barium, calcium, and strontium, these then being separated, first by the use of acetic acid, then dilute hydrochloric acid. Also, in precipitating calcium oxalate and strontium carbonate together, lead acetate might be used to dissolve calcium oxalate, leaving strontium carbonate, since the solubility of lead oxalate is less than that of calcium oxalate, but the solubility of lead carbonate is somewhat greater than that of strontium carbonate. The writer has not, however, carried out these separations. A *large* difference in solubility does not seem to be necessary; is not in fact desirable for the carrying out of such schemes.

A separation of copper and cadmium may be made by warming a suspension of the sulfides in water with lead nitrate solution. Cadmium sulfide dissolves; copper sulfide is not affected. The excess of lead is removed with ammonium sulfate, and cadmium precipitated as a sulfide. The objection to this method is that neither ammonium sulfate nor dilute sulfuric acid completely remove the lead, so that in testing for cadmium the solution is slightly discolored by lead sulfide. This, however, is the case in the usual scheme of analysis, whenever lead is present.

The writer expects to continue work on this subject.

PULLMAN, WASHINGTON.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF GRINNELL COLLEGE.]

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

BY W. S. HENDRIXSON.

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Quite recently Francis E. Dodge[1] suggested acid potassium phthalate as a satisfactory standard in acidimetry and alkalimetry, and also suggested acid sodium phthalate as a possible standard, though having no advantages over the potassium salt. His paper contains no analytical data, but is largely theoretical, and, so far as the writer has been able to learn, these substances have not been rigidly investigated with reference to their reliability for the purpose suggested. The two substances have certain properties, as pointed out by Dodge, that are very desirable in a standard, such as ease of preparation in the pure state, comparatively ready solubility, and high molecular weights. It seemed to me a matter of interest to subject them to a careful experimental study in comparison with other standards of undoubted accuracy, to determine whether they can be relied on to give accurate results in standardization. To this end a solution of hydrochloric acid was made up by the method of Hulett and Bonner,[2] which should contain 0.003647 g. of hydrochloric acid per cc., and it was then further standardized by means of silver chloride, by two samples of benzoic acid, by acid potassium and acid sodium phthalates.

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[1] *J. Eng. Ind. Chem.*, **7**, 29 (1915).

[2] THIS JOURNAL, **31**, 390 (1909).

**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. Platinum scrap was used to prevent bumping. Without interrupting the distillation the condenser tube was then inserted into the neck of a bottle cooled in ice water and the process was continued till about three-fourths of the remaining one-fourth had distilled. The second distillate was at once used to make up the solution of 0.1 *N* HCl by the method of Hulett and Bonner.

The pressure being 740, according to Hulett and Bonner, 17.9745 g. of the distillate (air weight) should contain one-tenth mol of HCl. The amount of the acid weighed was 53.997 g. and it was made up to 3004.08 cc., measuring the solution at 20° by the content, not delivery, of three flasks previously calibrated by myself by actually weighing them filled with water to the mark at 20°. Introducing the necessary corrections for water weighed in air at that temperature with brass weights the three flasks were found to contain, when filled to their marks, 3.0004 liters. The additional volume of water was measured from a buret also calibrated for 20°.

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 cc. 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 determined by means of silver chloride, filtered and weighed in platinum Gooch crucibles in the usual manner. In all precipitation and washing about 1% of nitric acid was present. The filtrates were measured and usually amounted to about 500 cc., and 1.4 mg. 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 subsequent titrations weighing burets were used.[1] They weigh scarcely 50 g., hold

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[1] 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 greatly indebted. They are essentially the same as described by Washburn, This Journal, 34, 1358 (1912) and used by him in his recent work on the value of the Faraday.

