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HEAT OF COMBUSTION OF STANDARD SAMPLE BENZOIC ACID

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ABSTRACT

The bomb calorimeter in use at this Bureau and the methods of calibrating it and determining heats of combustion are briefly described. In an extensive series of observations, the value obtained for the heat of combustion of standard sample benzoic acid is 26,419 international joules per gram mass (weight corrected for air buoyancy) when the sample is burned at 25° C in oxygen under an initial pressure of 30 atmospheres absolute, in a bomb of constant volume, the mass of sample and the mass of water placed in the bomb each being 3 g per liter of bomb volume. This value is in agreement within 0.03 percent with the values deduced from the data obtained in 1928 by Roth, Doepke, and Banse and by Jaeger and von Steinwehr, but is lower by 0.07 and 0.06 percent respectively than the values deduced from the data obtained by Fischer and Wrede in 1909 and by Dickinson in 1914.

CONTENTS

I. INTRODUCTION

The heat of combustion of benzoic acid, which is used as a standard substance for the calibration of bomb calorimeters, has been determined with a high degree of precision by a number of observers [1] [2] [3] [4] [5] in the last 25 years.

On account of possible differences in purity of lots of benzoic acid prepared at different times, it is desirable to determine the heat of combustion of each lot of the material used for the standard sample. A new determination is particularly desirable in view of the fact, recently pointed out by Washburn,[6] that the results obtained in bomb

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[1] Fischer and Wrede, Z.phys.Chem. **69**,218(1909).
[2] Wrede, Z.phys.Chem. **75**,81(1910).
[3] Dickinson, Bul.BS **11**,189(1914)S230.
[4] Roth, Doepke, and Banse, Z.phys.Chem. **133**,431(1928).
[5] Jaeger and von Steinwehr, Z.phys.Chem. **135**,305(1928).
[6] BS J.Research **10**,525(1933);RP546.

calorimetric determinations depends to some extent on such variables as initial oxygen pressure, amount of water placed in the bomb, mass of the charge burned, and volume of the bomb.

This paper describes the measurements, made at the National Bureau of Standards during the last 2 years, of the heat of combustion of 2 lots of benzoic acid, designated as standard samples 39d and 39e.

II. METHOD AND APPARATUS

1. METHOD

The method is practically the same as that used by Dickinson.[7] The electrical energy equivalent of a calorimetric system, consisting of calorimeter, bomb, oxygen, electric heater, thermometer, and a weighed amount of water, is determined by supplying a measured quantity of energy electrically and observing the resultant rise in temperature. The rise in temperature of the system due to the combustion of a known mass of a given material is then a measure of the heat of combustion of the material under the conditions of the bomb process.

2. APPARATUS

The calorimetric equipment is practically the same as that used by Dickinson, and is described in detail in the reference cited. A schematic diagram of the calorimeter is shown in figure 1.

The equipment used in the present work differs from that used by Dickinson in the following respects:

1. The temperature of the jacket was maintained constant within 0.005° C by means of an oscillating-contact type of thermoregulator, which has been described by Sligh.[8]

2. The temperature of the calorimeter was measured by means of a platinum resistance thermometer of the calorimetric type, previously described by Sligh.[9] It was calibrated by measuring its resistance at the ice and steam points and by comparison at 50° C with a strain-free platinum resistance thermometer which had been calibrated in accordance with the procedure [10] for realizing the international temperature scale. The constants of the thermometer are given in table 1, where R_0 represents the resistance at 0° C, F the change in resistance between 0 and 100° C, and δ the other constant in the Callendar formula:

$$\theta=\frac{R_\Theta-R_0}{F}100+\delta\left(\frac{\theta}{100}\right)\left(\frac{\theta}{100}-1\right)$$

Table 1.—*Constants of resistance thermometer*

Date	R_0	F	δ
August 20, 1920	25.6896	10.0563	1.474
June 30, 1926	25.6905	10.0569	1.455
August 28, 1931	25.6918	10.0565	----------
September 26, 1933	25.6920	10.0567	1.482

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[7] Bul. BS 11,189(1914);S230.

[8] J. Am. Chem. Soc. 42,60(1920).

[9] BS Sci. Pap. 17,49(1921);S407.

[10] BS J.Research,1,635(1928);RP22.

The changes in the constants given in table 1 result in a change of only about 0.01 percent in the slope of the resistance-temperature curve at 30° C. The change during the course of the present work is apparently much less than this, although unfortunately, the δ was not determined in 1931. For calorimetric measurements of heats of combustion the constants of the thermometer need not be accurately known. In the limiting case where the electrical-energy experiments and the combustion experiments are made over exactly the same temperature interval the relation between resistance of the thermometer and temperature is of no consequence whatever.

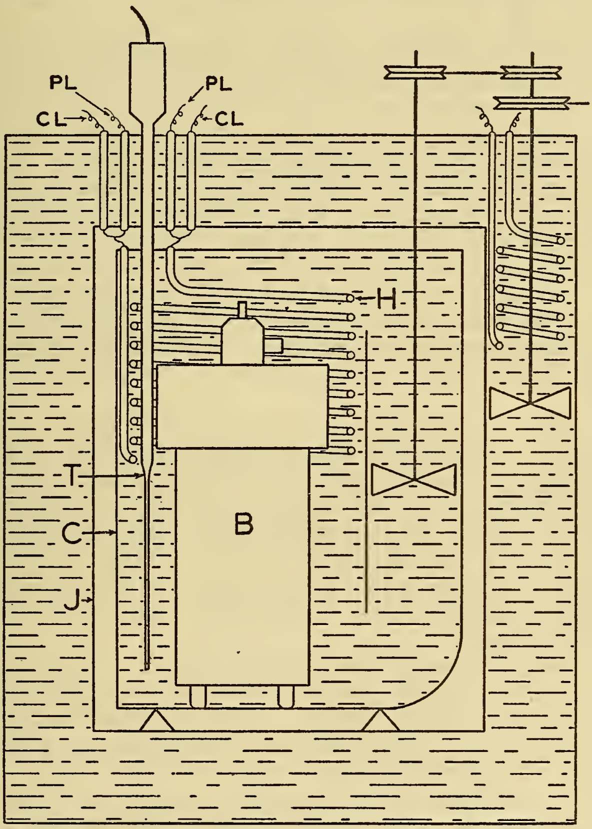

FIGURE 1.—*Schematic diagram of calorimeter.*

B, bomb; H, heater; C, calorimeter vessel; T, resistance thermometer; J, jacket; PL, potential leads; CL, current leads.

The Wheatstone bridge used in connection with the resistance thermometer has been described by Waidner, Dickinson, Mueller, and Harper.[11] The bridge was calibrated in terms of the international ohm by the method described in the reference cited.

3. The bomb is of the Parr type and is made of "illium", a corrosion-resisting alloy. This bomb has been used for several hundred combustions, but shows no signs of oxidation or corrosion. The cover

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[11] Bul. BS 11,571(1914);S241.

of the bomb was originally provided with a check valve, and the joint between the cover and the bomb was made gas-tight by means of a rubber gasket. This cover was discarded and a new cover was made having a needle valve, the base of which is an integral part of the cover. A tongue on the cover fits into a groove 1 mm wide in the top of the bomb. A gold washer in the groove makes a gas-tight joint between the cover and the bomb. The bomb was originally supported by 3 pins about 3 mm in height. These were replaced by pins 12 mm high so as to permit freer circulation of water beneath the bomb.

The electrode for firing the charge of combustible in the bomb is a conical pin of illium and is sealed into a conical hole in the cover of the bomb with a glass consisting of equal parts by weight of soda glass, zinc oxide, and borax. This glass is attacked slightly by the nitric acid formed in combustion, but the thermal effect of this action is negligibly small. This fact was established by a number of combustions of benzoic acid with a piece of the glass in the bomb. The surface area of this piece of glass was many times that of the exposed surface of the glass around the firing electrode, and although the glass was visibly etched by the acid, no appreciable effect was observed on the heat of combustion of the benzoic acid.

The crucible in which the charge of combustible is burned and the support for the crucible are of platinum. The capacity of the bomb is 377 cm^3.

4. The equipment used in measuring the power input to the calorimeter during the calibration experiments consists of a Diesselhorst potentiometer, an unsaturated cadmium standard cell, a 0.01-ohm resistance standard, and a 20,000-ohm volt box with a ratio of 1,000:1. Each of these instruments was calibrated in terms of the international electrical units by the electrical division of this Bureau, and was certified to be accurate within 0.005 percent. The standard cell was inclosed in a cork-lined box so as to reduce temperature changes and gradients in the cell.

5. The current through the heater in the calorimeter during the calibration experiments was turned on and off by means of a double-pole double-throw switch similar to the one described by Osborne, Stimson, and Fiock.[12] It is operated by a spring and a release which is actuated by an electric impulse from a standard clock.

Tests of the performance of the timing device were made by means of a tape chronograph. It was found that the time interval between the receipt of the impulse and the operation of the switch varied from 0.01 to 0.03 second depending on the adjustment of the timing device. However the difference in the time of turning on and the time of turning off of the current was independent of the adjustment within the accuracy of the measurements with the chronograph. The average time required to turn on the current was greater than the average time required to turn it off by 0.007 second. For a given adjustment of the timing device, the greatest error that could have been introduced by combining the shortest observed time of turning on with the longest observed time of turning off of the current, or vice versa, was 0.018 second, or just 0.01 percent of the shortest heating time used in any of the calibration experiments.

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[12] BS J.Research **5**, 429(1930);RP209.

6. The balance used for weighing the water of the calorimeter is sensitive to about 0.1 g, or about 0.003 percent of the total weight of calorimeter, heater, and water. The accuracy of the weights used with this balance is not important, since they were used only to obtain the same quantity of water in each experiment, and the same weights were always used.

The balance used for weighing the samples of benzoic acid is sensitive to a few hundredths of a milligram. The balance was tested, and the arms were found to be equal within the accuracy of the measurements (about 0.003 percent). The weights used with this balance were calibrated by the weights and measures division of this Bureau, and the corrections found were applied in calculating the weights of the samples of benzoic acid.

III. ELECTRICAL ENERGY EXPERIMENTS

The electrical energy equivalent of the calorimeter was determined by supplying a measured quantity of energy electrically and observing the temperature rise produced. A diagram of the power-measuring circuits is shown in figure 2. Current from a storage battery flows through either the stabilizing resistance, S, or the heater, H, in the calorimeter, depending on which way the switch, A, is thrown. The resistance, S, is adjusted to approximate equality with H so that when the switch, A, is thrown only a small change is made in the current drawn from the storage battery. The power circuit was grounded at G (fig. 2) to metal plates placed under the calorimeter, bridge, potentiometer, and galvanometers.

