Calorimetric Properties of Benzoic Acid from 0° to 410° K

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Heat capacity, enthalpy, and entropy of benzoic acid (C_6H_5COOH) are tabulated from 0° to 410° K, using experimental heat capacities obtained by means of an adiabatic vacuum-type calorimeter. The heat of fusion was measured to be 18,000 ±100 abs j mole^{-1}. The standard entropy, heat, and free energy of formation of benzoic acid at 298.16°K are calculated.

1. Introduction

For many years benzoic acid (C_6H_5COOH) has been issued by the National Bureau of Standards as a standard for acidimetry and for determining the energy equivalent of combustion bomb calorimeters. More recently this material has been used in standard thermometric cells in which its liquid-solid equilibrium temperature is used as a reference for thermometer calibration. At the meeting on April 21, 1948, the Low Temperature Calorimetry Conference,[1] which was organized for the purpose of promoting improved calorimetric techniques and setting up standards for testing and calibrating calorimeters of various designs, selected benzoic acid along with synthetic sapphire (α-aluminum oxide) and normal heptane as standards for the intercomparison of precision heat-capacity calorimeters in the temperature ranges from 10° to 350°K, 10° to 1,800° K, and 10° to 300°K, respectively. The three materials were prepared and packaged in suitable quantities at this Bureau and are of sufficient purity and uniformity that errors arising from these sources are well within the precision of experimental measurements.

The benzoic acid for the Calorimetry Conference was purified by procedures similar to those used in the preparation of the benzoic acid for the thermometric standard cells issued by this Bureau. The purity of this material is 99.997 mole percent, as calculated from the freezing curve. The purity of benzoic acid Standard Sample 39g, presently issued for acidimetry and for the calibration of the combustion-bomb calorimeters, is 99.99 weight percent, as determined by titration. Considering the high purities, the authors believe that within the accuracy with which calorimetric measurements can now be made the calorimetric properties of these two samples are the same. In this paper there are presented the results of the measurements, with an adiabatic vacuum-type calorimeter, of the heat capacity and the heat of fusion of the sample of benzoic acid prepared for distribution by the Calorimetry Conference. The enthalpy and entropy have been calculated from the results of the measurements, and these properties are tabulated from 0° to 410°K. The calorimetric measurements above 395°K, as indicated in the following sections, are less accurate due to a slight chemical reaction of benzoic acid with the container.

2. Experimental Procedure

2.1. Apparatus and Method

This investigation on benzoic acid was carried out with an adiabatic vacuum-type calorimeter similar to that used with diphenyl ether [1].[2] Since details of the design and operation of a similar calorimeter are given in the paper on 1,3-butadiene by R. B. Scott, et al. [2], only a brief account will be given. The sample was sealed in a copper container and suspended inside an adiabatic shield system. A series of heat-capacity experiments was made over the temperature range 13° to 410° K. After making the so-called curvature correction, which transforms observed values, $\Delta Q/\Delta T$, to the desired values, dQ/dT, these were plotted on a large scale as deviations from an approximate empirical equation. A smooth curve was drawn through the deviation points, and the heat-capacity values were obtained at equally spaced integral temperatures from this deviation curve combined with the approximate empirical equation. Similar heat-capacity experiments were made with the empty container, and the data obtained were treated in the same manner. The net heat capacities were computed by subtraction, using the smoothed tabulated values for the two sets of measurements at the corresponding temperatures. The vaporization correction is negligible for benzoic acid in the temperature range reported in this paper.

2.2. Sample

The benzoic acid sample for the Calorimetry Conference was prepared by F. W. Schwab[3] of this Bureau. Details of the purification by fractional crystallization and the subsequent removal of water and air are given in previous publications [3, 4]. The final treatment for the purification and the purity tests was carried out in thermometric cells similar to those described in one of the references cited [4]. The molten benzoic acid was transferred into platinum dishes and allowed to solidify in

a dessicator containing phosphorus pentoxide in order to prevent absorption of moisture from the atmosphere. The solid benzoic acid thus obtained was crushed and sieved; the particle sizes between number 10 and 50 sieves were thoroughly mixed and bottled in 70-g units. All units are considered to have a purity and identity well within the precision of heat-capacity measurements. The purity of this material from freezing-temperature studies was calculated to be 99.997 mole percent [5]. In order to determine whether the crushing and sieving processes would introduce any impurities, a crushed sample of benzoic acid was sieved 20 times. Spectrographic analysis by B. F. Scribner of this Bureau showed an increase of five parts per million of metallic impurities. It is considered, therefore, that a single sieving would introduce negligible amounts of impurities.

