0.47	0.47	0.47
ΔE, cor. to std. states[c], cal	9.62	9.62	9.62	9.62	9.62	9.62	9.62	9.63
$\Delta E^f_{oxid}(HBr)$, cal	-27.66	-27.67	-27.66	-27.67	-27.66	-27.67	-27.66	-27.68
$\Delta E_{dec}(HNO_3)$, cal	0.20	0.20	0.18	0.22	0.21	0.20	0.18	0.20
$\Delta E_{decomp}(As_2O_5)$, cal	99.64	99.64	99.64	99.52	99.52	99.55	99.64	99.56
$-m'''\Delta E^\circ_c/M$ (Fuse), cal	3.93	4.54	4.41	4.70	4.41	4.17	4.46	3.81
$m'\Delta E^\circ_c/M$ $(p\text{-}C_7H_5O_2Br)$, cal	-3870.52	-3870.78	-3868.92	-3870.04	-3869.29	-3870.76	-3869.23	-3873.03
$\Delta E^\circ_c/M$ $(p\text{-}C_7H_5O_2Br)$, cal g^{-1}	-3673.83	-3673.54	-3672.44	-3673.02	-3672.94	-3673.35	-3673.65	-3673.98

Mean and standard deviation of the mean for $\Delta E^\circ_c/M$, cal g^{-1} 3673.34 ± 0.18

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[a] 24.996 ml of 0.0633_6 M As_2O_3 was added to the bomb.

[b] See footnote c, Table I.

[c] See footnote b, Table I.

TABLE IV

ENERGY OF IDEALIZED COMBUSTION REACTION FOR *o*-BROMOBENZOIC ACID[a]

m'(*o*-$C_7H_5O_2Br$), g	1.05366	1.95371	1.05349	1.05317	1.05374	1.05357	1.05342	1.05361
m'''(Fuse), g	0.00121	0.00104	0.00109	0.00113	0.00095	0.00107	0.00092	0.00098
Δt_c, deg	0.99031	0.99033	0.99027	0.98988	0.99022	0.99006	0.99000	0.99022
$n^f(As_2O_3)$, mole	0.0002962	0.0002931	0.0002916	0.0002931	0.0002942	0.0002944	0.0002919	0.0002934
$\mathcal{E}_{app}(\text{calor})(-\Delta t_c)$, cal	-3960.35	-3960.43	-3960.19	-3958.60	-3959.99	-3959.36	-3959.12	-3959.99
$\mathcal{E}(\text{cont})(-\Delta t_c)^{*b}$, cal	-27.70	-27.70	-27.70	-27.69	-27.70	-2.70	-27.69	-27.70
ΔE_{ign}, cal	0.55	0.65	0.57	0.55	0.47	0.40	0.43	0.61
ΔE, cor. to std. states[c], cal	9.63	9.63	9.62	9.62	9.62	9.62	9.62	9.62
$\Delta E_{oxid}(HBr)$, cal	-27.67	-27.67	-27.66	-27.65	-27.67	-27.67	-27.66	-27.67
$\Delta E_{dec}(HNO_3)$, cal	0.17	0.18	0.18	0.21	0.19	0.20	0.19	0.21
$\Delta E_{decomp}(As_2O_5)$, cal	29.31	99.55	99.66	99.55	99.46	99.45	99.64	99.52
$-m'''\Delta E_c^o/M$ (Fuse), cal	4.90	4.21	4.41	4.58	3.85	4.33	3.73	3.97
$m'\Delta E_c^o/M$ (*o*-$C_7H_5O_2Br$), cal	3901.16	3901.59	3901.10	3899.44	3901.77	3900.71	3900.87	3901.42
$\Delta E_c^o/M$ (*o*-$C_7H_5O_2Br$), cal g^{-1}	3702.49	3702.71	3703.03	3702.58	3702.78	3702.38	3703.05	3702.91

Mean and standard deviation of the mean for $\Delta E_c^o/M$, cal g^{-1} 3702.74 ± 0.09

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[a] See footnote a, Table III.

[b] See footnote c, Table I.

[c] See footnote b, Table I.

TABLE V

DERIVED THERMOCHEMICAL DATA AT 298.15°K FOR THE CRYSTALLINE COMPOUNDS[a]

	$\Delta E_c^\circ/M$ cal g^{-1}	ΔE_c° kcal $mole^{-1}$	ΔH_c° kcal $mole^{-1}$	ΔHf° kcal $mole^{-1}$
<u>para</u>-Bromobenzoic Acid	-3673.34 ± 0.32	-738.44 ± 0.13	-738.59 ± 0.13	-90.56
<u>ortho</u>-Bromobenzoic Acid	-3702.74 ± 0.28	-744.35 ± 0.11	-744.50 ± 0.11	-84.65

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[a] The uncertainty given is equal to twice the final "over-all" standard deviation (29).

CHAPTER V

DISCUSSION

Comparison of Results

The immediate precisions (29) of the results for ortho-bromobenzoic acid and para-bromobenzoic acid were $0.005_0\%$ and $0.002_4\%$, respectively. These compare favorably with the best results of modern combustion calorimetry on other classes of compounds.

A test on the accuracy of the method of reduction to standard states can be made by comparing the results of the comparison and calibration experiments. The value of the heat equivalent of the calorimeter from the two calibration experiments (3999.01 cal deg^{-1}) agrees quite well with that from the comparison experiments (3999.09 cal deg^{-1}). Also, the value (3998.84 cal deg^{-1}) obtained by Smith (36) in work conducted a few months earlier for chlorine compounds with a significantly different composition of the solution initially in the bomb agrees well within the uncertainty interval.

An additional test on the accuracy of the results may be made by comparison of the value of the internal energy change of the idealized combustion reaction for para-bromobenzoic acid obtained in this work with that obtained by Bjellerup (4). The values for this work and Bjellerup's work, corrected for arsenic acid ionization, are 3673.34 ± 0.18 cal g^{-1} and 3674.06 ± 0.20 cal g^{-1}, respectively, and it can be seen that these agree to within 0.02%, less than the uncertainty interval.

This agreement does not prove that systematic errors are absent since similar procedures were employed in both investigations, but it does indicate that if such errors exist, they are a result of the reduction to standard states and not due to calorimetric observations.

Selection of a Reference Substance

Beckers (1) has indicated that a reference substance in combustion calorimetry must meet the following minimum requirements: (a) it should be obtainable in a pure state; (b) it should be stable; (c) it should not be hygroscopic; (d) it should not be too volatile; (e) it should be easily compressed into pellets; and (f) it should ignite readily and react completely in the bomb. It was found that both ortho-bromobenzoic acid and para-bromobenzoic acid satisfy these requirements.

There are advantages and disadvantages to each compound. ortho-Bromobenzoic acid is too soluble in the organic solvents commonly used for recrystallization, while para-bromobenzoic acid can be recrystallized from a variety of common solvents. ortho-Bromobenzoic acid, which melts at 150°C, is more conveniently zone-purified than para-bromobenzoic acid, which melts at 250°C, but it should be noted that only about one-half as many heater passes were required to remove the same amount of impurity from ortho-bromobenzoic acid. Each compound is stable at the required temperatures as shown by heating it above the melting point in the zone-purification procedure. Both compounds are essentially non-hygroscopic and non-volatile at room temperature. The compounds could be compressed into pellets which were not fragile, and no difficulties were encountered in the ignition of either compound. The ortho-bromobenzoic acid undergoes complete combustion. In a few cases in the combustion of *para*-bromobenzoic acid, small brown specks of no significant mass were noted in the crucible, and one experiment with this compound had to be rejected owing to incomplete combustion.

