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THE STANDARDIZATION OF HYDROCHLORIC ACID WITH POTASSIUM IODATE AS COMPARED WITH BORAX AND SODIUM CARBONATE AS STANDARD SUBSTANCES

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It has been known from earlier investigations¹ that potassium iodate is a very suitable standard substance for determining the strengths of solutions of sodium thiosulfate. By recrystallization from water and drying at 180° it may readily be obtained in a pure state. Moreover, it reacts instantaneously with iodide and acid liberating the calculated amount of iodine. I have also found it to be very suitable for the standardization of other solutions, for example, that of potassium permanganate.²

Potassium iodate may also be used for the direct standardization of hydrochloric acid, utilizing the reaction: $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$.

When a neutral solution of an alkali iodide and an excess of thiosulfate are added to a neutral iodate solution, the liberated iodine is continuously removed by the thiosulfate on the addition of hydrochloric acid. The liquid remains colorless and neutral until all of the iodate is used up. A drop of acid in excess gives the liquid an acid reaction and, therefore, the standardization of hydrochloric acid with potassium iodate may be carried out just as an ordinary acidimetric titration with the aid of some suitable indicator. In the following discussion it will be seen that the method gives accurate results.

Materials Used

The hydrochloric acid solutions were obtained by diluting a constant-boiling mixture with water. The solutions were free from chlorine.

¹ Kolthoff, *Pharm. Weekblad*, **56**, 644 (1919).

² Kolthoff, *Z. anal. Chem.*, **64**, 255 (1924).

The sodium carbonate was a preparation obtained by Professor Schoorl by heating pure sodium bicarbonate at 300° to constant weight. The first series of experiments made with this preparation always gave results that differed by about 0.1% from those obtained with iodate. This deviation appeared to be caused by the sodium carbonate taking up water during weighing. Initially the sodium carbonate was weighed in weighing bottles, which were repeatedly opened and closed until the required amount of salt had been obtained. During this process the sodium carbonate takes up some water. In order to get accurate results, however, the required amount of sodium carbonate was weighed in a small crucible placed in a weighing bottle. The crucible was then heated in an oven at 300° until the weight was constant the weighings being made with the weighing bottle kept closed. The rational equivalent weight of sodium carbonate (corrected for the buoyancy in the air) is 52.98.

The potassium iodate was a preparation obtained from Kahlbaum. No impurities in the salt could be detected, and on drying it did not lose in weight. Preparations obtained by recrystallization of the commercial product and subsequent drying gave the same results as the salt furnished by Kahlbaum. It was noticed that some of the preparations when kept in dark bottles became colored after some time, and developed an odor resembling that of iodoform. Moreover, the content of active substance decreased by a small amount. In bottles of colorless glass no such decomposition was ever detected and it is probable that in dark bottles the iodate is reduced to iodite. The rational equivalent weight of potassium iodate is 35.66.

The potassium iodide was a pure commercial preparation. A solution of 4 g. of this salt in 10 cc. of water gave with butter yellow (dimethylyellow)³ a color showing alkalinity; but after the addition of a drop of 0.1 *N* hydrochloric acid the liquid was pink-red; hence, alkaline-reacting substances were not present.

A solution of 4 g. of salt in air-free *N* hydrochloric acid did not turn yellow, nor did it color starch. This test shows the absence of iodate.

The sodium thiosulfate was a commercial preparation, purified by a repeated recrystallization from water. A solution of 10 g. of salt in 100 cc. of water showed an alkaline reaction with dimethylyellow; but after the addition of 1 drop of 0.1 *N* hydrochloric acid, the color changed to the acid. (After standing, the pink color disappears again, due to the decomposition of the thiosulfate to sulfite and sulfur.) In the standardization of hydrochloric acid in the presence of thiosulfate the latter, however, has no interfering action, as the thiosulfate is transformed during the titration into tetrathionate. The tetrathionic acid appeared to be as strong as hydrochloric acid; its second dissociation constant is much greater than that of sulfuric acid.

In the standardization of hydrochloric acid by means of borax, different samples of this salt were used. The borax supplied by Kahlbaum was sufficiently pure for our purpose. According to the analysis of Professor Schoorl it contained less than 0.002% of chloride, 0.001% of sulfate, 0.01% of carbonate, 0.01% of calcium, 0.002% of magnesium and 0.02% of silicic acid. The water content of this preparation was determined. This has to be done very carefully; first, the salt is dried on the water-bath, where it loses about five molecules of water. Afterwards, the temperature is raised very slowly. When the heating takes place too abruptly, the salt swells up, becomes very voluminous and may overflow the crucible. The last few percentages of water are removed very slowly; moreover, the hydrate with one molecule of water is stable at 200°. After the substance had been heated for 40 hours at 200° the weight remained constant and the loss in weight corresponded to a water content of 42.47%, whereas the calculated value for a loss of 9 molecules of water⁴ corresponds to 42.49%.