A sample (79.2409-g mass) of benzoic acid from two units was sealed in a copper container under pressure of helium of about 0.2 atm (0.0020 g). All heat-capacity experiments were completed below 320° K before the material was heated above this temperature for any further heat-capacity experiments or for the determination of the heat of fusion and purity by melting-temperature studies. This precaution was taken because the tests at 100° C performed by F. W. Schwab indicated that benzoic acid reacts slightly with copper and tin. The sample container, as described in the references cited [1, 2], is constructed with copper and coated with tin on the inside.

3. Results

3.1. Heat-Capacity Results

The heat capacity of the empty container was measured from 14° to 386° K. The deviation of individual experiments from the smoothed heat capacities is shown in figure 1. The heat capacities of the container plus benzoic acid were measured over the temperature range 13° to 410° K. The deviations of the experimental values from the smoothed heat capacities are given in figures 2 and 3. The deviation boundary of ±0.05 percent in the solid range and ±0.25 percent in the liquid range are expressed in terms of net heat capacities. The precision of ±0.02 percent obtained with the empty container arises from the high net heat capacity. The smoothed heat-capacity values of the empty container were extrapolated from 385° to 410° K in order to obtain the net heat capacities in this range. It is believed that the error in the extrapolation is less than the experimental precision. The heat capacity of benzoic acid was extrapolated below the experimental temperature range to 0° K by means of the Debye function,

$$C_{sat.} = 38.97 \, D \left(\frac{116.1}{T} \right), \tag{1}$$

which was fitted to the experimental values at 14°, 18°, and 22° K. The heat-capacity values are

tabulated in table 1 at intervals of 2 deg from 0° to 50° K and at intervals of 5 deg from 50° to 410° K.
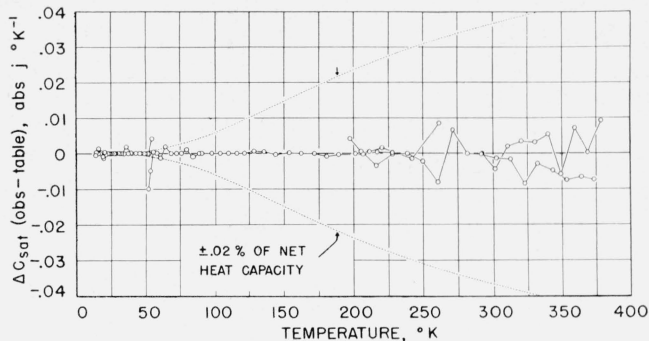

FIGURE 1. *Deviations of the experimental heat capacities (corrected for curvature) from smoothed values for the empty container.*

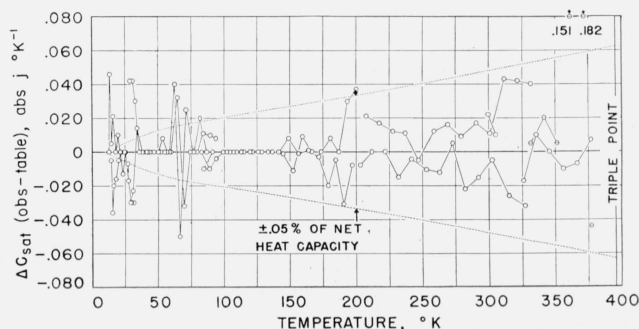Experiments in a single series are connected by lines.

