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HEAT OF COMBUSTION OF BENZOIC ACID, WITH SPECIAL REFERENCE TO THE STANDARDIZATION OF BOMB CALORIMETERS

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ABSTRACT

New measurements yielded the value 26428.4 ± 2.6 International joules per gram mass for the heat of combustion, Q_B, of benzoic acid at 25° C under the conditions of the standard bomb process. The difference, 0.036 percent, between the above value and that reported in 1934 is due to five factors: (1) An error in the previous value, resulting from the effect of dissolved carbon dioxide on the determination of the nitric acid formed in the bomb, (2) a change in the value used for the energy of formation of nitric acid in the bomb, (3) taking account in the present work (in the calculation of the value of Q_B at 25° from the observed value at 30°) of the temperature dependence of the Washburn reduction, (4) a change in the value used for the temperature coefficient of the heat of combustion, arising from the use of a new value for the specific heat of benzoic acid, and (5) a small difference in the results of the calorimetric measurements. The 1934 results, when corrected for the first four of the above effects, are in agreement within 0.01 percent with the results of the present measurements. The procedure for correcting the results of calibration experiments originally calculated on the basis of the 1934 value of Q_B is described.

With one exception, values of Q_B at 25° C calculated from the results of previous measurements are in satisfactory agreement with the value given above.

When the amount of benzoic acid burned in each experiment was calculated from the mass of carbon dioxide formed, the present measurements yield the value 3226.39 ± 0.32 International kilojoules per mole for $-\Delta H^\circ_{298.16}$, the decrease in heat content for the combustion reaction at 25° C when each of the gases involved in the reaction is in the thermodynamic state of the unit fugacity and the water formed in combustion is in the liquid state.

CONTENTS

I. INTRODUCTION

Benzoic acid has been used many years as a standard substance for calibrating bomb calorimeters, and has been selected as the primary standard substance for this purpose by the Standing Committee for Thermochemistry of the International Union of Chemistry [1].[1] Such use of benzoic acid requires an accurate value, in terms of some generally acceptable energy unit, for its heat of combustion under the conditions of the bomb process.

The results of heat of combustion measurements made at this Bureau on various lots of benzoic acid used as Standard Sample material have been reported previously [2, 3]. Because impurities might affect the heat of combustion of different lots of benzoic acid by significantly different amounts, it has been the practice at this Bureau to determine the heat of combustion of each lot of Standard Sample material.

The present paper gives the results of measurements of the heat of combustion of two lots of benzoic acid, designated as Standard Samples 39e and 39f, and of two samples of benzoic acid of a very high degree of purity that were prepared by Schwab and Wichers [4] of this Bureau.

These measurements were made primarily for the purpose of providing data for use in connection with the standardization of bomb calorimeters. For this purpose the quantity of interest is the heat of combustion per gram of sample under the conditions of the bomb process. However, since material of exceptionally high purity was available for this work, it seemed worth while to obtain also data on the heat of combustion per mole of benzoic acid. The values reported for the heat of combustion per mole apply for conditions other than those of the bomb process, and these values are not suitable for use in connection with the standardization of bomb calorimeters.

II. APPARATUS AND METHOD

The essential features of the apparatus and methods used in the present work have been described in detail [2, 3] previously, and only a brief description of them will be given here. The calorimeter system consists of a nickel-plated copper vessel, of about 3.5 liters capacity, containing a weighed amount of water, provided with a closely-fitting cover and an arrangement for stirring the water; an electric heater; a bomb of 377 ml capacity, made of a corrosion-resistant alloy (illium); and a platinum resistance thermometer. The calorimeter is completely inclosed by a jacket which can be maintained at a constant temperature by means of a thermostat, and which is separated from the calorimeter by a 1-cm air space.

The method consists in making two types of experiments with the calorimeter. In one of these a measured quantity of energy is supplied to the system electrically, and the resulting temperature rise of the calorimeter is observed. In the other type of experiment a weighed sample of a combustible material is burned in the bomb, and the resulting temperature rise is observed. The first type of experiment yields the energy equivalent (effective heat capacity) of the calorimeter system, and when the energy equivalent is known the

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[1] Numbers in brackets indicate the literature references at the end of this paper.

temperature rise of the calorimeter in the second type of experiment is a measure of the heat produced by the combustion. In both types of experiments the bomb contained 1 ml of water, and oxygen under a pressure of approximately 30 atmospheres. The procedure in both types of experiments was such that the final temperature of the calorimeter was very nearly the same as the constant temperature of the jacket.

The apparatus and methods used in the present work differ from those described in the report of measurements made at this bureau in 1934 [3] principally in the following respects:

1. The power measurements in the determination of the energy equivalent of the calorimetric system were referred to a saturated cadmium standard cell, which was maintained at a constant temperature by means of a temperature-control box [5]. The cell was calibrated before each series of energy-equivalent determinations, and its electromotive force remained constant to 2 microvolts over a period of 6 months. Unsaturated standard cells of the type used in the 1934 measurements have a very low temperature coefficient, but have been found to exhibit hysteresis effects [6] when exposed to varying temperature. Errors from this source could be avoided by keeping the cells at a constant temperature, but with the temperature kept constant the saturated cells have been found to be more satisfactory.
2. The Wolff-Diesselhorst potentiometer used for the measurements of power was calibrated in place. The potentiometer ratio (ratio of reading to electromotive force) was measured before each energy-equivalent determination, using two recently calibrated standard resistors [7].
3. The platinum resistance thermometer used to measure the temperature change of the calorimeter was of the same type as that used in the 1934 measurements [3], but it did not exhibit the erratic behavior of the latter.
4. The Wheatstone bridge used in connection with the platinum resistance thermometer was designed especially for bomb-calorimetric measurements [8].
5. The "constant range" method [9, 31] was used, that is, all calibration and combustion experiments were made over very nearly the same range of temperature. This procedure largely eliminates the effect of constant errors in calibration of the Wheatstone bridge and of peculiarities in the temperature scale defined by the thermometer.
6. In some of the measurements the amount of carbon dioxide formed in combustion was determined in the manner described in 1938 [10].

III. CALIBRATION OF THE CALORIMETER

The energy equivalent of the calorimeter was measured in the manner described in the 1934 report [3], except for the changes in apparatus and procedure mentioned in section II of this paper. The values obtained for the energy equivalent of the calorimetric system were all reduced to correspond to an absolute pressure of 30 atmospheres at 30° C. All the calibration experiments were made over very nearly the same temperature range, the temperature rise being about 3 degrees and the final temperature 30° C in all cases.

The results of the first series of calibration experiments are given in table 1. This series consisted of two groups of experiments, one made with 31 volts across the heater in the calorimeter and a time of heating of 7 minutes, the other with 47.5 volts and a time of heating of 3 minutes.

TABLE 1.—*Results of first series of electrical calibration experiments*

Experiment number	Date 1940	Approximate electromotive force across heater	Energy equivalent	Deviation from mean
		Volts	*Int.j/°C*	*Int.j/°C*
1	July 24	31	13733.9	+0.6
2	24	31	35.5	+2.2
3	Aug. 2	31	30.4	−2.9
4	2	31	32.7	−0.6
5	2	31	33.1	−.2
6	3	31	32.3	−1.0
7	5	31	31.3	−2.0
8	5	31	34.2	+0.9
9	5	31	33.2	−0.1
10	5	31	34.0	+0.7
11	6	31	35.6	+2.3
12	6	31	32.8	−0.5
Mean for group			13733.3	[a] $\pm 0.4_4$
13	Aug. 7	47.5	13732.8	−0.9
14	7	47.5	33.5	−0.2
15	7	47.5	34.1	+0.4
16	7	47.5	34.3	+0.6
17	8	47.5	33.2	−0.5
18	8	47.5	34.9	+1.2
19	8	47.5	34.0	+0.3
20	8	47.5	33.2	−0.5
Mean for group			13733.7	[a] $\pm 0.2_5$
Weighted mean			13733.6	[a] ±0.2

[a] The standard deviation of the mean.

Table 1 shows that the mean values of energy equivalent from the two groups of calibration experiments are in agreement within about 0.003 percent. The results of measurements on Standard Samples 39e and 39f given in table 4 were calculated on the basis of the weighted mean value given in table 1 for the energy equivalent of the calorimeter.

