we find for $E_{0Fe^{++}}^{Fe^{+++}}$ the value —**0.463**, instead of the value —0.456 derived from the direct measurements.

10. Summary.

The equilibrium constant at 25° of the reaction

$$Ag + Fe(NO_3)_3 = AgNO_3 + Fe(NO_3)_2$$

has been determined by analysis of the equilibrium mixture. The values of the constant are found to vary considerably with the concentration of the solution. By plotting the values of this constant against the total nitrate concentration and extrapolating to zero concentration, it is found that 0.128 is the value for the expression $\frac{(Fe^{++})(Ag^{+})}{(Fe^{+++})}$, at equilibrium.

The potential of the ferrous-ferric electrode and of the silver electrode at 25° have also been determined. The value —0.456 was found for the former and —0.516 for the latter, these being in good agreement with those previously obtained by Maitland and by Lewis, respectively.

From the equilibrium constant and the potential of the silver electrode, the potential of the ferrous-ferric electrode was calculated to be —0.463, in fair agreement with that derived from the direct electromotive force measurements.

BOSTON, June, 1912.

BENZOIC ACID AS AN ACIDIMETRIC STANDARD.[1]

BY GEORGE W. MOREY.

Received June 3, 1912.

The study of the suitability of benzoic acid as a primary standard in acidimetry and alkalimetry was suggested by experience gained in the purification of benzoic acid to be used as a calorimetric standard. During that work it was found that benzoic acid could be titrated with standard alkali to a high degree of accuracy, and that this titration afforded the most rapid and accurate method of comparing the purity of various samples. Since pure benzoic acid has been furnished for some time by the Bureau of Standards as a calorimetric standard, it would, of course, be advantageous to use it also for a standard in acidimetry, if found suitable.

A search of the literature showed that Wagner,[2] in a report presented to the Fifth International Congress of Applied Chemistry, in 1903, had mentioned benzoic acid among a number of other possibilities for the purpose named; and that Phelps and Weed[3] had later included it in a short study of the availability of several organic acids and acid anhydrides.

The method used in studying this problem was that of standardizing

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[1] Published by permission of the Director of the Bureau of Standards.

[2] Proc. Fifth Internat. Cong. Appl. Chem., Berlin, 1, 323 (1903).

[3] *Am. J. Sci.*, **26**, 141 (1908).

a hydrochloric acid solution by several well known and standard methods, and comparing the results so obtained with those obtained by standardizing the same hydrochloric acid against benzoic acid.

The methods chosen for the work were the distillation method of Hulett and Bonner, the gravimetric silver chloride method, comparison with a sulfuric acid solution standardized gravimetrically by the barium sulfate method, and comparison with the same sulfuric acid standardized volumetrically by the sodium oxalate method.

Preparation of Materials.

Two samples of benzoic acid were used in this work. Sample A was prepared from the "'Kahlbaum" grade by recrystallizing twice from alcohol, once from water, and then fractionally subliming *in vacuo*. Sample B was prepared in the same manner from a fifty pound lot furnished on specification by the Baker & Adamson Chemical Co. The final product in both cases was free from chloride and otherwise as pure as could be prepared.

The hydrochloric acid solution was prepared by diluting hydrochloric acid made by Hulett's method, with freshly boiled distilled water.

Two samples of sodium oxalate were used. Sample A was prepared by Mr. J. B. Tuttle, in the Bureau of Standards, from Merck's "Oxalsaures Natrium nach Sörensen." Sample B was prepared by Dr. Wm. Blum, also in the Bureau of Standards, from a sample furnished by J. T. Baker Chemical Co., by crystallizing twice from water and precipitating once by alcohol. This had been tested by Dr. Blum[1] and found to be identical in composition with the best material which could be prepared. The above samples were compared with five others of special purity by converting to the carbonate and titrating, and all were found to be identical within the limits of accuracy of the method.

The sulfuric acid solution was prepared by diluting C. P. acid with distilled water and boiling, after which the solution was transferred to a stock bottle, in which it was allowed to cool. Sodium hydroxide was prepared free from carbonate by adding a little barium hydroxide, precipitating the excess barium with sulfuric acid and filtering. Barium hydroxide was likewise prepared from the C. P. salt by dissolving in water and filtering.