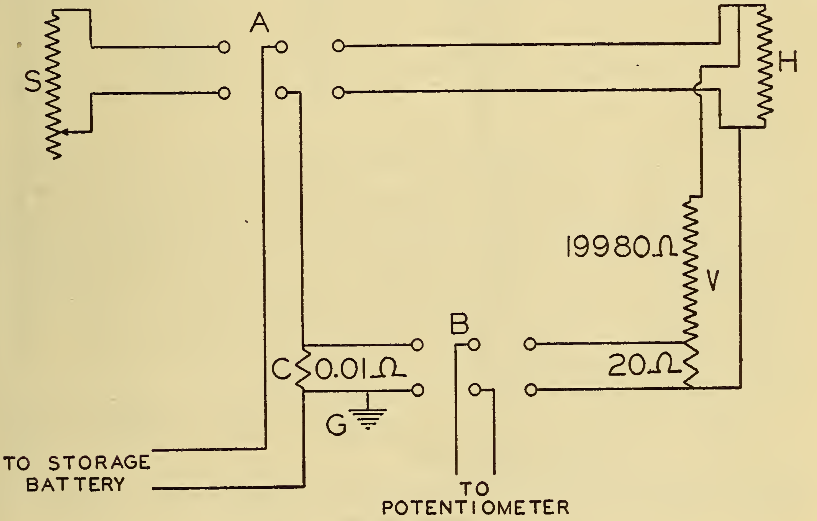

Figure 2.—*Power-measuring circuit.*

S, stabilizing resistance; A, switch operated by timing device; H, heater in calorimeter; C, 0.01 ohm resistance; G, ground; V, volt box.

The power input to the calorimeter is measured by observing the potential drops across the heater and the 0.01 ohm resistance standard, C (fig. 2). Before and after each experiment a zero reading is made on the potentiometer with the switch B (fig. 2) thrown as if to measure the potential drop across the 20 ohms of the volt box. This is to determine the magnitude of thermal emf's in the galvanometer circuit.

The relation between resistance of the thermometer and time in a heat-capacity determination is represented by the curve shown in figure 3, where AB, BC, and CD represent the relations between resistance and time for the initial, middle, and final periods, respectively.

Correction for heat transfer between calorimeter and jacket was made by Dickinson's [13] method. This consists in extrapolating the resistance-time curves of the initial and final periods to a time, t_M, so chosen that the areas BEF and FGC (fig. 3) are equal. The difference in the temperatures corresponding to the points E and G (fig. 3) is then the temperature rise of the calorimeter corrected for heat transfer between the calorimeter and its surroundings, and also for heat of stirring.

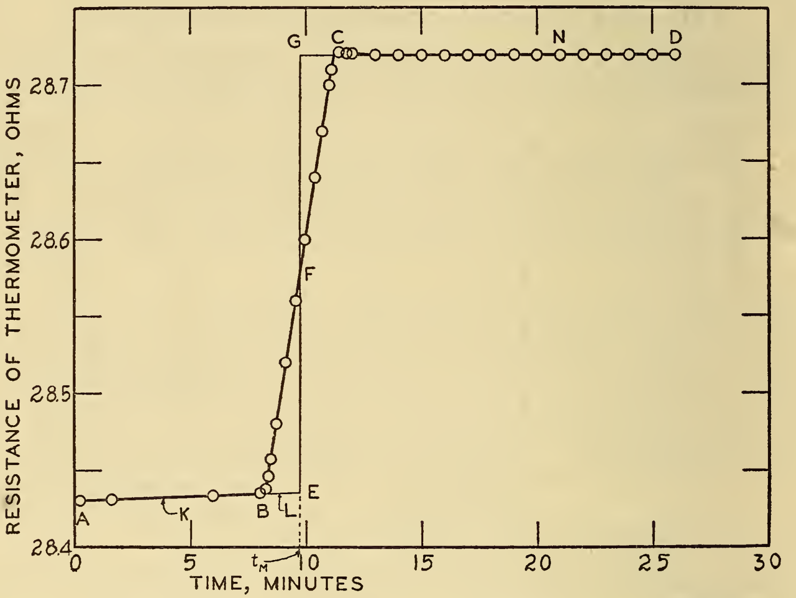

FIGURE 3.—*Relation between resistance of thermometer and time in a heat-capacity determination.*

This method of correcting for heat transfer is based on Newton's law of cooling in the form:

$$\frac{dR}{dt} = -\alpha(R-R')$$

where R is the resistance of the thermometer and R' its resistance at the convergence temperature of the calorimeter.

To determine whether this law is valid over the temperature range covered in the calibration and combustion experiments, measurements were made of $\frac{\Delta R}{\Delta t}$ for various calorimeter temperatures while the tem-

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[13] Bul.BS **11**, 189(1914);S230.

perature of the jacket was kept constant. The measured values of $\frac{\Delta R}{\Delta t}$ are compared in table 2 with the values calculated from the equation

$$\frac{\Delta R}{\Delta t} = -0.00004058\ (R - 28.7259)$$

where R is the average resistance of the thermometer during the time interval Δt.

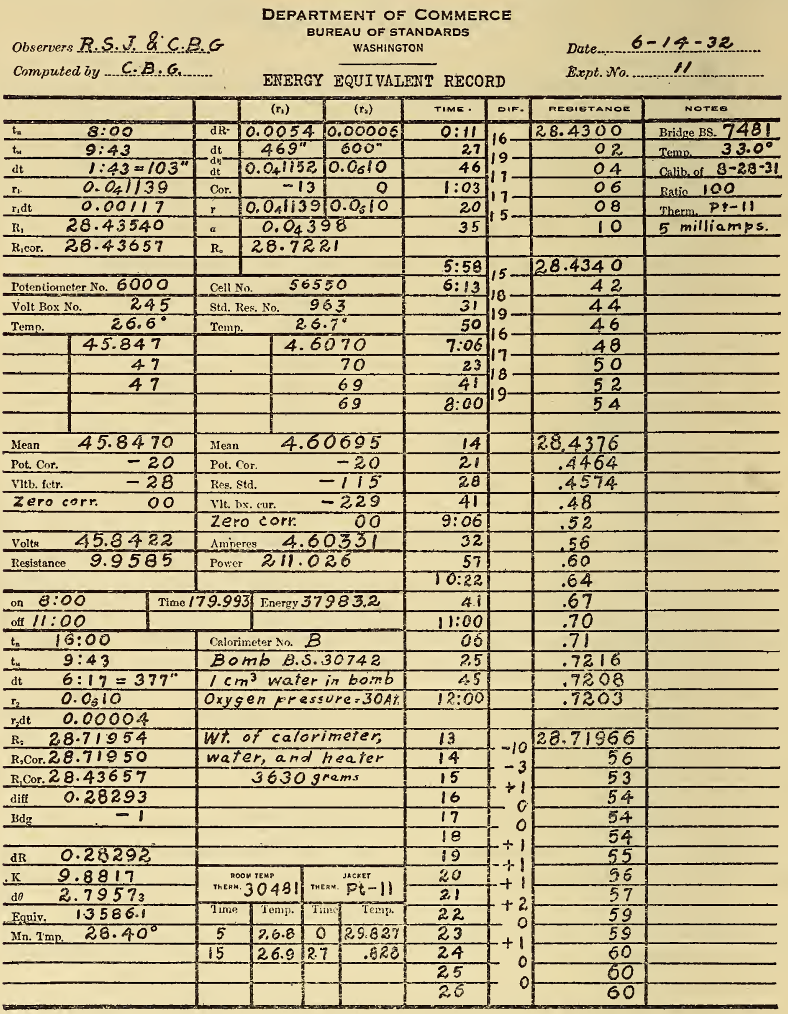
Table 2.—*Comparison of observed and calculated values of* $\frac{\Delta R}{\Delta t}$

R	$\frac{\Delta R}{\Delta t} \times 10^8_{\text{obs.}}$	$\frac{\Delta R}{\Delta t} \times 10^8_{\text{calc.}}$	$O-C$
ohms	*ohms/sec*	*ohms/sec*	*ohms/sec*
27.9447	3161	3170	−9
28.0657	2684	2679	+5
28.2098	2101	2094	+7
28.3317	1599	1600	−1
28.4498	1121	1120	+1
28.5507	712	711	+1
28.6556	280	285	−5
28.7648	−207	−158	−49
28.7639	−168	−154	−14
28.8818	−669	−633	−36
28.8778	−651	−616	−35

It will be seen from this table that for positive values of $\frac{\Delta R}{\Delta t}$, that is for the temperaure of the calorimeter below that of the jacket, the agreement between observed and calculated values is very satisfactory. The large differences between observed and calculated values, when the calorimeter temperature is higher than that of the jacket, are probably due to the variable evaporation of water from the calorimeter. The procedure in both the heat-capacity determinations and in the combustion experiments was such that the temperature of the calorimeter never exceeded that of the jacket by more than a few tenths of a degree.

Figure 4 is a sample of the records taken during an electrical-energy experiment. The observations in the columns headed "resistance" and "time" are the observed resistances of the thermometer and the corresponding times in minutes and seconds as read on a stop-watch. The items in the column headed "dif." are the differences between successive times of observation in the initial period, and differences between successive readings of resistance in the final period.

The items, dR, in the columns headed (r_1) and (r_2) are the total changes in resistance of the thermometer during the initial and final periods respectively, and the items dt are the corresponding elapsed times. The items, $\frac{dR}{dt}$, are the average time rates of change of resistance of the thermometer during the initial and final periods, respectively. The item, "cor.", in the column headed (r_1) is a correction which is applied to $\frac{dR}{dt}$ to take account of the fact that the resistance-time curve of the initial period is not quite linear. The sum of $\frac{dR}{dt}$ and cor. is equal to r_1[r in the column headed (r_1)], which is the value of $\frac{dR}{dt}$ corresponding to the thermometer resistance represented by the point L in figure 3, where L is midway between B and E. The correction, cor., is given by (see fig. 3):



DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
WASHINGTON

ENERGY EQUIVALENT RECORD

Observers R.S.J. & C.B.G
Computed by C.B.G.
Date 6-14-32
Expt. No. 11

			(r₁)	(r₂)		TIME.	DIF.	RESISTANCE	NOTES
t_a	8:00	dR·	0.0054	0.00006		0:11		28.4300	Bridge BS. 7481
t_m	9:43	dt	469"	600"		27	16	02	Temp. 33.0°
dt	1:43=103"	$\frac{dR}{dt}$	0.0₄1152	0.0₆10		46	19	04	Calib. of 8-28-31
r_1	0.0₄1139	Cor.	−13	0		1:03	11	06	Ratio 100
$r_1$dt	0.00117	r	0.0₄1139	0.0₆10		20	17	08	Therm. Pt-11
R_1	28.43540	α	0.0₄398			35	15	10	5 milliamps.
R_1cor.	28.43657	R_0	28.7221						
						5:58		28.4340	
Potentiometer No.	6000	Cell No.	56550			6:13	15	42	
Volt Box No.	245	Std. Res. No.	963			31	18	44	
Temp.	26.6°	Temp.	26.7°			50	19	46	
	45.847		4.6070			7:06	16	48	
	47		70			23	17	50	
	47		69			41	18	52	
			69			8:00	19	54	
Mean	45.8470	Mean	4.60695			14		28.4376	
Pot. Cor.	−20	Pot. Cor.	−20			21		.4464	
Vltb. fctr.	−28	Res. Std.	−115			28		.4574	
Zero corr.	00	Vlt. bx. cur.	−229			41		.48	
		Zero corr.	00			9:06		.52	
Volts	45.8422	Amperes	4.60331			32		.56	
Resistance	9.9585	Power	211.026			57		.60	
						10:22		.64	
on	8:00	Time	179.993	Energy 37983.2		41		.67	
off	11:00					11:00		.70	
t_a	16:00	Calorimeter No.	B			05		.71	
t_m	9:43	Bomb B.S. 30742				25		.7216	
dt	6:17 = 377"	1 cm³ water in bomb				45		.7208	
r_2	0.0₆10	Oxygen pressure = 30At.				12:00		.7203	
$r_2$dt	0.00004								
R_2	28.71954	Wt. of calorimeter,				13		28.71966	
R_2Cor.	28.71950	water, and heater				14	−10	56	
R_1Cor.	28.43657	3630 grams				15	−3	53	
diff	0.28293					16	+1	54	
Bdg	−1					17	0	54	
						18	0	54	
dR	0.28292					19	+1	55	
K	9.8817	ROOM TEMP THERM. 30481		JACKET THERM. Pt-11		20	+1	56	
dθ	2.7957₃					21	+1	57	
Equiv.	13586.1	Time	Temp.	Time	Temp.	22	+2	59	
Mn. Tmp.	28.40°	5	26.8	0	29.827	23	0	59	
		15	26.9	27	.828	24	+1	60	
						25	0	60	
						26	0	60	

