reagent than potassium iodide in neutral solution; its employment is only necessary, however, when absorption of the ozone in turpentine is the method followed. In the method of Schönbein, as used by Ladenburg and Quasig, either neutral or acid solutions of cadmium potassium iodide may be used; sharp end-points are obtained and the results are not too high.

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THE HEAT OF COMBUSTION OF ETHYLBENZENE.

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Sometime ago, together with Professor T. W. Richards, the writer carried out a comparison of the differences which exist between the heats of combustion of a number of isomeric substances, especially several of the octanes and the three xylenes.[1] In connection with the xylenes it was desirable to study the isomeric compound, ethylbenzene, and indeed, preliminary work was started at that time but lack of time prevented its completion. Facilities for further work with the calorimetric bomb have only recently become available. This paper presents the results of the completed study of ethylbenzene.

The preliminary work showed that it was difficult to free commercial samples of this compound completely from organic bromides. The sample used in these experiments was prepared by the Fittig synthesis from bromoethane and bromobenzene, with the former in excess in the hope of eliminating more completely the bromobenzene, whose boiling point is not far removed from that of ethylbenzene. The crude product after one distillation was fractionated seven times with the help of a long fractionating column. The sixth fraction (44 grams) boiled between 135.5–136.4° (745.5 mm.). This portion was distilled again, 7 grams coming over between 135.5–135.8° and 35 grams between 135.9–136.1°. The determinations later showed that these two fractions were identical in so far as thermochemical means could decide.

The bomb used in this work was one made by Professor S. W. Parr of this laboratory from a special alloy of nickel, copper, and chromium.[2] This alloy is so resistant to the attack of acids that it is proposed to use bombs made of it as substitutes for those with the expensive platinum linings. Analyses of the washings from eight runs showed that the amounts of metal dissolved in an average determination were 0.2 mg. of copper and 0.8 mg. of nickel.[3] The heat of formation of the nitrates

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[1] THIS JOURNAL, 31, 268 (1910).

[2] See *Proc. Eighth Intern. Congr. Appl. Chem.* where there is a full description of this bomb.

[3] A fuller description of the behavior of this bomb under actual working conditions has been given in the *Proc. Eighth Intern. Congr. Appl. Chem.*

corresponding to these quantities is about 1.8 calories, which is 0.02% of the total amount of heat measured in the average determination of this series. This is beyond the limit of accuracy claimed for these experiments, so this correction has not been applied to the results. The mercury thermometer of the Beckmann type was calibrated by the Bureau of Standards.

The method of adiabatic calorimetry devised by Professor Richards was again used. In this method the calorimeter can of nickel-plated copper, holding the bomb, stirrer, and 3 liters of water was placed inside of a larger copper vessel. A cover provided with tubes for the thermometer, stirrer, and electrical connections was clamped down upon the face of a rubber gasket which fitted between the cover and a suitable flange on this outer copper vessel, making a water-tight joint. The whole was immersed in a bath of caustic soda solution, whose temperature was so adjusted that it was the same as that in the calorimeter can. The temperature of this bath was readily changed by the addition of proper amounts of sulfuric acid so that its temperature was at all times the same as that in the calorimeter, even when the latter was changing.[1]

In order to obtain suitable standards of comparison, determinations were made of the heats of combustion of three samples of cane sugar and two of benzoic acid. The sugar samples were all supplied by the Bureau of Standards at different times during the past three years. One sample of benzoic acid was also from the Bureau of Standards. The other sample was purified from Kahlbaum's best benzoic acid by two distillations under diminished pressure, followed by three crystallizations from water, each crop of crystals being centrifugally drained. Afterwards the sample was dried for several hours at 110° and was allowed to stand over fused potassium hydroxide for two months before use. The determination on this sample is marked No. 10 in the table. The agreement between the several samples was excellent.

