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Acid Potassium and Acid Sodium Phthalates as Standards in Alkalimetry and Acidimetry

W. S. Hendrixson
Grinnell College

ACID POTASSIUM AND ACID SODIUM PHTHALATES AS STANDARDS IN ALKALIMETRY AND ACIDIMETRY.

W. S. HENDRIXSON.

Quite recently Francis D. Dodge[1] suggested acid potassium phthalate and acid sodium phthalate as standards in alkalimetry and acidimetry. His paper contains no analytical data and is largely theoretical, and so far as the writer can determine no such data are available. The two substances have certain very desirable features as standards, which Dodge has pointed out. The question is whether they are true acid salts. It seemed to me a matter of interest to subject them to a somewhat rigorous examination to determine whether they can be relied upon to give accurate results in standardization.

The primary solution used in the study of the acid phthalates was an approximately tenth normal solution of hydrochloric acid. It was made up according to the method of Hulett and Bonner,[2] and its concentration was further determined by means of silver chloride, and by comparison with two samples of benzoic acid, one made from the pure commercial acid and the other the standard benzoic acid from the Bureau of Standards.

Solution of Hydrochloric Acid.—Concentrated, chemically pure hydrochloric acid was distilled from a glass stoppered distilling flask till three-fourths of it had passed over. The distillate was then collected in a bottle placed in ice water. The end of the condenser tube extended well into the bottle. About three-fourths of what remained in the flask was distilled. The distillation was not interrupted from first to last, and bumping was controlled with platinum scrap.

The pressure being 740, according to Hulett and Bonner 17.9745 grams of this latter distillate should contain one mole. of HCl, (air weight). The amount weighed from a weight buret was 53.997 grams and it was made up to 3.00408 liters with pure water, by using the content, not the delivery of three calibrated liter flasks, whose total capacity was 3.0004 true liters as cali-

[1]Journal of Engineering and Industrial Chemistry, Vol. 7, p. 29.
[2]Journal of the American Chemical Society, Vol. 31, p. 393.

brated by myself by weighing when filled to the marks with water at 20°. The few centimeters remaining to be added were added with a buret.

In making up the hydrochloric acid solution and at all other essential points redistilled water was used. The boiler was of copper and it was fitted with a Kjeldahl distilling bulb to prevent the passage of spray. The condenser tube was of block tin and extended well into the receiving bottle. A seal of cotton between the tube and the neck of the bottle prevented currents of air. The collection of the water was begun only after about 500 c. c. of water had passed over, so as to eliminate carbon dioxide. The water was kept stored in glass stoppered, covered bottles till required.

The concentration of the hydrochloric acid solution thus prepared was further determined by means of silver chloride, filtered and weighed in platinum Gooch crucibles in the usual manner. In all precipitation and washing about 1 per cent of nitric acid was present. The filtrates were measured and usually amounted to about 500 c. c., and 1.4 milligrams of silver chloride was added to the weight for one liter of filtrate. The portions of the acid taken for precipitation were weighed.

In the early part of this work ordinary calibrated burets and flasks were used, but changing temperature, want of uniformity of drainage and the limit of volume in the case of burets to rather less than 50 cc. soon proved their inadequacy, and all results thus secured were rejected. In the determination of the hydrochloric acid and in all titrations here recorded weighing burets were used. They were made by the glass blower at the Chemical Laboratory, University of Illinois, at the instance of Professor W. A. Noyes to whom I am very greatly indebted. They are essentially the same as described by Washburn,[3] and used by him in his recent work on the value of the Farad. They weigh scarcely 50 grains, hold about 175 cc., and have long slender delivery tubes to insert into other vessels, and very small tips so as to give small drops.

The following are the results of the determination of the concentration of the acid by means of silver:

[3]Journal American Chemical Society, vol. 34, 1358.

	Grams of Solution. (Air weight.)	Weight of AgCl.	HCl to 1 Gram of Solution.
1.	64.215	.9221	.0036535
2.	57.318	.8232	.0036541
3.	63.945	.9185	.0036546
4.	107.876	1.5489	.0036532
5.	99.748	1.4323	.0036534

Average of five determinations.....0036536

This value is for 1 gram of the HCl solution weighed in air. However, if the weight of the acid be reduced to vacuum standard the value becomes .0036497. The density of the solution was determined with a Sprengel picnometer at 20° as compared with water at the same temperature and was found to be 1.0018, and since the density of 1 cc. of water at this temperature is .9982, the density of the solution at 20°=.9982×1.0018=1.0000. Therefore one has also the value of 1 cc.=.0036497, of HCl.

Alkali Solution. Solutions of both barium and sodium hydroxides were prepared but the former seemed to have no advantage over the latter and had the disadvantage that the precipitates formed in titration interfered somewhat with judging the end points. It was soon discarded in favor of the sodium hydroxide.