Since ease of purification plays such a dominant role in the selection of reference substances, it appears that *para*-bromobenzoic acid is more suitable for use as a secondary reference compound in the combustion of organic bromine compounds than *ortho*-bromobenzoic acid even though the former compound presented minor difficulties in obtaining complete combustion; this difficulty possibly could have been a result of experimental technique, since Bjellerup (4) reported no such difficulty. Another factor favoring the use of *para*-bromobenzoic acid is that its heat of combustion now has been determined independently in two laboratories.

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APPENDIX A

CALCULATION OF THE CORRECTED TEMPERATURE RISE[1]

In rotating bomb calorimetry, the temperature rise of the calorimetric system includes the temperature rises due to (a) the energy from the processes occuring within the bomb, (b) the mechanical energy from the stirring and rotation, and (c) the exchange energy resulting from heat transfer between the calorimetric vessel and its environment. The contribution from item (a) is called the corrected temperature rise and is the quantity usually desired for further thermodynamic calculations. In the experiments described in Chapter III, the corrected temperature rise was determined by the mid-point time method introduced by Dickenson (15). This method and how it is related to a method not involving the mid-point time will be discussed in this section.

To understand the limitations and the range of use of the corrected temperature rise, it is helpful to begin the derivation of the equations necessary for calculating this result by expressing the differential equation describing the time rate of temperature change, $\dot{\theta}$, of the calorimetric vessel in terms of the following four factors: (a) $\dot{\theta}$(process) which is some unknown function for the rate due to the processes occurring in the bomb; (b) $\alpha(\theta_o - \theta)$ which is the rate due to heat transfer, according to Newton's law of cooling, where α is the leakage modulus, and θ and

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[1] The reader is referred to the selected references (13,14,15,41) for additional information concerning this type calculation.

θ_o are the temperatures of the calorimetric vessel and its environment, respectively; (c) $\dot{\theta}_{rot}$(during rotation) which is the rate due to rotation; and (d) $\dot{\theta}_{stir}$ which is the rate due to stirring. Thus,

$$\dot{\theta} = \dot{\theta}(\text{process}) + \alpha(\theta_o - \theta) + \dot{\theta}_{stir} + \dot{\theta}_{rot}(\text{during rotation}). \qquad (I)$$

Since the temperature is determined in terms of the platinum resistance thermometer, and since its resistance is nearly a linear function of temperature, it is possible and expedient to work with the observed resistances and convert the corrected resistance change to the temperature scale (12). In terms or resistance, R, the above equation becomes

$$\dot{R} = \dot{R}(\text{process}) + \alpha(R_o - R) + \dot{R}_{stir} + \dot{R}_{rot}(\text{during rotation}). \qquad (II)$$

Integration of this equation from the initial to the final time of the reaction period gives the observed resistance change as follows:

$$\Delta R_{obs} = \int_{t_i}^{t_f} \dot{R}(\text{process})dt + \int_{t_i}^{t_f} [\alpha(R_o - R) + \dot{R}_{stir} + \dot{R}_{rot}(\text{during rotation})]dt. \qquad (III)$$

The first integral on the right is the corrected resistance change ultimately desired. If one designates this term as ΔR_c, then

$$\Delta R_c = R_{obs} - \int_{t_i}^{t_f} [\alpha(R_o - R) + \dot{R}_{stir} + \dot{R}_{rot}(\text{during rotation})]dt. \qquad (IV)$$

If the "instantaneous" heat equivalent of the calorimetric vessel does not change appreciably during an experiment, the parameters α, $\dot{R}_{stir}$, and $\dot{R}_{rot}$ are constant, so the remaining integral of the last equation is as follows:

$$\Delta R_{cor} = \alpha\int_{t_i}^{t_f} (R_o - R)dt + \dot{R}_{stir}(t_f - t_i) + \dot{R}_{rot}(t_f - t_{mp}), \qquad (V)$$

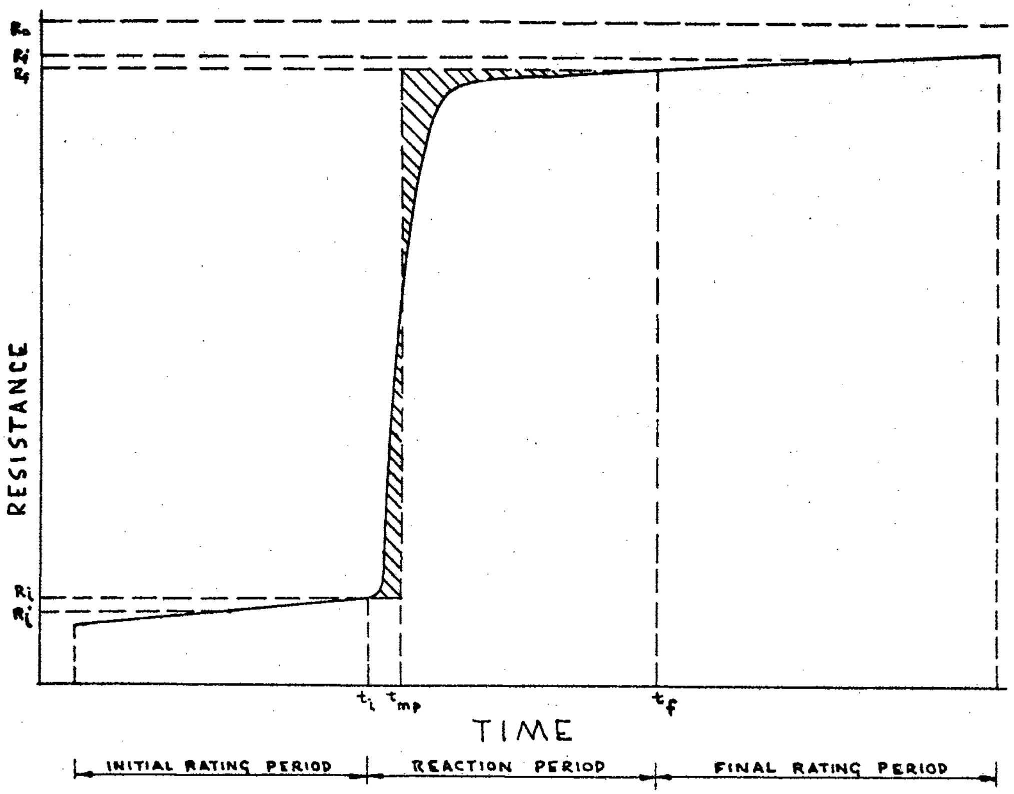

Figure 2. Time-resistance curve for a bomb-calorimetric experiment

where rotation starts at t_{mp} and continues throughout the experiment as in the method introduced by Good et al. (20).

