presence of atomic oxygen in each case. Ozone may or may not be formed by means of gaseous ions. Because of the few species of ions present in oxygen its transformation into ozone is a suitable reaction for the study of the connection between ionization and chemical reaction. The corona apparatus gives a very favorable form of discharge for this purpose.

An equilibrium results between the oxygen and ozone caused by the presence of two opposing effects, ozonizing and deozonizing. At equilibrium in the corona it is probable that gases have the same concentration regardless of whether the wire is charged positively or negatively. Coincident with the increase in temperature in the discharge tube, caused by the degradation of energy, there is an increase in resistance.

The study of ozone formation is being continued.

URBANA, ILL.

[CONTRIBUTION FROM THE H. LOUGININE THERMAL LABORATORY OF THE PHYSICAL INSTITUTE OF MOSCOW UNIVERSITY.]

ON THE STANDARD UNIT IN THE THERMOCHEMISTRY OF ORGANIC COMPOUNDS.

BY W. SWIENTOSLAWSKI.

Received September 19, 1917.

In 1908, Em. Fischer and Wrede[1] published a paper about the heat of combustion of benzoic acid and cane sugar. As the measurement of heat capacity of calorimeteric systems, carried out in the Reichsanstalt by Jaeger and Steinwehr, has been expressed in kilo-joules, therefore, these quantities also were expressed in kilo-joules.

1 g. benzoic acid weight in air................	26,497 kilo-joules.
1 g. cane sugar weight in air..................	16,555 kilo-joules.

The authors proposed that the cited quantities might be used as standard units for the measurements of the heat capacity of all the calorimetric bombs. Verifying the constants of calorimetric bombs, used in W. Louginine's Thermal Laboratory of Moscow University, I noticed that the real heat capacity of the bombs was smaller than the one determined from the combustion of benzoic acid or cane sugar. These constants were computed with the aid of the Reichsanstalt data using 4.189 as the equivalent of the joule instead of a more probable value between 4.179 and 4.182.

This induced Popov and myself to determine the heat capacity of the Peters bomb of the Thermal Laboratory by two methods, which were described in our preceding papers,[2] and to measure again the heat of combustion of benzoic acid.

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[1] *Sitzb. k. akad. Wiss. Math. Nat. Klasse,* 1908, 129.

[2] *J. Russ. Phys. Chem. Soc.,* **46,** 935, 1284, 1293, 1302 (1914).

The following values were obtained in the five different series of measurements:

Method applied.	Heat of combustion of benzoic acid (v = const.). 1 g. (weight in vacuum).	Heat of combustion of benzoic acid (v = const.). 1 g. (weight in air).
The ordinary calorimeter (radiation and evaporation)....	6310 Cal.	6315 Cal.
The ordinary calorimeter (radiation and evaporation)....	6312 Cal.	6317 Cal.
The ordinary calorimeter (radiation)...................	6307 Cal.	6312 Cal.
The adiabatic method, series 1.........................	6305 Cal.	6310 Cal.
The adiabatic method, series 2.........................	6305 Cal.	6310 Cal.
Average heat of combustion in 15° calories...........	*6306 Cal.*	*6311 Cal.*

As the quantities so obtained did not agree with the data of Fischer and Wrede and were smaller by about 0.4–0.5% and as it was clear that it was impossible to find the cause of this incongruity by polemics or correspondence, I went in June, 1914, to Berlin and Charlottenburg in order to discuss the following propositions with E. Fischer and Jaeger:

1. It is indispensible to choose a substance and to accept the heat of combustion of this substance as the standard unit in thermochemistry of organic compounds. The constants of all calorimetric systems ought to be determined by the combustion of this substance.

2. This substance should be benzoic acid.

3. The heat of combustion of benzoic acid ought to be determined with the greatest accuracy and to be accepted by the International Committee of Standards.

4. The heat of combustion of benzoic acid ought to be determined by the adiabatic method.

5. At present the heat of combustion of benzoic acid ought to be expressed in terms of calories, for it would be impossible now to express this quantity in absolute units with necessary accuracy.

6. All the other methods of determination of the heat capacity of calorimetric systems ought to be excluded. Other methods could be applied, if it was desired to verify the heat of combustion of the standard unit in the thermochemistry of organic compounds.

7. When publishing the materials used in the thermochemistry of organic compounds the author should indicate the value for the heat of combustion of benzoic acid, accepted by him in determining the constant of his calorimetric bomb. This may be necessary for future computation and correction, if the value of the standard unit in thermochemistry should be changed.

8. The number of corrections necessary for computing the heat of combustion must be fixed, because all corrections have not been made by several investigators in their measurements. To all, the correction for isothermic heat of combustion

$$(C_6H_5CO_2H + 7.5O_2)_t = (7CO_2 + 3H_2O)_t \ldots\ldots + Ais$$

should be applied.