Somewhat more than the required weight of sodium hydroxide, purified by alcohol, was weighed, sprayed with a little water to remove superficial carbonate and dissolved in about a liter of water. A slight excess of barium hydroxide solution was added to precipitate the carbonate and the excess of barium was precipitated with sodium sulfate. It was filtered rapidly, without waiting for all of it to pass through, into a large bottle which had been filled with air free from carbon dioxide. It was then made up to about four liters with the twice distilled water. The bottle was fitted with a glass stoppered buret which was filled through its side tube also provided with a glass stopper. Both buret and bottle were provided with long calcium chloride tubes filled with bits of solid potassium hydroxide. The tube connected with the bottle was in turn connected with a bottle containing a solution of concentrated caustic potash over which the air remained till drawn into the bottle containing the standard alkali, in filling the buret. Over the tip of the buret was kept a rubber cap. The weight buret was filled from the volume buret, the tip of the latter being inserted far into the neck of the weight buret. A small amount of carbonate in the alkali

even if present, but if constant, would have mattered little, since in the series of titrations hydrochloric acid, sodium hydroxide, benzoic acid, for example, the influence of the carbonate would have been eliminated. For the same reason no correction was made for the error due to the fact that phenoltalein, which was used as the indicator, shows the pink color only after the hydroxyl ions are slightly in excess.

All titrations were made in air free from carbon dioxide. A small Erlenmeyer flask was fitted with a thin section cut from a two-hole rubber stopper. One hole received the long delivery tube of the weight buret, and through the other was a tube reaching to the bottom of the flask, and connected with an apparatus to purify the air. The compressed air was contained in a large steel cylinder and passed from it to a large storage bottle with a layer a few centimeters deep of strong caustic potash. It then passed through three gas-washing bottles containing potash, through a similar bottle with water and finally to the titration flask.

In titrating the acid against the alkali both were weighed in weight burets, and the alkali was run into the hydrochloric acid. The air was allowed to run through the flask a short time before the addition of alkali was begun. This stream of air also served to agitate the liquid, and so obviated any need of shaking or stirring. Five closely agreeing titrations gave the ratio in grams of alkali to acid as 1 to 1.10991. A second solution of sodium hydroxide was prepared in the same way and its ratio to the acid was 1 to 1.1859 grams. Which value applies in any series of titrations will be indicated.

Standardizing with Benzoic Acid. The benzoic acid used by Morey[4] in his investigation as to its reliability as a volumetric standard was fractionally sublimed in vacuo, which demands an amount of time and labor that might seem excessive in ordinary volumetric work. It seemed desirable, therefore, to make titration of the best acid on the market after purifying by crystallization only. A quantity of such acid was recrystallized from dilute alcohol and from water. The air-dried acid was fused in an oven heated at 130°. After fusion the platinum dish was placed in cold water which caused the cake of acid to crack loose. In weighing the acid for titration a platinum crucible was used since platinum is far less hydroscopic than glass. The

[4]Bureau of Standards, Bulletin 8, p. 643.

crucible was never handled with the bare hands. The weighed portions were dissolved in the titration flask in about 20 cc. of pure alcohol, whose neutrality had been tested, about an equal volume of water was added, and the titration was carried out as described under standardization of the sodium hydroxide. The following are the results, using the alkali having the relation to the acid 1 to 1.10991.

	Weight of NaOH.	Weighed benzoic acid.	Calculated HCl in 1 gram of solution of HCl.
1.	91.829	1.2470	.0036559
2.	82.139	1.1148	.0036547
3.	89.695	1.2169	.0036525
4.	79.778	1.0838	.0036574
		Average of all titrations.....	.0036551

As under silver chloride reducing the weight of the HCl solution in air to volume, the HCl in 1 cc. is .0036511.

Another series of titrations was made using the special sublimed benzoic acid prepared by the Bureau of Standards for calorimetric and volumetric work. It was fused, weighed and titrated in the same way as the benzoic acid prepared by myself, but the more concentrated alkali having the ratio to the hydrochloric acid 1 to 1.1859 was used.

	Weight of NaOH.	Weighed benzoic acid.	Calculated HCl in 1 gram of solution of HCl.
1.	34.903	.5062	.0036544
2.	54.767	.7941	.0036536
3.	96.481	1.3990	.0036536
4.	139.791	2.0264	.0036526
5.	133.900	1.9410	.0036525
		Average of all determinations.....	.0036533

Reducing the weight of the HCl solution to volume as explained under the silver chloride method, these results give the value of HCl to 1 cc., .0036494.

Acid Potassium Phthalate. This salt is anhydrous. It is moderately soluble in cold water, very soluble in hot water, and may be easily purified by repeated crystallization. Its molecular weight is high, 204.14, so that the amounts that may be weighed for titration are large, thus reducing the influence of the unavoidable errors in weighing.

Acid potassium phthalate was prepared by dissolving in hot water pure sublimed phthalic anhydride and a little more than the calculated weight of pure potassium carbonate necessary to form the acid phthalate. The salt was recrystallized five times

from pure water in platinum. A second preparation was made with specially prepared potassium carbonate, made by repeated precipitation of the acid carbonate from the normal carbonate with carbon dioxide. After drying in the air each sample was heated in a platinum dish in an air bath for several hours at 125°.