The value of R_o cannot be measured directly since the environment temperature differs slightly from the jacket temperature as a result of heat transfer along the electrical leads and the mechanical shafts between the calorimetric vessel and the room. It is therefore necessary to relate this entity to other experimentally accessible quantities; this is the purpose of the mid-point time method. For this method, Dickenson defined t_{mp} so that the cross-hatched areas of Figure 2 be equal; this condition is represented by the equation

$$\alpha\int_{t_i}^{t_{mp}} (R - R_i)dt + \alpha\int_{t_{mp}}^{t_f} (R - R_f)dt = 0, \qquad \text{(VI)}$$

where R_i and R_f are the resistances at t_i and t_f, respectively. Rearrangement of equation V followed by addition of the last equation gives

$$\Delta R_{cor} + 0 = \alpha\int_{t_i}^{t_{mp}} (R_o - R_i)dt + \alpha\int_{t_{mp}}^{t_f} (R_o - R_f)dt + \dot{R}_{stir}(t_f - t_i) + \dot{R}_{rot}(t_f - t_{mp}). \tag{VII}$$

If one recognizes the integrands of this equation are constant, then further integration and rearrangement gives the following equation:

$$\Delta R_{cor} = [\alpha(R_o - R_i) + \dot{R}_{stir}](t_{mp} - t_i) + [\alpha(R_o - R_f) + \dot{R}_{stir} + \dot{R}_{rot}(t_f - t_{mp}), \tag{VIII}$$

but $\alpha(R_o - R_i)$ and $\alpha(R_o - R_f)$ are the rates due to Newtonian heat exchange at t_i and t_f respectively, so the combined rates due to exchange and mechanical factors at these times are

$$\dot{R}_i = \alpha(R_o - R_i) + \dot{R}_{stir} \tag{IX}$$

$$\dot{R}_f = \alpha(R_o - R_f) + \dot{R}_{stir} + \dot{R}_{rot}. \tag{X}$$

Thus, the resistance correction becomes

$$\Delta R_{cor} = \dot{R}_i(t_{mp} - t_i) + \dot{R}_f(t_f - t_{mp}). \tag{XI}$$

This is the point at which the derivation for the mid-point time method is stopped and the factors entering the calculation are evaluated from experimental data, but this equation may be simplified further. In order to make this simplification, it is necessary to see how t_{mp} is evaluated. By the requirement that the cross-hatched areas of Figure 2 be equal, it follows that area C in Figure 3 meets the following condition:

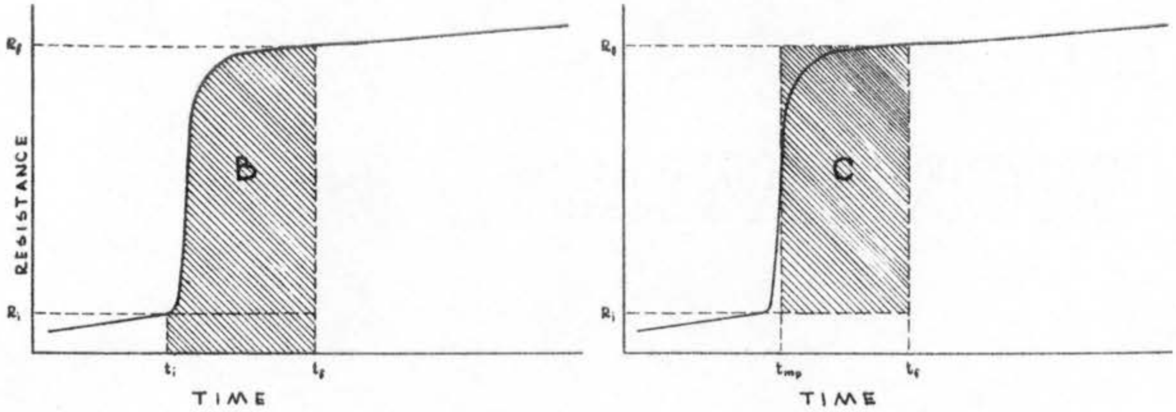

Figure 3. Areas associated with the time-resistance curve used for calculating the mid-point time.

$$C = B - R_i(t_f - t_i) = (t_f - t_{mp})(R_f - R_i), \qquad \text{(XII)}$$

where area B is shown in Figure 3 and is determined by

$$B = \int_{t_f}^{t_i} R\,dt. \qquad \text{(XIII)}$$

Solving equation XII for t_{mp}, one obtains

$$t_{mp} = t_f - [B - R_i(t_f - t_i)]/(R_f - R_i). \qquad \text{(XIV)}$$

If one substitutes

$$\dot{R}_i = \dot{R}_f + \alpha(R_f - R_i) - \dot{R}_{rot} \qquad \text{(XV)}$$

into equation XI, then factors out $\dot{R}_{rot}(t_{mp} - t_i)$ and redesignates it $\dot{R}_{rot}(t_{rot} - t_i)$ and finally substitutes t_{mp} in the resulting equation, one obtains

$$\Delta R_{cor} = \dot{R}_f(t_f - t_i) + \alpha[R_f(t_f - t_i) - B] - \dot{R}_{rot}(t_{rot} - t_i). \qquad \text{(XVI)}$$

This equation is essentially the same as another equation used for calculating the corrected temperature rise [for an example, see Coops (14)], and this result also may be obtained by introducing R_f in equation V in the following manner:

$$\Delta R_{cor} = \alpha\int_{t_i}^{t_f} (R_f - R)dt + \alpha(R_o - R_f)(t_f - t_i) + \dot{R}_{stir}(t_f - t_i) + \dot{R}_{rot}(t_f - t_{mp}), \qquad \text{(XVII)}$$

but by use of equation IX, this becomes

$$\Delta R_{cor} = \alpha\int_{t_i}^{t_f} (R_f - R)dt + \dot{R}_f(t_f - t_i) - \dot{R}_{rot}(t_{rot} - t_i), \qquad \text{(XVIII)}$$

and integration of this equation gives equation XVI.

It remains to be shown how the factors t_i, R_f, $\dot{R}_i$, $\dot{R}_f$, and B are determined analytically from experimental data. Straight lines are fitted by the method of least-squares to the data of the initial and final rating periods to obtain the values of t_i as well as the slopes. The slopes of these lines are considered to be equal to the tangents at the mid-points of the rating periods. The final rate normally contains the essentially constant contribution due to rotation, and one may determine this contribution in an independent experiment as the difference in the rates observed successively with and without rotation. The rotation rate is subtracted from the final rate to obtain the final rate due to exchange and stirring at the mid-points of the inital and final periods. One may determine α, the leakage modulus, from the equation

$$\alpha = - \frac{(\dot{R}_i)_{obs} - [(\dot{R}_f)_{obs} - \dot{R}_{rot}]}{(R_i' - R_f')}, \qquad \text{(XIX)}$$

where $(\dot{R}_i)_{obs}$ and $(\dot{R}_f)_{obs}$ are the least-squares slopes for the initial and final observed rates and where R_i' and R_f' are the resistances at the mid-points of the rating periods. One may determine the rates $\dot{R}_i$ and $\dot{R}_f$ by use of α as follows:

$$\dot{R}_i = (\dot{R}_i)_{obs} - \alpha(\Delta R/2)_i; \tag{XX}$$

$$\dot{R}_f = (\dot{R}_f)_{obs} + \alpha(\Delta R/2)_f, \tag{XXI}$$

where the ΔR's are the resistance changes during the rating periods.