The results of a second series of calibration experiments, made after some necessary repairs to the calorimeter, are given in table 2. All experiments in this group were made with an electromotive force of about 31 volts across the heater in the calorimeter, and with a heating period of 7 minutes. The results of measurements on Standard Samples 39e and 39f given in table 5, and the results of measurements on purified benzoic acid given in table 8 were calculated on the basis of the mean value given in table 2 for the energy equivalent of the calorimeter.

TABLE 2.—*Results of second series of electrical calibration experiments*

Experiment number	Date 1941	Energy equivalent	Deviation from mean	Experiment number	Date 1941	Energy equivalent	Deviation from mean
		Int. j/° C	*Int. j°/ C*			*Int. j/° C*	*Int. j/° C*
1	Feb 18	13732.0	−0.2	9	24	32.1	−.1
2	18	33.5	+1.3	10	24	31.7	−.5
3	19	32.6	+0.4	11	25	32.1	−.1
4	21	31.2	−1.0	12	25	31.3	−.9
5	21	30.8	−1.4	13	25	32.8	+.6
6	21	33.6	+1.4				
7	21	32.3	+0.1	Mean		13732.2	[a]$\pm 0.2_5$
8	24	32.7	+.5				

[a] The standard deviation of the mean.

IV. COMBUSTION EXPERIMENTS

1. MATERIAL

From the freezing behavior of Standard Samples 39e and 39f, Schwab and Wichers [4] have estimated the purity of these lots of benzoic acid to be 99.983 and 99.977 mole percent, respectively. From specific-heat measurements on the solid at temperatures near the melting point, the purity of Sample 39e was estimated to be 99.990 mole percent [4, 12].

The two samples of purified benzoic acid were prepared by Schwab and Wichers from Standard Sample 39e, one by eight fractional crystallizations from aqueous solution, the other by eight fractional crystallizations from benzene solution. The purity of the first of the purified samples was estimated from freezing behavior to be 99.995 mole percent, whereas that of the second sample was estimated from both freezing behavior and specific-heat measurements to be 99.999 mole percent [4, 12].

As noted by Schwab and Wichers [4], the estimates of purity from specific-heat measurements were made on samples that had been dried by passing dry air through liquid benzoic acid at a temperature a few degrees above the melting point. It was later found that this treatment results in the very slow formation of benzoic anhydride. It is possible, therefore, that these samples may have contained slightly larger amounts of impurity than the corresponding samples for which the estimates of purity were made on the basis of freezing behavior. On the other hand, the drying treatment may have removed some excess water from Standard Sample 39e, so that for this Sample the net effect of the drying treatment may have been either an increase or a decrease in purity. In view of the facts that the rate of formation of benzoic anhydride under the conditions of the drying treatment is extremely small, and that only a very small amount of water was found in the Standard Sample material in the special tests described later in this paper, it is not believed that the formation of anhydride or the removal of water caused any significant change in purity of the Samples.

It should be emphasized that both of the tests of purity mentioned above are sensitive only to impurities that are soluble in the liquid and insoluble in the solid benzoic acid. The Standard Sample material is known to contain some insoluble material, but the amount of this is so small as to be practically negligible.

Combustible impurities were removed from the oxygen used by passing the gas through a tube filled with copper oxide maintained at a temperature of about 750°C.

2. IGNITION ENERGY

The samples of benzoic acid were ignited by passing electric current from a small transformer through a helix made from a 2-cm length of No. 36 AWG iron wire (about 0.13 mm in diameter). The procedure was the same as in the measurements reported in 1934 [3], except that the secondary voltage of the transformer in the present measurements was 9 instead of 14 as in the previous work. The energy, q_i, used to ignite the charge (q_i=electric energy plus heat of combustion of iron wire) was determined calorimetrically in a number of blank experiments in which only the iron wire was burned. The results of these measurements are given in table 3. The standard deviation of the mean of the results and the maximum deviation from the mean correspond to 0.001 and 0.005 percent, respectively, of the heat of combustion of a 1.5-g sample of benzoic acid.

TABLE 3.—*Energy used to ignite the charge*

Experiment number	q_i	Deviation from mean
	Int. j	*Int. j*
1	17.1	−1.5
2	20.6	+2.0
3	19.3	+0.7
4	19.0	+0.4
5	17.3	−1.3
6	18.2	−0.4
7	19.7	+1.1
8	17.5	−1.1
Mean	18.6	[a]$\pm 0.4_5$

[a] Standard deviation of the mean.

In another method of ignition, which has been described by Huffman and Ellis [13], an electrically heated platinum wire ignites a small piece of filter paper, which in turn ignites the charge. In some preliminary experiments of the present work the method of Huffman and Ellis was compared with the iron-wire method of ignition by using the two methods alternately in a series of calorimetric experiments in which Standard Sample benzoic acid was burned in the bomb. These experiments yielded the following values for the energy equivalent of the calorimeter, which differed in some respects from the calorimeter used in the other experiments described in this paper:

Method of ignition	Number of experiments	Mean value of energy equivalent	Standard deviation of the mean
		Int. j/°C	*Int. j/°C*
Iron wire	6	13733.6	$\pm 0.6_5$
Platinum wire and filter paper	6	13732.4	$\pm 0.7_5$

These results indicate that the precision of the two methods is about the same. The difference between the two mean values of energy equivalent is no larger than might be expected if the procedure in the two sets of measurements had been identical in all respects, and is in the direction opposite to that of the difference which might be expected to result from action of nitric acid on the products of combustion of the iron wire. The iron-wire technique is somewhat more convenient than the platinum-wire–filter-paper technique, and has the further advantage that it does not complicate the determination of the amount of carbon dioxide formed in the combustion of the charge.

3. CORRECTION FOR HEAT OF FORMATION OF NITRIC ACID

The amount of nitric acid formed in the bomb in each combustion experiment was determined by titrating the bomb washings against an 0.1 *N* solution of potassium hydroxide, using phenolphthalein[2] as an indicator. The correction, q_{HNO_3}, for the energy of formation of nitric acid in the bomb was calculated, using for the energy decrease, $-\Delta U_{HNO_3}$, for the reaction $1/2\ N_2\ (g)+5/4\ O_2\ (g)+1/2\ H_2O\ (liq)=HNO_3\ (aq)$ at 30° C the rounded value 60 kj/mole of nitric acid. This value is very near the mean of the value derived from the results of Becker and Roth [14], and that derived from data given by Bichowsky and Rossini [15]. The correction for the heat of formation of nitric acid rarely exceeded 0.02 percent of the heat produced in the bomb, and was usually less than this.

4. CALCULATION OF RESULTS

The corrected temperature rise, Δt, of the calorimeter for each calibration experiment and each combustion experiment was computed on the basis of Newton's law of cooling from data obtained in two "rating periods", using Dickinson's method [2] of calculation. It has been shown that the effect of the lag of the bomb and other parts of the calorimetric system is almost completely eliminated by this procedure [16, 17, 25].

The quantity of heat produced in each combustion experiment was computed by multiplying the corrected temperature rise, Δt, by the energy equivalent of the system, represented by $C=C_0+1.21\ m_s+0.32\ (P-30)$, where C_0 is the energy equivalent, determined by the calibration experiments, of the calorimetric system, including the bomb containing 1 g of water, and oxygen under an absolute pressure of 30 atm; m_s is the mass of the sample of benzoic acid; P is the initial oxygen pressure, in atmospheres, at 30° C. The factor 1.21 is the value recently obtained at this Bureau [12] for the specific heat of benzoic acid at 28.5° C (at constant pressure); and the factor 0.32 was calculated from the specific heat of oxygen at constant volume [18], the volume of the bomb, and the density of oxygen.

The value for the heat of combustion per gram of sample under the conditions of the actual bomb process was calculated for each experiment by means of the relation

$$q_B=\frac{C\Delta t-q_i-q_{HNO_3}}{m_s}.$$

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[2] Phenolphthalein is sensitive to dissolved carbon dioxide, and its use resulted in high values for nitric acid unless precautions were taken to remove dissolved carbon dioxide from the bomb washings before titrating. It is shown later in this paper that under the conditions of the present measurements the effect of dissolved carbon dioxide amounted to about 0.017 percent of the heat of combustion. The use of an indicator that is practically insensitive to carbon dioxide, such as methyl orange, would have been better.