FIGURE 2. *Deviations of the experimental heat capacities (corrected for curvature) from smoothed values for the container plus benzoic acid in the solid range.*

Experiments in a single series are connected by lines. The heat-capacity experiments after melting are indicated by ⊖.
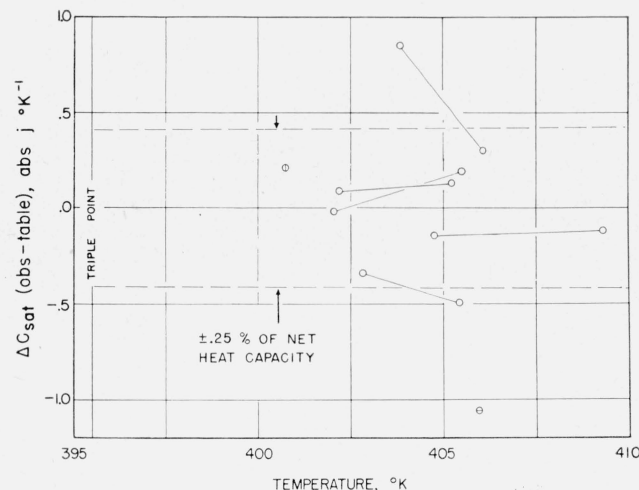

FIGURE 3. *Deviations of the experimental heat capacities from smoothed values for the container plus benzoic acid in the liquid range.*

Experiments in a single series are connected by lines. The points indicated by ⊕ and ⊖ are single separate measurements.

257

T	$C_{sat.}$	$(H_{sat.} - E_0^s)$	$(S_{sat.} - S_0^s)$
		Solid	
°K	abs j °K^{-1} mole^{-1}	abs j mole^{-1}	abs j °K^{-1} mole^{-1}
0.0	0.0	0.0	0.0
2	.0155	.0078	.0052
4	.1242	.1242	.0414
6	.4191	.6287	.1397
8	.9924	1.987	.3313
10	1.923	4.838	.6454
12	3.242	9.928	1.107
14	4.932	18.063	1.729
16	6.824	29.790	2.509
18	8.854	45.446	3.429
20	11.00	65.294	4.473
22	13.17	89.458	5.623
24	15.46	118.09	6.867
26	17.61	151.16	8.189
28	19.78	188.56	9.574
30	21.92	230.26	11.012
32	24.03	276.22	12.494
34	26.08	326.33	14.012
36	28.05	380.48	15.560
38	29.91	438.46	17.126
40	31.68	500.06	18.706
42	33.36	565.12	20.293
44	34.98	633.48	21.882
46	36.55	705.02	23.472
48	38.06	779.63	25.060
50	39.50	857.20	26.643
55	42.81	1063.1	30.565
60	45.88	1284.9	34.424
65	48.65	1521.4	38.207
70	51.24	1771.2	41.908
75	53.52	2033.1	45.522
80	55.85	2306.5	49.050
85	58.13	2591.5	52.505
90	60.14	2887.3	55.886
95	62.04	3192.8	59.189
100	63.93	3507.7	62.419
105	65.82	3832.1	65.584
110	67.69	4165.8	68.689
115	69.60	4509.1	71.740
120	71.51	4861.8	74.742
125	73.38	5224.1	77.700
130	75.27	5595.7	80.614
135	77.18	5976.8	83.491
140	79.09	6367.5	86.332
145	80.99	6767.7	89.141
150	82.90	7177.4	91.919
155	84.81	7596.7	94.668
160	86.75	8025.6	97.391
165	88.72	8464.2	100.09
170	90.70	8912.8	102.77
175	92.69	9371.3	105.43
180	94.70	9839.7	108.07
185	96.72	10318	110.69
190	98.75	10807	113.29
195	100.80	11306	115.89
200	102.89	11815	118.46
205	104.99	12335	121.03
210	107.11	12865	123.59
215	109.25	13406	126.13
220	111.40	13958	128.67
225	113.58	14520	131.20
230	115.78	15093	133.72
235	117.99	15678	136.23
240	120.22	16273	138.74
245	122.46	16880	141.24
250	124.71	17498	143.74
255	126.97	18127	146.23
260	129.24	18768	148.71
265	131.52	19419	151.20
270	133.81	20083	153.68
273.16	135.26	20508	155.24
275	136.10	20758	156.15
280	138.40	21444	158.63
285	140.71	22142	161.10
290	143.03	22851	163.56
295	145.35	23572	166.03
298.16	146.81	24033	167.59
300	147.66	24304	168.49
305	149.98	25049	170.95
310	152.30	25804	173.41
315	154.63	26572	175.86
320	156.96	27351	178.32
325	159.28	28141	180.77
330	161.60	28943	183.22
335	163.91	29757	185.67
340	166.22	30582	188.11
345	168.53	31419	190.56
350	170.84	32268	193.00
355	173.17	33128	195.44
360	175.52	34000	197.88
365	177.90	34883	200.31
370	180.34	35779	202.75
375	182.81	36687	205.19
380	185.25	37607	207.62
385	187.64	38539	210.06
390	190.05	39483	212.50
395	192.47	40440	214.93
395.522	192.74	40541	215.19
		LIQUID	
395.522	250.60	58541	260.70
400	253.33	59669	263.54
405	256.59	60944	266.70
410	259.86	62235	269.87