It was not possible to propose sugar instead of benzoic acid as the standard substance for the following reasons: (1) The heat of combustion of sugar is small; (2) it is hygroscopic; (3) it is not easy to obtain a completely dry preparation; (4) dry sugar is difficult to ignite.

All these questions were discussed by Em. Fischer and Jaeger and accepted by them, excepting the fifth, because therein lay the cause of the difference between Fischer's results and mine. Fischer, Jaeger and myself decided to find out the cause of the observed difference in the cited measurements but the war made it impossible to carry out our intention. It was probable, however, that the observed difference was caused by the electrical units of the volt or of the ampere, which may appear greater than the real ones.

After Dickinson's investigation,[1] published in 1915, I may now give my definite opinion on these questions.

Dickinson determined the heat of combustion of three substances: naphthalene, benzoic acid and sugar. The results obtained expressed in 15° calories for 1 g. substance weight in air are:

Substance.	Heat of combustion.
Naphthalene	9612 Cal.
Benzoic acid	6323 Cal.
Cane sugar	3945 Cal.

The author cites the values of the heats of combustion obtained by previous authors but does not explain the cause of the difference between Fischer and Wrede's data and his own, although the first ones have been expressed in calories by using the too large equivalent, J = 4.189.

Author.	$C_{10}H_8$.	$C_6H_5CO_2H$.	$C_{12}H_{22}O_{11}$.
Dickinson	9612	6323	3945
Fischer and Wrede	..	6325	3952
Wrede	9633	6323	3952

The heat of combustion of benzoic acid as determined by Wrede and Dickinson is exactly the same, 6323, while the values of heat of combustion of sugar and naphthalene differ about 0.22% and 0.18%.

The comparison of Dickinson's data with mine also shows a deviation of +0.19%.

Dickinson	6323 Cal.
Swientoslawski	6311 Cal.

It is interesting, however, that the heat capacity of the Peter's bombs, measured by different methods by Dickinson and myself, shows the following coinciding number:

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[1] Bur. Standards, *Sci. Paper* **230**.

Author.	Bombs.	15°.	20°.	25°.
Dickinson	6312 platinum lining	272.7	274.9	276.3
Dickinson	6312 porcelain lining	272.9	275.1	276.5
Swientoslawski	platinum lining	272.6	274.1	275.6
Swientoslawski	porcelain lining	...	275.0	...

As the weight, dimension and heat capacity of a great many Peters bombs, which I used, showed only slight differences, the coinciding of the cited values prove that the measurements of M. Dickinson and mine were performed with sufficient accuracy. But the above-mentioned difference in the measurements of heat of combustion of benzoic acid can be explained only by supposing the presence of systematic errors or impurities of the preparation.

In order to explain the cause of this incongruity I have burned four samples of naphthalene: three times in ordinary Berthelot's calorimeter, three times in adiabatic calorimeter of my own construction[1] and three times in adiabatic calorimeter, in such a manner that the temperature of the jacket was continually equal to the final temperature t_n of calorimeter. The following results were obtained:

The ordinary Berthelot's calorimeter	9614 Cal.
The adiabatic calorimeter (adiabatic process)	9611 Cal.
The adiabatic calorimeter (temperature of jacket = t_n)	9615 Cal.
Average heat of combustion for 1 g. substance, weight in air	9613 Cal.

The complete conformity of Dickinson's data and mine shows that the discrepancy of data obtained by combustion of benzoic acid by Dickinson and myself is caused not by systematical errors in measurements but by some accidental circumstances. In the future the cause of this discrepancy will, perhaps, be made clear.

THE ANALYSIS OF THE DATA.

	Heat of combustion in calories or in kilo-joules.		
Author.	$C_{10}H_8$.	$C_6H_5CO_2H$.	$C_{12}H_{22}O_{11}$.
Fischer and Wrede	......	26,497 Kj.	16,555 Kj.
Wrede	40,350 Kj.	26,488 Kj.	16,558 Kj.
Hohmann	9,328 Cal.	6,322 Cal.	3,955 Cal.
Dickinson	9,612 Cal.	6,323 Cal.	3,945 Cal.
Swientoslawski	9,613 Cal.	6,311 Cal.	....

and computing the proportions:

$$\frac{\text{Heat of combustion of } C_{10}H_8}{\text{Heat of combustion of } C_6H_5CO_2H} = \alpha_1;$$

$$\frac{\text{Heat of combustion of } C_{10}H_8}{\text{Heat of combustion of } C_{12}H_{22}O_{11}} = \alpha_2;$$

$$\frac{\text{Heat of combustion of } C_6H_5CO_2H}{\text{Heat of combustion of } C_{12}H_{22}O_{11}} = \alpha_3.$$

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[1] *J. Russ. Phys. Chem. Soc.*, 46, 1284 (1914).