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 hydrochloric acid solution by means of silver:

|  | G. of soln. (air weight). | Wt. of AgCl. | HCl in 1 g. of soln. |
|---|---|---|---|
| 1 | 64.215 | 0.9221 | 0.0036535 |
| 2 | 57.318 | 0.8232 | 0.0036541 |
| 3 | 63.945 | 0.9185 | 0.0036546 |
| 4 | 107.876 | 1.5489 | 0.0036532 |
| 5 | 99.748 | 1.4323 | 0.0036534 |
|  |  | Average, | 0.0036536 |

Since the concentrations of volumetric solutions are given commonly for 1 cc., this and all other values obtained per gram air weight should be calculated for 1 cc. To this end the density of the solution of hydrochloric acid was determined with a Sprengel picnometer by weighing the solution at 20° and comparing with the weight of water the instrument contained at the same temperature. The result was 1.0018. The density of water at 20 being 0.9982 and the product of these two values being almost exactly 1, it follows that the mass of 1 g. of the solution weighed in air is greater than 1 cc. only by the amount of the net buoyancy of air on 1 g. of water when weighed with brass weights. The buoyancy under the conditions is calculated to be 0.00107 gram. Therefore dividing the silver value 0.0036536 by 1.00107 the content of HCl in 1 cc. becomes 0.0036497. All subsequent values found for the HCl in 1 g. of the solution are calculated to 1 cc. in the same way.

**Comparison of the HCl and an Alkali Solution.**—Solutions of both barium and sodium hydroxides were made up, but the former seemed to have no advantage over the latter and had the disadvantage that the precipitates formed in titration interfered somewhat in judging the end points. It was soon discarded in favor of the sodium hydroxide.

Somewhat more than the required amount of sodium hydroxide (purified by alcohol) was weighed, sprayed with a little water to remove most of the superficial carbonate, and dissolved in about a liter of water. A slight excess of barium hydroxide was added to precipitate any carbonate and the excess of barium was removed by precipitation with a slight excess of sodium sulfate. The solution was filtered rapidly into a large bottle which had been filled with air free from carbon dioxide. Without exposing to the air till all the solution had run through, the filtration was stopped and enough pure water was added to the bottle to make the total volume about four liters. The bottle was fitted with a glass-stoppered buret which was filled through its side tube, also provided with a glass stopper. To prevent access of carbon dioxide the buret and bottle were provided with long calcium chloride tubes filled with bits of solid potassium hydroxide. The guard 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 constant amount of carbonate in the alkali, if present, 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 phenolphthalein, which was used as the indicator in all titrations 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, obviating 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. Which value applies in any given series of titrations will be indicated.

**Standardizing with Benzoic Acid.**—The benzoic acid used by Morey[1] in his investigation was fractionally sublimed *in vacuo*, which demands an amount of work and time that might seem excessive for ordinary purposes, student practice for example. It seemed desirable to make titrations of the best acid obtainable in the market after further purifying it by crystallization from alcohol and water and from water alone. The acid thus purified was melted in a platinum dish in an oven at 130°. The dish was placed in water and the cake of acid cracked loose. It was broken up and placed in a desiccator. In weighing the acid a platinum crucible was used, since it was less hygroscopic than glass. Weighed

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[1] THIS JOURNAL, **34**, 1027 (1912), Bureau of Standards, *Bull.* **8**, p. 643.

portions were dissolved without heating in the titration flask in about 20 cc. of purified alcohol whose neutrality was tested. About an equal volume of pure water was added and the titration was carried out as already described, using as in all other instances phenolphthalein as indicator. The following are the results, the alkali having the ratio alkali to acid as 1 to 1.10991 being used:

| | Wt. of NaOH. | Wt. benzoic acid. | Calcd. HCl in 1 g. of soln. |
|---|---|---|---|
| 1 | 91.829 | 1.2470 | 0.0036559 |
| 2 | 82.139 | 1.1148 | 0.0036539 |
| 3 | 89.695 | 1.2169 | 0.0036525 |
| 4 | 79.778 | 1.0838 | 0.0036574 |

Av. of all titrations ........ 0.0036549

The calculated amount of HCl in 1 cc. is, therefore ........ 0.0036510

The calculated weight of HCl to 1 cc. is here found as described under standardization by means of silver chloride.