FIGURE 4.—*Sample of records made in an electrical energy equivalent determination*

$$\text{cor.} = -\alpha\ (R_L - R_K)$$

where

$$\alpha = -\frac{d}{dR}\left(\frac{dR}{dt}\right) = -\frac{\left(\frac{dR}{dt}\right)_N - \left(\frac{dR}{dt}\right)_K}{R_N - R_K}$$

R_K=average resistance in initial period
R_N=average resistance in final period.
The corresponding value of the correction to the rate in the final period is usually negligible.

The item, t_R, at the extreme left at top of figure 4 is the time of the last observation of resistance in the initial period, t_M has already been defined, dt is (t_M-t_R), r_1 is the value of r from the column headed (r_1), R_1 is the final reading of resistance in the initial period, and R_1 cor. the sum of R_1 and $r_1\,dt$. R_1 cor. is therefore the value of resistance obtained by extrapolating the initial resistance-time curve to the time, t_M.

The corresponding items for the final period are given at the left of figure 4 and a little below the middle of the page. The item, "diff.", below R_1 cor. is (R_2 cor.$-R_1$ cor.). The item, "Bdg." is the difference in the corrections to the bridge for the initial and final readings, and dR is the corrected change in resistance of the thermometer, (R_G-R_E) in figure 3. The item, K, is the value of $\frac{d\theta}{dR}$ corresponding to the mean of R_1 cor. and R_2 cor. (where θ is temperature), and is obtained by differentiating the Callendar equation as described by Dickinson and Mueller.[14] The item $d\theta$ is the corrected temperature rise corresponding to the resistance change dR.

The recorded values of voltage near the middle of figure 4 are the readings of potential drop across 20 ohms of the volt box multiplied by 1,000, the nominal value of the volt-box ratio. The recorded values of current are the readings of potential drop across the resistance standard divided by 0.01, the nominal resistance of the standard. The corrections to current and voltage, and other items of the figure are self-explanatory.

The results of the electrical-energy experiments are listed in table 3. Conditions were varied in order to detect possible systematic errors. Voltage was varied from 28 to 55, time of heating from 3 to 7 minutes, and temperature rise from 1.7 to 4.8° C. The final temperature in each experiment was within 0.1 or 0.2° of 30.0° C, so that the mean temperatures varied from 27.6 to 29.2°. The results were not corrected to a common mean temperature since the rate of change with temperature of the electrical energy equivalent of the system is negligibly small at this temperature.

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[14] Bul.BS 9,483(1913);S200.

TABLE 3.—*Results of electrical energy experiments*

[First Series, Dec. 14 to 18, 1931]

Experiment number	Potential drop across heater E	Current through heater E/R	Time of heating t	Energy supplied to cal. $Q=(E^2/R)t$	Temperature rise (corrected) $\Delta\theta$	Observed electrical energy equivalent $Q/\Delta\theta$	Weight of calorimeter +water+ heater W	Electrical energy equivalent for W=3,630 g	Deviation from mean of group	Mean of group	Deviation from mean of all observations
	Int. volts	*Int. amp.*	*Seconds*	*Int. joules*	°*C*	*Int. j/°C*	*g*	*Int. j/°C*	*Int. j/°C*	*Int. j/°C*	*Int. j/°C*
1	55.277_9	5.5535_4	179.99_3	$55255._7$	4.0555_1	$13624._8$	3640.0	$13583._0$	−1.0	$13584._0$	−3.2
2	55.257_5	5.5513_4	179.99_3	$55213._4$	4.0521_1	$13625._8$	3640.0	$13584._0$	0.0		
3	55.237_2	5.5493_4	179.99_3	$55173._3$	4.0488_5	$13626._9$	3640.0	$13585._1$	+1.0		
5	27.827_6	2.7922_6	419.99_3	$32634._3$	2.4011_9	$13590._9$	3630.0	$13590._9$	+2.1	$13590._0$	+2.8
6	27.745_9	2.7841_1	419.99_3	$32443._5$	2.3876_1	$13588._3$	3630.0	$13588._3$	−0.5		
7	27.760_3	2.7855_8	419.99_3	$32477._4$	2.3900_6	$13588._5$	3630.0	$13588._5$	−0.3		
8	27.756_5	2.7851_7	419.99_3	$32468._2$	2.3890_9	$13590._2$	3630.0	$13590._2$	+1.4		
9	27.751_0	2.7846_3	419.99_3	$32455._5$	2.3888_5	$13586._2$	3630.0	$13586._2$	−2.6		
16	28.320_7	2.8418_0	419.99_3	$33801._8$	2.4866_7	$13593._2$	3630.0	$13593._2$	+2.1		
17	28.318_3	2.8416_0	419.99_3	$33796._5$	2.4870_3	$13589._1$	3630.0	$13589._1$	−2.0		
18	28.313_9	2.8411_8	419.99_3	$33786._2$	2.4859_9	$13590._6$	3630.0	$13590._6$	−0.5		
19	28.309_2	2.8407_2	419.99_3	$33775._2$	2.4847_3	$13593._1$	3630.0	$13593._1$	+2.0		
20	28.302_3	2.8400_2	419.99_3	$33758._6$	2.4841_4	$13589._7$	3630.0	$13589._7$	−1.4		
10	46.038_4	4.6230_6	179.99_3	$38309._4$	2.8184_5	$13592._4$	3630.0	$13592._4$	+3.6	$13588._8$	+1.6
11	45.930_0	4.6121_3	179.99_3	$38128._8$	2.8059_7	$13588._5$	3630.0	$13588._5$	−0.5		
12	45.886_7	4.6077_5	179.99_3	$38056._7$	2.8006_4	$13588._6$	3630.0	$13588._6$	−0.2		
13	45.837_7	4.6029_6	179.99_3	$37976._6$	2.7949_4	$13587._6$	3630.0	$13587._6$	−1.2		
14	45.792_0	4.5981_8	179.99_3	$37899._3$	2.7892_1	$13587._8$	3630.0	$13587._8$	−1.9		
15	45.743_7	4.5934_0	179.99_3	$37820._0$	2.7833_5	$13587._9$	3630.0	$13587._9$	−0.9		
Mean of first series								$13588._6$			

[Second Series, May 16 to 20, 1932]

(wt of cal.+heater+water=3630.0 g in all experiments)

1	46.395$_9$	4,6589$_4$	179.99$_3$	38906.$_5$	2.8623$_4$	----	----	13592.$_6$	+3.1	13589.$_5$	+2.3
2	46.366$_9$	4.6559$_7$	179.99$_3$	38857.$_4$	2.8589$_3$	----	----	13591.$_6$	+2.1		
11	46.773$_9$	4.6970$_7$	180.99$_3$	39764.$_2$	2.9267$_5$	----	----	13586.$_5$	−3.0		
12	46.733$_5$	4.6930$_0$	179.99$_3$	39476.$_1$	2.9053$_6$	----	----	13587.$_3$	−2.2		
3	46.327$_2$	4.6520$_2$	299.99$_3$	64653.$_0$	4.7584$_8$	----	----	13586.$_9$	+2.0	13584.$_9$	−2.3
4	46.290$_4$	4.6483$_3$	299.99$_3$	64550.$_4$	4.7513$_5$	----	----	13585.$_7$	+0.8		
13	46.634$_2$	4.6830$_0$	299.99$_3$	65514.$_9$	4.8224$_3$	----	----	13585.$_4$	+0.5		
14	46.580$_6$	4.6776$_0$	299.99$_3$	65364.$_1$	4.8124$_6$	----	----	13582.$_3$	−2.6		
15	46.507$_8$	4.6702$_7$	304.99$_3$	66245.$_7$	4.8766$_7$	----	----	13584.$_2$	−0.7		
16	46.429$_2$	4.6624$_1$	299.99$_3$	64940.$_1$	4.7803$_6$	----	----	13584.$_8$	−0.1		
5	55.557$_0$	5.5813$_8$	179.99$_3$	55813.$_1$	4.1088$_6$	----	----	13583.$_6$	+0.5	13583.$_1$	−4.1
6	55.483$_7$	5.5739$_3$	179.99$_3$	55665.$_0$	4.0986$_0$	----	----	13581.$_5$	−1.6		
7	55.371$_7$	5.5627$_5$	179.99$_3$	55441.$_3$	4.0822$_5$	----	----	13581.$_1$	−2.0		
8	55.330$_0$	5.5585$_0$	179.99$_3$	55357.$_2$	4.0756$_2$	----	----	13582.$_5$	−0.6		
9	55.295$_7$	5.5551$_3$	179.99$_3$	55289.$_3$	4.0704$_2$	----	----	13583.$_2$	+0.1		
10	55.276$_7$	5.5532$_5$	179.99$_3$	55251.$_6$	4.0666$_9$	----	----	13586.$_4$	+3.2		
17	36.888$_8$	3.7027$_3$	359.99$_3$	49171.$_2$	3.6186$_0$	----	----	13588.$_5$	+4.2	13584.$_3$	−2.9
18	36.885$_3$	3.7024$_3$	359.99$_3$	49162.$_5$	3.6197$_9$	----	----	13581.$_6$	−2.7		
19	36.942$_8$	3.7081$_7$	359.99$_3$	49315.$_5$	3.6309$_0$	----	----	13582.$_2$	−2.1		
20	36.894$_0$	3.7032$_9$	359.99$_3$	49185.$_5$	3.6211$_7$	----	----	13582.$_8$	−1.5		
21	36.871$_5$	3.7010$_3$	359.99$_3$	49125.$_6$	3,6159$_7$	----	----	13585.$_7$	+1.4		
22	36.863$_3$	3.7001$_9$	359.99$_3$	49103.$_5$	3.6144$_8$	----	----	13585.$_2$	+0.9		
23	27.987$_5$	2.8084$_2$	299.99$_3$	23579.$_6$	1.7349$_4$	----	----	13591.$_0$	+4.8	13586.$_2$	−1.0
24	27.973$_3$	2.8070$_0$	299.99$_3$	23555.$_8$	1.7343$_0$	----	----	13582.$_3$	−3.9		
25	27.961$_9$	2.8058$_3$	299.99$_3$	23536.$_3$	1.7321$_0$	----	----	13588.$_3$	+2.1		
26	27.947$_7$	2.8044$_0$	299.99$_3$	23512.$_4$	1.7304$_7$	----	----	13587.$_3$	+1.1		
27	27.937$_3$	2.8033$_5$	299.99$_3$	23494.$_9$	1.7296$_0$	----	----	13584.$_0$	−2.2		
28	27.927$_3$	2.8024$_0$	299.99$_3$	23478.$_5$	1.7284$_9$	----	----	13583.$_2$	−3.0		
Mean of second series	----	----	----	----	----	----	----	13585.$_3$	----	----	----