All these solutions were carefully protected from the carbon dioxide of the air by suitable guard tubes, and were tested for the presence of carbonate from time to time by titrating both in the cold and while boiling, using phenolphthalein as indicator. A difference between the two titrations would indicate the presence of carbonate, but the titrations were always within the limit of error of the method. Weight burets

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[1] THIS JOURNAL, 34, 127 (1912).

were used for all titrations, which were made in a 300 cc. flask through which passed a stream of air free from carbon dioxide.

Direct Standardizations of Hydrochloric Acid.

The hydrochloric acid was first standardized in its preparation, having been prepared by the method of Hulett and Bonner,[1] which is based on the constancy of composition, at a definit atmospheric pressure, of the constant boiling mixture formed by hydrochloric acid and water. A liter of HCl ($d_{25} = 1.098$) was distilled, and a portion of the last quarter of the distillate collected, the barometric pressure being 755.5 mm. Of this acid 89.293 g. were diluted with 4855.9 g. of freshly boiled distilled water. From the above data and those given by Hulett and Bonner,[2] the resulting solution was calculated to contain 0.0036396 gram HCl per gram solution, corresponding to a 0.1 N factor of 0.9980.

The next standardization was by the gravimetric silver chloride method. About 50 cc. of the solution were diluted with 150 cc. of distilled water, precipitated with excess of silver nitrate, heated rapidly to boiling, and allowed to stand over night in a dark closet. The precipitate was then collected on a weighed Gooch crucible, washed free from silver with nitric acid (1%), then washed with water and dried at 130° to constant weight. The hydrochloric acid in the filtrate and washings was determined with the nephelometer, and the amount found added to that calculated from the weight of silver chloride. The results are given in Table I:

TABLE I.

No.	Wt. HCl, g.	Wt. AgCl, g.	HCl in filtrate, mg.	Total HCl, g.	HCl per gram solution, g.
1	57.26	0.8188	0.2	0.2085	0.0036403
2	50.11	0.7167	0.1	0.1824	0.0036400
3	59.03	0.8440	0.3	0.2150	0.0036414
4	50.635	0.7245	0.1	0.1844	0.0036417
Mean of four determinations					0.0036411
Corresponding 0.1 N factor					0.9984

The hydrochloric acid was standardized from the sulfuric acid by comparing the two solutions through a solution of sodium hydroxide. The mean of six determinations of the ratio HCl : NaOH was 1.0464; of four determinations of the ratio H_2SO_4 : NaOH, 0.8454. These determinations were very concordant, the maximum difference between any two being 1 part in 2500. The ratio HCl : H_2SO_4 is therefore 1.2378. For the gravimetric standardization of the sulfuric acid the following method was used: About 50 g. of the sulfuric acid were diluted with 150 cc. hot water, heated to boiling, and 15 cc. of a 10% barium chloride solution

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[1] Hulett and Bonner, THIS JOURNAL, 31, 390–3 (1909).

[2] *Loc. cit.*

added slowly (1.5 min.) with constant stirring. This solution was then evaporated to dryness on the steam bath, taken up with 10 cc. hot water, filtered and washed free from chlorine. The filtrate and wash water were united and evaporated to dryness, taken up again, etc., the precipitate was collected on a small filter and added to the main portion. After igniting and weighing in the usual manner the precipitates were tested for occluded barium chloride by the method of Hulett and Duschak,[1] but the amount was always less than 0.1 mg., a negligible quantity. The results are given in Table II:

TABLE II.