The area B is determined by numerical integration (trapezoidal rule) according to the following equation:

$$B = \sum_{t_j = t_i}^{t_{j+1} = t_f} (t_{j+1} - t_j)(R_{j+1} + R_j)/2 \ . \tag{XXII}$$

From the foregoing development, one may formulate the corrected temperature rise in terms of variables which are readily evaluated as follows: for the mid-point time method

$$\Delta\theta_c = k[(R_i - R_f) - \dot{R}_i(t_{mp} - t_i) - \dot{R}_f(t_f - t_{mp})], \tag{XXIII}$$

and for the expression not involving the mid-point time

$$\Delta\theta_c = k[(R_i - R_f) - \dot{R}_f(t_f - t_i) - \alpha\int_{t_i}^{t_f} (R_f - R)dt + \dot{R}_{rot}(t_{rot} - t_i)], \tag{XXIV}$$

where k is the proportionality constant between the temperature and the resistance of the platinum resistance thermometer. The methods used for evaluating this correction give a sufficient degree of accuracy when one employs calibration experiments that yield time-resistance curves nearly identical to those obtained in combustion experiments since this near duplication ultimately cancels the small errors arising from the individual calculations.

APPENDIX B

TABULATION FOR THE REDUCTION TO STANDARD STATES

The form below closely follows that of Bjellerup (7) and is extended so that either bromine or chlorine compounds may be treated. This extension was made for writing the computer program. The data incorporated in the computation form and the auxiliary data necessary for the calculations was obtained from similar tabulations of this type or by similar procedures employed for such tabulations (7, 19, 24, 36). The calculations for a comparison experiment was chosen for an illustration. The reference temperature, t_h, for the reaction is $25^\circ C$.

(a) Initial State

(1*)	Formula of compound, $C_{a'}H_{b'}O_{c'}X_{d'}$	$C_7H_6O_2$
(2*)	m', mass of compound	0.56964 g
(3*)	M', molecular weight of compound	122.125 g $mole^{-1}$
(4)	$n' = m'/M'$	0.0046644 mole
(5*)	ρ', density of compound	1.320 g ml^{-1}
(6)	$V' = m'/1000\,\rho'$	0.0004 l.
(7*)	Formula of auxiliary material, $C_{a''}H_{b''}O_{c''}$	$C_4H_6O_4$
(8*)	m", mass of auxiliary material	0.11961 g
(9*)	M", molecular weight of auxiliary material	118.090 g $mole^{-1}$
(10)	$n'' = m''/M''$	0.0010129 mole
(11*)	ρ'', density of auxiliary material	1.564 g ml^{-1}

(12)	$V'' = m''/1000\,\rho''$	0.0001 l.
(13*)	Formula of fuse, $C_{a'''}H_{b'''}O_{c'''}$	$CH_{1.774}O_{0.887}$
(14*)	m''', mass of fuse	0.00110 g
(15*)	M''', molecular weight of fuse	27.991 g mole^{-1}
(16)	$n''' = m'''/M'''$	0.0000393 mole
(17*)	ρ''', density of fuse	1.5 g ml^{-1}
(18)	$V''' = m'''/1000\rho'''$	0.0000 l.
(19)	$a = n'a' + n''a'' + n'''a'''$	0.0367416
(20)	$b = n'b' + n''b'' + n'''a'''$	0.0341334
(21)	$c = n'c' + n''c'' + n'''a'''$	0.0134151
(22)	$d = n'd' + n''d'' + n'''a'''$	0.0000000
(23)	$m(\text{sub.}) = m' + m'' + m'''$	0.69035 g
(24)	$M(\text{sub.}) = 12.0111a + 1.0097b + 15.999c$	
	(if $x = Br$) $+ 79.909d$ or	
	(if $x = Cl$) $+ 35.543d$	0.69035 g
(25)	$n(\text{sub.}) = m(\text{sub.})/M(\text{sub.})$	1.00000
(26*)	$V(\text{bomb})$	0.3403 l.
(27*)	$V^i(\text{soln.})$	0.02503 l.
(28*)	$P^i(\text{gas})$	30.00 atm
(29*)	$C^i(As_2O_3)$	0.01172 mole l.$^{-1}$
(29a*)	$C^i(As_2O_5)$	0.05170 mole l.$^{-1}$
(29b*)	$C^i(HX)$	0.2093 mole l.$^{-1}$
(29c)	$n^i(As_2O_3) = C^i(As_2O_3)V^i(\text{soln.})$	0.0002934 mole
(29d)	$n^i(As_2O_5) = C^i(As_2O_5)V^i(\text{soln.})$	0.0012943 mole
(29e)	$n^i(HX) = C^i(HX)V^i(\text{soln.})$	0.005241 mole
(29f)	$\rho^i(\text{soln.}) = 0.997 + [0.785n^i(As_2O_3)197.84$	
	$+ 0.808n^i(As_2O_5)229.84 + 0.710n^i(HBr)30.917$	
	$+ 0.49n^i(HCl)36.461]/m^i(\text{soln.})$	1.0201 g ml^{-1}

The value of ρ^i(soln.) was determined by reiteration; in the first calculation, m^i(soln.) was approximated by $0.997V^i$(soln.).

(29g) g^i 0.9920

(29h) $K^i(O_2) = 0.001296 - 0.0000845C^i(HX)$ 0.001279 mole l.$^{-1}$ atm^{-1}

This equation was determined from a combination of the data of Bohr and Boch (9) and Geffcken (17), where it it was assumed that the solubility of O_2 in the bomb solutions was the same as in HCl solutions.

(29j) $D^i(O_2) = 0.951 - 0.0023[P^i(\text{gas}) - 20]$ 0.928

(29k) $K^{*i}(O_2) = D^i(O_2)K^i(O_2)$ 0.001186 mole l.$^{-1}$ atm^{-1}

(30) $n^i(H_2O \text{ tot.}) = [V^i(\text{soln})\rho^i(\text{soln})$
$- 197.84n^i(As_2O_3) - 229.84n^i(As_2O_5)$
$- 80.917n^i(HBr) - 36.461n^i(HCl)]/18.015$ 1.3743 mole

(31) $V^i(\text{gas}) = V(\text{bomb}) - V^i(\text{soln})$
$- V' - V'' - V'''$ 0.3147 l.