TABLE 3.—*Results of electrical energy experiments*—Continued

[Third Series, June 1932]

Experiment number	Potential drop across heater E	Current through heater E/R	Time of heating t	Energy supplied to cal. $Q=(E^2/R)t$	Temperature rise (corrected) $\Delta\theta$	Observed electrical energy equivalent $Q/\Delta\theta$	Weight of calorimeter +water+ heater W	Electrical energy equivalent for W=3,630 g	Deviation from mean of group	Mean of group	Deviation from mean of all observations
	Int. volts	*Int. amp.*	*Seconds*	*Int. joules*	°*C*	*Int. j/°C*	*g*	*Int. j/°C*	*Int. j/°C*	*Int. j/°C*	*Int. j/°C*
1	55.270$_7$	5.5526$_5$	179.99$_3$	55239.$_6$	4.065$_7$			13586.$_7$	−1.3	13588.$_0$	+0.8
2	55.161$_4$	5.5418$_2$	179.99$_3$	55022.$_8$	4.050$_0$			13585.$_9$	−2.1		
3	55.120$_0$	5.5375$_8$	179.99$_3$	54939.$_6$	4.043$_4$			13587.$_5$	−0.5		
4	55.088$_0$	5.5342$_7$	179.99$_3$	54874.$_8$	4.038$_1$			13589.$_3$	+1.3		
5	55.069$_0$	5.5325$_2$	179.99$_3$	54838.$_6$	4.035$_4$			13589.$_4$	+1.4		
6	55.070$_7$	5.5325$_7$	179.99$_3$	54840.$_8$	4.035$_6$			13589.$_3$	+1.3		
7	45.923$_2$	4.6114$_2$	179.99$_3$	38117.$_3$	2.805$_5$			13586.$_7$	−0.7	13587.$_4$	+0.2
8	45.907$_2$	4.6098$_5$	179.99$_3$	38091.$_1$	2.803$_0$			13589.$_4$	+2.0		
9	45.885$_5$	4.6077$_1$	179.99$_3$	38055.$_4$	2.800$_8$			13587.$_4$	0.0		
10	45.863$_9$	4.6054$_6$	179.99$_3$	38018.$_9$	2.798$_1$			13587.$_4$	0.0		
11	45.842$_2$	4.6033$_1$	179.99$_3$	37983.$_2$	2.795$_8$			13586.$_1$	−1.3		
12	45.824$_2$	4.6015$_1$	179.99$_3$	37953.$_4$	2.793$_2$			13587.$_8$	+0.4		
13	46.442$_2$	4.6637$_2$	299.99$_3$	64976.$_5$	4.781$_8$			13588.$_3$	+1.3	13587.$_1$	−0.1
14	46.415$_8$	4.6610$_6$	299.99$_3$	64902.$_5$	4.777$_4$			13585.$_3$	−1.8		
15	46.367$_2$	4.6562$_6$	300.99$_3$	64983.$_7$	4.782$_7$			13587.$_3$	+0.2		
16	46.321$_3$	4.6516$_0$	299.99$_3$	64638.$_9$	4.757$_1$			13587.$_9$	+0.8		
17	46.285$_4$	4.6479$_4$	299.99$_3$	64538.$_4$	4.750$_0$			13587.$_0$	−0.1		
18	46.248$_6$	4.6442$_7$	299.99$_3$	64435.$_8$	4.742$_6$			13586.$_6$	−0.5		
19	28.072$_4$	2.8169$_8$	299.99$_3$	23723.$_2$	1.746$_0$			13587.$_2$	−0.3	13587.$_5$	+0.3
20	28.058$_9$	2.8155$_9$	299.99$_3$	23700.$_1$	1.743$_9$			13590.$_3$	+2.8		
21	28.045$_3$	2.8142$_5$	299.99$_3$	23677.$_3$	1.742$_6$			13587.$_4$	−0.1		
22	28.034$_8$	2.8131$_8$	299.99$_3$	23659.$_5$	1.741$_3$			13587.$_3$	−0.2		
23	28.025$_1$	2.8122$_1$	299.99$_3$	23643.$_1$	1.740$_0$			13588.$_1$	+0.6		
24	28.014$_6$	2.8111$_6$	299.99$_3$	23625.$_5$	1.739$_1$			13584.$_9$	−2.6		
25	28.447$_5$	2.8546$_4$	419.99$_3$	34106.$_5$	2.510$_1$			13587.$_7$	−0.7	13588.$_4$	+1.2
26	28.341$_9$	2.8440$_0$	419.99$_3$	33853.$_2$	2.491$_3$			13588.$_6$	+0.2		
27	28.227$_6$	2.8325$_2$	419.99$_3$	33580.$_5$	2.471$_3$			13588.$_3$	−0.1		
28	28.161$_5$	2.8258$_5$	419.99$_3$	33423.$_1$	2.460$_0$			13586.$_5$	−1.9		
29	28.114$_3$	2.8211$_2$	419.99$_3$	33311.$_2$	2.451$_2$			13589.$_8$	+1.4		
30	28.079$_1$	2.8175$_9$	419.99$_3$	33227.$_9$	2.445$_1$			13589.$_6$	+1.2		
31	37.144$_9$	3.7284$_8$	359.99$_3$	49856.$_8$	3.668$_4$			13590.$_9$	+1.8	13589.$_1$	+1.9
32	37.105$_0$	3.7244$_8$	359.99$_3$	49749.$_9$	3.661$_0$			13589.$_1$	0.0		
33	37.072$_2$	3.7210$_6$	359.99$_3$	49660.$_2$	3.654$_3$			13589.$_5$	+0.4		
34	37.049$_9$	3.7189$_1$	359.99$_3$	49601.$_7$	3.650$_1$			13589.$_1$	0.0		
35	37.031$_1$	3.7170$_3$	359.99$_3$	49551.$_5$	3.647$_1$			13586.$_5$	−2.6		
36	37.009$_4$	3.7148$_5$	359.99$_3$	49493.$_4$	3.642$_0$			13589.$_6$	+0.5		
Mean of third series								13587.$_9$			
Mean of all observations								13587.$_2$			

The determinations were made with the calorimeter as nearly as possible in the same condition as in the combustion experiments. One cm^3 of water was placed in the bomb, which was filled with oxygen to a pressure of 30 atmospheres absolute. Hence for the combustion experiments at this pressure it is necessary to add only the heat capacity of the sample of combustible material to obtain the total electrical energy equivalent of the system.

In the first series of determinations 3 groups of measurements were made, in which the voltages impressed on the heater were approximately 55, 28, and 46 and the corresponding temperature changes of the calorimeter were 4.0, 2.4, and 2.8°, respectively. The means of the results obtained in the second and third groups (28 and 46 volts) are in agreement within less than 0.01 percent, while the results obtained in the first group are lower by 0.04 percent. It was noticed that if the results were plotted against the temperature rise of the calorimeter the points would lie very nearly on a straight line. Such an effect as this could not possibly be an actual change in the energy equivalent of the calorimeter with temperature rise, but might be the result of some pecularity of the thermometer, possibly arising from mechanical strain in the platinum wire.

In order to check the results of the first series of electrical energy experiments a second series was made, consisting of 5 groups of experiments, in which the temperature rise of the calorimeter was varied from 1.7 to 4.8°. It will be seen from table 3 that the results obtained in the second series of experiments for temperature rises of 2.9 and 4.1° are in agreement within 0.01 percent with the corresponding groups of the first series, and that the results obtained with a 3.6° temperature rise are intermediate between those obtained with temperature rises of 2.9 and 4.1°. These 3 groups of experiments therefore appear to confirm the apparent variation of energy equivalent with temperature rise observed in the first series of experiments. However, the results obtained with temperature rises of 1.7 and 4.8° do not confirm this apparent variation.

In order to determine whether the differences in the results obtained were due to erratic behavior of the thermometer, it was carefully compared over the temperature range 25 to 30° with a strain-free thermometer. It was found that when the resistances of the calorimetric thermometer at 10 temperatures in this range were plotted against the corresponding resistances of the strain-free thermometer, the points lay on a smooth curve with a maximum deviation of $0.0000 2_5$ ohm ($.0002_5$°C) and an average deviation of 0.00001 ohm (.0001°C). These results suggested that the variations in the results of the electrical energy experiments were not caused by erratic behavior of the thermometer.

Following these experiments a third series of electrical energy experiments was made, using a different potentiometer and standard cell from those used in the first and second series, all other equipment being the same as in the first two series. This series consisted of six groups of experiments made under the same conditions as those of the second series. It will be seen from table 3 that the results were remarkably consistent, showing no sign of any variation of energy equivalent with temperature rise. It was concluded at the time that the variations observed in the first 2 series could be attributed to the potentiometer or standard cell used in these series. However, it was found in making heat of combustion measurements with different amounts of benzoic acid in the bomb, that the results in some cases were consistent with the apparent variation of the energy equivalent of the calorimeter with temperature rise observed in the first two series of calibration experiments, while others were consistent with a value for the energy equivalent independent of temperature rise. It was finally found that the indications of the thermometer depend to some extent on its previous history, and it is believed that this explains the differences in the results obtained in the various groups of experiments.

It was found, for example, that the apparent variation of energy equivalent of the calorimeter with temperature rise was somewhat greater if the thermometer was cooled to about 23° C before each experiment, than if it was heated to 33° C before each experiment. It was also found that the resistance of the thermometer at 30° C was greater by 0.0001_4 ohm (0.001_4 ° C) if it had been recently cooled to 23° than if it had been heated to 33°. This was shown by comparisons with a strain-free thermometer which was left in a constant-temperature bath throughout the comparisons, while the calorimetric thermometer was occasionally removed from the bath and cooled to 23° or heated to 33° C.

Although the results obtained under various conditions differ by more than had been expected, it is believed that by taking the mean of all the results of the calibration experiments as the electrical energy equivalent of the calorimeter, and the mean of the results of a large number of combustion experiments made under various conditions as the heat of combustion of benzoic acid, the effect of the differences is largely eliminated. The justification for this belief lies in the fact that the means of the results in the 3 series of calibration experiments are in good agreement with the mean of all the results.