We notice that the ratios α_1, α_2, α_3 derived from the values of each separate investigator can vary in limits ±0.1%, because the liquid of the relative error by determination of heat of combustion is ±0.03 to ±0.05%.

The following comparison clears up the difficulty. The ratios α_1 and α_2 are computed by Fischer and Wrede from Wrede's data for the heat of combustion of naphthalene, 40,350 Kj.; while in my computation of the ratios, α_1 and α_3, the heat of combustion of sugar was taken corresponding to Dickinson's value, 3945 cal.

Author.	α_1.	%.	α_2.	%.	α_3.	%.
Wrede	1.52333	..	2.43689	..	1.59971	..
Fischer and Wrede	1.52281	—0.03%	2.43733	+0.02%	1.60054	+0.05%
Hohmann	1.52294	—0.03%	2.43439	—0.10%	1.59848	—0.08%
Dickinson	1.52016	—*0.21*%	2.43650	—0.02%	1.60279	+*0.20*%
Swientoslawski	1.52321	—0.01%	2.43676	+0.01%	1.59975	+0.00%

The cited data do not require any explanation. The ratios α_1, α_2, α_3 vary between ±0.1% (the ratios computed by Wrede were taken for comparison as 100%), excepting in two cases. So we find an exception when the number *6323*, which expresses the heat of combustion of benzoic acid according to Dickinson, is used as denominator or numerator in computing the ratios α_1 and α_3. I cannot indicate what caused this discrepancy yet it is by no means probable, that all these investigators, except Dickinson, used impure benzoic acid and that this was the only cause of the difference in data up to —0.2%.

The complete coincidence of the values of heat capacity of calorimetric bombs and of heat of combustion of naphthalene obtained by Dickinson and by myself indicates that our measurements were performed with sufficient relative and absolute accuracy.

It is also remarkable that the ratios α_1, α_2, α_3 computated with my number 9613, 6311 (naphthalene, benzoic acid) and with Dickinson's number 3945 (sugar) differ from Wrede's coefficients only by about ±0.01%, and therefore, the relative accuracy of all these measurements and the purity of preparations cannot be bettered.

I, therefore, propose that the following data can be accepted at present in thermochemistry for determining the heat capacity of calorimetric bombs:

Substance.	Heat of combustion in 15 cal. 1 g. weight in air.	Author.
Naphthalene	9612 Cal.	Dickinson, Swientoslawski
Benzoic acid	6311 Cal.	Swientoslawski
Cane sugar	3945 Cal.	Dickinson

These quantities cannot be compared with the data of Hohmann, as this investigator had not introduced the correction of the hydrogen scale of temperature and all the other corrections, which now must be introduced in contemporary investigations. The amount of all these corrections changes the results of measurements to +0.3% (more precisely +0.29%).[1] After having introduced the due corrections into Hohmann's data, we will obtain the following results:

Substance.	1 g. weight in air.	Deviation.
Naphthalene	9599 Cal.	—0.13%
Benzoic acid	6303 Cal.	—0.13%
Cane sugar	3943 Cal.	—0.05%

The discrepancies with the data of Dickinson and myself are small but a little greater than the limit of accuracy of the discussed measurements.

Summary.

1. Agreement in thermochemical data will be obtained if the heat capacity of all calorimetric bombs is measured by *one method* and if one substance, accepted as standard, is burned in determining the constant of calorimetric bombs.

2. The next International Congress ought to appoint a special commission to adopt a standard unit for the thermochemistry of organic compounds.

3. The International Congress ought to fix standards by which the heat capacity of all calorimetric bombs may be determined by only one method —namely, by burning of the standard substance.

4. It would be desirable that all the bureaus of standards be provided with a sufficient quantity of the pure substance chosen as standard and that the bureaus cease to use other methods for determining the constant of calorimetric bombs.

5. The International Congress ought to fix the terms in which the heat of combustion of standard may be expressed as calories or as absolute units.

6. The heat of combustion of a standard in the thermochemistry of organic compounds ought to be determined with the greatest accuracy. The number of the corrections to be introduced should be fixed.

Until the standard unit is fixed, it is desirable to determine the heat of capacity of calorimetric bombs by burning naphthalene, benzoic acid or cane sugar and by accepting the following values for the computations:

Substance.	Heat of combustion in 15° cal. for 1 g. weight in air. (v=const.)
Naphthalene	9612 Cal.
Benzoic acid	6311 Cal.
Cane sugar	3945 Cal.

MOSCOW, RUSSIA.

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[1] *Loc. cit.*