

UNITED STATES DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON 25, D. C.

National Bureau of Standards
Certificate

Standard Sample 39h

Benzoic Acid

Calorimetric Standard

This lot of benzoic acid was prepared to insure material of high purity and uniformity. Although it is known to contain a small amount of impurity, its heat of combustion has been found to be the same, within the estimated uncertainty of the measurements, as that of specially purified samples of benzoic acid. On the basis of titration, a purity of 99.98 percent is indicated. It has been found that benzoic acid will not absorb moisture from the atmosphere if the relative humidity does not exceed 90 percent. The heat of combustion of the sample will not change with time if adequate precautions are taken to avoid the introduction of impurities.

The quantity of heat evolved by combustion of Standard Sample 39h of benzoic acid has been found to be 26.434 abs kj/g mass¹ (weight in vacuum) with an estimated uncertainty of ± 0.003 when the sample is used under the following conditions:

- A. The combustion reaction is referred to 25° C.
- B. The sample is burned in a bomb of constant volume in pure oxygen at an initial absolute pressure of 30 atmospheres at 25° C.
- C. The number of grams of sample burned is equal to three times the volume of the bomb in liters.
- D. The number of grams of water placed in the bomb before combustion is equal to three times the volume of the bomb in liters.

In the use of the standard sample, it will be advantageous to observe the following procedure:

1. The material should be made into a briquet and weighed in this form in the crucible in which it is to be burned.
2. The conditions stated above under A, B, C, and D should be adhered to as closely as practicable. If it is necessary to depart from these conditions, the value given for the heat evolved should be multiplied by the following factor, if this factor is found to differ from unity to a significant extent:

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

where

- P =initial absolute pressure of oxygen in atmospheres at the temperature t ,
 m_s =mass of sample in grams,
 m_w =mass, in grams, of water placed in bomb before combustion,
 V =volume of bomb in liters,
 t =temperature to which the reaction is referred, in degrees Celsius (centigrade).

3. The charge should be fired by passing electric current through a short length of iron or platinum fuse wire (about No. 34 Awg). The correction for the energy used in firing the charge (elec-

¹ The reduction of weight in air to weight in vacuum was made using the value 1.320 g/cm³ for the density of benzoic acid at 25° C.

trical energy plus heat of combustion of iron wire if used) may be determined by blank calorimetric experiments on the fuse alone. A battery of 3 to 5 storage cells or 6 to 10 dry cells in series or a small transformer with a secondary voltage of about 10 can be used for ignition.

4. The charge should be burned in pure oxygen, or in commercially pure oxygen containing not more than 1 percent of nitrogen and no combustible gases. The amount of nitric acid formed in the combustion may be determined by titration with 0.1 *N* solution of sodium hydroxide by the use of methyl orange as indicator. The correction for the formation of aqueous nitric acid is 59 kJ/mole, or 0.94 kJ/g of HNO₃.

If the heat of combustion of the sample in calories per gram is desired, the following conversion factor may be used: 1 calorie=0.0041840 abs kj. The calorie thus defined is being used in connection with practically all of the thermochemical work done in the United States.

The results of calorimetric tests of fuels for steam power plants may be expressed in terms of the International Steam Tables calorie (I. T. cal), which is defined by the relation, 1 I. T. cal=0.0041868 abs kj. The Btu used in modern steam tables is defined by means of the relation, 1 I. T. cal/g=1.8 Btu/lb.

In the ordinary use of the bomb calorimeter, where an accuracy of not better than 0.1 percent is required, as in fuel calorimetry, the use of the factor given under (2) may be omitted and the heat evolved expressed as 26.453 abs kj (kw-sec)/g weight against brass weights in air (6,323 cal/g weight in air, or 6,318 I. T. cal/g weight in air, or 11,373 Btu/lb weight in air). Also for work of this order of accuracy, the corrections for the energy used in firing the charge may be omitted, if the length of the iron wire and the temperature rise of the calorimeter are about the same in the calibration of the calorimeter as in the determination of heats of combustion. In determining the heating values of fuels it is desirable to follow a standardized procedure such as that specified by the American Society for Testing Materials in their Standard D-271-48 for coal or Standard D-240-50 for fuel oil.

Methods of calculating heats of reaction at a constant pressure of 1 atmosphere, from bomb calorimetric data, are given by Prosen² and Hubbard, Scott, and Waddington.²

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² Experimental Thermochemistry, Edited by F. D. Rossini, Interscience Publishers, New York, 1956; Chapter 6 by E. J. Prosen; Chapter 5 by Hubbard, Scott, and Waddington.