TABLE 1. *Heat capacity, enthalpy, and entropy of benzoic acid at saturation pressure—Continued*

3.2. Reliability of the Heat-Capacity Results

The possible sources of errors in the adiabatic calorimeter were discussed previously [1]. As a test on the performance of the calorimeter, the heat capacity of water was measured between 274° and 332° K under conditions as nearly identical as possible to those of the benzoic acid experiments. These results agree within 0.02 percent of the values previously published [6]. Considering the precision and the various known sources of errors a probable error [4] of ±0.2 percent is assigned to the heat-capacity values from 60° to 395° K. Above 395° K the probable error is ±0.3 percent, due to the increased uncertainty arising from the chemical reaction of benzoic acid with the container. In order to determine the effect of the chemical reaction on the heat capacity of benzoic acid, a series of heat-capacity measurements was carried out after two experiments in which the material had been melted. Figure 2 shows, except for the two points indicated by the deviations of 0.151 and 0.182 abs j deg^{-1}, which are considered to be experimental errors, the results for the solid benzoic acid are essentially the same as prior to melting. No unusual thermal drifts were observed in the higher temperature range to indicate the evolution of a large heat of chemical reaction. Below 60° K the probable error increases to ±1 percent at 14° K because of the greatly diminished absolute heat capacity and uncertainties in the measurement of temperature.

[4] For these experiments a true probable error cannot be computed statistically. The values given are estimates reached by examining contributions to the inaccuracy from all known sources. The authors estimate that there is a fifty-fifty chance that the error is no larger than that indicated.

3.3. Purity and Heat of Fusion

In order to follow the extent of chemical reaction when the material was melted, three purity determinations were made with two meltings before each measurement. The purity was calculated from the equilibrium melting curves [1]. The results in the order of the measurements were 99.93, 99.92, and 99.92 mole percent purity, indicating that the purity did not change greatly with the number of meltings. These figures are considerably lower than the value, 99.997 mole percent, obtained from the freezing-point curve. Judging from the appearance of the interior surface of the container and the fact that the container lost about 0.45-g mass, it seems the purity determined is higher than expected. It is possible, however, that the reaction products are insoluble in benzoic acid. This method only gives liquid soluble-solid insoluble impurities.

The heat of fusion was determined by the usual method of heating continuously from a temperature slightly below the triple point to just above it [1]. The total heat input was corrected for the heat capacity of the container and sample below and above the triple point and for the premelting of the sample due to impurities. Three determinations were made, and the results were 18,006, 18,003, and 18,011 abs j mole^{-1}. The heat of fusion is taken to be 18,000 abs j mole^{-1}. It is believed, upon considering the chemical reaction that took place with the container, the uncertainty in the heat-capacity correction, and the uncertainty in the premelting correction, that the probable error in the heat of fusion may be as much as 100 abs j mole^{-1}. In the temperature range of this investigation the amount of benzoic anhydride formed was probably not greater than 0.03 mole percent, as estimated from the work of Schwab and Wichers [4, 7]. It is considered that the error in the heat of fusion from this source is negligible.

