

Chemistry. — "*The use of Salicylic acid as a standard in Calorimetry.*"

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Introductory.

The investigations of recent years had led to the conviction that, when determining the heats of combustion of substances, the first desideratum is to ascertain with great accuracy the heats of combustion of one or more "standard-substances", and since that time similar studies have been taken up by more than one scientist ¹⁾. Contrary to the opinion of some investigators VERKADE and COOPS have pointed out that not only of one standard-substance the heat of combustion ought to be fixed with great accuracy, but at least of two of such substances.

As the result of an extensive investigation they have recommended *salicylic acid* as second standard with *benzoic acid* as first standard ²⁾.

As ERNST COHEN and VAN DOBBENBURCH ³⁾ had found that this acid, when recrystallized, without further precautions, from water, can contain rather considerable quantities of occluded water, which cannot be removed by drying in vacuo over P_2O_5 , the question arose if the few considerations mentioned by VERKADE and COOPS in their paper just cited, relating to the previous history of the preparates they had investigated, could be considered sufficient to guarantee a *salicylic acid* preparate which was perfectly free from water. For, at that time, a complete formula for the preparation of a standard-preparate, had not yet been given.

While later on we shall return in extenso to this subject, we give here the results of our investigation in this direction; it has proved that, indeed, the determination of the heat of combustion of *salicylic acid* which has been recrystallized from water, without further precautionary measures, can give quite arbitrary values. However, we can add the assurance that *if, after recrystallizing from water, the acid is crystallized from dry ether, we always find the same value for the heat of combustion, viz. the one which VERKADE and COOPS have fixed for it.*

¹⁾ See for literature f. i. P. E. VERKADE, *Chemisch Weekblad* 21, 13 (1924).

²⁾ *Rec. d. Trav. Chim. des Pays Bas* 43, 561 (1924).

³⁾ *These Proceedings* 28, 702, (1925).

The Method of Procedure.

§ 1. The different preparates under discussion have been prepared at Utrecht or at Rotterdam, at which latter place the calorimetric measurements were made in the Laboratory of the Handels-Hoogeschool, with the apparatus used by VERKADE and COOPS in their previous investigations. The preparates which were got ready at Utrecht were taken to Rotterdam sealed in glass bottles, which had been well dried. When the calorimetric determinations had been made we transported the rest of the preparations used to Utrecht in the same way, and here we determined ¹⁾, if necessary, the solubility in dry benzene at 30°.00 C. This was done after the manner minutely described in the paper by ERNST COHEN and VAN DOBBENBURGH ²⁾. In the course of this paper we shall indicate this communication by the letters V. C. D.

The solubility determinations have all been made by SABURO MIYAKE. The names behind the preparates indicate their maker.

The preparates used.

§ 2. The preparates of salicylic acid which were calorimetrically investigated were :

A. Standard preparete (MIYAKE). A newly received quantity of salicylic acid (KAHLBAUM, für kalorimetrische Bestimmungen) was recrystallized (V.C.D § 2, 2), from dry ether (V.C.D. § 1, c), kept for some weeks over P₂O₅ in vacuo, and powdered every day.

B. Ether preparete I (V. D. HOEVE). Prepared in quite the same way as A. On the 9th of October the air-dry preparete was placed in vacuo over P₂O₅, and, in flat weighing bottles, in which a thin layer of acid (± 7 gms) had been spread, the weight was occasionally determined. Before weighing the preparete into the bottles it had been powdered a few times. Thus we found : October 12 : 43.9791 ; October 19 : 43.9789 ; October 20 : 43.9789 ; October 21 : 43.9790 gms.

C. Ether preparete 2 (V. D. HOEVE). Quite as B. Placed in vacuo (± 5 gms. of acid) on October 11. Found : October 16 : 39.7814 ; October 19 : 39.7810 ; October 20 : 39.7809 ; October 21 : 39.7812 ; October 22 : 39.7814 gms.

D. Water preparete I (V. D. HOEVE). The acid had been slowly crystallized from the aqueous solution. After sucking off on a hardened filter the crystals were left on a glass plate to become air-dry. When the mass had been in vacuo for some time, it was powdered and for 72 hours placed in vacuo over P₂O₅. When the weight had become constant a part was kept as "Water preparete I" (± 10 gms. of acid). Found October

¹⁾ Not at 30°.50 C., as was previously done by COHEN and VAN DOBBENBURGH.

²⁾ These Proceedings 28, 702, (1925).

23 : 44.4869 gms. ; October 24 : 44.4867 gms. ; October 26 : 44.4866 gms., while the rest was powdered a few times, and then also dried to constant weight in vacuo over P_2O_5 (± 10 gms. of acid). Found : October 26 : 43.4416 gms. ; October 28 : 43.4366 gms. ; October 29 : 43.4363 gms. ; October 30 : 43.4363 gms.

E. Water prepareate II is this last mentioned part. (V. D. HOEVE).

F. Water prepareate, chilled on ice, (V. D. HOEVE). Pure ice was washed with distilled water ; on 1 K.G. of ice was poured a boiling saturated aqueous solution of about 30 gms. of salicylic acid. The crystals were sucked off and made air-dry. Then it was placed in vacuo, 48 hours later it was powdered, and dried in the desiccator to constant weight.

G. Water prepareate. After continual powdering we allowed prepareate E to stand for a week in vacuo over P_2O_5 ; the prepareate thus treated is called G.

