LI.—*The Ratio of the Heats of Combustion of Benzoic Acid and Salicylic Acid.* (*A Reply to P. E. Verkade and J. Coops.*)

By ENDRE BERNER.

RECENTLY Verkade and Coops (J., 1926, 1437), in a reply to me (J., 1925, **127**, 2747), held that their previously determined value of the heat of combustion of salicylic acid, 5241·7 cal.$_{15}$. per g. (air) (*Rec. trav. chim.*, 1924, **43**, 561), is correct, as new determinations have given the same result. They conclude from this that my value for this heat of combustion, 5237·4 cal.$_{15}$. per g. (air), is too low and that the reason for this might be an error in the heat capacity of my calorimeter. In support of the correctness of their value, they refer to the results of Roth and of Swientoslawski, who found very nearly the same value, *viz.*, 5241·3 and 5242·4, respectively. Notwithstanding this, I am obliged to consider my value of the heat of combustion of salicylic acid to be the correct one, especially as a new comparison of the heat of combustion of a fresh standard sample of benzoic acid, from the Bureau of Standards, with that of purified salicylic acid gave very nearly the same ratio of the heats of combustion of the two substances, *viz.*, 1·2074 (vac.), as that found previously [1·2073 (vac.)]. In this comparison, as will be seen below, the heat capacity of the calorimeter was not introduced at all into the calculation of the result, the ratio being calculated directly from the rise in temperature when the two substances were burned.

In my previous paper, I was of the opinion that the difference between my value and that of Verkade and Coops was due to insufficient purity of the samples used by these authors, because we found about the same value for Merck's salicylic acid ("für kalorimetrische Bestimmungen"), and also because I found that this value was altered after purification of the sample. However, later investigations have shown that the sample from Merck, which I used, was an impure one. Another sample, obtained from Merck during 1926, has the same heat of combustion as my purified samples. Verkade and Coops also have burned two of my samples and found the same value as for their original samples. The discrepancy between their value and my own cannot, therefore, be due to impurity of the samples, but must be caused by a systematic error in the determinations.

Verkade and Coops submit that they have no reason to doubt the correctness of their value, because the ratios of the heats of combustion of benzoic acid and naphthalene and of benzoic acid and cane-sugar, determined by themselves, are in full agreement with those which have been obtained in careful work by other authors, and at present are generally accepted. They suggest, therefore, the possibility that in burning naphthalene and cane-sugar I may find other values for these ratios. I cannot believe this to be relevant to the present discussion, which only concerns the ratio of the heats of combustion of benzoic acid and salicylic acid. Presumably it should be easier to determine the exact ratio in the case of the chemically similar substances benzoic acid and salicylic acid than in the case of benzoic acid and the chemically different substances naphthalene and cane-sugar. As is well known, naphthalene has a relatively high vapour pressure and therefore evaporates appreciably even at the ordinary temperature. Cane-sugar, which is completely purified only with difficulty, generally needs auxiliary substances for ignition, and even then incomplete combustion is often the result. As a matter of course, these facts make the heats of combustion of naphthalene and cane-sugar less trustworthy than those of benzoic and salicylic acids, which are not volatile and do not need auxiliary substances for ignition.

EXPERIMENTAL.

The ratio of the heats of combustion of benzoic and salicylic acids has now been redetermined as follows.

A series of 22 combustions was carried out, under exactly the same conditions, with benzoic acid and salicylic acid alternately, *i.e.*, 11 combustions with each. The quantities of the substances used, about 0·64 and 0·78 g., respectively, always caused an equal rise, of about 1°, in the temperature of the calorimeter, the mean temperature being 19°. An oxygen pressure of 35 atm. was used, as this sufficed for the complete combustion of both substances. The ignition was effected electrically by means of a very thin platinum wire and without the aid of auxiliary substances. A detailed description of the calorimeter and method has recently been published in another journal (*Archiv for Mathematik og Naturvidenskab, Oslo,* 1926, **39**, Nr. 6).