Another series of titrations was made using the special 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 first sample, but the more concentrated alkali having the ratio to the hydrochloric acid 1 to 1.1859 was used.

| | Wt. of NaOH. | Wt. benzoic acid. | Calcd. HCl to 1 g. of soln. |
|---|---|---|---|
| 1 | 34.903 | 0.5062 | 0.0036544 |
| 2 | 54.767 | 0.7941 | 0.0036536 |
| 3 | 96.481 | 1.3990 | 0.0036536 |
| 4 | 139.791 | 2.0264 | 0.0036526 |
| 5 | 133.900 | 1.9410 | 0.0036525 |

Av. of all titrations ........ 0.0036536

Calculating the HCl in 1 cc. as already described, the value is found to be ........ 0.0036497

**Standardization with Acid Potassium Phthalate,** $HKC_8H_4O_4$.—This salt is anhydrous.[1] It is moderately soluble in cold water and its solubility is greatly increased by heat, and it can, therefore, be easily purified by crystallization from hot water. It was prepared by dissolving pure, sublimed phthalic anhydride and slightly more than the calculated weight of pure potassium carbonate to form the acid salt. This salt was purified by recrystallizing five times from hot water. Specially purified water was used throughout, and a platinum vessel in the later crystallizations. After drying in air the sample was heated several hours at 125°, and its constancy of weight tested.

The following are the results obtained by titration of the first prepara-

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[1] Dodge, *Loc. cit.*

tion: The first three titrations were made with the alkali solution having the ratio by weight to the hydrochloric acid solution 1 to 1.10991. All the remaining titrations were made with the alkali having the ratio 1 to 1.1859.

Weighed portions of the acid salt were dissolved in about 50 cc. of water in the titration flask, which was kept loosely stoppered and usually was warmed slightly to hasten solution. Phenolphthalein was of course used as the indicator.

| | Wt. of NaOH. | Wt. of $HKC_8H_4O_4$. | Calcd. HCl to 1 g. of soln. |
|---|---|---|---|
| 1 | 64.275 | 1.4583 | 0.0036517 |
| 2 | 68.479 | 1.5531 | 0.0036503 |
| 3 | 96.585 | 2.1933 | 0.0036548 |
| 4 | 59.670 | 1.4483 | 0.0036565 |
| 5 | 49.471 | 1.2000 | 0.0036542 |
| Av. wt. HCl in 1 g. of soln | | | 0.0036535 |

The calculated value of HCl to 1 cc. of the solution is, therefore, 0.0036495.

The second preparation of the acid salt from which the following titrations were made was prepared from a new sample of the anhydride and special potassium carbonate made by repeated precipitation of the acid potassium carbonate from the normal carbonate with carbon dioxide. It was purified with the same or even greater care, as was used in the first preparation. The results of its titration are practically the same as in the first series.

| | Wt. of NaOH. | Wt. of $HKC_8H_4O_4$. | Calcd. HCl in 1 g. of soln. |
|---|---|---|---|
| 1 | 71.733 | 1.7380 | 0.0036500 |
| 2 | 56.660 | 1.3733 | 0.0036513 |
| 3 | 71.243 | 1.7287 | 0.0036554 |
| 4 | 78.108 | 1.8943 | 0.0036535 |
| 5 | 52.367 | 1.2692 | 0.0036512 |
| Av. of all titrations | | | 0.0036523 |

Calculating the weight of HCl to 1 cc. of the solution the result obtained is 0.0036484.

**Standardization with Acid Sodium Phthalate,** $HNaC_8H_4O_4$.—This salt has about the same solubility in hot and cold water as the potassium salt. It crystallizes with approximately one-half a molecule of water as determined by Dodge,[1] and the writer has confirmed his work both by titration of the salt and by loss on heating. Three preparations of this salt were made by the author with the same care described under the potassium salt. It was usually crystallized six times from hot water. Numerous titrations were made to determine whether

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[1] *Loc. cit.*

the hydrous salt would give constant results but the figures were disappointing. The results thus obtained from the air-dried salt varied from about 1 part in 700 lower to about the same amount higher than corresponds to the formula $HNaC_8H_4O_4.{}^1/_2\ H_2O$. The hydrous salt when considered for titration purposes belongs to the same class, apparently, as oxalic acid and sodium tetroxalate. In the experience of the writer, however, it showed less variation from theory than the oxalates showed in the course of an extended and careful study of these under the same conditions. The study was made in the hope that oxalic acid and potassium tetroxalate might be used to compare with the acid phthalates as to their reliability, but so great was their variation from formula and want of constancy that the attempt had to be given up. In fact, determinations of the potassium in the potassium tetroxalate seemed to show definitely that this salt becomes more nearly neutral with repeated crystallization, and I hope to give this matter further study.