Moreover we have investigated :

H. Prepareate "KAHLBAUM für kalorimetrische Bestimmungen" (new consignment), coarse crystalline, was, without further treatment, powdered and kept over P_2O_5 in vacuo for 288 hours.

I. Prepareate POULENC ("Standard pour calorimétrie"). On November 12 this prepareate was quickly recrystallized from water, stirring the solution continuously (VERKADE). After sucking off and washing with water it was placed in vacuo over P_2O_5 without first powdering it. The heat of combustion was determined on November 14, 17 and 24.

K. Prepareate I, without special preliminary treatment, was heated for 6 hours at 100° — 105° (VERKADE).

L. Another part of prepareate I was powdered and then heated for six hours at 100° — 105° (VERKADE).

The results.

§ 3. The results of the determinations of the heat of combustion of the different preparates are given in Table 1. Before the combustion every prepareate was always carefully made homogeneous.

When the preparates had been transported to Utrecht their solubility was determined in dry benzene (MIYAKE). The benzene had been treated in the same way as previously described (V.C.D. § 1. b.). The solubilities thus found are also given in Table 1.

§ 4. First of all we wish to point out that the heat of combustion of the preparates A, B, and C, all recrystallized from dry ether, is exactly the same as the one found by VERKADE and COOPS for preparates of very different origin, viz. 5242 cal.₁₅₀ per gramme (air).

The satisfactory agreement between the values which we found in the different determinations of each of these preparates indicates that they were homogeneous. The fact that the solubility determinations for different samples in dry benzene give concurring figures is in correspondence with it.

TABLE 1.

Name of the preparate	Heat of combustion in cal. 15° per gram (air)	Solubility at 30°0 C. in dry benzene gms in 100 gms, of saturated solution	
		First determination	Second determination
<i>A</i>	5243.1 } 5242.3 } 5243.4 5244.7 }	0.98 ²	0.98 ²
<i>B</i>	5242.4 } 5244.5 } 5243.4	0.98 ²	0.97 ⁵
<i>C</i>	5239.9 } 5243.6 } 5241.7	0.97 ⁹	0.98 ²
<i>D</i>	5232.8 } 5232.6 } 5233.8 5237.3 } 5232.4 }	0.98 ⁵	1.00 ⁰
<i>E</i>	5237.4 } 5229.7 } 5231.8 5230.0 } 5229.4 }	0.99 ²	0.97 ⁷
<i>F</i>	Nov. 3-4 5219.7 } 5223.3 } 5216.3 } Nov. 14 5240.8 } 5228.7 5240.8 } 5228.0 } 5232.0 }	1.00 ¹	1.00 ⁸
<i>G</i>	5235.6 } 5232.1 } 5236.2 5235.1 } 5242.0 }	—	—
<i>H</i>	5243.1 } 5242.5 } 5242.4 5244.4 } 5239.6 }	—	—
<i>I</i>	5222.1 } 5216.8 } 5220.3 5221.9 }	—	—
<i>K</i>	5231.4 } 5233.8 } 5232.6	—	—
<i>L</i>	5237.8 } 5238.0 } 5237.9	—	—

§ 5. The course is totally different with the preparates D, E, F and I, all of which are crystallized from water. Without exception they give for the heat of combustion values which are far too low. Moreover the figures obtained from one and the same preparate in different experiments are often greatly divergent, which proves that the samples taken from the same mass differ from each other in composition, which is self evident, as it must be held impossible to divide homogeneously 0.2—0.4 weight percentage of water in the crystals.

In agreement with this the solubility figures in dry benzene also show divergencies. It is quite in agreement with the results of ERNST COHEN and VAN DOBBENBURGH's experiments that they give higher values than in the preparates which are crystallized from ether.

§ 6. Very instructive are the determinations with the preparates K and L; heating to 100°—105° C. is not sufficient to remove the occluded water completely.

The distinct difference in heat of combustion between the powdered preparate L and the preparate K, which was not powdered, further shows that powdering, as was to be expected, opens part of the capillary pores. No doubt it would be possible to obtain a preparate of about the exact heat of combustion by alternate powdered and heating.

§ 7. Furthermore we call attention to the conduct of preparate H, of whose previous history we know only that in the factory-works it was recrystallized from water. We are not acquainted with the further operations in the factory. Meanwhile it given values for the heat of combustion which are identical with those previously found by VERKADE and COOPS.

§ 8. Summarizing, we see that preparates finally recrystallized from water must never be used as standard-preparates, even after drying to constant weight in vacuo over P_2O_5 , or after heating for six hours to 100°—105° C., as they give values for the heat of combustion which must be considered as accidental.

On the contrary, preparates finally crystallized from dry ether give constant values, which are in good agreement with those found by VERKADE and COOPS for preparates which had been finally crystallized from ether or chloroform.

Summary.

It was demonstrated that, if salicylic acid is to be used as a "standard-substance" for the determination of the heat of combustion, the prescriptions for its preparation must be formulated more sharply — especially as regards the final crystallization — than was done up to this time. It was seen that

constant values which can be reproduced, can be expected only if the final crystallization has been made from dry ether. A special investigation will have to establish what other solvents may be used for this final crystallization.

The disturbances which occur when crystallizing from water can be accounted for by the presence of occluded water in the crystals, which cannot be completely removed, neither by drying in vacuo over P_2O_5 , nor by heating to 100° — 105° C. for six hours.

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