(32) $n^i(H_2O \text{ vap.}) =$
$g^i[0.02304 + 0.00008P^i(\text{gas})]V^i(\text{gas})/18.015$ 0.000441 mole

(33) $n^i(H_2O \text{ liq.}) = n^i(H_2O \text{ tot.})$
$- n^i(H_2O \text{ vap.})$ 1.3738 mole

(34) $n^i(\text{gas}) = \dfrac{P^i(\text{gas})V^i(\text{gas})}{24.465[1 - 0.000608P^i(\text{gas})]}$ 0.3931 mole

(35) $n^i(O_2 \text{ diss.}) =$
$K^{*i}(O_2)V^i(\text{soln.})[P^i(\text{gas}) - P^i(H_2O \text{ vap.})]$ 0.000890 mole

(36) $n^i(O_2 \text{ tot.}) =$
$n^i(\text{gas}) - n^i(H_2O \text{ vap.}) + n^i(O_2 \text{ diss.})$ 0.3936 mole

(b) Final State

(37*)	$n^f(HNO_3)$	0.000014 mole
(38*)	$n^f(As_2O_3)$	0.0002818 mole
(38a)	$\Delta n(As_2O_5) = n^i(As_2O_3) - n^f(As_2O_3)$	0.0000116 mole
(38b)	$n^f(As_2O_5) = n^i(As_2O_5) + \Delta n(As_2O_5)$	0.0013060 mole
(39)	$n^f(HX) = d + n^i(HX)$	0.005241 mole
(40)	$n^f(H_2O\ liq.) = n^i(H_2O\ liq.)$ $+ (b - d)/2 - 1/2\ n^f(HNO_3)$	1.3909 mole
(41)	$m^f(soln.) = 18.015n^f(H_2O\ liq.)$ $+ 197.84n^f(As_2O_3) + 229.84n^f(As_2O_5)$ $+ 80.917n^f(HBr) + 36.461n^f(HCl)$	25.837 g
(44)	$\rho^f(soln.) = 0.9970 + [0.785n^f(As_2O_3)197.84$ $+ 0.808n^f(As_2O_5)229.84 + 0.710n^f(HBr)80.917$ $+ 0.49n^f(HCl)36.461]/m^f(soln.)$	1.0199 g ml^{-1}
(45)	$V^f(soln.) = m^f(soln.)/\rho^f(soln.)$	0.02533 l.
(49)	$V^f(gas) = V(bomb) - V^f(soln.)$	0.3149 l.
(50)	$n^f(CO_2\ tot.) = a$	0.036742 mole
(51)	$K(CO_2)$	0.0336 mole $l.^{-1}$ atm^{-1}
(52)	$D(CO_2) = 0.914 - x(CO_2)[0.14 - 0.025x(CO_2)]$ $- [P^f(gas) - 30][0.0041 + 0.005x(CO_2)$ $- 5\{P^f(gas) - 20\}\ 10^{-6}]$	0.859

This item and the items through 63 also were calculated by a reiterative process. The mole fraction of CO_2 for the first calculation was approximated by

$$x(CO_2) \doteq n^f(CO_2\ tot.)/n^f(O_2\ tot.) + n^f(H_2O\ vap.) + n^f(CO_2\ tot.).$$

(53)	$K^*(CO_2) = D(CO_2)K(CO_2)$	0.02886 mole $l.^{-1}$ atm^{-1}

(54) $n^f(\mathrm{CO_2\ diss.}) = \dfrac{24.465K^*(\mathrm{CO_2})V^f(\mathrm{soln.})/V^f(\mathrm{gas})}{1 + 24.465K^*(\mathrm{CO_2})V^f(\mathrm{soln.})/V^f(\mathrm{gas})}$ 0.001974 mole

(55) $n^f(\mathrm{CO_2\ gas}) = n^f(\mathrm{CO_2\ tot.}) - n^f(\mathrm{CO_2\ diss.})$ 0.034767 mole

(56) $n^f(\mathrm{O_2\ tot.}) = n^i(\mathrm{O_2\ tot.})$
$- \{a + [(b - d)/2 - c]\}/2 - \Delta n(\mathrm{As_2O_5})$
$- 7/4\ n^f(\mathrm{HNO_3})$ 0.3550 mole

(57) $K^f(\mathrm{O_2}) = 0.001296$
$-0.0000845n^f(\mathrm{HX})/V^f(\mathrm{soln.})$ 0.001278 mole $\mathrm{l.}^{-1}$ atm^{-1}

See item 29h for comments.

(58) $D^f(\mathrm{O_2}) = 0.951 - x(\mathrm{CO_2})[0.04 - 0.025x(\mathrm{CO_2})]$
$- [P^f(\mathrm{gas}) - 20][0.0023 + 0.002x(\mathrm{CO_2})]$ 0.924

(59) $K^{*f}(\mathrm{O_2}) = D^f(\mathrm{O_2})K^f(\mathrm{O_2})$ 0.001181 mole $\mathrm{l.}^{-1}$ atm^{-1}

(60) $n^f(\mathrm{O_2\ diss.}) = \dfrac{24.465K^{*f}(\mathrm{O_2})V^f(\mathrm{soln.})/V^f(\mathrm{gas})}{1 + 24.465K^{*f}(\mathrm{O_2})V^f(\mathrm{soln.})/V^f(\mathrm{gas})}$ 0.000823 mole

(61) $n^f(\mathrm{O_2\ gas}) = n^f(\mathrm{O_2\ tot.}) - n^f(\mathrm{O_2\ diss.})$ 0.3542 mole

(62) $n^f(\mathrm{gas}) = n^f(\mathrm{O_2\ gas}) + n^f(\mathrm{CO_2\ gas})$
$+ n^f(\mathrm{H_2O\ vap.})$ 0.3894 mole

(63) $x(\mathrm{CO_2}) = n^f(\mathrm{CO_2\ gas})/n^f(\mathrm{gas})$ 0.08929

(64) $\mu^f(\mathrm{gas}) =$
$0.000608\{1 - 3.12x(\mathrm{CO_2})[1 + 1.33x(\mathrm{CO_2})]\}$ 0.000802 atm

(65) $P\ (\mathrm{gas}) = \dfrac{1}{\mu^f(\mathrm{gas}) + [V^f(\mathrm{gas})/24.465n^f(\mathrm{gas})]}$ 29.53 atm

(66) g^f 0.992

(67) $n^f(H_2O\ \text{vap.}) = g^f\{0.02304 + [0.00008 + 0.000040x(CO_2)]P^f(\text{gas})\}V^f(\text{gas})/18.015$ 0.000459 mole

(c) Energy Factors and Calorimetric Data

(68*) $(\partial E/\partial P)_T' = -24.22T_h(\partial V/\partial T)_P'$ -0.0028 cal g^{-1} atm^{-1}

(68a*) $(\partial E/\partial P)_T'' = -24.22T_h(\partial V/\partial T)_P''$ -0.0028 cal g^{-1} atm^{-1}

(68b*) $(\partial E/\partial P)_T''' = -24.22T_h(\partial V/\partial T)_P'''$ -0.007 cal g^{-1} atm^{-1}

(69) $(\partial E/\partial P)_T^i(\text{soln.}) = -24.22T_h(\partial V/\partial T)_P^i(\text{soln.})$ -0.00170 cal g^{-1} atm^{-1}

(69a) $(\partial E/\partial P)_T^f(\text{soln.}) = -24.22T\ (\partial V/\partial T)_P^f(\text{soln.})$ -0.00170 cal g^{-1} atm^{-1}

(70) $\Delta E'(HX)$ -5280 cal $mole^{-1}$

This term may be the molar value, either for the heat of dilution of the initial hydrogen halide solution as in the method employed by Smith (36), or for the heat of oxidation of the initial hydrogen halide solution as in the method employed by Bjellerup (7). The value for this example is the heat of oxidation.

