CLXXXVII.—*The Heat of Combustion of Salicylic Acid.* (*A Reply to E. Berner.*)

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DURING the last few years investigations on thermochemical standard substances, carried out in various places, have led to the adoption of benzoic acid, by international consent, as the exclusive standard substance to be used in determinations of heats of combustion. The value 6324 cal.$_{15°}$ per g. (air) (v = constant), *i.e.*, 6319 cal.$_{15°}$ per g. (vac.), has been accepted for the heat of combustion of this substance. At the same time, it was decided that, for scientific work, use should always be made of benzoic acid furnished for this purpose by the Bureau of Standards, Washington (*Compt. rend. de la troisième Conférence Internationale de la Chimie*, Lyons, 1922, p. 54; compare Verkade, *Chem. Weekblad*, 1922, **19**, 389; 1924, **21**, 13).

For some time we have tried to make it clear that this regulation is not quite sufficient. The heat capacity of a calorimetric system, found exclusively by means of this benzoic acid, is always somewhat uncertain; accidental errors, caused by contamination of the standard preparation, during packing or in the course of time, can be brought to light only with difficulty, if at all. We therefore emphasised strongly the desirability of introducing one or more further thermochemical standard substances (which, if so desired, could be considered as *secondary* standards) and, on the grounds of an extensive research, recommended salicylic acid for this purpose (Verkade and Coops, *Rec. trav. chim.*, 1924, **43**, 561).

The heats of combustion of various samples of salicylic acid were determined with the following results, valid for an isothermal reaction at 19·5°, at constant volume and on the assumption that the above-mentioned heat of combustion of benzoic acid holds for the same temperature (compare Verkade, *Rec. trav. chim.*, 1925, **44**, 799).

Sample.	Heat of combustion per g. (air).
Poulenc (" Standard pour calorimétrie ")	5241·4 cal.$_{15°}$
Merck (" Präparat von bestimmter Verbrennungswärme ")	5241·7 ,,
Merck (crystallised from ether)	5241·3 ,,
Von Heyden (" Acid. Salicylicum recrystallis. puriss.")	5242·8 ,,
Kahlbaum (" für kalorimetrische Bestimmungen ")	5242·6 ,,
Commercial (" Acid. Salicyl. praec. pulv.") (crystallised twice from water and once from chloroform)	5242·3 ,,

Thus a number of the purest samples obtainable commercially, most of them supplied especially for calorimetric purposes, furnished values for the heat of combustion which agreed within the error of observation. The heat of combustion of one of these samples remained unchanged when the substance was recrystallised from ether. A technical preparation taken from the Dutch market gave the same heat of combustion after purification. On the basis of these facts, we considered ourselves completely justified in regarding the mean of all our measurements as the heat of combustion of *pure* salicylic acid. This heat of combustion is 5241·9 cal.$_{15°}$ per g. (air) (v = constant; 19·5°), *i.e.*, 5238·3 cal.$_{15°}$ per g. (vac.). The ratio of the heats of combustion of benzoic acid and salicylic acid is then 6324/5241·9 = 1·2064 (air).

Our work has recently been criticised by Berner (J., 1925, **127**, 2747). Let it be said that this author shares our views regarding the desirability of introducing a second or secondary thermochemical standard substance and admits the particular suitability of salicylic acid for this purpose. However, we are said not to have taken the necessary care to ensure the greatest possible purity of our samples of salicylic acid and, on that account, to have found too high a heat of combustion; according to Berner, the heat of combustion of salicylic acid is only 5237·4 cal.$_{15°}$ per g. (air) (v = constant; about 18°), *i.e.*, 5233·8 cal.$_{15°}$ per g. (vac.). The ratio of the heats of combustion of benzoic and salicylic acids should then be 6324/5237·4 = 1·2075 (air).

Berner seems to have overlooked the fact that the heat of combustion found by us was already confirmed from two sides :

1. Roth burnt salicylic acid in the micro-bomb and micro-calorimeter which he has constructed and found 5241·5 cal.$_{15°}$ per g. (air) for the heat of combustion, which deviates from our value by only − 0·08 part per 1000 parts (*Z. Elektrochem.*, 1924, **30**, 607). Also, Roth has investigated salicylic acid in a bomb of normal dimensions and the well-known calorimetric apparatus of Stohmann-Hugershoff (*Naturwiss.*, 1924, **12**, 652); it is, however, simply stated there that the heat of combustion found agreed exactly with ours. We have learned some details from a private

communication, which, by kind permission of Prof. Roth, we are able to publish. Various samples of salicylic acid from von Heyden gave concordant heats of combustion; an arbitrarily chosen commercial sample was purified by crystallisation from alcohol and after careful drying gave the same heat of combustion, which did not alter when the sample was recrystallised from alcohol and from water. The mean value of all these measurements was 5241·3 cal.$_{15°}$ per g. (air) (v = constant; 18·3°); the deviation from our value amounted therefore to only − 0·11 part per 1000 parts.