The corresponding value for the heat of combustion per mole of benzoic acid was calculated from

$$-\Delta U_B = \frac{C\Delta t - q_i - q_{\mathrm{HNO_3}}}{N/7},$$

where N is the number of moles of carbon dioxide formed in the combustion, the molecular weight of carbon dioxide being taken as 44.010. Since the value of C used in the above equations is the energy equivalent of the calorimetric system, including the oxygen and charge of benzoic acid rather than the products of combustion, the values of q_B and $-\Delta U_B$ are referred to the final temperature of the calorimeter, which was 30° C in all experiments.

With the aid of an equation similar to Washburn's [19] eq 81 (which applies at 20° C), but calculated by the writer for 30° C, there was computed from each value of q_B the corresponding value of Q_B, which is the heat of combustion (at 30° C) per gram of sample for the standard bomb process defined by the following initial conditions

$$m_S/V = 3.0 \text{ g/liter}$$
$$m_W/V = 3.0 \text{ g/liter}$$
$$P = 30 \text{ atm at } 30^\circ \text{ C},$$

where V is the volume of the bomb, and m_W is the mass of water placed in the bomb before the experiment. The other symbols have been defined previously.

The values of $-\Delta U_B$ per mole of benzoic acid were reduced, with the aid of the modified Washburn equation, to the corresponding values of $-\Delta U_R$, which is the energy decrease for the reaction

$$C_6H_5COOH(c) + 7\tfrac{1}{2}O_2(g) = 7CO_2(g) + 3H_2O(\text{liq.}) \text{------}, \qquad (1)$$

where each of the reactants and products is under a pressure of 1 atm. at 30° C.[3]

5. RESULTS

In table 4 are given the results of the first series of measurements on Standard Samples 39e and 39f. The mean values of Q_B at 30° C given in this table are in good agreement with the corresponding mean values, 26415.3 and 26413.1 International joules per gram (mass), which were obtained for Samples 39d and 39e, respectively, in 1934[3]. In table 5 are given the results of the second series of measurements on Samples 39e and 39f. The measurements of the first and second series were made under the same conditions, except that in the second series the mass of carbon dioxide[4] formed in each experiment was determined by absorption in Ascarite in the manner described in 1938[10].

It will be seen from tables 4 and 5 that the values of Q_B at 30° C from the second series of measurements on both Samples are systematically higher by about 0.03 percent than those from the first series. It will also be seen that the correction for the heat of formation of nitric acid is systematically lower in the second series than in

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[3] Washburn's eq 81 gives the value of $100\frac{\Delta U_B - \Delta U_R}{-\Delta U_B}$, that is, the percentage difference between $-\Delta U_B$ and $-\Delta U_R$. The percentage difference between the quantities q_B and Q_B is the difference between the values of $100\frac{\Delta U_B - \Delta U_R}{-\Delta U_B}$ for the actual and standard bomb processes.

[4] The results of the measurements of the mass of carbon dioxide formed in experiments 17 to 25, inclusive, were discarded because of a leak in the apparatus which was discovered after experiment 25.

TABLE 4.—*Results of first series of measurements on Samples 39e and 39f*

Experiment number	Date 1940	Mass of sample (weight in vacuum)	Initial oxygen pressure at 30° C	Total heat produced	Correction for heat of formation of HNO_3	Correction for ignition energy	Heat produced by combustion of benzoic acid	Observed heat of combustion, q_B	Reduction to standard bomb process	Q_B (30°C)	Deviation from mean
MEASUREMENTS ON SAMPLE 39e											
		g	*atm*	*Int. j*	*Int. j*	*Int. j*	*Int. j*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*
1	June 13	1.51865	31.7	40145.3	−11.9	−18.6	40114.8	26414.8	−1.7	26413.1	−2.0
2	13	1.52115	31.6	40215.6	−11.9	−18.6	40185.1	26417.6	−1.6	16.0	+0.9
3	13	1.52080	31.7	40211.5	−13.1	−18.6	40179.8	26420.2	−1.7	18.5	+3.4
4	14	1.51746	31.7	40116.3	−12.5	−18.6	40085.2	26416.0	−1.7	14.3	−0.8
13	21	1.53468	31.9	40578.9	−13.1	−18.6	40547.2	26420.6	−1.8	18.8	+3.7
14	24	1.52120	31.9	40214.5	−13.1	−18.6	40182.8	26415.2	−1.8	13.4	−1.7
15	24	1.52044	31.8	40195.7	−11.9	−18.6	40165.2	26416.8	−1.7	15.1	0.0
16	24	1.52153	31.8	40220.2	−12.5	−18.6	40189.1	26413.6	−1.7	11.9	−3.2
Mean										26415.1	[a]±1.0
MEASUREMENTS ON SAMPLE 39f											
5	June 14	1.51922	31.6	40164.5	−12.5	−18.6	40133.4	26417.1	−1.6	26415.5	+0.8
6	14	1.51711	31.8	40117.6	−10.1	−18.6	40088.9	26424.5	−1.7	22.8	+8.1
7	20	1.52153	31.9	40225.8	−10.7	−18.6	40196.5	26418.5	−1.8	16.7	+2.0
8	20	1.51974	31.9	40162.3	−11.3	−18.6	40132.4	26407.4	−1.8	05.6	−9.1
9	20	1.52141	31.8	40214.0	−11.9	−18.6	40183.5	26412.0	−1.7	10.3	−4.4
10	21	1.52050	32.0	40203.2	−12.5	−18.6	40172.1	26420.3	−1.9	18.4	+3.7
11	21	1.52111	32.0	40203.6	−11.3	−18.6	40173.7	26410.8	−1.9	08.9	−5.8
12	21	1.52075	32.0	40210.8	−12.5	−18.6	40179.7	26421.0	−1.9	19.1	+4.4
Mean										26414.7	[a]±2.1

[a] The standard deviation of the mean, calculated from the data of both calibration and combustion experiments.