4. Derived Thermal Properties

4.1. Enthalpy and Entropy

The enthalpy and entropy of solid and liquid benzoic acid are given in columns 3 and 4 of table 1, respectively, at 2-degree intervals from 0° to 50° K and at 5-degree intervals from 50° to 410° K. The enthalpy was evaluated using the relation

$$(H_{sat.} - E_0^s) = \int_0^T C_{sat.} \, dT + L_f, \qquad (2)$$

in which $(H_{sat.} - E_0^s)$ is the enthalpy along the saturation curve relative to the internal energy of the solid benzoic acid at absolute zero; and L_f is the heat of fusion. The entropy was evaluated using the relation

$$(S_{sat.} - S_0^s) = \int_0^T \frac{C_{sat.}}{T} \, dT + \frac{L_f}{T_t}, \qquad (3)$$

in which $(S_{sat.} - S_0^s)$ is the entropy of the solid benzoic acid along the saturation curve relative to absolute zero (S_0^s is considered to be zero in all calculations made in this work); and T_t is the triple-point temperature. The equations were evaluated above 12° K by numerical integration, using four-point Lagrangian integration coefficients [8] and below this temperature by analytical methods. The integrations were checked by evaluating the thermodynamic identity

$$\int_0^T (S_{sat.} - S_0^s) \, dT = T(S_{sat.} - S_0^s) - (H_{sat.} - E_0^s). \quad (4)$$

The tabulated enthalpy values are considered to have a probable error of ±0.2 percent between 60° and 395° K, ±1 percent below 60° K, and ±0.3 percent above 395° K. The entropy values have a probable error of ±0.1 abs j °K^{-1} mole^{-1} in the temperature range below 395° K and ±0.5 abs j °K^{-1} mole^{-1} above this temperature. The increase in uncertainty above 395° K as previously stated is due to the chemical reaction of benzoic acid with the container. In all calculations the triple-point temperature was taken to be 395.522°K,[5] as given by Schwab and Wichers [4].

4.2. The Standard Entropy, Heat, and Free Energy of Formation

The standard entropy of formation of benzoic acid at 298.16° K was calculated by using the entropy value directly from table 1 without correction to standard state, since this correction is negligible for all practical purposes. The standard entropies of graphite, hydrogen, and oxygen used in the calculation are 5.720 ±0.050 [9], 130.574 ±0.010 [10, 11] and 205.073 ±0.010 [12, 13] abs j °K^{-1} mole^{-1}, respectively. The value so obtained is

$$\Delta S_{f\,298.16°K}^{\circ} = -469.25 \pm 0.37 \text{ abs j °K}^{-1} \text{ mole}^{-1}.$$

The standard heat of formation was calculated using the standard heat of combustion of benzoic acid, −3226.92±0.32 abs kj mole^{-1} [14, 15, 16] with the standard heats of formation of carbon dioxide, −393.513±0.045 abs kj mole^{-1} [17], and liquid water, −285.840±0.042 abs kj mole^{-1} [17]. The value obtained is

$$\Delta H_{f\,298.16°K}^{\circ} = -385.19 \pm 0.46 \text{ abs kj mole}^{-1}.$$

The standard free energy of formation was calculated using the above values of standard entropy and heat of formation. The result is

$$\Delta F_{f\,298.16°K}^{\circ} = -245.28 \pm 0.47 \text{ abs kj mole}^{-1}.$$

The probable error given with each of these values was obtained from a statistical combination of the probable errors of the data used in computing the value.

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[5] Temperatures in degrees Kelvin were obtained from the relation °K=°C+ 273.160.

5. Comparison With Other Results

Hess [18] measured the enthalpy of benzoic acid relative to 0° C, using a Bunsen ice calorimeter and formulated a linear heat-capacity equation to fit the interval from 0° to 122° C. His heat-capacity values are 25 percent lower at 275° K and 32 percent higher at 395° K than the values in table 1. Andrews, et al. [19], using a drop method similar to Hess but with the receiving vessel at 22° C, obtained linear relations for the heat capacity of solid and liquid benzoic acid in the temperature range 22° to 200° C. Comparing their work in the range of this work, their values are about 5.4 percent higher at 300° K and 6.7 percent lower at 395° K. Using a cooling method Hrynakowski and Smoczkiewiczowa [20] measured the heat capacity at 25° C. This value is 6.5 percent higher than the value in table 1. Parks, et al. [21], using an aneroid type calorimeter, measured the heat capacities from 90° to 295° K. These values are within 1 percent of the values in table 1. Jessup [14] measured the heat capacity of benzoic acid at 28.5° C; this value is 0.4 percent lower. The heat-capacity values obtained by Andrews, et al., Parks, et al., and Jessup are compared in figure 4 with the values in table 1.