2. Swientoslawski (*Bull. Soc. chim.*, 1925, **37**, 84) found 5242·4 cal.$_{15°}$ per g. (air) for the heat of combustion of a commercial sample of salicylic acid, which was crystallised several times from water. This value deviates from ours only by about + 0·10 part per 1000 parts. Details of these measurements were not published.

These facts made it *a priori* scarcely possible for us to believe in the accuracy of Berner's results. It was improbable that the numerous preparations used by Verkade and Coops, by Roth, and by Swientoslawski—notwithstanding their different origins and different modes of purification—should all show a large surplus of exactly the same magnitude in the heat of combustion.

Nevertheless, we considered that our work ought to be controlled. In the first place, we again burnt one of the preparations which we had used previously (namely, that of Merck), making use of another bomb and of a calorimetric apparatus of considerably greater heat-capacity than that used previously. Secondly, we carefully subjected the previously used sample from von Heyden to various purification processes and measured the heat of combustion after each purification in the same apparatus. The results of these measurements are in the following table.

Material.	Heat of combustion per g. (air). (v=constant; 19·5°).
Merck	5242·3
Von Heyden (crystallised twice from water, once from chloroform)	5241·4
Von Heyden (further crystallised from ether)	5241·5
,, (further crystallised from benzene)	5241·9

Thus we see that continued purification of von Heyden's salicylic acid brings about no change in the heat of combustion. The mean value of our 15 experiments with this acid in its various stages of purification is 5241·7 cal.$_{15°}$ per g. (air) (v = constant; 19·5°). This new value for the heat of combustion of salicylic acid deviates from the one we found previously by only − 0·04 part per 1000 parts. For the ratio of the heats of combustion of benzoic and salicylic acids we now obtain the value 6324/5241·7 = 1·2065 (air), which is practically identical with that found previously. We have no reason to doubt the correctness of this value, as the ratios of the heats of combustion of benzoic acid and naphthalene, and of benzoic acid and cane-sugar, obtained by us at about the same time (Verkade, Coops, and Hartman, *Rec. trav. chim.*, 1922, **41**, 241; Verkade and Coops, *ibid.*, 1923, **42**, 205) are in full agreement with those obtained recently in very careful work by other authors (Dickinson, *Bull. Bureau of Standards*, 1914, **11**, 243; Swientoslawski and Starczewska, *Bull. Soc. chim.*, 1922, (4), **31**, 654; Schläpfer and Fioroni, *Helv. Chim. Acta*, 1923, **6**, 713), and at present generally accepted.

Hence we reach the conclusion that Berner found a value for the heat of combustion of salicylic acid which is too low, and that his results are subject to an error of about 0·8 part per 1000 parts. We are not able to indicate the cause of this error. At our request, Mr. Berner had the kindness to provide us with small quantities of two samples of salicylic acid which he had used in his research. These were the samples designated by Berner as 571II (Merck's acid, crystallised twice from water and once from chloroform) and 572IV (Kahlbaum D.A.B.5, subjected to sublimation in a vacuum and to several crystallisations from water, chloroform, and benzene). These samples yielded in our hands values for the heats of combustion of 5241·6 and 5241·9 cal.$_{15°}$ per g. (air), respectively. These values are practically identical with those obtained by us for our own specimens. Berner as well as ourselves used benzoic acid from the Bureau of Standards, Washington (Standard Sample 39*b*) in the calibration of the calorimetric apparatus.

As far as we know, Berner has not burnt standard samples of naphthalene and cane-sugar in his apparatus. The possibility therefore exists that, on burning these substances, this author may find, for the ratios mentioned above, values different from those now generally accepted as correct. In this case, the low heat of combustion of salicylic acid found by this author would be due to a slight error in the determination of the heat capacity of his apparatus.

EXPERIMENTAL.

The following alterations have been made in the calorimetric apparatus used for our previous measurements of the heat of combustion of salicylic acid (Verkade and Coops, *loc. cit.*) and described in detail in our first communication on heats of combustion of organic compounds (Verkade, Coops, and Hartman, (*Rec. trav. chim.*, 1922, **41**, 241).

We now used a silver calorimeter can of greater capacity than that used formerly, so that the quantity of water could be increased to about 2600 g., as well as a bomb of rustless V_2A steel, supplied by the firm of Hugershoff, Leipzig, and especially suited, in our experience, for work of high precision.