The mean of these 3 series, and of all of the calibration experiments are as follows:

First series	$13588._6$ int. joules/° C
Second series	$13585._3$ int. joules/° C
Third series	$13587._9$ int. joules/° C
All experiments	$13587._2$ int. joules/° C

The means of the various series are within less than 0.015 percent of the mean of all experiments. The maximum deviation of the mean of a single group of experiments made under the same conditions, from the mean of all experiments is 0.030 percent.

IV. COMBUSTION EXPERIMENTS

1. MATERIALS

(a) BENZOIC ACID

Measurements were made on 2 lots of benzoic acid, designated as standard samples 39d and 39e. These samples were of a high degree of purity and uniformity, but were not entirely free from small amounts of impurity. Chemical data on the 2 samples are given in table 4.

Table 4.—*Chemical data on standard samples 39d and 39e of benzoic acid*

Sample number	Purity of dried or fused sample on basis of titration [1]	Sulphur	Chlorine	Nonvolatile matter at 600° C	Heavy metals	Insoluble in diluted NH_4OH (1+3)
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	
39d	99.98	0.001	0.001	0.003	----------	----------
39e	99.99	0.001	0.001	0.002	0.0005	none

[1] Compared with HCl which was standardized by weighing AgCl.

Freezing point measurements were made on sample 39d by means of a platinum resistance thermometer, in accordance with the technic described by Mair.[15] The initial freezing point was found to be 122.30_5° C, and the freezing range 0.095° C. The purity estimated on the basis of these data is 99.88 mole percent. No freezing point measurements were made on sample 39e.

As a further check on the purity of the material, measurements were made of the amounts of carbon dioxide formed in the combustion of known masses of sample 39d. The carbon dioxide formed was absorbed in "ascarite" and weighed in the manner described by Rossini.[16]

In table 5 are given the ratios of the masses of CO_2 found to those calculated on the assumption that the material is pure benzoic acid. The atomic weights used in calculating this table are $O=16.000$, $H=1.0078$, and $C=12.000$. There is some evidence which indicates that the atomic weight of carbon is somewhat higher than 12.000.[17] If 12.007 had been used in calculation of the data of table 5, the average value of the ratio CO_2 found/CO_2 calculated would have been 0.9998_3.

Table 5.—*Results of measurements of* CO_2 *formed in combustion of standard sample 39d*

Experiment number	$\frac{CO_2 \text{ found}}{CO_2 \text{ calculated}}$	Deviation from mean
1	0.9998_3	+0.00024
2	$.9994_4$	−.00015
3	$.9996_3$	+.00004
4	$.9994_5$	−.00014
Mean	$.9995_9$	±.00014

(b) OXYGEN

Commercial oxygen containing a small amount of nitrogen was used. Before being admitted to the bomb the oxygen was passed through a tube containing copper oxide heated to a temperature of about 750° C, in order to burn out any combustible impurities

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[15] BS J.Research **9**, 457(1932);RP482.

[16] BS J.Research **6**, 37(1931);RP260.

[17] 1934 report of International Committee on Atomic Weights, J. Am. Chem. Soc. **56**, 753(1934).

which might be present. The use of oxygen purified in this way resulted in a value for the heat of combustion of benzoic acid which was lower by about 0.03 percent than the value obtained with unpurified oxygen.

2. EXPERIMENTAL PROCEDURE AND CALCULATION OF RESULTS

The samples of benzoic acid were compressed into briquets, and weighed in that form in the platinum crucible in which they were to be burned. One cm^3 of water was placed in the bomb to saturate the space with water vapor at the beginning of the experiment. In most experiments the air initially in the bomb was washed out by filling the bomb several times with oxygen to 3 or 4 atmospheres pressure, and then allowing the oxygen to escape until the pressure was reduced to 1 atmosphere. The experimental procedure in the combustion experiments was as nearly as possible the same as in the calibration experiments.

The charge was ignited by means of an electric fuse consisting of a 2 cm length of iron wire about 0.13 mm in diameter (no. 36 B. & S. gage). The iron wire was connected to platinum leads, 0.20 to 0.25 mm in diameter. The current for firing the charge was obtained from a toy transformer having a secondary voltage of 14.

The energy used in firing the charge, that is the heat developed in the combustion of the iron plus the electric energy used to ignite the wire, was determined in a series of blank experiments in which only the iron wire was burned. The results obtained in these experiments are given in table 6.

TABLE 6.—*Energy required to ignite charge*

Experiment number	Firing energy	Deviation from mean
	int. joules	*int. joules*
1	22.6	−0.4
2	22.6	−.4
3	25.1	+2.1
4	23.8	+0.8
5	20.9	−2.1
Mean	23.0	±1.6

In the combustion experiments, as in the calibration experiments, the observed temperature rise of the calorimeter was corrected for heat transfer between calorimeter and jacket, and heat of stirring by Dickinson's method. The heat produced by the combustion of a sample of benzoic acid was calculated by multiplying the corrected temperature rise by the electrical energy equivalent of the system. The total electrical energy equivalent of the system is given by

$$C=C_0+1.26m_s+0.34\ (p_{O_2}-30)$$

where m_s is the mass of the sample of benzoic acid, p_{O_2} is the initial oxygen pressure in the bomb in atmospheres, at 30° C, and C_0 is the observed electrical energy equivalent of the calorimeter, including the bomb, containing 1 gram of water and oxygen under a pressure of 30 atmospheres absolute at 30° C.

From the total quantity of heat, Q, produced in an experiment were subtracted the energy, q_i (=23.0 joules), used to ignite the sample, and the energy, $-\Delta U_{HNO_3}$, of formation of the nitric acid produced in the combustion. The energy of formation of nitric acid in the reaction

$$\frac{1}{2}\ N_2(\text{gas})+\frac{5}{4}\ O_2(\text{gas})+\frac{1}{2}\ H_2O\ (\text{liq.})=HNO_3(\text{aq.})(30°C)$$

is taken as 63,000 joules, a figure which is based on data given in International Critical Tables, vol. 5, 179.

The observed heat of combustion of the sample of benzoic acid at the final temperature of the calorimeter is given by

$$-\Delta U_B=\frac{Q-q_i+\Delta U_{HNO_3}}{m_s}$$

where m_s is the mass of the sample, and $-\Delta U_B$ is the heat evolved in the combustion of unit mass of the sample under the conditions of the bomb process.

The experimental conditions were varied over a wide range in order to detect possible systematic errors. The mass of sample was varied from 0.7 to 2.0g, the corresponding temperature rise varying from 1.4 to 3.9° C, and the oxygen pressure was varied from 20 to 30 atmospheres.

There was no indication of unburned carbon remaining in the crucible after combustion. The gaseous products of combustion in a number of experiments were examined for carbon monoxide by the method described by Eiseman, Weaver, and Smith.[18] No carbon monoxide was found although the method is capable of detecting amounts as small as 0.001 to 0.003 percent of the total amount of gas in the bomb at the end of the experiments.

3. RESULTS.

The results obtained for standard samples 39d and 39e are given in tables 7 and 8, respectively. The observed values of heat of combustion have been reduced by the method given by Washburn [19] to the heat of combustion for standard initial conditions. The standard conditions chosen are:

Initial oxygen pressure=30 atmospheres absolute at 30° C;
Mass of sample=3 g per liter of bomb volume;
Volume of water placed in bomb=3 cm^3 per liter of bomb volume;
Temperature to which reaction is referred=30° C.

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[18] BS J.Research 8,669(1932);RP446.
[19] BS J.Research, 10,525(1933);RP546.

TABLE 7.—*Measurements of heat of combustion of standard sample 39d*

[Oxygen not purified in experiments 1 to 6; oxygen purified in experiments 7 to 63]