TABLE 5.—*Results of second series of measurements on Samples 39e and 39f*

Experiment number	Date	Mass of sample (weight in vacuum)	Initial oxygen pressure at 30°C	Total heat produced	Correction for heat of formation of HNO_3	Correction for ignition energy	Heat produced by combustion of benzoic acid	Observed heat of combustion, q_B	Reduction to standard bomb process	Q_B (30°C)	Deviation from mean	CO_2 formed in combustion	Observed heat of combustion, $-\Delta U_B$	Washburn reduction, $\Delta U_B - \Delta U_R$	$-\Delta U_R$ (30°C)	Deviation from mean
MEASUREMENTS ON SAMPLE 39f																
	1940	*g*	*atm*	*Int. j*	*Int. j*	*Int. j*	*Int. j*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Moles×7*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*
17	Nov. 29	1.52275	32.4	40267.7	−6.0	−18.6	40243.1	26427.9	−2.1	26425.8	+2.6	------	------	------	------	------
18	Dec. 3	1.52111	32.6	40219.2	−6.0	−18.6	40194.6	26424.5	−2.2	22.3	−0.9	------	------	------	------	------
19	27	1.52120	32.4	40223.5	−6.0	−18.6	40198.9	26425.8	−2.1	23.7	+0.5	------	------	------	------	------
20	31	1.52077	32.3	40209.7	−6.0	−18.6	40185.1	26424.2	−2.1	22.1	−1.1	------	------	------	------	------
	1941															
21	Jan. 2	1.52075	32.3	40205.0	−2.4	−18.6	40184.0	26423.8	−2.1	21.7	−1.5	------	------	------	------	------
22	22	1.52182	32.3	40236.0	−5.4	−18.6	40212.0	26423.6	−2.1	21.5	−1.7	------	------	------	------	------
23	27	1.52051	32.5	40200.1	−4.8	−18.6	40176.7	26423.2	−2.2	21.0	−2.2	------	------	------	------	------
24	28	1.52144	32.4	40228.2	−2.4	−18.6	40207.2	26427.1	−2.1	25.0	+1.8	------	------	------	------	------
25	30	1.52172	32.4	40235.3	−4.2	−18.6	40212.5	26425.7	−2.1	23.6	+0.4	------	------	------	------	------
26	Feb. 6	1.52058	32.3	40212.6	−5.4	−18.6	40188.6	26429.8	−2.1	27.7	+4.5	0.0124527	3227.30	−2.53	3224.77	+0.16
27	7	1.52115	32.1	40214.9	−3.0	−18.6	41193.3	26423.0	−2.0	21.0	−2.2	.0124554	3226.98	−2.52	4.46	−0.15
Mean	------	------	------	------	------	------	------	------	------	26423.2	[a] ±0.8	------	------	------	3224.61	[a] ±0.17
MEASUREMENTS ON SAMPLE 39e																
28	Mar. 20	1.52141	32.2	40225.0	−6.6	−18.6	40199.8	26422.7	−2.0	26420.7	−1.8	0.0124582	3226.77	−2.53	3224.24	−0.04
29	25	1.51952	32.2	40185.2	−9.0	−18.6	40157.6	26427.8	−2.0	25.8	+3.3	.0124438	3227.12	−2.53	4.59	+0.31
30	26	1.52033	32.2	40201.3	−9.0	−18.6	40173.7	26424.3	−2.0	22.3	−0.2	.0124510	3226.54	−2.53	4.01	−0.27
31	27	1.52157	32.1	40228.4	−9.0	−18.6	40200.8	26420.6	−2.0	18.6	−3.9	$.0124577_5$	3226.97	−2.52	4.45	+0.17
32	Apr. 25	1.52175	32.2	40233.5	−5.4	−18.6	40209.5	26423.2	−2.0	21.2	−1.3	.0124623	3226.49	−2.53	3.96	−0.32
33	28	1.51853	32.2	40158.6	−7.8	−18.6	40132.2	26428.3	−2.0	26.3	+3.8	.0124365	3226.97	−2.53	4.44	+0.16
Mean	------	------	------	------	------	------	------	------	------	26422.5	[a] ±1.3	------	------	------	3224.28	[a] ±0.12

[a] Standard deviation of the mean, calculated from the data of both calibration and combustion experiments.

the first. The fact that the carbon dioxide was completely removed from the bomb before the nitric acid determinations in the second series of measurements, but not in the first, suggests that the nitric acid determinations of the first series may have been in error because of the sensitivity of the indicator, phenolphthalein, to carbon dioxide dissolved in the washings from the bomb.

In table 6 are given the values of the correction for nitric acid per gram of benzoic acid in the first and second series of measurements on Sample 39f.[5] The difference in the mean values of the correction for the two series is 4.5 j/g of benzoic acid (standard deviation ±0.4 j/g). If it is assumed that the difference is the result of dissolved carbon dioxide in the washings from the bomb in the first series of measurements, and the results of this series are corrected accordingly, the mean values of Q_B for the two series are brought into satisfactory agreement. The final values of Q_B at 30° C obtained in this way for the Standard Samples are given in table 7.

TABLE 6.—*Correction for nitric acid per gram of benzoic acid in the two series of measurements on Standard Sample 39f*

First series			Second series		
Experiment number	Correction	Deviation from mean	Experiment number	Correction	Deviation from mean
	Int. j.	*Int. j.*		*Int. j.*	*Int. j.*
5	8.2	+0.6	17	3.9	+0.8
6	6.7	−.9	18	3.9	+.8
7	7.0	−.6	19	3.9	+.8
8	7.4	−.2	20	4.0	+.9
9	7.8	+.2	21	1.6	−1.5
10	8.2	+.6	22	3.6	+0.5
11	7.4	−.2	23	3.2	+.1
12	8.2	+.6	24	1.6	−1.5
			25	2.8	−0.3
Mean	7.6	[a] ±0.2	26	3.6	+.5
			27	2.0	−1.1
			Mean	3.1	[a] ±0.3

[a] The standard deviation of the mean.

TABLE 7.—*Final values of Q_B at 30° C for the Standard Samples*

Series	Mean value of Q_B for Standard Sample 39e	Standard deviation of mean	Mean value of Q_B for Standard Sample 39f	Standard deviation of mean
	Int. j/g	*Int. j/g*	*Int. j/g*	*Int. j/g*
First	26419.6	[a] $\pm 1.0_5$	26419.2	[a] $\pm 2.1_5$
Second	26422.5	±1.3	26423.2	±0.8
Mean	26420.7	±0.8	26422.7	±0.7

[a] The results of the first series have been corrected for the effect of dissolved carbon dioxide in the washings from the bomb. The standard deviations for the results of the first series of measurements include the standard deviation (±0.4 j/g) of the correction for dissolved carbon dioxide.

The improved concordance of the results brought about by the application of the above correction is consistent with the hypothesis regarding the cause of the original differences, but it is not conclusive proof of this hypothesis. It was desirable, therefore, to make inde-

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[5] The same oxygen tank was used in both series of measurements on Sample 39f, but different tanks were used in the two series of measurements on Sample 39e. The nitric acid determinations for the two series of experiments on Sample 39e are therefore not comparable.

pendent tests to ascertain the effect of dissolved carbon dioxide on the determination of nitric acid formed in the bomb. To this end, a measured volume of a dilute solution of nitric acid was placed in the bomb, which was then filled to a pressure of 30 atm with a mixture of oxygen and carbon dioxide. The mass and concentration of the nitric acid solution placed in the bomb and the composition of the O_2–CO_2 mixture were such as to duplicate approximately the conditions in the bomb after combustion of a 1.5-g sample of benzoic acid. After an hour or more had been allowed for the establishment of equilibrium, the pressure was released, the bomb opened and immediately washed out, and the washings were titrated, the procedure being as nearly as possible the same as in the first series of measurements on the Standard Samples. In other experiments the procedure was the same, except that after opening the bomb, it was flushed out with air and allowed to stand for a measured length of time before washing it out and titrating the washings.

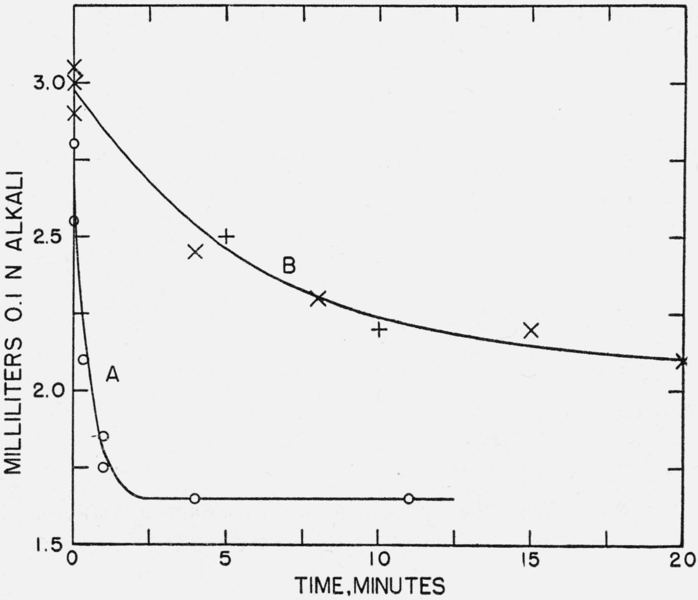

Figure 1. *Results of the tests to ascertain the effect of dissolved carbon dioxide on the determination of nitric acid.*

The results of these experiments are given by curve *A*, figure 1, where the amount of 0.1 *N* alkali solution required to neutralize the washings from the bomb is plotted as ordinate, and the time after opening and flushing out the bomb is plotted as abscissa. Curve *B* shows the results of two similar series of experiments, in which the carbon dioxide and nitric acid were formed by combustion of a 1.5-g sample of benzoic acid. Both curves are consistent, within the uncertainty of the measurements, with the conclusions drawn from the data of table 6 as to the magnitude of the effect of dissolved carbon dioxide. It is believed that this fact justifies the correction of the results of the first series of measurements on the basis of the data of table 6.