For the method of carrying out the measurements reference may be made to the literature cited above.

Heat Capacity of the Calorimetric Apparatus.—This was determined by burning three samples of benzoic acid, namely, two standard preparations (Standard Samples 39*a* and 39*b*) from the Bureau of Standards, Washington, and one prepared by ourselves, which had already served for earlier work. At an oxygen pressure of 35 atms. the heat capacity was 3051·2 cal._{15° at a temperature of 19·5°. It seems unnecessary for us to give full details of our measurements, but we give a statement of results :

Sample.	Heat capacity.	Sample.	Heat capacity.
39*a*	3050·0	39*b*	3050·0
,,	3049·6	,,	3051·4
,,	3051·4	,,	3051·8
,,	3051·6	,,	3052·4
,,	3051·3	Rotterdam	3050·9
,,	3050·2	,,	3052·3
,,	3051·2	,,	3051·8
		,,	3052·5

For some observations regarding the heat capacity found in this way (*i.e.*, by the combustion of a standard substance), reference may be made to a paper by one of us (Verkade, *Rec. trav. chim.*, 1925, **44**, 799).

We were able to verify this heat capacity repeatedly by indirect methods, namely, by burning substances which we had already burnt before introducing the above-mentioned alterations in the calorimetric apparatus. Completely concordant results were obtained in both cases. Also (*e.g.*, in the case of *n*-butyl alcohol), we could obtain with our new apparatus complete concordance with the extremely accurate thermochemical work of Richards (compare Verkade and Coops, *Rec. trav. chim.*, 1926, in course of publication).

Salicylic Acid Preparations.—Von Heyden's " Acidum Salicylicum recrystallis. puriss " (used in our previous measurements) was crystallised twice from water. After drying in the air, it was very finely powdered and warmed to about 100° for 4 hours ; during the heating it was again finely powdered several times. We have shown already (*Rec. trav. chim.*, 1924, **43**, 575) that salicylic acid can be heated for 20 hours at about 115° without undergoing even the slightest decomposition. This heating is necessary, since it has been shown recently (*e.g.*, Cohen, Verkade, Saburo Miyake, Coops, and van der Hoeve, *Versl. Kon. Akad. Wetensch. Amsterdam*, 1926, **35**, 48) that on crystallisation from water, salicylic acid may occlude several parts of water per thousand, which is not removed even by very long drying in a vacuum over phosphorus pentoxide. However, this occluded water can be removed for the most part in the way described above, as was proved by determinations of the heat of combustion carried out expressly for this purpose. The sample obtained in this way was then recrystallised from dry chloroform (sample II); the last traces of water in the crystals were removed by distilling off a part of the solvent from the boiling solution, the water then passing over with the solvent. After a part of this sample had been burnt, the remainder was crystallised from dry ether (sample III) and finally from dry benzene (sample IV). All three samples were finely powdered and dried for several days in a vacuum over phosphorus pentoxide.

Merck's salicylic acid (" Präparat von bestimmter Verbrennungswärme) and Berner's samples 571II and 572IV were finely powdered and dried in the same way without other treatment.

Heat of Combustion of the Salicylic Acid Preparations.—On account of a small difference in the composition of the products of combustion of benzoic and salicylic acids, a correction of +0·1 cal.$_{15°}$ must be introduced in the above-mentioned heat capacity in combustions of the latter acid (compare *Rec. trav. chim.*, 1924, **43**, 566). We shall give no details of the measurements. We found the following values for the heat of combustion of salicylic acid per g. (air) (v = constant; 19·5°).

Sample.	Heat of combustion.	Mean.
Merck	5242·4, 5242·7, 5240·7, 5242·4, 5243·2	5242·3
II	5241·5, 5241·8, 5242·2, 5240·0, 5241·6	5241·4
III	5242·5, 5242·5, 5240·4, 5241·5, 5240·8	5241·5
IV	5242·6, 5240·8, 5241·6, 5241·7, 5242·9	5241·9
571 II	5241·6, 5241·5, 5241·7	5241·6
572 IV	5241·2, 5240·1, 5244·5	5241·9

Summary.

Our previous determinations of the heat of combustion of salicylic acid have been submitted to a control. The heat of combustion of this compound was found to be 5241·7 cal.$_{15°}$ per g. (air) (v = constant; 19·5°), a value practically identical with that found previously. Hence the heat of combustion found by Berner, namely, 5237·4 cal.$_{15°}$ per g. (air) (v = constant; about 18°), is too low.

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