Experiment number	Weight of sample in air vs. brass weights	Initial oxygen pressure at 30° C	Total heat produced	Correction for heat of formation of HNO_3	Correction for iron wire and electric energy	Heat produced by combustion of benzoic acid	Observed heat of combustion	Reduction to standard initial conditions	Heat of combustion for standard initial conditions	Deviation from mean of group	Mean of group	Deviation from mean of all observations
	g	*atm*	*int. joules*	*int. joules*	*int. joules*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*
1	1.5193$_7$	30.2	40,286.$_7$	77.$_0$	23.$_0$	40,186.$_7$	26,449.$_6$	−1.0	26,448.$_6$	+4.3	26444.$_3$	+8.4
2	1.4987$_7$	30.2	39,748.$_4$	75.$_8$	23.$_0$	39,649.$_6$	26,454.$_8$	−0.9	26,453.$_9$	+9.6		
3	1.5185$_8$	30.2	40,246.$_2$	67.$_6$	23.$_0$	40,155.$_6$	26,442.$_9$	−1.0	26,441.$_9$	−2.4		
4	1.4674$_8$	30.2	38,894.$_0$	72.$_3$	23.$_0$	38,798.$_7$	26,439.$_0$	−0.9	26,438.$_1$	−6.2		
5	1.5121$_1$	30.2	40,085.$_9$	72.$_8$	23.$_0$	39,990.$_1$	26,446.$_6$	−1.0	26,445.$_6$	+1.7		
6	1.5869$_0$	30.2	42,055.$_0$	76.$_3$	23.$_0$	41,955.$_7$	26,438.$_8$	−1.0	26,437.$_8$	−6.5		
7	1.5905$_3$	30.5	42,422.$_1$	85.$_5$	23.$_0$	42,313.$_6$	26,603.$_5$	−1.2	(26,602.$_3$)			
8	1.7976$_1$	30.4	47,642.$_9$	89.$_6$	23.$_0$	47,530.$_3$	26,440.$_8$	−1.3	26,439.$_5$	+1.4	26438.$_1$	+3.2
9	1.5704$_4$	30.4	41,606.$_0$	79.$_1$	23.$_0$	41,503.$_9$	26,428.$_2$	−1.1	26,427.$_1$	−11.0		
10	1.6851$_7$	30.2	44,664.$_0$	85.$_0$	23.$_0$	44,556.$_0$	26,440.$_0$	−1.0	26,439.$_0$	+0.9		
11	1.5726$_2$	30.2	41,678.$_1$	82.$_0$	23.$_0$	41,573.$_1$	26,435.$_5$	−0.7	26,434.$_8$	−3.3		
12	1.5143$_0$	30.2	40,134.$_0$	77.$_9$	23.$_0$	40,033.$_1$	26,436.$_7$	−0.9	26,435.$_8$	−2.3		
13	1.2569$_2$	30.2	33,325.$_2$	66.$_5$	23.$_0$	33,235.$_7$	26,442.$_1$	+0.1	26,442.$_2$	+4.1		
14	1.4605$_2$	30.5	38,700.$_1$	70.$_2$	23.$_0$	38,606.$_9$	26,433.$_6$	−0.9	26,432.$_7$	−5.4		
15	1.6654$_7$	30.1	44,135.$_3$	75.$_8$	23.$_0$	44,036.$_5$	26,440.$_9$	−1.2	26,439.$_7$	+1.6		
16	1.6352$_3$	30.1	43,330.$_6$	78.$_9$	23.$_0$	43,228.$_7$	26,435.$_8$	−1.1	26,434.$_7$	−3.4		
17	1.4323$_6$	30.0	37,969.$_0$	66.$_5$	23.$_0$	37,879.$_5$	26,445.$_5$	−0.6	26,444.$_9$	+6.8		
18	1.4452$_4$	30.1	38,257.$_3$	19.$_9$	23.$_0$	38,214.$_4$	26,441.$_5$	−0.7	26,440.$_8$	+2.7		
19	1.4493$_6$	30.1	38,355.$_7$	19.$_2$	23.$_0$	38,313.$_5$	26,434.$_8$	−0.7	26,434.$_1$	−4.0		
20	1.5080$_0$	30.1	39,919.$_1$	15.$_5$	23.$_0$	39,880.$_6$	26,445.$_9$	−0.8	26,445.$_1$	+7.0		
21	1.4692$_2$	30.1	38,883.$_8$	15.$_5$	23.$_0$	38,845.$_3$	26,439.$_4$	−0.7	26,438.$_7$	+0.6		
22	1.4921$_7$	30.1	39,498.$_0$	14.$_9$	23.$_0$	39,460.$_1$	26,444.$_7$	−0.8	26,443.$_9$	+5.8		
23	1.6444$_2$	30.1	43,514.$_4$	15.$_5$	23.$_0$	43,475.$_9$	26,438.$_4$	−1.1	26,437.$_3$	−0.8		
50 [a]	1.5385$_8$	32.5	40,722.$_9$	17.$_6$	23.$_0$	40,682.$_3$	26,441.$_4$	−2.2	26,439.$_2$	+1.1		
51 [a]	1.5208$_0$	32.5	40,255.$_4$	16.$_9$	23.$_0$	40,215.$_5$	26,443.$_6$	−2.2	26,441.$_4$	+3.3		
52 [a]	1.5081$_7$	32.5	39,910.$_2$	17.$_6$	23.$_0$	39,869.$_6$	26,435.$_7$	−2.2	26,433.$_5$	−4.6		
24	1.4566$_3$	22.2	38,583.$_5$	57.$_8$	23.$_0$	38,502.$_7$	26,432.$_7$	+3.5	26,436.$_2$	−0.9	26437.$_1$	+2.2
25	1.6082$_8$	22.2	42,590.$_8$	65.$_4$	23.$_0$	42,502.$_4$	26,427.$_2$	+3.1	26,430.$_3$	−6.8		
26	1.5638$_1$	22.2	42,419.$_7$	59.$_8$	23.$_0$	41,336.$_9$	26,433.$_4$	+3.2	26,436.$_6$	−0.5		
27	1.4620$_2$	22.2	38,707.$_2$	48.$_0$	23.$_0$	38,636.$_2$	26,426.$_6$	+3.5	26,430.$_1$	−7.0		
28	1.5375$_3$	22.7	40,717.$_5$	52.$_0$	23.$_0$	40,642.$_5$	26,433.$_6$	+2.9	26,436.$_5$	−0.6		
29	1.4803$_9$	22.7	39,224.$_3$	54.$_6$	23.$_0$	39,146.$_7$	26,443.$_5$	+3.1	26,446.$_6$	+9.5		
30	1.5293$_4$	22.7	40.505.$_6$	51.$_9$	23.$_0$	40,430.$_7$	26,436.$_7$	+3.0	26,439.$_7$	+2.6		
31	1.5429$_8$	22.7	40,884.$_6$	68.$_2$	23.$_0$	40,793.$_4$	26,438.$_0$	+3.0	26,441.$_0$	+3.9		
32	1.5398$_5$	22.5	40,792.$_0$	57.$_2$	23.$_0$	40,711.$_8$	26,438.$_8$	+3.1	26,441.$_9$	+4.8		
33	1.6394$_0$	22.7	43,407.$_1$	55.$_7$	23.$_0$	43,328.$_2$	26,429.$_2$	+2.8	26,432.$_0$	−5.1		

34	1.0292_4	30.7	$27227._7$	$13._9$	$23._0$	$27190._8$	$26418._2$	+0.2	$26418._4$	−17.4	$26435._8$	+0.9
35	1.2169_3	32.1	$32212._0$	$16._8$	$23._0$	$32172._2$	$26437._2$	−1.1	$26436._1$	+0.3		
36	$.9927_8$	32.3	$26294._9$	$13._2$	$23._0$	$26258._7$	$26449._7$	−0.7	$26449._0$	+13.2		
37	1.0494_7	32.3	$27780._2$	$15._3$	$23._0$	$27741._6$	$26434._1$	−0.7	$26433._4$	−2.4		
38	$.9912_7$	32.3	$26252._7$	$14._5$	$23._0$	$26215._2$	$26446._1$	−0.7	$26445._4$	+9.6		
39	1.0643_2	32.3	$28175._8$	$15._2$	$23._0$	$28137._6$	$26437._1$	−0.8	$26436._3$	+0.5		
40	$.9746_0$	32.3	$25902._2$	$13._2$	$23._0$	$25866._0$	$26540._1$	−0.6	($26539._5$)			
41	1.0302_6	30.5	$27285._7$	$16._5$	$23._0$	$27246._2$	$26445._9$	+0.3	$26446._2$	+10.4		
53	1.0291_1	32.3	$27232._6$	$13._0$	$23._0$	$27196._6$	$26427._2$	−0.7	$26426._5$	−9.3		
54	1.0036_1	32.3	$26561._2$	$12._4$	$23._0$	$26525._8$	$26430._4$	−0.7	$26429._7$	−6.1		
55	1.0457_7	32.3	$27686._5$	$11._1$	$23._0$	$27652._4$	$26442._1$	−0.7	$26441._4$	+5.6		
56	1.0326_5	32.3	$27001._4$	$13._0$	$23._0$	$26965._4$	$26112._8$	−0.7	($26112._1$)			
57	1.0002_6	32.3	$26474._2$	$12._4$	$23._0$	$26438._8$	$26431._9$	−0.7	$26431._2$	−4.6		
58 [b]	1.0301_8	32.3	$27264._1$	$11._7$	$23._0$	$27229._4$	$26431._7$	−0.7	$26431._0$	−5.0	$26436._0$	+1.1
59 [b]	$.9958_8$	32.3	$26363._5$	$10._4$	$23._0$	$26330._1$	$26439._0$	−0.7	$26438._3$	+2.3		
60 [b]	1.0020_3	32.3	$26517._0$	$10._4$	$23._0$	$26483._0$	$26429._9$	−0.7	$26429._2$	−6.8		
61 [b]	$.9697_7$	32.3	$25676._2$	$10._4$	$23._0$	$25642._8$	$26442._1$	−0.7	$26441._4$	+5.4		
62 [b]	1.0022_7	32.2	$26533._3$	$10._4$	$23._0$	$26499._9$	$26439._9$	−0.7	$26439._2$	+3.2		
63 [b]	1.0107_4	32.1	$26754._0$	$10._4$	$23._0$	$26721._2$	$26437._3$	−0.7	$26436._6$	+0.6		
42	$.9791_2$	22.0	$25904._8$	$13._9$	$23._0$	$25867._9$	$26419._4$	+4.9	$26424._3$	−5.8	$26430._1$	−5.9
43	$.9917_9$	21.9	$26251._2$	$15._2$	$23._0$	$26213._0$	$26430._0$	+4.9	$26434._9$	+4.8		
44	1.0012_7	21.9	$26495._8$	$13._9$	$23._0$	$26458._9$	$26425._3$	+4.9	$26430._2$	+0.1		
45	1.0102_9	21.9	$26771._6$	$44._2$	$23._0$	$26704._4$	$26432._4$	+4.9	$26437._3$	+7.2		
46	1.0318_2	22.5	$27300._5$	$13._2$	$23._0$	$27264._3$	$26423._4$	+4.5	$26427._4$	−2.2		
47	1.0149_7	22.5	$26852._1$	$14._5$	$23._0$	$26814._6$	$26419._1$	+4.5	$26423._6$	−6.5		
48	$.9865_2$	22.3	$26104._7$	$11._2$	$23._0$	$26070._5$	$26426._8$	+4.7	$26431._5$	+1.4		
49	$.9849_2$	21.3	$26064._7$	$14._5$	$23._0$	$26027._2$	$26425._7$	+5.2	$26430._9$	+0.8		
Mean of all observations on standard sample 39d except experiments 1 to 7, inclusive, 40, 56, and 58 to 63, inclusive									$26436._0$			

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[a] Fused samples.

[b] Large piece of low-melting-point glass in bomb.

TABLE 8.—*Measurements of heat of combustion of standard sample 39e*

MATERIAL DRIED AT 105° C

Experiment number	Wt. of sample in air vs. brass weights	Initial oxygen pressure at 30° C	Total heat produced	Correction for heat of formation of HNO_3	Correction for iron wire and electric energy	Heat produced by combustion of benzoic acid	Observed heat of combustion	Reduction to standard initial conditions	Heat of combustion for standard initial conditions	Deviation from mean of group	Mean of group	Deviation from mean of all observations
	g	*atm*	*int. joules*	*int. joules*	*int. joules*	*int. joules*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*	*int. j/g (air)*
1	1.5263_6	29.9	$40394._0$	$10._3$	$23._0$	$40360._7$	$26442._4$	−0.8	$26441._6$	+3.5	$26438._1$	+3.2
2	1.4943_5	30.3	$39540._7$	$11._6$	$23._0$	$39506._1$	$26436._9$	−0.9	$26436._0$	−2.1		
3	1.5422_3	22.2	$40791._4$	$11._6$	$23._0$	$40756._8$	$26427._1$	+3.2	$26430._3$	−7.8		
4	1.5172_3	22.0	$40170._9$	$11._6$	$23._0$	$40136._3$	$26453._7$	+3.5	$(26457._2)$			
5	1.5070_5	21.9	$39883._9$	$11._6$	$23._0$	$39849._3$	$26441._9$	+3.5	$26445._4$	+7.3		
6	1.4870_3	21.8	$39339._3$	$12._3$	$23._0$	$39304._0$	$26431._2$	+3.6	$26434._8$	−3.3		
7	1.4764_3	22.1	$39067._8$	$13._6$	$23._0$	$39031._2$	$26436._2$	+3.4	$26439._6$	+1.5		
8	1.5034_4	22.1	$39769._6$	$12._9$	$23._0$	$39733._7$	$26428._5$	+3.4	$26431._9$	−6.2		
9	1.5044_9	22.0	$39817._5$	$11._0$	$23._0$	$39783._5$	$26443._2$	+3.5	$26446._7$	+8.6		
10	1.4995_0	21.8	$39672._6$	$12._3$	$23._0$	$39637._3$	$26433._6$	+3.6	$26437._2$	−0.9		
11	1.4939_6	21.8	$39526._7$	$12._3$	$23._0$	$39491._4$	$26434._0$	+3.6	$26437._6$	−0.5		