A surprising feature of figure 1 is the difference in form of the curves *A* and *B*, which indicates that the carbon dioxide was removed from solution much more slowly in the experiments represented by curve *B* than in those represented by curve *A*. It would be expected that the difference would be in the opposite direction, since in the experiments represented by curve *A* all the nitric acid solution was in the bottom of the bomb, whereas in those represented by curve *B* the solution was distributed over the entire inner surface of the bomb and therefore had a much larger free surface. No satisfactory explanation of this phenomenon has been found. A series of experiments similar to those represented by curve *B*, but in which naphthalene was burned instead of benzoic acid, gave results which were represented by a curve more nearly resembling curve *A* than curve *B*.

In addition to the values of Q_B per gram of sample, there are given in table 5 values of $-\Delta U_R$ (at 30° C) per mole of benzoic acid for the Standard Sample material. The results for the two Samples are in agreement within the uncertainty of the measurements.

In table 8 are given the results of measurements on the purified samples of benzoic acid. These samples were received in sealed glass containers, and in opening one of them some particles of glass were introduced into the sample. This made impossible an accurate determination of the mass of the sample burned in each experiment, and consequently only the values per mole of benzoic acid are given for this sample. In opening the other container great care was taken to avoid getting glass into the benzoic acid, and values of both Q_B per gram of sample and $-\Delta U_R$ per mole of benzoic acid are given for this sample.

The mean value of Q_B at 30° C given in table 8 for the benzoic acid purified by crystallization from benzene is in satisfactory agreement with the values given in table 7 for the Standard Samples. The values given in table 8 for $-\Delta U_R$ at 30° C for the purified samples of benzoic acid, and the corresponding values given in table 5 for the Standard-Sample materials are also in satisfactory agreement.

In view of the agreement of the results for the purified and Standard Sample materials, it may be concluded that the impurities in the Standard Sample materials are of such a nature that they have no appreciable effect on the heat of combustion. The weighted mean values of all results on both Standard-Sample and purified materials may therefore be taken as the results of the present measurements for pure benzoic acid or for the Standard Sample materials.

The weighted mean value of Q_B was obtained by taking the mean of all results on Standard Samples 39e and 39f that were obtained on the basis of the first calibration of the calorimeter, and the mean of all results on the Standard Samples and the purified materials that were obtained on the basis of the second calibration of the calorimeter, and weighting these two mean values inversely as the squares of their standard deviations. The final value of $-\Delta U_R$ is the mean of all results on both Standard Sample and purified materials.

The values obtained in the manner just described are Q_B (30° C)= 26422.4 Int. j/g (mass) and $-\Delta U_R$ (30° C)=3224.70 Int. kj/mole. The standard deviations of these mean values are, respectively, $\pm 0.6_5$ j/g and ± 0.12 kj/mole. Multiplication of these values of the standard deviation by appropriate factors will yield values of other measures of precision, such as "probable error" (factor=

TABLE 8.—*Results of measurements on samples of purified benzoic acid*

Experiment number	Date	Mass of sample (weight in vacuum)	Initial oxygen pressure at 30° C	Total heat produced	Correction for heat of formation of HNO_3	Correction for ignition energy	Heat produced by combustion of benzoic acid	Observed heat of combustion, q_B	Reduction to standard bomb process	Q_B (30° C)	Deviation from mean	CO_2 formed in combustion	Observed heat of combustion, $(-\Delta U_B)$	Washburn reduction, $(\Delta U_B - \Delta U_R)$	$-\Delta U_R$ (30°C)	Deviation from mean
SAMPLE 39e PURIFIED BY EIGHT CRYSTALLIZATIONS FROM WATER																
	1941	*g*	*atm*	*Int. j*	*Int. j*	*Int. j*	*Int. j*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Int. j/g*	*Moles ×7*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*	*Int. kj/mole*
34	Apr. 30	----------	32.1	40199.4	−8.7	−18.6	40172.1	----------	----------	----------	----------	0.0124504	3226.57	−2.52	3224.05	−0.76
35	May 12	----------	32.4	40216.2	−4.6	−18.6	40193.0	----------	----------	----------	----------	.0124568	6.59	−2.54	4.05	−.76
36	13	----------	32.3	40241.8	−5.8	−18.6	40217.4	----------	----------	----------	----------	.0124629	6.97	−2.53	4.44	−.37
37	26	----------	32.0	402.9.5	−3.5	−18.6	40197.4	----------	----------	----------	----------	.0124553$_5$	7.32	−2.52	4.80	−.01
38	28	----------	32.2	40207.5	−2.9	−18.6	40186.0	----------	----------	----------	----------	.0124512	7.48	−2.53	4.95	+.14
39	29	----------	31.5	40213.1	−4.1	−18.6	40190.4	----------	----------	----------	----------	.0124513	7.81	−2.48	5.33	+.52
40	June 12	----------	32.1	40176.6	−4.6	−18.6	40153.4	----------	----------	----------	----------	.0124400	7.77	−2.52	5.25	+.44
41	18	----------	32.4	40203.8	−1.2	−18.6	40184.0	----------	----------	----------	----------	.0124484	8.05	−2.54	5.51	+.70
42	19	----------	32.0	40138.1	−2.3	−18.6	40117.2	----------	----------	----------	----------	.0124305	7.32	−2.52	4.80	−.01
43	20	----------	31.9	40214.5	−3.5	−18.6	40192 4	----------	----------	----------	----------	.0124514	7.94	−2.51	5.43	+.62
44	23	----------	31.5	40116.0	−3.5	−18.6	40093.9	----------	----------	----------	----------	.0124253	6.80	−2.48	4.32	−.49
Mean	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------	3224.81	[a] ±0.18
SAMPLE 39e PURIFIED BY EIGHT CRYSTALLIZATIONS FROM BENZENE																
45	June 25	1.52107	31.7	40205.4	−2.9	−18.6	40183.9	26418.2	−1.7	26416.5	−6.8	0.0124543	3226.51	−2.49	3224.02	−0.87
46	26	1.52061	31.7	40209.7	−7.5	−18.6	40183.6	26426.0	−1.7	24.3	+1.0	.0124510	7.34	−2.49	4.85	−.04
47	27	1.52123	31.8	40228.4	−4.1	−18.6	40205.7	26429.7	−1.8	27.9	+4.6	.0124564$_5$	7.70	−2.50	5.20	+.31
48	30	1.52096	31.5	40220.1	−4.1	−18.6	40197.4	26429 0	−1.6	27.4	+4.1	.0124535	7.80	−2.48	5.32	+.43
49	July 21	1.52069	31.7	40199.0	−3.5	−18.6	40176.9	26420.2	−1.7	18.5	−4.8	.0124525	6.41	−2.49	3.92	−.97
50	22	1.52122	31.9	40217.8	−1.7	−18.6	40197.5	26424.5	−1.8	22.7	−0.6	.0124556$_5$	7.26	−2.51	4.75	−.14
51	23	1.52137	32.0	40226.3	−1.2	−18.6	40206.5	26427.8	−1.9	25.9	+2.6	.0124567$_5$	7.69	−2.51	5.18	+.29
52	24	1.52159	31.7	40227.3	−1.2	−18.6	40207.5	26424.7	−1.7	23.0	−0.3	.0124545	8.35	−2.49	5.86	+.97
Mean	----------	----------	----------	----------	----------	----------	----------	----------	----------	26423.3	[a] ±1.5	----------	----------	----------	3224.89	[a] ±0.24

[a] Standard deviation of the mean, calculated from the data of both calibration and combustion experiments.

0.6745), and the "uncertainty" (factor=2.0) proposed by Rossini and Deming [11] for the final results of thermochemical measurements. An estimated uncertainty of ±0.010 percent (±2.6 j/g, or ±0.32 kj/mole) is here assigned to the final results of the present measurements. In arriving at this figure, consideration was given to the precision of the data, the probable magnitudes of systematic errors, and the agreement of the results with those of previous measurements.