No.	Wt. H_2SO_4 solution, g.	Wt. $BaSO_4$, g.	H_2SO_4 per gram solution, g.
1	47.74	0.6891	0.006065
2	52.62	0.7587	0.006059
3	49.21	0.7096	0.006059
4	51.13	0.7375	0.006061
5	55.37	0.7992	0.006065
6	54.06	0.7793	0.006058
Mean of six determinations			0.006061
Corresponding 0.1 *N* factor for H_2SO_4			1.2358
Corresponding 0.1 *N* factor for HCl			0.9984

The standardization by means of sodium oxalate was made with great care, after a series of experiments to compare various samples of the salt. The samples were dried at 230° in an electric oven for an hour, a weighed amount was placed in a platinum crucible and the covered crucible heated with an alcohol lamp, first very gently, then more strongly, but in no case was the resulting sodium carbonate fused. Though an alcohol flame was used, it was found advisable to place the crucible in a perforated asbestos shield as recommended by Lunge,[2] to avoid loss of material due to mechanical carrying away by the gaseous current. The contents of the cooled crucible were carefully washed into a 300 cc. flask, diluted to 200 cc., and a slight excess of the standard sulfuric acid (0.1 to 0.5 cc.) was added. The solution was reduced by boiling to two-thirds its original volume, while a current of air free from carbon dioxide was passed through to expel carbon dioxide, after which the excess acid was titrated with sodium hydroxide, using phenolphthalein as indicator. The end point chosen in this case, as well as in all other titrations, is that described under the standardization with benzoic acid. While concordant results were obtained by strict adherence to a certain procedure in the transformation of the oxalate to the carbonate, it was found that slight variations in the rate or manner of heating might produce very discordant results. The data are given in Table III:

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[1] *Z. anorg. Chem.*, 40, 196 (1904).

[2] *Z. angew. Chem.*, 18, 1520–28 (1905).

TABLE III.

No.	Sample.	Wt. $Na_2C_2O_4$. g.	Wt. solution. g.	H_2SO_4 per gram solution, g.
1	A	0.5013	60.56	0.006059
2	A	0.5027	60.75	0.006057
3	A	0.5001	60.38	0.006063
4	A	0.5018	60.62	0.006059
5	B	0.5037	60.84	0.006061
6	B	0.5021	60.66	0.006059
7	B	0.5011	60.53	0.006060
8	B	0.5015	60.61	0.006058
9	B	0.5007	60.46	0.006062
Mean of nine determinations				0.006060
Corresponding 0.1 *N* factor for H_2SO_4				1.2356
Corresponding 0.1 *N* factor for HCl				0.9982

Standardization of Hydrochloric Acid by Benzoic Acid.

The next step was the standardization of the hydrochloric acid solution with benzoic acid. Because of the bulkiness of the sublimed benzoic acid, it was found convenient to fuse or compress it before weighing. Fusion has the advantage of diminishing the possibility of large surface effects. A platinum dish was filled with the sublimed benzoic acid and the covered dish placed in an oven heated to about 140°. When melted, the liquid was poured into a test tube, and after solidifying the stick so obtained was broken into pieces of convenient size and preserved in a glass stoppered bottle. Samples so prepared can be kept indefinitely and used without preliminary drying.

About 1 gram of this material was weighed and placed in a 300 cc. flask which had been swept free from carbon dioxide; 20 cc. of alcohol were added, the flask was stoppered and let stand until the sample had dissolved. Three drops of a 1% solution of phenolphthalein were then added and the solution titrated directly with 0.1 *N* alkali, a current of air free from carbon dioxide bubbling through the solution until the titration was completed. The end point chosen was that of a 7% transformation of the indicator added, that being the end point which should give the best results.[1] The effect of the alcohol on the end point was determined in a blank experiment and the titrations were corrected by this amount. This blank ranged from 0.06–0.08 cc.

In the first series of experiments a solution of barium hydroxide was used, this being the most convenient alkali to use when exclusion of carbon dioxide is necessary. The mean of four concordant determinations of the ratio HCl : $Ba(OH)_2$ was 1.3790. The results are given in Table IV:

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[1] Noyes, THIS JOURNAL, **32**, 857 (1910).

TABLE IV.