MATERIAL NOT DRIED

Experiment number	Wt. of sample in air vs. brass weights	Initial oxygen pressure at 30° C	Total heat produced	Correction for heat of formation of HNO_3	Correction for iron wire and electric energy	Heat produced by combustion of benzoic acid	Observed heat of combustion	Reduction to standard initial conditions	Heat of combustion for standard initial conditions	Deviation from mean of group	Mean of group	Deviation from mean of all observations
12	1.4840_2	21.4	$39256._4$	$9._0$	$23._0$	$39224._4$	$26431._1$	+3.8	$26434._9$	+1.0	$26433._9$	−1.0
13	1.4723_4	21.0	$38952._8$	$10._3$	$23._0$	$38919._5$	$26433._7$	+4.0	$26437._7$	+3.8		
14	1.5589_7	20.8	$41244._4$	$16._1$	$23._0$	$41205._3$	$26431._1$	+4.0	$26435._1$	+1.2		
15	1.4766_1	20.6	$39061._6$	$23._2$	$23._0$	$39015._4$	$26422._2$	+4.2	$26426._4$	−7.5		
16	1.5310_1	20.2	$40509._1$	$16._8$	$23._0$	$40469._3$	$26433._0$	+4.4	$26437._4$	+3.5		
17	1.5104_7	20.0	$39952._3$	$11._6$	$23._0$	$39917._7$	$26427._3$	+4.5	$26431._8$	−2.1		

MATERIAL FUSED

Experiment number	Wt. of sample in air vs. brass weights	Initial oxygen pressure at 30° C	Total heat produced	Correction for heat of formation of HNO_3	Correction for iron wire and electric energy	Heat produced by combustion of benzoic acid	Observed heat of combustion	Reduction to standard initial conditions	Heat of combustion for standard initial conditions	Deviation from mean of group	Mean of group	Deviation from mean of all observations
18	1.4920_7	20.1	$39465._6$	$15._5$	$23._0$	$39427._1$	$26424._4$	+4.5	$26428._9$	−5.4	$26434._3$	−0.6
19	1.5286_2	20.2	$40434._4$	$9._7$	$23._0$	$40401._7$	$26430._2$	+4.4	$26434._6$	+0.3		
20	1.5167_2	20.1	$40126._1$	$11._6$	$23._0$	$40091._5$	$26433._0$	+4.5	$26437._5$	+3.2		
21	1.5174_0	20.2	$40145._8$	$12._9$	$23._0$	$40109._9$	$26433._3$	+4.4	$26437._7$	+3.5		
22	1.5243_4	20.0	$40320._5$	$11._6$	$23._0$	$40285._9$	$26428._4$	+4.5	$26432._9$	−1.4		

MATERIAL DRIED AT 105° C											
36	1. 5159$_6$	29. 4	40108.$_3$	10.$_0$	23.$_0$	40075.$_3$	26435.$_6$	−0. 5	26435.$_1$	+1. 6	26433.$_5$	−1. 4
37	1. 5151$_1$	29. 4	40090.$_9$	9.$_7$	23.$_0$	40058.$_2$	26439.$_1$	−0. 5	26438.$_6$	+5. 1		
38	1. 5236$_2$	29. 5	40293.$_9$	9.$_0$	23.$_0$	40261.$_9$	26425.$_1$	−0. 5	26424.$_6$	−8. 9		
39	1. 5222$_9$	29. 7	40276.$_1$	9.$_0$	23.$_0$	40244.$_1$	26436.$_5$	−0. 7	26435.$_8$	+2. 3		
40	1. 5120$_1$	29. 6	40001.$_8$	10.$_0$	23.$_0$	39968.$_8$	26434.$_2$	−0. 6	26433.$_6$	+0. 1		
MATERIAL FUSED											
23	0. 9892$_7$	20. 4	26170.$_8$	9.$_0$	23.$_0$	26138.$_3$	26422.$_2$	+5. 7	26427.$_9$	−2. 1	26430.$_0$	−4. 9
24	. 9991$_3$	20. 2	26431.$_7$	7.$_7$	23.$_0$	26401.$_0$	26424.$_0$	+5. 9	26429.$_9$	−0. 1		
25	. 9988$_0$	20. 1	26418.$_8$	9.$_0$	23.$_0$	26386.$_8$	26418.$_5$	+5. 8	26424.$_3$	−5. 7		
26	1. 0166$_3$	20. 4	26765.$_8$	10.$_3$	23.$_0$	26732.$_5$	26425.$_2$	+5. 6	26430.$_8$	+0. 8		
27	. 9973$_6$	20. 2	26392.$_7$	8.$_4$	23.$_0$	26361.$_3$	26431.$_1$	+5. 8	26436.$_9$	+6. 9		
MATERIAL NOT DRIED											
41	0. 9997$_7$	21. 5	26436.$_3$	7.$_1$	23.$_0$	26406.$_2$	26412.$_3$	+5. 1	26417.$_4$	−12. 7	26430.$_1$	−4. 8
42	1. 0035$_0$	22. 5	26564.$_2$	8.$_7$	23.$_0$	26532.$_5$	26440.$_0$	+4. 7	26444.$_7$	+14. 6		
43	. 9954$_4$	21. 6	26333.$_7$	6.$_0$	23.$_0$	26304.$_7$	26425.$_2$	+5. 1	26430.$_3$	+0. 2		
44	1. 0146$_0$	21. 6	26837.$_6$	7.$_3$	23.$_0$	26807.$_3$	26421.$_5$	+5. 0	26426.$_5$	−3. 6		
45	1. 0075$_4$	21. 4	26655.$_1$	7.$_3$	23.$_0$	26624.$_8$	26425.$_5$	+5. 1	26430.$_6$	+0. 5		
46	. 9960$_3$	21. 3	26353.$_4$	9.$_1$	23.$_0$	26321.$_3$	26426.$_2$	+5. 2	26431.$_4$	+1. 3		
MATERIAL DRIED AT 105° C											
28	0. 7026$_6$	20. 5	18592.$_0$	5.$_2$	23.$_0$	18563.$_8$	26419.$_3$	+6. 4	26425.$_7$	−4. 6	26430.$_3$	−4. 6
29	. 6800$_1$	20. 1	17995.$_7$	5.$_8$	23.$_0$	17966.$_9$	26421.$_4$	+6. 7	26428.$_1$	−2. 1		
30	. 6987$_0$	20. 1	18496.$_9$	7.$_1$	23.$_0$	18466.$_8$	26430.$_3$	+6. 7	26437.$_0$	+6. 7		
31	. 6992$_0$	20. 0	18484.$_7$	3.$_2$	23.$_0$	18458.$_5$	26399.$_5$	+6. 7	(26406.$_2$)	----------		
MATERIAL DRIED AT 105° C											
32	1. 9955$_1$	29. 8	52788.$_7$	11.$_6$	23.$_0$	52754.$_1$	26436.$_4$	−2. 0	26434.$_4$	−0. 7	26435.$_1$	+0. 2
33	2. 0188$_9$	29. 6	53419.$_8$	12.$_3$	23.$_0$	53384.$_5$	26442.$_4$	−1. 9	26440.$_5$	+5. 4		
34	2. 0242$_0$	29. 6	53542.$_0$	11.$_6$	23.$_0$	53507.$_4$	26433.$_8$	−1. 9	26431.$_9$	−3. 2		
35	2. 0294$_1$	29. 5	53685.$_4$	14.$_2$	23.$_0$	53648.$_2$	26435.$_3$	−1. 8	26433.$_5$	−1. 6		
Mean of all observations except experiments 4 and 31									26433.$_8$	----------	----------	----------
Mean of 39d and 39e									26434.$_9$	----------	----------	----------

Reduction to the standard state practically always brought the results of groups of experiments made under different conditions into better agreement. It is seen from tables 7 and 8, however, that even after reduction to the standard state there are small systematic differences between the results of measurements made at different times and under different conditions. Thus the results obtained with 1.5 g samples of benzoic acid are, in general, somewhat higher than those obtained with 1.0 g samples. This difference is consistent with the apparent variation of the electrical energy equivalent of the calorimeter with temperature rise discussed in section III of this paper. However, since this variation was not observed in all cases, either in the calibration of the calorimeter or in the combustion experiments, it seems best to take the mean of the results of all experiments as the best value deducible from the present work for the heat of combustion of the standard samples.

In taking the mean of the results on sample 39d, experiments 1 to 6, inclusive, were disregarded, as the oxygen used in these experiments was not purified, and may have contained combustible impurities. The mean of the results of these experiments is definitely higher than the mean of the results of any other group of experiments, and 0.03 percent higher than the mean result obtained for this sample. Experiments 58 to 63 were also disregarded (although including them would not have changed the mean of all of the experiments) because in these experiments a large piece of the glass used to insulate the firing electrode was placed in the bottom of the bomb. The results of these experiments indicate that the action on the glass of the nitric acid formed in the combustion does not produce any appreciable thermal effect. Experiments 7, 40, and 56 were disregarded on account of very large differences from the other experiments.

In taking the mean of the results on sample 39e experiments 4 and 31 were disregarded, the former on account of a short circuit in the firing circuit which resulted in a large firing energy, and the latter on account of a large change in the temperature of the jacket during the experiment.

The mean results for samples 39d and 39e are, respectively, 26,436 and 26,434 international joules per gram weight in air against brass weights. As the 2 values differ by less than the estimated uncertainty of the results, the average of the 2 values, 26,435 international joules per gram weight of air, or 26,414 international joules per gram mass (weight corrected for air buoyancy)[20] may be taken as the heat of combustion of either sample under the standard conditions mentioned above.

The average deviation of the individual results of electrical energy experiments from the mean is 2.1 int. joules per degree, or 0.015 percent. The average deviation of the individual results of heat of combustion determinations from the mean is 5.0 int. joules per gram, or 0.019 percent. On account of the large number of observations the probable errors of the final results of both the electrical energy experiments and the heat of combustion measurements are absurdly small (less than 0.002 percent). The probable error of a single electrical energy experiment is 1.8_5 international joules per degree (0.014

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[20] The correction for air buoyancy is based on the assumption that the densities of benzoic acid, weights, and air are, respectively, 1.26, 8.4, and 0.00117 g/cm³. The value used for the density of air is the average value calculated from 16 observations of temperature and barometric pressure made during the course of the work. The individual values of density of air varied from 0.00115 to 0.00120 g/cm³.

percent). The probable error of a single heat of combustion measurement is 4.3 international joules per gram (0.016 percent). The estimated uncertainty in the final result is 6 international joules per gram (0.023 percent). The value for the heat of combustion obtained by combining the highest mean observed electrical energy equivalent of the calorimeter for a group of experiments (experiments 5 to 9 and 16 to 20 in table 3), with the highest mean observed heat of combustion for a group of experiments (experiments 8 to 23 and 50 to 52 in table 7, or experiments 1 to 11 in table 8), would be higher than that given above by 0.04 percent. Similarly, the value obtained by combining the lowest mean observed electrical energy equivalent for a group of experiments with the lowest mean heat of combustion for a group of experiments, would be lower than the value given above by 0.05 percent.

The measurements were made at 30° C as a matter of convenience, since often during the summer months it is not possible to keep the jacket at a lower temperature. Most thermochemical data are, however, referred to 25° C. Using specific heat data given in International Critical Tables, vol. 5, 80 and 104, the temperature coefficient of the heat of combustion of benzoic acid is found to be −0.94 joule per gram per °C. The heat of combustion at 25° C is then 26,440 international joules per gram weight of air against brass weights, or 26,419 international joules per gram mass, when the sample is burned at 25° C in oxygen under an initial pressure of 30 atmospheres,[21] the mass of sample and the mass of water placed in the bomb initially each being 3 g per liter of bomb volume.[22] This value is for the heat of combustion of the standard samples 39d and 39e, neither of which is absolutely pure benzoic acid, although the amount of impurity is known to be small.