In order to obtain the value of Q_B at 25° C corresponding to the value given above for 30° C, it is necessary to take account of the temperature coefficient of $-\Delta U_R$, and of the change in the Washburn reduction with temperature. The temperature coefficient of $-\Delta U_R$ was calculated from the specific heats of benzoic acid [12], water [7], oxygen and carbon dioxide [18] to be −118.5 j/mole-degree (−0.97 j/g° C). The Washburn reduction, $(\Delta U_B - \Delta U_R)$, at 30° and 25°C is −2.30 and −2.44 kj/mole (−18.8 and −20.0 j/g), respectively. With these data it is calculated that for the standard bomb process

$$Q_B\ (25^\circ\ \mathrm{C}) = 26428.4 \pm 2.6\ \mathrm{Int.\ j/g\ (mass).}^{6}$$

The value of $-\Delta H$ for the reaction (1) at 30° C, corresponding to the value of $-\Delta U_R$ (30° C) given above is 3226.03 ±0.32 Int. kj/mole. Using the value 115.5 j/mole-degree for the temperature coefficient of ΔH, and correcting for the departures of the gases, oxygen, and carbon dioxide, from the standard state of unit fugacity (1 atm), there is obtained for reaction (1) $-\Delta H^\circ 298.16 = 3226.39 \pm 0.32$ Int. kj/mole.[7]

It should be emphasized that the quantity of interest in connection with the standardization of bomb calorimeters is Q_B, the heat of combustion per gram under the conditions of the standard bomb process. The values of heat of combustion per mole are not suitable for this purpose, since they apply for conditions other than those of the bomb process and are based on the mass of carbon dioxide formed in combustion rather than on the mass of sample burned.

V. CORRECTION OF 1934 RESULTS

The procedure in the combustion experiments reported in 1934 [3] was the same as that in the first series of combustion experiments of the present work, and the same indicator, phenolphthalein, was used in the nitric acid determinations. It is inferred, therefore, that the 1934 results are low because of dissolved carbon dioxide in the bomb washings, and they have been corrected accordingly. The correction is somewhat uncertain because of the fact that the data of table 6 apply when a 1.52-g sample of benzoic acid is burned under an initial oxygen pressure of about 32 atm, whereas in the 1934 measurements the mass of sample was varied from 0.7 to 2.0 g and the oxygen pressure from 20 to 32 atm. In calculating the correction to be applied

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[6] The heat of combustion under conditions differing by small amounts from those of the standard bomb process at 25° C is obtained by multiplying the value given for Q_B (25° C) by the factor

$$1 + 10^{-6}\,[20\,(P-30) + 42\,(m_s/V-3) + 30\,(m_w/V-3) - 45\,(t-25).]$$

[7] As noted previously, this value was derived by calculating the number of moles of benzoic acid burned in each experiment from the mass of carbon dioxide formed in combustion. The value of $-\Delta H^\circ 298.16$ obtained by calculating the number of moles of benzoic acid burned from the mass of sample, using 122.118 for the molecular weight of benzoic acid, is 3226.04 ±0.32 Int. kj/ mole. Inert impurity in the sample would affect the value of heat of combustion per mole based on the weight of sample but not the value based on the weight of carbon dioxide formed. The effect of an error in the atomic weight of carbon would be 2.5 times as great in the value based on the weight of sample as in the value based on the weight of carbon dioxide.

to the 1934 results, it was assumed that the effect of dissolved carbon dioxide in any experiment is proportional to the mole fraction of carbon dioxide in the gas phase and to the total mass of water in the bomb at the end of the experiment.

The 1934 results have also been corrected for the change from 63 to 60 kj/mole in the value used for the energy of formation of nitric acid in the bomb, for the change in the value used for the temperature coefficient of $-\Delta U_R$, and for the dependence on temperature of the Washburn reduction. The last-named effect was neglected in 1934 in calculating the value of Q_B at 25° C from the observed value at 30° C.[8]

The values of Q_B at 25° calculated from the data of the 1934 measurements in the manner outlined above are given in table 9, together with the corresponding values resulting from the present measurements on Standard Samples 39e, 39f, and the sample of 39e that was purified by fractional crystallization from benzene.

TABLE 9.—*Values of Q_B at 25°C for Standard Samples, and for the sample purified by crystallization from benzene*

Date	Sample	Values for individual samples	Standard deviation of the mean	Mean of values for all samples	Standard deviation of the mean
		Int. j/g	*Int. j/g*	*Int. j/g*	*Int. j/g*
1934 [1]	39d	26427.7	±1.1	26426.6	±0.85
	39e	26425.6	±1.0		
1942	39e	26426.7	±0.7$_5$	26428.4	±0.65
	39f	26428.8	±0.7		
	Purified [2]	26429.3	±1.5		

[1] The results reported in 1934 have been corrected as described in the test.
[2] Sample 39e purified by crystallization from benzene.

It will be seen from table 9 that the corrected results of the 1934 measurements are in satisfactory agreement with those of the present work. The mean values of Q_B from the two investigations differ by only 0.007 percent, and the total range of values for the different lots of benzoic acid is 0.014 percent.

VI. PROCEDURE FOR CORRECTING RESULTS REPORTED ON THE BASIS OF THE 1934 VALUE OF Q_B

The mean value reported in 1934 for Q_B at 25° C, 26,419 International joules per gram mass, is lower by 9.4 j/g (0.036 percent) than the value obtained in the present measurements. The elements which enter into this difference may be summarized as follows:

1. Effect of dissolved CO_2	5.5 j/g
2. Temperature dependence of Washburn reduction	1.2 j/g
3. Change in temperature coefficient of $-\Delta U_R$	0.1 j/g
4. Change in nitric acid correction	0.8 j/g
5. Difference in calorimetric measurements	1.8 j/g
Total	9.4 j/g

The results of calibration experiments by means of benzoic acid which were calculated on the basis of the 1934 value of Q_B can be re-

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[8] In other words, the temperature coefficient of $-\Delta U_R/M$, calculated from data on Cv at atmospheric pressure, was used in 1934 in deriving the value of Q_B at 25° C from the observed value at 30° C. The temperature coefficient of Q_B involves the temperature coefficients of both $-\Delta U_R/M$ and the Washburn reduction.

duced to the basis of the new value with the aid of the above data. The reduction will not in all cases involve all of the above elements of the difference between the two values of Q_B, and in deciding which of the elements are involved in any particular case, consideration will have to be given to the conditions under which the calibration experiments were performed. For example, consider the case of a bomb calorimeter calibrated with benzoic acid under the same (average) conditions as in the 1934 combustion experiments with respect to temperature, oxygen pressure, mass of sample, mass of water placed in the bomb, amount of nitric acid formed, procedure followed in the nitric acid determinations, and value used for the heat of formation of nitric acid. Under these circumstances the conversion of the value obtained for the energy equivalent of the calorimeter to the basis of the new value of Q_B would involve only that part of the difference between the old and new values which resulted from the difference in the calorimetric measurements (1.8 j/g=0.007 percent).

In the case where the calibration experiments were made under the same conditions as in the above example, except that the procedure was such that dissolved carbon dioxide did not affect the nitric acid determinations, the conversion to the basis of the new value of Q_B would involve both the difference in the calorimetric measurements (1.8 j/g) and the effect of dissolved carbon dioxide (5.5 j/g) on the nitric acid corrections in the 1934 experiments. If the calibration experiments were referred to some temperature other than 30° C, account would have to be taken of the change in the temperature coefficient of Q_B.

The following data on the average conditions in the 1934 measurements will be of use in reducing results originally calculated on the basis of the 1934 report to the basis of the present report:

Temperature to which experiments were referred	30° C
Mass of sample of benzoic acid	1. 35 g
Nitric acid correction per gram of benzoic acid	17. 4 j
Mole fraction of CO_2 in final gas phase in bomb	0. 206
Water in bomb at end of experiment	0. 089 mole
Effect of dissolved CO_2 per gram of benzoic acid	5. 5 j

The value given above for the nitric acid correction was calculated, using the 1934 value, 63 kj/mole, for the heat of formation of nitric acid in the bomb.