The following are the titrations made with the first preparation. The first three were made with the solution of sodium hydroxide having the ratio to the hydrochloric acid 1 to 1.10991; all the remaining ones in this paper with the alkali having the ratio 1 to 1.1859.

	Weight of NaOH.	Weighed acid potassium phthalate.	Calculated HCl in 1 gram of solution of HCl.
1.	64.275	1.4583	.0036517
2.	68.479	1.5531	.0036503
3.	96.585	2.1933	.0036548
4.	59.670	1.4483	.0036565
5.	49.471	1.2000	.0036542
	Average of five determinations.....		.0036535

The data of the second series give practically the same value.

	Weight of NaOH.	Weighed acid potassium phthalate.	Calculated HCl in 1 gram of solution of HCl.
1.	71.7335	1.7380	.0036500
2.	56.660	1.3733	.0036513
3.	71.243	1.7287	.0036554
4.	78.108	1.8943	.0036535
5.	52.367	1.2692	.0036512
	Average.....		.0036523

The amount of HCl in 1 cc. of the solution, calculated under silver chloride is .0036484.

Acid Sodium Phthalate. This salt has about the same solubility in hot and cold water as the acid potassium salt. It crystallizes with approximately one-half molecule of water. Its equivalent is also high, 188.04.

Three preparations of this salt were made by the same method and with the same care as described under the potassium salt. It was crystallized six times from hot water, and dried in the atmosphere of the laboratory. Many titrations were made to determine whether the hydrous salt would show sufficient constancy to serve as a standard. Three determinations of the water of crystallization were made using large quantities of the salt each time. All these determinations showed considerable variation depending apparently on the state of the atmosphere

and conditions of crystallization. The titrations showed a variation of about 1 part in 700 too low to 1 part in 700 too high. The hydrous salt belongs to the same class as other hydrous substances used as standards such as oxalic acid and potassium tetroxalate. In this connection it may be stated that in the course of this study the writer prepared with great care samples of oxalic acid and potassium tetroxalate and made many titrations. The results were always too low. In the case of the tetroxalate the difference between the acidity found and the theory was so marked as to suggest some other reason than hygroscopic water. The potassium contained in the salt was therefor determined. Two determinations as sulfate and one as carbonate gave the per cents, 15.74, 15.77 and 15.73, while the theory requires 15.38. While not a perfect standard, hydrous acid sodium phthalate will give much more nearly correct results than either oxalic acid or potassium tetroxalate according to my experience. For this purpose, however, the salt should be dehydrated.

Dehydrated Acid Sodium Phthalate. Before the acid sodium phthalate was dehydrated for use in titration it was subjected to tests to ascertain its degree of stability when heated. A portion of it in a boat was heated in a tube through which passed a current of pure air, and the air then passed through a bottle of clear baryta water. The heat was gradually raised to 225°, the time occupying about two hours. No trace of carbon dioxide could be detected but a small amount of phthalic anhydride sublimed above 200°. The salt may, therefore, safely be heated much higher than the necessary temperature to dehydrate it within reasonable time, which is 120°. It was heated at that temperature and attained constant weight in about three hours, though the heating continued much longer. It was then used in the following titrations:

	Weight of NaOH	Weighed acid sodium phthalate.	Calculated HCl in 1 gram of solution of HCl.
1.	42.754	.9548	.0036524
2.	43.610	.9737	.0036515
3.	52.897	1.1824	.0036557
4.	51.337	1.1470	.0036540
5.	61.626	1.3758	.0036511
6.	77.619	1.7354	.0036565
7.	51.479	1.1494	.0036516
	Average of seven titrations.....		.0036533

The value of HCl in 1 cc. of the hydrochloric acid solution is .0036494.

To summarize, we have the concentration of the solution of hydrochloric acid determined by five different methods and standards. The first three are of undoubted accuracy, though the method of Hulett and Bonner has the disadvantage that neither the boiling point of hydrochloric acid nor the distillate is perfectly constant at any concentration, though very nearly so. With these three old methods the acid phthalates are compared. The following are the concentrations for 2 cc. found by the different methods:

1. Method of Hulett and Bonner.....0036470
2. Silver chloride 0036497
3. Benzoic acid, series I and II.....0036502
4. Acid Potassium Phthalate, series I and II.....0036490
5. Acid Sodium Phthalate 0036494

It will be seen that these results agree within the limits of ordinary volumetric work. Leaving out the method of Hulett and Bonner whose slight defect has been mentioned and was fully recognized by its founders in their original publication,[3] the other results are almost identical.

From this study it would seem that benzoic acid, acid potassium phthalate and dehydrated acid sodium phthalate may with equal confidence be used as standards. The acid phthalates have the advantage of much higher equivalent weights, ready solubility in water and ease of preparation in the pure state.

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[3]Loc. cit.