(70a) $\Delta E'_{decomp}(As_2O_5) =$

$$\left\{77.04 + \frac{3.38(0.00562)}{[H^+] + 0.00562}\right\}10^3$$ 77130 cal $mole^{-1}$

This value is a combination of values for the reactions $H^+(aq) + H_2AsO_4^-(aq) = H_3AsO_4(aq)$ and $As_2O_5(aq) = As_2O_3(aq) + O_2(g)$. From a combination of recent experimental data (33) and Bjellerup's (3) value, it may be shown that

$$\Delta E_{decomp}(As_2O_5) = 77.04 + \frac{3.88K_a}{[H^+] + K_a} \text{ kcal mole}^{-1}$$

where $[H^+]$ is the activity of the hydrogen ion and K_a is the ionization constant for the first ionization step of H_3AsO_3.

(71) $\Delta E'_{soln}(O_2) = -2410 + 460C^i(HX)$ -2315 cal mole^{-1}

This relationship was determined from a combination of the data of Bohr and Boch (9) and Geffcken (17), where the heat of solution of oxygen was assumed to be the same as for hydrochloric acid solutions.

(71a) $\Delta E''_{soln}(O_2) = -2410$
$+ 460n^f(HX)/V^f(\text{soln.})$ -2315 cal mole^{-1}

(71b) $\Delta E_{soln}(CO_2)$ -3890 cal mole^{-1}

(71c) $\Delta E''(HX)$ -5279 cal mole^{-1}

See item 70 for comments.

(71d) $\Delta E''_{decomp}(As_2O_5)$ 77130 cal mole^{-1}

See item 70a for comments.

(72*) $\Delta E_c^o/M$ (auxiliary material) -3019.80 cal g^{-1}

(73*) $\Delta E_c^o/M$ (fuse) -4050 cal g^{-1}

(74*) $\mathcal{E}_{app}(\text{calor.})$ 3999.05 cal deg^{-1}

For a comparison experiment, this is the last item to be calculated and is determined by

$$\mathcal{E}_{app}(\text{calor.}) = -[\Delta E_{I.B.P.} - \mathcal{E}^i(\text{cont.})(t_i - 25) - \mathcal{E}^f(\text{cont.})(25 - t_f + \Delta t_{corr}) - \Delta E_{ign}]/\Delta t_c$$

(75) $\mathcal{E}^i(\text{cont.}) = 5.056n^i(O_2 \text{ tot.})$
$+ A^iV^i(\text{soln.})\rho^i(\text{soln.}) + 550n^i(H_2O \text{ vap.})$
$+ B(O_2)n^i(O_2 \text{ diss.}) + C_p'm' + C_p''m'' + C_p'''m'''$
$+ 0.0317m(Pt) + 0.17m(\text{glass})$ 27.38 cal deg^{-1}

See Chapter IV for the definition of $B(O_2)$ and $B(CO_2)$. For evaluating $B(O_2)$, the temperature coefficient can be represented by the equation,

$$\frac{d\Delta E^*_{soln}(O_2)}{dT} = 32.5 + 25C(HX) \text{ cal mole}^{-1} \text{ deg}^{-1};$$

this equation was obtained with the same data and assumptions that were used in items 71 and 71a.

(76) $\mathcal{E}^f(\text{cont.}) = 5.056n^f(O_2\text{ tot.})$
$+ 7.251n^f(CO_2\text{ tot.}) + A^f m^f(\text{soln.})$
$+ 550n^f(H_2O\text{ vap.}) + B(O_2)n^f(O_2\text{ diss.})$
$+ B(CO_2)n^f(CO_2\text{ diss.}) + 0.0317m(\text{Pt})$
$+ 0.17m(\text{glass})$ 27.81 cal deg^{-1}

The temperature coefficient (44 cal mole^{-1} deg^{-1}) from the data of Harned and Davis (21) was used to evaluate $B(CO_2)$.

(77*) ΔE_{ign} 0.47 cal

(78*) t_i 24.000°C

(79*) t_f 24.991°C

(80*) Δt_{corr} 0.00400 deg

(80a*) Δt_c, corrected temperature rise 0.98677 deg

(d) <u>Changes in Internal Energy</u>

(81) $\Delta E^i_{\text{vap}}(H_2O) = 9922n^i(H_2O\text{ vap.})$ 4.37 cal

(82) $\Delta E^i(\text{soln.})\Big]_1^{P^i(\text{gas})} =$
$(\partial E/\partial P)^i_T(\text{soln})V^i(\text{soln.})\rho^i(\text{soln.})[P^i(\text{gas}) - 1]$
-1.26 cal

(83) $\Delta E^i(\text{sub.})\Big]_1^{P^i(\text{gas})} = [m'(\partial E/\partial P)'_T$
$+ m''(\partial E/\partial P)''_T + m'''(\partial E/\partial P)'''_T][P^i(\text{gas}) - 1]$ -0.06 cal

(84) $\Delta E^i_{\text{soln}}(O_2) = \Delta E'_{\text{soln}}(O_2)n^i(O_2\text{ diss.})$ -2.06 cal

(85) $\Delta E^i(\text{gas})\Big]_0^{P^i(\text{gas})} =$
$-1.574P^i(\text{gas})n^i(\text{gas})$ -18.56 cal

(85a) $\Delta E^i(HX) = -\Delta E'(HX)n^i(HX)$ 27.67 cal

(85b) $\Delta E^{i}_{decomp}(As_2O_5) =$

$- \Delta E'_{decomp}(As_2O_5) n^{i}(As_2O_5)$ -99.83 cal

(86) $\Delta E_{I.B.P.} = -\mathcal{E}_{app}(calor.) \Delta t_c$

$+ \mathcal{E}^{i}(Cont.)(t_i - 25) + \mathcal{E}^{f}(cont.)(25 - t_f + \Delta t_{corr})$

$+ \Delta E_{ign}$ -3972.69 cal

For a comparison experiment, this item is calculated after the items which follow are calculated. In such a case, $\Delta E_{I.B.P.}$ is the difference between item 95 and the sum of items 85 through 94.

(87) $\Delta E^{f}_{soln}(CO_2) =$

$\Delta E_{soln}(CO_2) n^{f}(CO_2 \text{ diss.})$ 7.68 cal

(88) $\Delta E^{f}_{soln}(O_2) =$

$\Delta E''_{soln}(O_2) n^{f}(O_2 \text{ diss.})$ 1.90 cal

(89) $\Delta E^{f}(soln.)\Big]^{1}_{P^f(gas)} =$

$(\partial E/\partial P)^{f}_{T}(soln) m^{f}(soln.)[1 - P^{f}(gas)]$ 1.25 cal

(90) $\Delta E^{f}_{decomp}(As_2O_5) =$

$\Delta E''_{decomp}(As_2O_5) n^{f}(As_2O_5)$ 100.73 cal

(91) $\Delta E^{f}(HX) = \Delta E''(HX) n^{f}(HX)$ -27.66 cal

(92) $\Delta E^{f}_{decomp}(HNO_3) =$

$\Delta E_{decomp}(HNO_3) n^{f}(HNO_3)$ 0.19 cal

(93) $\Delta E^{f}(gas)\, {}^{0}_{P^f(gas)} =$

$\left\{1.574 + 1 + 1.69x(CO_2)[1 + x(CO_2)]\right\} P^{f}(gas) n^{f}(gas)$

21.07 cal

(94) $\Delta E^{f}_{vap}(H_2O) = -9922 n^{f}(H_2O \text{ vap.})$ -4.55 cal

(95) $n \Delta E^{o}_{c}(sub.)$, sum of items 81-84 incl. -3961.79 cal

For a comparison experiment, this item is the sum of items 96, 97, and 98.