The conversion of the results of calibration experiments by means of benzoic acid, originally calculated, using the 1934 value of Q_B, to the basis of the new value will be illustrated by a specific example. It is assumed that the calibration experiments were performed under the following conditions:

Volume of bomb	0. 4 liter
Mass of sample burned	1. 50 g
Mass of water placed in bomb	1. 00 g
Nitric acid correction per gram of benzoic acid burned	6. 8 j
Temperature to which experiments were referred	28. 0° C
Initial oxygen pressure at 28° C	33. 0 atm

The value for the heat of combustion of benzoic acid under these conditions would be 26418.6 Int. j/g, according to the 1934 report, and 26426.8 Int. j/g, according to the present report. The difference, 8.2 j/g, between these two values is less than the difference, 9.4 j/g, between the values of Q_B at 25° C reported in 1934 and in the present paper. The discrepancy is due (1) partly to the fact that the coefficients of $(P-30)$, $(m_s/V-3)$, and $(m_w/V-3)$ in the formula given in footnote 6, page 161 differ slightly from the coefficients in the corresponding formula in the 1934 report, (2) partly to the fact that the change in the value used for the heat of formation of nitric acid does not enter into the calculations, and (3) partly to the fact that in the calculation of the heat of combustion at 28° C, according to data given in the 1934 report, the effect of the error in the temperature coefficient is reduced to 40 percent of its effect in the calculation of Q_B at 25° C from the observed value at 30° C.

The changes mentioned above in the coefficients of $(P-30)$, $(m_s/V-3)$, and $(m_w/V-3)$ are taken account of by applying a correction of $-0.4_5 j/\text{g}$ to the value of the heat of combustion of benzoic acid calculated on the basis of the 1934 report.

The other corrections that should be applied to the above value for the heat of combustion of benzoic acid calculated according to the 1934 report are related to the elements of the difference between the old and new values of Q_B at 25° C, and will be discussed in the order that these elements are listed on page 262.

1. The correction for the effect of dissolved carbon dioxide will depend upon how the nitric acid determinations were made in the calibration experiments under consideration. If the procedure in these experiments was the same as in the 1934 measurements, and in the first series of combustion experiments of the present measurements, then the effect of dissolved carbon dioxide in the calibration experiments here considered will partially cancel the effect in the 1934 value of Q_B. In this case the correction for dissolved carbon dioxide may be calculated as follows: Under the conditions of the calibration experiments under consideration the mole fraction of carbon dioxide in the bomb after combustion of the sample of benzoic acid is calculated to be 0.157, and the amount of water in the bomb after combustion is 0.092 mole. On the assumption that the total effect of dissolved carbon dioxide is proportional to the mass of water and the mole fraction of carbon dioxide, the above data, together with the data given previously regarding the average conditions in the 1934 combustion experiments, lead to 3.9_1 j/g of benzoic acid burned for the effect of dissolved carbon dioxide. This partially cancels the effect, 5.5 j/g of benzoic acid, in the 1934 value of Q_B, leaving a net correction of $+1.5_9$ j/g to be applied to the value of the heat of combustion calculated on the basis of the 1934 report.

On the other hand, if the procedure in the nitric acid determinations in the calibration experiments under consideration was such that these determinations were not affected by dissolved carbon dioxide, then a correction equal to the total effect of dissolved carbon dioxide in the 1934 value of Q_B, +5.5 j/g, will be necessary.

2 and 3. As noted previously, the effect (1.3 j/g) on Q_B at 25° C of the error in the value used in 1934 for the temperature coefficient of Q_B is partially eliminated in the calculation, on the basis of the 1934 report, of the heat of combustion of benzoic acid under the conditions of the calibration experiments here considered. There remains, however, 40 percent of the effect, or $+0.5_2$ j/g, which should be applied as a correction to the value of the heat of combustion calculated on the basis of the 1934 report.

4. The 1934 value of Q_B was too low by 0.8 j/g because of the

error in the nitric acid correction. This error in Q_B is partially cancelled in the original calculation of the results of the calibration experiments under consideration by the use of the value given in the 1934 report for the heat of formation of nitric acid in the bomb. A correction is necessary, however, for the error in the difference in the nitric acid corrections in the 1934 experiments and in the calibration experiments. This correction amounts to $+0.5_0$ j/g of benzoic acid burned.

5. A correction of +1.8 j/g is necessary to take account of the difference in the results of the calorimetric measurements of 1934 and the present work.

Taking account of the various factors discussed above, the value for the heat of combustion of benzoic acid which should be used in calculating the corrected value for the energy equivalent of the calorimeter from the data of the calibration experiments under consideration is obtained as follows:

(a) If the procedure in the nitric acid determinations was the same as in the 1934 experiments and in the first series of combustion experiments described in this paper:

Heat of combustion calculated on basis of 1934 report	26418.6	Int. j/g
Changes in coefficients of (P−30), etc	$-.4_5$	Int. j/g
Dissolved CO_2	$+1.5_9$	Int. j/g
Change in temperature coefficient of Q_B	$+0.5_2$	Int. j/g
Error in nitric acid correction	$+0.5_0$	Int. j/g
Difference in calorimetric measurements	+1.8	Int. j/g
Corrected value of heat of combustion	26422.6	Int. j/g

The correction to be applied to the original value of the energy equivalent of the calorimeter in this case is +0.015 percent.

(b) If the procedure in the nitric acid determinations was such that these determinations were not affected by dissolved carbon dioxide, the calculation of the corrected value for the heat of combustion of benzoic acid would differ from the above calculation only in that the correction for dissolved carbon dioxide in this case would be equal to the total effect, 5.5 j/g, in the 1934 experiments. The corrected value for the heat of combustion of benzoic acid in this case would be 26426.5 Int. j/g, and the correction to be applied to the original value of the energy equivalent of the calorimeter would be +0.030 percent.

The difference between the corrected value for the heat of combustion of benzoic acid given under (b) and the value 26426.8 Int. j/g calculated on the basis of the present measurements arises from the fact that a part of the change in the nitric acid correction does not appear in the above calculations but is taken care of in the original calculation of the energy equivalent of the calorimeter on the basis of the 1934 report.

VII. PREVIOUS WORK

Results of measurements of the heat of combustion of benzoic acid by various observers [2, 3, 20, 21, 22, 23, 32] are given in table 10. The correction of the 1934 results of Jessup and Green is discussed in section V of this paper.

The value of Q_B at 25° C attributed to Roth, Doepke, and Banse [22] in the 1934 report [3] was calculated from their published results, on

TABLE 10.—*Results of the measurements of the heat of combustion of benzoic acid by various observers*

Observer	Date	Material	Original value	Q_B at 25° C	Standard deviation of the mean	Deviation from result of present measurements
			Int. j/g (mass)	*Int. j/g* (mass)	*Int. j/g*	*Percent*
Fischer and Wrede	1909		26,475 at 17.5° C	26, 436	±4. 5	+0. 029
Wrede	1910		26, 466 at 17. 5° C	26, 427	±6. 5	−. 005
Dickinson	1914		26,441 at 25° C	26, 434	[b] ±4. 0	+. 021
Roth, Doepke, and Banse	1928	Kahlbaum-Verkade [a]	26.433 at 20° C	26, 405	±6. 0	−. 088
Jaeger and von Steinwehr	1928	Kahlbaum-Verkade [a] and National Bureau of Standards.	26,437 at 19.3° C {NBS 26,426 K−V [a] 26,411± }	26, 418	{±9. 0 ±9. 0} ±7. 5	{−0. 009 −0. 066} −. 039
Jessup and Green	1934	Standard Samples 39d and 39e	26,419 at 25° C	[c] 26, 426. 6	$\pm 0.8_5$	−. 007
Prosen and Rossini	1939–41	Standard Sample 39e		26, 428. 9	±1. 1	+. 002
Present work	1942	Standard Samples 39e, 39f, and a specially purified sample.		26, 428. 4	$\pm 0.6_5$	

[a] Obtained from Kahlbaum and compared with National Bureau of Standards material by P. Verkade [24], according to whom the two materials had the same heat of combustion. The National Bureau of Standards material was probably Standard Sample 39d.

[b] Dickinson did not give the necessary data for calculating the standard deviation. The value given was estimated by the present writer.