V. PREVIOUS WORK

Fischer and Wrede [23] in 1909 reported the results of 7 determinations of the heat of combustion of benzoic acid. The mean of the 7 observations was 26,475 joules per gram mass at about 17.5 °C, with an average deviation from the mean of 6 joules per gram.

The oxygen pressure used in these measurements was 45 atmospheres, the volume of the bomb 275 cm^3, the mass of charge about 0.9 g, and the mass of water placed in the bomb before each experiment 0.5 g.

The calorimeter was calibrated electrically by Jaeger and von Steinwehr,[24] who made 13 determinations, the average deviation from the

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[21] Strictly speaking the value given for the heat of combustion at 25° corresponds to an initial oxygen pressure of 29.5 atmospheres, since it is derived from the value at 30° and 30 atmospheres by the use of data on C_V, and since on cooling from 30 to 25° C the initial pressure would decrease by 0.5 atmosphere. The difference is of no importance as a difference of 0.5 atmosphere in the initial pressure results in a change of only 0.001 percent in the observed heat of combustion.

[22] The heat of combustion under conditions differing from the standard conditions is obtained by multiplying the value given by the factor

$$1+10^{-6}\left[25(P-30)+49\left(\frac{M_s}{V}-3\right)+38\left(\frac{M_w}{V}-3\right)-36(t-25)\right]$$

where

P=initial absolute pressure of oxygen in atmospheres.
M_s=mass of sample of benzoic acid, in grams.
M_w=mass of water in bomb before combustion, in grams.
V=volume of bomb in liters.
t=temperature to which reaction is referred, in °C.

[23] Z.phys.Chem. 69,218(1909).

[24] Ann.d.Phys. 21,23(1906).

mean being 0.04 percent. The unit of electromotive force used in this calibration was based on the value 1.01860 volts for the emf of the Weston cell, whereas the accepted value of the emf of the Weston cell in terms of the present international volt is 1.01830.

Hence the value obtained by Fischer and Wrede, when expressed in terms of the present international electrical units, will be less than the value given above by 0.06 percent, or 16 joules per gram. According to Jaeger and von Steinwehr [25] a further correction of −8 joules per gram should be applied to take account of the firing energy. The value is still further lowered by 7 joules per gram by reduction to the standard temperature of 25° C, and by 7 joules per gram by reduction to the standard initial conditions. The finally recomputed value is therefore 26,437 international joules per gram mass.

Wrede [26] in 1910 made 7 additional measurements of the heat of combustion of benzoic acid in the same calorimeter and under the same conditions as in the measurements of Fischer and Wrede. The mean of the results obtained was 26,466 joules per gram mass. Application of the corrections mentioned above yields the value 26,428 international joules per gram mass at 25° C and under the standard initial conditions.

Dickinson[27] in 1914 reported the value 6,329 calories_{20} per gram weight in air against brass weights, as the mean of a large number of measurements of the heat of combustion of benzoic acid. The measurements were made at about 25° C, the initial oxygen pressure was 30 atmospheres, the volume of the bomb 275 cm^3, the mass of charge 1.5 g, and the mass of water placed in the bomb before each experiment was 0.5 g. The calorimeter was calibrated in terms of the present international electrical units, and the method of reduction to calories is equivalent to the use of a conversion factor of 4.181 joules per calorie_{20}.

Upon converting to electric units by means of the factor given above, and correcting for air buoyancy, Dickinson's value becomes 26,441 international joules per gram mass. Reduction to the standard initial conditions lowers this value to 26,439 international joules per gram mass.

It has recently been pointed out by D. R. Harper, 3d[28] that, in calculating the heat capacity of the oxygen in his bomb, Dickinson used C_p rather than C_v. The difference amounts to 0.02 percent in the total heat capacity of the calorimeter, and the resulting value for the heat of combustion of benzoic acid is therefore too high by this amount. On reducing the value given above by 0.02 percent, the finally recomputed value becomes 26,434 international joules per gram mass.

Roth, Doepke, and Banse[29] in 1928 reported the results of 2 series of measurements with an electrically calibrated calorimeter, of the heat of combustion of benzoic acid. The material used was supplied by Kahlbaum, and tested by P. Verkade, in Rotterdam, according to whom it was identical, so far as heat of combustion measurements indicated, with material obtained from the National Bureau of Standards. (Probably standard sample 39d.)

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[25] Z.Phys.Chem. **135**,305(1928).
[26] Z.phys.Chem. **75**,81(1910).
[27] Bul. BS **11**,189 (1914); S230.
[28] Private communication.
[29] Z. phys. Chem. **133**, 431 (1928).

The first series consisted of 7 calibration experiments in which the average deviation from the mean was 0.04 percent, and 7 combustion experiments with an average deviation from the mean of 0.035 percent. The second series consisted of 6 calibration experiments and 5 combustion experiments, the average deviations from the means being 0.05 and 0.025 percent, respectively. The difference in the values of the heat of combustion obtained in the 2 series was 0.02 percent.

Temperatures were measured by means of a Beckmann thermometer. The initial oxygen pressure was 35 atmospheres; the mass of the sample varied from 0.5 to 0.9 g. The volume of the bomb and the mass of water placed in it are not given. Washburn[30] in reducing the result to the standard initial state, has assumed that the bomb volume was 0.3 liter, and the mass of water placed in the bomb was 1.0 g.

The value reported by Roth, Doepke, and Banse is 26,433 international joules per gram mass, at 20° C. Reduction to the standard initial state and to 25° C lowers this value to 26,426 international joules per gram mass.

According to measurements made in 1931 and reported by Vinal,[31] there is a difference in the value of the watt derived from electrical standards maintained at the Physikalischtechnische Reichsanstalt, and that derived from standards maintained at the National Bureau of Standards, the latter being larger by 0.013 percent. Hence the result obtained by Roth, Doepke, and Banse, when expressed, for the purpose of comparision with the results of the present work, in terms of the electric units maintained at this Bureau, becomes 26,423 international joules per gram mass at 25° C.

Jaeger and von Steinwehr[32] in 1928 reported the results of measurements of the heat of combustion of benzoic acid, using the calorimeter and bomb which had been used by Fischer and Wrede. Two lots of material were used, one obtained from the National Bureau of Standards and the other supplied by Kahlbaum and tested by Verkade. The oxygen pressure used was 45 atmospheres, the volume of the bomb 280 cm^3, and the mass of the charge of benzoic acid 0.9 g. The mass of water placed in the bomb is not given, but may be assumed to be 0.5 g as in the measurements of Fischer and Wrede.

The calorimeter was calibrated electrically, and a platinum resistance thermometer used for temperature measurements. Two series of determinations of the heat capacity were made, which gave results differing by 0.067 percent. The average deviation from the mean in the first series was 0.07 percent and in the second 0.08 percent.

Seven combustion measurements on the National Bureau of Standards material gave the value 26,444 international joules per gram mass at 20° C, while 9 determinations with the Kahlbaum material gave the value 26,433 international joules per gram mass. The average deviation from the mean for each material was ±17 joules per gram. On reducing to 25° C and the standard initial state, and correcting for the difference in the watt, these 2 values become 26,426 and 26,415 respectively, in terms of the international electrical units maintained at the National Bureau of Standards. The mean of all of the experiments on both materials is 26,420 international joules

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[30] BS J. Research **10**, 525 (1933); RP546.
[31] BS J. Research, 8, 729 (1932); RP448.
[32] Z. phys. Chem. **135**, 305(1928).

per gram mass, which is practically identical with the value obtained in the present work for the National Bureau of Standards material.

The results obtained by the various observers are summarized in table 9. The value obtained in the present work is seen to be in agreement within 0.03 percent[33] with the values obtained by Roth, Doepke, and Banse, and by Jaeger and von Steinwehr. The value obtained by Wrede in 1910 is higher by 0.03_4 percent, while those of Fischer and Wrede and of Dickinson are, respectively, 0.07 and 0.06 percent higher than the value obtained in the present work.

Table 9.—*Results obtained by various observers*

Observer	Date	Heat of combustion at 25° C and standard initial state
		int. joules/g (vac)
Fischer and Wrede	1909	26, 437
Wrede	1910	26, 428
Dickinson	1914	26, 434
Roth, Doepke, and Banse	1928	26, 423
Jaeger and von Steinwehr	1928	[1] 26, 426 [2] 26, 415
Present work	1933	26, 419

[1] National Bureau of Standards Material.
[2] Kahlbaum-Verkade Material.

It is not possible to say how much of these differences is due to differences in material and how much to experimental errors. The results obtained in the present work indicate that a part of the differences may be due to combustible impurities in the oxygen used. Fischer and Wrede analyzed their oxygen for hydrogen and hydrocarbons, and state that no detectable amount of either was present. They give no data on the accuracy of their analyses, but their method can be used with sufficient accuracy to detect an amount of impurity which would cause an error of 0.01 percent in the heat of combustion. Dickinson used atmospheric oxygen which was obtained commercially and did not determine or remove combustible impurities. If this oxgyen contained the same amount of combustible impurities as that used in the present work, and if the error caused by these impurities is proportional to the mass of oxygen in the bomb, a correction of −0.02 percent should be added to Dickinson's value which would bring it within 0.04 percent of the value obtained in the present work. Roth, Doepke, and Banse give no data regarding the oxygen used in their work. Jaeger and von Steinwehr state that they used commercial oxygen which was obtained from liquid air, and was "very pure."

VII. SUMMARY

Measurements of the electrical energy equivalent of a bomb calorimeter, and of the heat of combustion of two lots of benzoic acid are described. The value obtained for the heat of combustion of these lots at 25° C is 26,419 international joules per gram mass (weight corrected for air buoyancy) when the sample is burned in an enclosure of constant volume, in oxygen under an initial pressure of 30 atmos-

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[33] Within 0.015 percent if the results of Jaeger and von Steinwehr are all averaged together.

pheres absolute, the mass of sample and mass of water placed in the bomb each being 3 g per liter of bomb volume. This is in agreement within 0.03 percent with measurements reported in 1928 by Roth, Doepke, and Banse, and by Jaeger and von Steinwehr, but is 0.07 percent lower than the value obtained by Fischer and Wrede, and 0.04 or 0.06 percent lower than that obtained by Dickinson. The differences may be due partly to differences in material, and partly to combustible impurities in the oxygen used by the previous investigators.

The work described in this paper was done under the direction of H. C. Dickinson and E. F. Mueller, both of whom have contributed valuable suggestions during the course of the work.

The chemical data on sample 39d were obtained by A. Isaacs, and those on sample 39e by J. I. Hoffman and H. A. Buchheit. The freezing point measurements on sample 39d were made by F. W. Rose. Several analyses of gaseous products of combustion for carbon monoxide were made by C. Creitz.

WASHINGTON, July 31, 1934.