A few authors have published their experimental values in terms of mean heat capacities. These are compared in table 2 with the values in table 1. The comparisons were made by interpolating the tabulated enthalpies at the proper temperature intervals. Hess [18] and Satoh and Sogabe [22] used ice calorimeters in their experiments.

The heats of fusion of benzoic acid obtained by previous investigators are compared in table 3. Hess [18] obtained mean heat capacities of solid and liquid benzoic acid at the melting point relative to 0° C and from these values calculated the heat of fusion. Garelli and Montanari [23] determined the cryoscopic constant of benzoic acid using different solutes at various concentrations and from the average of the cryoscopic constants calculated the heat of fusion. Mathews [24] similarly calculated the heat of fusion from the cryoscopic constant
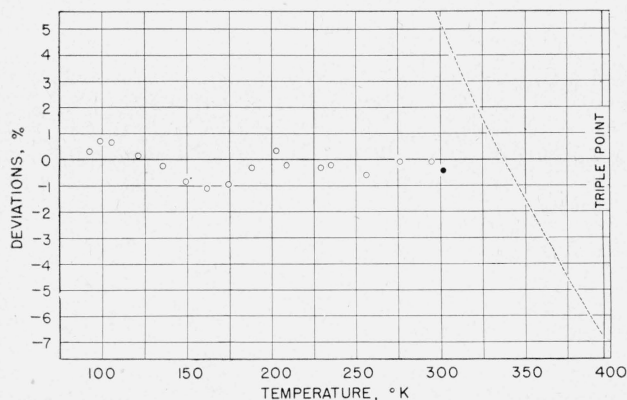
TABLE 2. *Comparison of mean heat capacities of benzoic acid with the values obtained by other investigators*

Investigator	Temperature interval	Mean heat capacity	
		Other investigator	This work
	° C	abs j deg^{-1} mole^{-1}	abs j deg^{-1} mole^{-1}
Hess [18]	0 to 50	131. 4	146.82
Do	0 to 94	159. 3	157. 03
Do	0 to 110	169. 6	160.79
Satoh and Sogabe [22]	0 to 99. 6	160. 2	158. 34

TABLE 3. *Comparison of heat of fusion of benzoic acid with the values obtained by other investigators*

Investigator	L_f
	abs j mole^{-1}
Hess [18]	9, 810
Garelli and Montanari [23]	20, 260
Mathews [24]	17, 780
Andrews, et al. [19]	17, 320
Klosky, et al. [25]	16, 760
Hrynakowski and Smoczkiewiczowa [26]	15, 530
This work	18, 000

obtained using anthracene as a solute at different concentrations. Andrews, et al. [19] obtained their value for the heat of fusion from the enthalpy curves for the solid and liquid benzoic acid determined by the drop method. Klosky, et al. [25] calculated the heat of fusion from the vapor pressure curves for solid and liquid benzoic acid. Hrynakowski and Smoczkiewiczowa [26] determined the heat of fusion by a cooling method.

6. Discussion

The results of this investigation show that benzoic acid is a suitable heat-capacity standard in the temperature range 10° to 350° K prescribed by the Calorimetry Conference. As this material becomes corrosive above the upper temperature limit, particularly in the liquid state, it should be used only below 350° K. The benzoic acid, packaged in 70-g units in particle sizes between number 10 and 50 sieves, can be easily poured into calorimeter sample containers. As long as this material is used below 350° K, most of it can be poured out after use, but once fused the task of removing the sample becomes more difficult.

The original purpose of the benzoic acid standard as proposed by the Calorimetry Conference is for the intercomparison of precision heat-capacity calorimeters. It seems appropriate that the heat capacity of benzoic acid be determined by other laboratories so that calorimeters of various design and the results obtained with them can be compared.

7. References

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FIGURE 4. *Comparison of heat capacities of benzoic acid with those from other investigators.*

The base-line represents the values in table 1. ○, Parks, Hoffman, and Barmore; ●, Jessup; _____, Andrews, Lynn, and Johnston.

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