[c] Corrected as described in the text.

the assumption that they had placed 1 g of water in the bomb before each experiment. Professor Roth has since informed the writer that actually 10 g of water was placed in the bomb, and that the effect of the difference between 10 g and 1 g of water was found by experiment in his laboratory to be 0.064 percent. The difference between 0.064 percent and the value 0.10 percent calculated from the Washburn [19] equation was attributed to the lack of equilibrium between the gaseous carbon dioxide and the aqueous solution. On the basis of the information supplied by Roth, a correction of −0.064 percent has been applied to the value attributed to Roth, Doepke, and Banse in the 1934 report.

An additional correction of about 1 j/g has been applied to the values of Q_B at 25° C attributed in the 1934 report to Fischer and Wrede [20], Wrede [21], Roth, Doepke, and Banse [22], and Jaeger and von Steinwehr [23] to take account of the temperature dependence of the Washburn reduction, an effect which was partially neglected in the 1934 report.

The value attributed to Prosen and Rossini [32] in table 10 is the result of unpublished measurements made at this Bureau entirely independently of the measurements described in the present paper, and with different apparatus [34].

Because of uncertainty as to experimental procedure in the various investigations, and as to precautions taken to avoid the effect of dissolved carbon dioxide on the determinations of nitric acid, no correction for this effect has been applied to any previous results except those of the 1934 measurements at this Bureau. The results of Dickinson and those of Roth, Doepke, and Banse are probably not in error from this cause because the indicators they used, methyl orange and Congo red, respectively, are insensitive to carbon dioxide. The results of Prosen and Rossini are not in error from this cause, since they flushed out their bomb sufficiently to remove dissolved carbon dioxide. Fischer and Wrede, and Wrede do not state what indicators they used. Jaeger and von Steinwehr used phenolphthalein, and therefore their nitric acid determinations may have been in error because of dissolved carbon dioxide.

All of the final values given in table 10, with the exception of that due to Roth, Doepke, and Banse, are in as good agreement with the result of the present measurements as could be expected on the basis of the precision of the various measurements. The fact that the values obtained for the Kahlbaum-Verkade material by Jaeger and von Steinwehr and by Roth, Doepke, and Banse are in good agreement with each other and are lower than the other values in the table suggests that a difference in material may be responsible for the low values for the Kahlbaum-Verkade material. However, Verkade [24] has compared the Kahlbaum-Verkade and National Bureau of Standards materials and found no difference in their heats of combustion. It may be noted also that the values obtained for the two materials by Jaeger and von Steinwehr are in as good agreement with each other and with the value obtained in the present work for National Bureau of Standards material as could be expected from the precision of the measurements. Except for the low values for the Kahlbaum-Verkade material, there is nothing in the data of table 10 to indicate any differences in the materials used in the various investigations.

As noted in the 1934 report, the results of all measurements previous to that time may be too high because of combustible impurities in the oxygen. The estimate of 0.02 percent made in the 1934 report as the probable effect of combustible impurities on Dickinson's results is practically equal to the difference between Dickinson's value and that resulting from the present measurements.

VIII. SUITABILITY OF BENZOIC ACID AS A STANDARD SUBSTANCE FOR BOMB CALORIMETRY

The requirements that a standard substance for bomb calorimetry should satisfy have been summarized [28] as follows:

1. It should be easily obtainable in a pure state.
2. It should be stable.
3. It should not be hygroscopic.
4. It should not be too volatile.
5. It should be easily compressible into pellets.
6. It should burn completely in the bomb.

The tests of purity of Standard Samples 39e and 39f of benzoic acid [4], and the agreement of the results of measurements of heat of combustion of different samples given in table 10 indicate that benzoic acid satisfies the first of the above requirements. The low values given in table 10 for the heat of combustion of the Kahlbaum-Verkade material cast some doubt on this conclusion. However, as noted previously, the low values for this material are not in accord with results obtained by Verkade [24].

While it has been reported [29] that benzoic acid decomposes at temperatures above about 150° C, it appears to be quite stable under conditions to which it is likely to be subjected when used as a Standard Sample material. Thus no significant change in heat of combustion of Standard Sample 39e was observed during the period between the 1934 measurements and those of the present work.

In order to determine whether benzoic acid is appreciably hygroscopic, Schwab and Wichers [33] made measurements of the water content of Standard Sample 39f in its original condition and after exposure for 6 weeks at a relative humidity of 90 percent at about 23° C. Ten-gram samples of benzoic acid were fused in a glass apparatus, which was then evacuated through a trap immersed in liquid air. The trap was then closed off from the rest of the apparatus, and the liquid air was removed, allowing the trap to warm up to room temperature. The amount of water removed from the benzoic acid was estimated from the pressure, measured by means of a mercury manometer, and the temperature and volume of the closed system. The results indicated a water content of the untreated benzoic acid of 0.0015 to 0.0018 percent, and of the benzoic acid, after exposure to the high humidity, of 0.0014 to 0.0019 percent.

A less precise test of the hygroscopicity of benzoic acid was made by the writer by calibrating a calorimeter with (a) Standard Sample 39e from a recently opened bottle, (b) some of the same material which had been kept for about a year in an open bottle under conditions such that no appreciable amount of dust could get into the bottle, (c) some of the same material which had been kept for about a year in an open bottle in a desiccator vessel containing a saturated solution of ammonium chloride, which maintains a relative humidity of about

79 percent [27]. The values of the energy equivalent of the calorimeter obtained in these measurements are as follows:

Number of experiments	Treatment of benzoic acid sample	Energy equivalent of calorimeter	Standard deviation of the mean
		Int. j/°C	*Int. j/°C*
6	(a)	13730.6	0.6_5
2	(b)	13731.6	.7
4	(c)	13730.8	1.2_5
Mean		13731.0	0.4_5

Both of the above sets of data indicate that benzoic acid is not appreciably hygroscopic. However, data obtained by Weaver [29] indicated a moisture content of about 0.08 percent by weight in a sample of benzoic acid that had been kept in a glass-stoppered bottle for about a year. By a very sensitive test, Weaver also found small amounts of moisture in several other samples. In all cases the moisture could be removed by fusing the sample.

A number of years ago the writer found that a sample of benzoic acid obtained from another laboratory had a heat of combustion per gram that was lower by 0.2 percent than that of National Bureau of Standards material. The discrepancy disappeared after fusing the sample.

It appears, therefore, that some samples of benzoic acid may contain appreciable amounts of moisture. The source of such moisture is not known, but it is possible that samples crystallized from aqueous solution may contain trapped water unless special precautions are taken to dry them. Whatever the source of the water in the samples referred to, it appears that it is relatively easy to prepare benzoic acid which is substantially free from water, and that it will not absorb moisture from the atmosphere. It may be concluded, therefore, that benzoic acid is entirely satisfactory as a standard substance so far as hygroscopicity is concerned.

To determine the volatility of benzoic acid a pellet of 1.5 g was placed in a platinum crucible and weighed at intervals over a period of about 3 weeks. During this time the temperature of the room during the daytime varied from 29° to 32° C. The benzoic acid lost weight at the rate of about 0.15 mg, or 0.01 percent, per day. Evaporation at this rate is not serious, since not more than half an hour need elapse from the time a sample is weighed until it is ignited in the bomb.

Experience at this Bureau indicates that benzoic acid satisfies requirements 5 and 6, page 268. Some observers have reported negligible amounts of soot left in the crucible after burning a sample of benzoic acid, but no soot or other evidence of incomplete combustion was observed in any of the 1934 experiments at this Bureau or in those of the present work. In these experiments the samples were burned in a cylindrical platinum crucible ¾ in. in diameter and ⅝ in. high, weighing a little less than 8 g.

IX. SUMMARY

The present measurements yield the value 26428.4 International joules per gram mass for the heat of combustion, Q_B, of benzoic acid under the conditions of the standard bomb process.

When the amount of the reaction is determined from the mass of carbon dioxide formed in combustion, the present measurements yield for the combustion of benzoic acid $-\Delta H^\circ_{298.16}=3226.39$ International kilojoules per mole when each of the gases involved in the reaction is in the thermodynamic state of unit fugacity. The estimated uncertainty of the final values of Q_B and $-\Delta H^\circ_{298.16}$ is ±0.010 percent (±2.6 j/g, or ±0.32 kj/mole).

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