The preparations used in the present investigation are: A standard sample of benzoic acid (39*c*) from the Bureau of Standards, Washington; a sample of benzoic acid (590) purified in the same way as sample 517 in my previous paper; three samples of salicylic acid, 571 II*b*, 572 III, and 572 IV, which were also used in my first investigation; and a sample of salicylic acid " von Heyden," purified by Verkade by crystallising it twice from water and once from chloroform (designated " Verk.").

After the necessary corrections had been applied for loss of heat and for formation of nitric acid, the rise in temperature of the calorimeter was calculated on the basis of 1 g. of the substance (weighed in a vacuum) being burned. The following are the results of the 22 combustions.

Benzoic Acid.

Sample.	Rise in temp. for 1 g. of subst. (vac.).
39*c*	1·5549°, 1·5549°,
,,	1·5551 , 1·5550 ,
,,	1·5550 , 1·5550 ,
,,	1·5554 , 1·5548 ,
,,	1·5550 .
590	1·5550 , 1·5555 .
Mean	1·55505

Salicylic Acid.

Sample.	Rise in temp. for 1 g. of subst. (vac.).
571 II*b*	1·2883°, 1·2879°.
572 III	1·2878 , 1·2878 .
572 IV	1·2883 , 1·2878 .
Verk.	1·2876 , 1·2879 ,
,,	1·2879 , 1·2880 ,
,,	1·2878 .
Mean	1·28792

The ratio of the heats of combustion of benzoic acid and salicylic acid is accordingly 1·55505/1·28792 = 1·2074$_1$ (vac.). Previously 1·2073$_4$ (vac.) was found. The mean of the two determinations is 1·2073$_7$ (vac.). As the heat of combustion of benzoic acid is fixed at 6319 cal.$_{15}$. per g. (vac.), the heat of combustion of salicylic acid is 5233·7 cal.$_{15}$. per g. (vac.), or 5237·3 per g. (air).

The possible errors arising in this determination will be considered briefly. The accuracy of the measurement of the heat evolved during combustion is dependent only on the accuracy of the determination of the rise in temperature, as the heat capacity of the calorimeter was always the same. Thus the same quantity of water and the same pressure of oxygen were used, and, further, the difference between the heat capacities of the products of combustion and that of the oxygen necessary for the combustion is very nearly the same in the case of the quantities used of the two substances. By means of a trustworthy platinum resistance thermometer the temperature could be read accurately to 0·0001° or less. The correction for loss of heat generally amounted to about 0·2% of the total heat evolved. Even an error of 10% in the calculation of this correction would, therefore, result in an error of only 2 parts per 10,000 in the final result. The heat of formation of nitric acid varied from 0·4 to 0·6 cal. The total corrections in my experiments amounted, accordingly, to only 2—2·5 parts per 1000.

Another cause of error is to be found in the combustion process in the bomb. Here, an error might arise either from incomplete combustion of the substance or from the contamination of the oxygen by combustible impurities. In my experiments, the combustion of the substance was complete, as no soot could be detected in the bomb and no carbon monoxide could be found in the products of combustion. Even very small quantities of carbon monoxide can be detected when about 2 litres of the gaseous products of combustion are collected in a bottle and shaken thoroughly with 15 c.c. of a dilute solution of palladium chloride. I have previously shown that oxygen, prepared from liquid air, often contains small quantities of combustible impurities (see the detailed description), and that special attention should always be paid to the oxygen used in calorimetric work. The oxygen used in the present case was free from such impurities, as ensured by passing it, before it was filled into the bomb, through a heated, thick-walled copper tube filled with palladium asbestos and pieces of platinum.

In conformity with what has been said above, I must abide by the correctness of my value of the ratio of the heats of combustion of benzoic acid and salicylic acid, *viz.*, 1·2074 (vac.).

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