(96)	$m'' \Delta E_c^\circ/M$ (auxiliary material)	-361.20 cal
(97)	$m''' \Delta E_c^\circ/M$ (fuse)	-4.46 cal
(98)	$n' \Delta E_c^\circ(\text{compound}) = n \Delta E_c^\circ(\text{sub.})$ $- m'' \Delta E_c^\circ/M$ (auxiliary material) $- m''' \Delta E_c^\circ/M$ (fuse) For a comparison experiment, this item is $m' \Delta E_c^\circ/M$ (benzoic acid).	-3596.14 cal
(99)	$\Delta E_c^\circ/M(\text{compound}) = n' \Delta E_c^\circ(\text{compound})/m'$	-6313.01 cal g^{-1}
(100)	$\Delta E_c^\circ(\text{compound}) = n' \Delta E_c^\circ(\text{compound})/1000n'$	-770.98 kcal $mole^{-1}$

APPENDIX C

LIMITATIONS AND APPLICATIONS OF THE COMPUTER PROGRAM

Time and space will not permit an inclusion of all of the details pertaining to the computer program written in this research. Its range of use, the information necessary for its use, and the information one may obtain from it will be indicated in this section.

The program was written in symbolic machine language (SOAP) for the IBM-650 to reduce data for organic chlorine and bromine compounds (for which As_2O_3 is used as a reducing agent) to standard states. It does not reduce weights to in vacuo or calculate the corrected temperature rise. It will calculate from one to eight combustion, comparison, or calibration experiments per pass.

The necessary input data may be determined from Table VI. The numbers shown in this table indicate the drum locations where the information must be stored. If chlorine compound data is calculated, then the heat of dilution of the hydrogen chloride must also be entered in location 0549 for the inital value and in locations 0550 through 0557 for the final values.

An example of the data output is shown in Table VII; the meaning of the symbolism in this table may be inferred from Appendix B and Table IV. If figures appear only in the first column of results in this table, the items are considered constant for a set of experiments and are calculated one time for that particular set. The decimal point is in the seventh place from the right for items 1 through 67 and is in the fifth place from the right for the items thereafter. The sign of each number is to the right of the number. Any black spaces should be considered zeros.

TABLE VI

INPUT DATA SHEET FOR THE COMPUTER PROGRAM

Name of compound ____________ Experiment Type Date ____________

Type of compound	Br	0	0249
	Cl	1	

Combustion		0	0000
Comparison		1	

Title	1	2	3	4	5	6	7	8	# Exp's
Exp. #									0268
m'	0050	0051	0052	0053	0054	0055	0056	0057	
m''	0060	0061	0062	0063	0064	0065	0066	0067	
m'''	0070	0071	0072	0073	0074	0075	0076	0077	
ΔE_{ign}	0210	0211	0212	0213	0214	0215	0216	0217	R_i
R_f	0230	0231	0232	0233	0234	0235	0236	0237	0229
Δt_c	0240	0241	0242	0243	0244	0245	0246	0247	
$n^f(As_2O_3)$	0280	0281	0282	0283	0284	0285	0286	0287	
$n^f(HNO_3)$	0270	0271	0272	0273	0274	0275	0276	0277	
m(glass)	0220	0221	0222	0223	0224	0225	0226	0227	

	a	b	c	d	density	MW	c_p	$(\partial E/\partial P)_T$	$\Delta E^o_c/M$
Compound	0250	0253	0256	0259	0004	0001	0030	0033	
Aux. mat.	0251	0254	0257	0260	0005	0002	0031	0034	0045
Fuse	0252	0255	0258	0261	0006	0003	0032	0035	0046

m(Pt)	0269	Glass	0024		0026
$c^i(As_2O_3)$	0278	$c^i(As_2O_5)$	0288	$c^i(HBr)$	0298

	g	$\partial E/\partial P$ (soln)	$E_{sol}(O_2)$	A	Apprx. t°C
Initial	0012	0048	0268	0021	0266
Final	0022	0044	0043	0040	0267

Therm. Consts.	
R_o	0263
	0264
	0265

V_i(soln.)	0027
V(bomb)	0016
P_i(gas)	0028
$B(O_2)$	0679
$K^{*i}(O_2)$	0037
$K^f(O_2)$	0019
$K^f(CO_2)$	0018
$\Delta E_{sol}(CO_2)$	0042