The sugar was burnt in powdered form, but the benzoic acid was pressed into pellets. The corrections for the burning of the iron ignition wire and for the heat of formation of the nitric acid[2] were applied in the usual manner. The voltage of the line connected with the motor which actuated the stirrer varied so much from day to day that corrections for the heat gained by friction had to be determined for each individual run. After each experiment when the thermometer became stationary the stirring was continued for as many minutes as had elapsed between the ignition and the time when the final temperature had been reached, and the in-

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[1] For details see THIS JOURNAL, 31, 273.

[2] The correction for the iron was made on the basis of Berthelot's equation, $Fe \longrightarrow Fe_3O_4 + 270,800$ cal. The correction for nitric acid was made on the basis of Thomsen's equation, $2N + 5O + H_2O + Aq = 2HNO_3Aq + 29,800$ cal.

crease in temperature was considered the stirring correction. The rate of stirring varied between 85 and 100 strokes per minute; the corrections varied between 0.003 and 0.005°.

The results on sugar and benzoic acid follow.

TABLE I.—CANE SUGAR.

No.	Weight substance in air. Grams.	Rise produced in calorimeter. All corrections made.	Rise per gram.	Deviation from mean. Per cent.
1	2.4994	2.898+°	1.1596°	+0.05
2	2.5018	2.898+°	1.1585°	—0.05
3	2.4987	2.898—°	1.1597°	+0.06
4	2.5004	2.899—°	1.1593°	+0.02
5	2.5035	2.900 °	1.1583°	—0.07
6	2.2743	2.636 °	1.1590°	±0.00

Average rise per gram sugar (weighed in air) = 1.1591°.
Average rise per gram sugar (vacuum standard) = 1.1584°.

BENZOIC ACID.

7	1.5089	2.802°	1.8570°	+0.02
8	1.5390	2.858°	1.8570°	+0.02
9	1.5059	2.797°	1.8574°	+0.04
10	1.4467	2.687°	1.8572°	+0.03
11	1.5635	2.902°	1.8561°	—0.04
12	1.5630	2.901°	1.8560°	—0.04
13	1.6584	3.078°	1.8560°	—0.04

Average rise per gram benzoic acid (weighed in air) = 1.8567°.
Average rise per gram benzoic acid (vacuum standard) = 1.8552°.

The ratio of benzoic acid and sugar (vacuum weights) is 1.6014. Fischer and Wrede[1] have made two series of determinations on these substances. Their value for sugar is practically identical in the two series. Their ratio from the first series on benzoic acid, which is the most concordant one, is 1.6003; the ratio from the average of the two series is 1.6000. These ratios are 0.07% and 0.09% lower than the one found here. If the ratio of the three highest results of these investigators is used it differs from the present one by only 0.035%. These differences are probably within experimental error of both series. The figures used by the Bureau of Standards are (*in vacuo*): 1 gram sugar = 3943 cal.; 1 gram benzoic acid = 6315 cal., the ratio between them being 1.6016 which is practically identical with that found in this paper. The *ratios* of Fischer and Wrede and the Bureau are in sufficiently satisfactory agreement in spite of the fact that their *absolute values* appear to differ by about 0.3%.

The method of burning the ethylbenzene was similar in every way to that used in the former work. The liquid was sealed into glass bulbs, with very thin walls, flattened on two sides. When completely filled

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[1] *Z. physik. Chem.*, **69**, 218 (1909); **75**, 81 (1910).

with liquid these bulbs withstand pressures at least as high as 45 atmospheres without breaking. A bulb of this kind was placed in the bottom of a narrow platinum crucible and a thin platform of glass carrying a weighed pellet of sugar was fixed above it in the crucible. The sugar was ignited by the passage of an electric current through an iron wire suspended just above it. The ignition of the sugar burst the bulb and the vapor passing through the flame from the sugar was completely burned. No odor of bromine could be detected in the gases from the bomb after combustion. The washings from the bomb gave no opalescence with silver nitrate.

It may be remembered that before this method was perfected the amount of nitrogen present in the bomb hindered complete combustion. In one experiment, No. 18, the nitrogen in the bomb was reduced by admitting oxygen until the pressure was 15 atmospheres and allowing it to escape. This was repeated five times so that practically all the nitrogen of the air originally in the bomb was displaced by oxygen. The only effect of this treatment was to diminish the amount of nitric acid formed. The pressure of oxygen in all these experiments was 35 atmospheres.