No.	Sample.	Wt. $C_6H_5CO_2H$, g.	Wt. $Ba(OH)_2$, g.	$C_6H_5CO_2H$ per gram $Ba(OH)_2$ solution, g.
1	B	1.0425	62.02	0.016809
2	B	1.0798	64.27	0.016801
3	B	1.0290	61.25	0.016800
4	B	1.0020	59.61	0.016809
5	B	1.0350	61.57	0.016810
6	A	1.0090	60.04	0.016805
7	A	1.0250	61.01	0.016801
8	A	1.0580	62.96	0.016804
9	A	1.0348	61.58	0.016804
10	A	1.0114	60.18	0.016806
11	A	1.0048	59.92	0.016808
12	B	1.0249	61.00	0.016802
13	B	1.0225	60.82	0.016811
14	B	1.0228	60.84	0.016810
15	B	1.0224	60.84	0.016804

Mean for fifteen determinations.......................... 0.016805

Corresponding 0.1 *N* factor for $Ba(OH)_2$.................. 1.3769

Factor for HCl = 1.3768 ÷ 1.3790 = 0.9984

In a second series of experiments the sodium hydroxide solution used in comparing the hydrochloric and sulfuric acids was used, for which the ratio HCl : NaOH was 1.0464. The data are given in Table V:

TABLE V.

No.	Sample.	Wt. $C_6H_5CO_2H$, g.	Wt. NaOH, g.	$C_6H_5CO_2H$ per gram NaOH solution, g.
1	B	1.0067	78.97	0.012748
2	B	1.0108	79.29	0.012748
3	B	1.0208	80.08	0.012747
4	B	1.0440	81.89	0.012749

Mean of four determinations............................. 0.012748

Corresponding 0.1 *N* factor for NaOH.................... 1.0445

Factor for HCl = 1.0445 ÷ 1.0464 = 0.9981

Summary and Conclusion.

The results of the foregoing standardizations are summarized in the following table:

TABLE VI.

Method.	0.1 N factor for HCl.
Direct by Hulett	0.9980
Direct by AgCl	0.9984
H_2SO_4–$BaSO_4$–NaOH–HCl	0.9984
H_2SO_4–$Na_2C_2O_4$–NaOH–HCl	0.9982
$C_6H_5CO_2H$–$Ba(OH)_2$–HCl	0.9984
$C_6H_5CO_2H$–NaOH–HCl	0.9981

The close agreement of these results proves the accuracy of the benzoic acid method. Moreover, benzoic acid has many advantages. Its high molecular weight permits the use of large samples, thus reducing the error of weighing; its stability and lack of hygroscopicity make it very convenient, and the method is rapid, since a single weighing and a titration are all the operations involved. These considerations, combined with the ease of obtaining it in a high state of purity, make benzoic acid an excellent material to use as a standard in acidimetry and alkalimetry.

WASHINGTON, D. C., May, 1912.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE ESTIMATION OF HALOGENS IN ORGANIC COMPOUNDS, INCLUDING A DEVICE FOR THE COMBUSTION OF VOLATIL SUBSTANCES.

BY E. EMMET REID.

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In the ordinary combustion methods for the estimation of carbon and hydrogen, it has long been customary, when burning compounds containing halogens, to insert a roll of silver foil to absorb the halogens and so prevent them from reaching the absorption train. This would suggest the absorption of the halogens on weighed silver foil as a possible method for their estimation. However, in the old methods of combustion, in which copper oxide or lead chromate served as sources of oxygen, more or less of the halogen was retained by the copper and lead. Experience[1] with the elegant electrical combustion methods of Morse and his co-workers[2] suggested that the combustion might be carried on without the use of metallic oxidizing agents, and the halogen absorbed by silver.

To test this idea, an experiment was made in which 0.2283 gram of ethyl *p*-bromobenzoate was burned and the halogen absorbed in a boat, 100 mm. long, of silver foil, filled with silver clippings. The gain in weight of the boat was 0.0703 gram, corresponding to 30.8% of halogen out of a calculated 34.9%. The combustion was carried out with great care, taking 1½ hours. The portion of the tube containing the boat was kept at 250°.

A consideration of conditions in the combustion tube shows that the vapors of the substance being burned may be more or less decomposed by the heat before they come into a region in the tube in which there is an excess of oxygen. As is well known, organic halogen compounds give hydrogen halides when decomposed by heat in absence of excess of oxygen, and may give more or less of such halides even in presence of an abundance of oxygen. It is also well known that the complete oxidation of such halides is difficult. Hence provision must be made for the

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[1] *Am. Chem. J.*, **47**, 416.

[2] *Ibid.*, **33**, 590; **35**, 451.