TABLE VII

EXAMPLE OF OUTPUT DATA FROM THE COMPUTER PROGRAM

```
 COMBUSTN   EXPMNTS      FOR ORTHO    BROMO        BENZOIC      ACID

1    FORM1
2    M1        10536600+    10537100+    10534900+    10531700+    10537400+    10535700+    10534200+    10536100+
3    MW1     2010260000+
4    N1           52414+       52417+       52406+       52390+       52418+       52410+       52402+       52412+
5    RHO1      19290000+
6    V1            5462+        5462+        5461+        5460+        5463+        5462+        5461+        5462+
7    FORM2
8    M2
9    MW2     1180900000+
10   N2
11   RHO2      15640000+
12   V2
13   FORM3
14   M3           12100+       10400+       10900+       11300+        9500+       10700+        9200+        9800+
15   MW3      279908000+
16   N3             432+         372+         389+         404+         339+         382+         329+         350+
17   RHO3      15000000+
18   V3               8+           7+           7+           8+           6+           7+           6+           7+
19   A           367331+      367288+      367229+      367132+      367266+      367250+      367144+      367232+
20   B           262837+      262742+      262719+      262665+      262693+      262726+      262594+      262679+
21   C           105212+      105163+      105157+      105138+      105137+      105158+      105096+      105134+
22   D            52414+       52417+       52406+       52390+       52418+       52410+       52402+       52412+
23   MSSUB     10548700+    10547500+    10545800+    10543000+    10546900+    10546400+    10543400+    10545900+
24   MWSUB     10548684+    10547484+    10545784+    10542984+    10546885+    10546384+    10543384+    10545884+
25   NSUB      10000015+    10000015+    10000015+    10000015+    10000014+    10000015+    10000015+    10000015+
26   VBOMB      3402794+
27   VISOL       249960+
28   PIGAS    300000000+
29   CIAO3       633600+
29A  CIAO5
29B  CIHX
29C  NIAO3        15837+
29D  NIAO5
29E  NIHX
29F  DISOL     10067739+
29G  GI         9980000+
29H  KSIO2        12020+
30   NIHOT     13794937+
31   VIGAS      3147364+     3147365+     3147366+     3147367+     3147365+     3147366+     3147367+     3147366+
32   NIHOV         4436+        4436+        4436+        4436+        4436+        4436+        4436+        4436+
33   NIHOL     13790501+
34   NIGAS      3931315+     3931317+     3931318+     3931319+     3931317+     3931317+     3931319+     3931318+
35   NIODS         9002+
36   NIO2T      3935881+     3935883+     3935884+     3935885+     3935883+     3935883+     3935885+     3935884+
37   NFHNO          121+         126+         130+         150+         133+         141+         132+         151+
38   DASO5        12875+       12906+       12921+       12906+       12895+       12893+       12918+       12903+
38A  NFAO3         2962+        2931+        2916+        2931+        2942+        2944+        2919+        2934+
38B  NFAO5        12875+       12906+       12921+       12906+       12895+       12893+       12918+       12903+
39   NFHX         52414+       52417+       52406+       52390+       52418+       52410+       52402+       52412+
40   NFHOL     13895652+    13895601+    13895593+    13895564+    13895572+    13895589+    13895531+    13895559+
41   MFSOL    258120830+   258121110+   258120560+   258118260+   258120350+   258119910+   258119060+   258119850+
42   OMIT
43   OMIT
44   DFSOL     10198432+    10198473+    10198467+    10198416+    10198465+    10198444+    10198457+    10198460+
45   VFSOL       253099+      253098+      253097+      253096+      253097+      253097+      253096+      253097+
46   OMIT
47   OMIT
48   OMIT
49   VFGAS      3149696+     3149697+     3149697+     3149698+     3149697+     3149697+     3149698+     3149698+
50   NFCOT       367331+      367288+      367229+      367132+      367266+      367250+      367144+      367232+
51   KCO2        336000+
52   DCO2       8586772+     8586801+     8586831+     8586876+     8586810+     8586820+     8586866+     8586836+
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TABLE VII (Continued)

53	KSFCO	288516+	288517+	288518+	288519+	288517+	288517+	288519+	288518+
54	NFCOD	19716+	19713+	19710+	19705+	19712+	19711+	19705+	19710+
55	NFCOG	347616+	347575+	347519+	347427+	347554+	347539+	347438+	347521+
56	NFO2T	3555463+	3555468+	3555506+	3555584+	3555489+	3555493+	3555592+	3555484+
57	KFO2	12780+							
58	DO2	9239180+	9239191+	9239201+	9239216+	9239194+	9239198+	9239211+	9239205+
59	KSFO2	11808+	11808+	11808+	11808+	11808+	11808+	11808+	11808+
60	NFO2D	8234+	8234+	8234+	8234+	8234+	8234+	8234+	8234+
61	NFO2G	3547229+	3547234+	3547272+	3547350+	3547255+	3547259+	3547358+	3547251+
62	NFGAS	3899434+	3899398+	3899380+	3899366+	3899398+	3899387+	3899386+	3899361+
63	XCO2	891451+	891355+	891216+	890983+	891302+	891265+	891008+	891226+
64	MUFGS	8020+	8019+	8019+	8018+	8019+	8019+	8018+	8019+
65	PFGAS	295684850+	295682310+	295681240+	295680630+	295682410+	295681660+	295681970+	295679780+
66	GF	9920000+							
67	NFHOV	4589+	4589+	4589+	4589+	4589+	4589+	4589+	4589+
68A	PEPC1	280-							
68B	PEPC2	280-							
68C	PEPC3	700-							
69A	PEPIS	186-							
69B	PEPFS	170-							
70	DEIHX								
71	ESIO2	241000000-							
71A	ES2O2	231500000-							
71B	ESCO2	389000000-							
71C	DEFHX	527873060-	527873430-	527871940-	527869780-	527873640-	527872480-	527871490-	527872770-
71D	EASO5	7713000000+							
71E	OMIT								
72	ECM2	301980000-							
73	ECM3	405000000-							
74	ECAL	399909440+	399909440+	399909440+	399909440+	399909440+	399909440+	399909440+	399909440+
75	E1CTS	2797242+	2797236+	2797234+	2797230+	2797233+	2797235+	2797226+	2797232+
76	EFCTS	2778199+	2778195+	2778184+	2778152+	2778186+	2778180+	2778162+	2778176+
77	DEIGN	55000+	65000+	57000+	55000+	47000+	40000+	43000+	61000+
78	TI	2399998+							
79	TF	2499464+	2499434+	2499444+	2499365+	2499385+	2499474+	2499414+	2499404+
80	DTEXC	435+	404+	419+	380+	365+	470+	416+	385+
80A	TDELT	99031+	99033+	99027+	98988+	99022+	99006+	99000+	99022+
81	EIVAP	440101+	440101+	440101+	440101+	440101+	440101+	440101+	440101+
82	EISOL	135742-							
83	EISUB	8580-	8577-	8576-	8575-	8576-	8577-	8572-	8575-
84	EISO2	216937-							
85	E1GAS	1856367-	1856368-	1856368-	1856369-	1856368-	1856368-	1856369-	1856368-
85A	EIHX								
85B	EIAO5								
86	DEIBP	398750040-	398748100-	398732320-	398574460-	398722200-	398665160-	398638410-	398708200-
87	EFSCO	766933+	766843+	766721+	766519+	766797+	766764+	766543+	766725+
88	EFSO2	190609+	190609+	190611+	190615+	190610+	190610+	190615+	190610+
89	EFSOL	125360+	125359+	125358+	125357+	125359+	125358+	125358+	125357+
90	EFAO5	9930847+	9954757+	9966327+	9954757+	9946273+	9944730+	9964013+	9952443+
91	EFHX	2766800-	2766933-	2766348-	2765496-	2767013-	2766561-	2766162-	2766667-
92	EHNO3	17153+	17862+	18429+	21264+	18854+	19988+	18712+	21406+
93	EFGAS	2112615+	2112542+	2112474+	2112379+	2112524+	2112499+	2112407+	2112458+
94	EFVAP	455329-	455326-	455323-	455319-	455325-	455325-	455320-	455323-
95	ECSUB	390606180-	390579910-	390551590-	390401900-	390561640-	390504620-	390459760-	390538710-
96	ECAUX								
97	ECFUS	490050-	421200-	441450-	457650-	384750-	433350-	372600-	396900-
98	ECCPD	390116130-	390158710-	390110140-	389944250-	390176890-	390071270-	390087160-	390141810-
99	ECO/M	370248590-	370271430-	370302650-	370257650-	370278140-	370237640-	370305440-	370290530-
100	ECO	74429593-	74434184-	74440461-	74431414-	74435533-	74427392-	74441021-	74438024-
101	AVE	370274000-							
102	DEV	25410+	2570+	28650-	16350+	4140-	36360+	31440-	16530-
103	STDVM	8805+							
				RESUME	FOR TABLE				
	CR ST ST	962663+	962504+	962319+	962030+	962442+	962384+	962085+	962306+
	E(CNT)DT	2770324-	2770374-	2770208-	2769102-	2770068-	2769628-	2769456-	2770067-
	E(CLR)DT	396034720-	396042720-	396019120-	395860360-	395999130-	395935540-	395911950-	395999130-
	DE(HX)	2766800-	2766933-	2766348-	2765496-	2767013-	2766561-	2766162-	2766667-
	DE(ASO5)	9930847+	9954757+	9966327+	9954757+	9946273+	9944730+	9964013+	9952443+

VITA

Bruce Edwin Gammon

Candidate for the Degree of

Master of Science

Thesis: COMBUSTION CALORIMETRY OF ORGANIC BROMINE COMPOUNDS

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Biographical:

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