The temperature range for all the experiments described in this paper was between the limits 21° and 25°.

TABLE II.—HEAT OF COMBUSTION OF ETHYLBENZENE.

No.	Wt. $C_6H_5C_2H_5$ in air. Gram.	Wt. sugar in air. Gram.	Rise corrected for bore, stem, iron wire and stirring.	Correction for HNO_3.	Rise due to sugar.	Rise due to $C_6H_5C_2H_5$.	Rise per gram $C_6H_5C_2H_5$.	Deviation from mean. Per cent.
14	0.6870	0.2023	2.289°	—0.003°	0.234°	2.052°	2.987°	±0.00
15	0.8702	0.1934	2.826°	—0.003°	0.224°	2.599°	2.987°	±0.00
16	0.5912	0.2657	2.077+°	—0.003°	0.308°	1.766+°	2.988°	+0.03
17	0.7063	0.2005	2.109°	—0.003°	0.232°	2.109°	2.986°	—0.03
18	0.8091	0.2712	2.731°	—0.001°	0.314°	2.416°	2.986°	—0.03
19	0.6548	0.2705	2.270°	—0.003°	0.314—°	1.953—°	2.989°	+0.06

Average rise per gram ethylbenzene (weighed in air) = 2.987+°.
Average rise per gram ethylbenzene (vacuum standard) = 2.984°.

The agreement of the determinations of this series is all that could be expected. In the experiment marked No. 19 the fraction boiling at 135.5–135.8° was used. The other determinations are on the fraction 135.9–136.1°. The two fractions are thus identical within experimental error.

The ratio of ethylbenzene to sugar (vacuum standard) is 2.577. The ratios found for the xylenes are 2.605 for ortho- and metaxylene and 2.596 for paraxylene. Ethylbenzene has a heat of combustion 1.05% lower than that of ortho- and metaxylene and 0 7% lower than paraxylene. These aromatic isomers thus show much greater differences than was encountered in the aliphatic octane series.

If the value of Fischer and Wrede for sugar be accepted (1 gram = 16.545 kilojoules) the heat of combustion of 1 gram of ethylbenzene (weighed in vacuum) is 42.63 kilojoules. The heat of combustion of 1 gram mole (106.023 grams) is 4520 kilojoules. If a large calorie be considered equivalent to 4.179 kj. a gram-mole of ethylbenzene has a heat of combustion of 1081.5 Calories. On the other hand, if the value of the Bureau of Standards (1 gram sugar *in vacuo* = 3943 calories) be accepted, the heat of combustion of a gram-mole of ethylbenzene is 1077.3 Calories. This is the first determination of this constant.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

THE IODINE COULOMETER AND THE VALUE OF THE FARADAY.[1]

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PART I.—REVIEW OF PREVIOUS COULOMETER INVESTIGATIONS.

1. Introduction.

Although Faraday's law of electrochemical change has been universally accepted for many years, there still exists a considerable degree of uncertainty regarding the exact value of the Faraday. Theoretically, any chemical reaction which can be brought about by means of the electric current, might be employed for the determination of the value of the Faraday, but as a matter of fact, very few reactions have been studied in this connection and the value at present accepted for this constant is practically based upon measurements with a single electrochemical reaction, the deposition of silver from an aqueous solution of one of its salts. When we consider the amount of care and labor expended and the variety of reactions which it is deemed necessary to employ in order to fix the atomic weight of a single element, it is certainly remarkable that, in the case of such an important and universal a constant as the Faraday, scarcely any serious consideration has ever been given to any electrochemical reaction except that which occurs in the silver coulometer. And when we add to this the fact that this particular reaction is known to be affected by numerous sources of error and uncertainty which have not been entirely removed by years of laborious investigation participated in by many chemists and physicists, it must be apparent to all that serious

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[1] Presented before the Eighth International Congress of Applied Chemistry at New York, Sept. 9, 1912. Abstract of a thesis presented by Mr. Bates to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.