Much better results were obtained with dehydrated sodium phthalate. Before dehydrating the salt for use in titrations, it was subjected to certain tests to determine its stability when heated. A portion of the salt, contained in a porcelain boat, was heated in a tube through which passed a current of pure air, and this air was then passed through clear baryta water. It was gradually heated to 225° during an hour and held at that temperature an hour longer. No trace of carbon dioxide was indicated by the baryta water, but a very small amount of phthalic anhydride appeared in the cooler part of the tube after 200° had been reached. Since the salt can be completely dehydrated at 120°, no decomposition need be feared if reasonable care is taken. No such test of the stability of the potassium salt was made, since drying it is merely a matter of driving off hydroscopic water, and a temperature much above a hundred is not required.

The acid sodium phthalate used in the following titrations was dehydrated by heating at 120°. About 10 g. of it in a platinum dish attained constant weight in about three hours, but was heated longer in order to be perfectly sure of the constancy.

| | Wt. of NaOH. | Wt. of $HNaC_8H_4O_4$. | Calcd. HCl to 1 g. of the soln. |
|---|---|---|---|
| 1 | 42.754 | 0.9548 | 0.0036524 |
| 2 | 43.610 | 0.9737 | 0.0036515 |
| 3 | 52.897 | 1.1824 | 0.0036557 |
| 4 | 51.337 | 1.1470 | 0.0036540 |
| 5 | 61.626 | 1.3758 | 0.0036511 |
| 6 | 77.619 | 1.7354 | 0.0036565 |
| 7 | 51.479 | 1.1494 | 0.0036516 |
| | | | 0.0036533 |

The average for the seven experiments is 0.0036533 g. of HCl for 1 g. air weight of the HCl solution, which, as already explained, gives 0.0036494 g. HCl in 1 cc. of the solution.

To sum up the work we have the following values for the weight of HCl in 1 g. of the hydrochloric acid solution, prepared according to the method of Hulett and Bonner:

| | |
|---|---|
| 1. Constant boiling point, Hulett and Bonner | 0.0036470 |
| 2. By means of silver chloride | 0.0036497 |
| 3. By means of benzoic acid, first series | 0.0036510 |
| 4. By means of benzoic acid, second series | 0.0036497 |
| 5. By means of acid potassium phthalate, first series | 0.0036495 |
| 6. By means of acid potassium phthalate, second series | 0.0036484 |
| 7. By means of anhydrous acid sodium phthalate | 0.0036494 |
| Average of all methods | 0.0036492 |

There are, therefore, seven values based upon five standards and methods from which to determine the concentration of the solution of hydrochloric acid. The agreement is very close. The extreme difference is between the constant boiling-point method and the first series of titrations of benzoic acid. Even here the difference is 1 in more than 900 parts, which is yet within the limits of accuracy of ordinary titration in which the delivery of flasks and volume burets is used. The difference between the boiling-point method and the average of the titrations of benzoic acid is 1 part in more than 1100. It differs from the average of all results by 1 part in more than 1600, and its greatest difference from the results of any series where a phthalate was used is 1 part in 1460 too low. The experience of the writer is in close agreement with that of Morey[1] in whose work on benzoic acid as an acidimetric standard the method of Hulett and Bonner gave the concentration of the hydrochloric acid lower than any other standard, and by about the same amounts as just stated.

It may be observed that the results obtained by using silver, benzoic acid and the two acid phthalates as standards are almost identical. So far as the results go they indicate that one of the organic standards is as good as another in point of accuracy. The acid phthalates have some advantage in their much higher molecular weights, their greater solubility, and the fact that they can be prepared pure and true to the formulae accepted for the anhydrous salts without the use of unusual and time-consuming methods of purification. They may easily and quickly be prepared in large quantity for class use, and in fact their preparation may be considered easily within the powers of comparatively elementary students in volumetric analysis.

GRINNELL, IOWA.

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[1] *Loc. cit.*