³ Dimethylyellow is dimethylamino-azobenzene.

⁴ Compare Hoffmann, *Chem. Zentr.*, (I) **88**, 304 (1917).

The final experiments were performed as follows. After the substance had been dried at 200°, the crucible was placed in an electric oven at a temperature of 400–450°, until constant weight was attained. When afterwards it was heated at 800°, at which temperature the salt fuses, the weight did not change. We cannot confirm the statement of H. V. A. Briscoe, P. L. Robinson and G. E. Stephenson,⁵ who state that fused borax loses sodium oxide. Even after the substance had been heated for two hours at 800° the weight did not change.

In the way described above I found in the salt of Kahlbaum 47.24 and 47.22% of water, respectively. In preparations, obtained by three recrystallizations of a commercial product and subsequent drying in a sodium bromide desiccator (NaBr.2H₂O sat. sol., relative vapor tension, 60%) to constant weight, a water constant was found of 47.23 and 47.24%, respectively.

There is some uncertainty in the calculated value due to the uncertainty in the atomic weight of boron. In 1916 the international atomic weight was 11.0. From the investigations of Hönigschmid and Birckenbach⁶ and also from those of Briscoe and Robinson⁷ it follows that the most probable value is 10.82; this is accepted in the International Table of 1925.⁸ Using the values given in this table, the molecular weight of Na₂B₄O₇.10H₂O is calculated to be 381.434 (in a vacuum). If we take for borax a specific gravity of 1.72 (Gmelin-Kraut), we then find for weighings in normal air a molecular weight of 381.214.⁹ As the molecular weight of water in the air is 17.997 the water content of borax is calculated to be 47.21%. This value is in close agreement with the average of our experimental values, 47.23%. As we shall see below, the results of our titrations are only in correspondence with those obtained with other standard substances, if we accept the atomic weight of borax as equal to 10.82.

The rational equivalent weight of borax, then, is 190.61.

Performance of the Experiments

In all cases a 100cc. special buret was used, consisting of a bulb and a narrow tube, the latter being graduated in 0.1 cc. from 95 to 105 cc. The readings certainly are as accurate as 0.02 cc. The titrations with 0.1 *N* as well as with 0.5 *N* hydrochloric acid were made as follows.

Sodium Carbonate as Standard Substance.—The accurately weighed amount of sodium carbonate (comp. sub. 2) was dissolved in 100 cc. of water, and 8 drops of 0.1% dimethylyellow solution were added. In order to avoid losses from mechanical removal of liquid by the action of the

⁵ Briscoe, Robinson and Stephenson, *J. Chem. Soc.*, **127**, 150 (1925).

⁶ Hönigschmid and Birckenbach, *Ber.*, **56**, 1467 (1923).

⁷ Briscoe and Robinson, *J. Chem. Soc.*, **127**, 696 (1925).

⁸ THIS JOURNAL, **47**, 600 (1925).

⁹ Compare Schoorl, *Chem. Weekblad*, **15**, 547 (1918).

evolved carbon dioxide, the acid was allowed to run down the wall of the flask; the latter was not shaken until in the immediate neighborhood of the equivalent point. In other cases the acid was added to the flask through a funnel.

An objection to the use of sodium carbonate as a standard substance is the difficulty of detection of the end-point of the titration. W. Küster¹⁰ has already shown that a saturated solution of carbon dioxide in water colors methyl orange to a faintly acid shade. The same holds for dimethyl-yellow. Moreover, the salt formed during the titration increases the acid reaction of the indicators mentioned. Consequently, a change in the alkaline color of the indicator is observed before the equivalent point is reached. The color change is not sharp; a difference from the color with water is visible even at 0.5 to 0.8% from the end-point in titrations with 0.1 *N* hydrochloric acid. With the use of 0.5 *N* liquids the color change is visible at about 0.3% from the end-point. When a saturated carbon dioxide solution containing the same amount of salt as the liquid at the equivalent point is taken as comparison liquid, the results are better, but still are not accurate enough for our purpose, since in the titrations the carbonic acid concentration at the end-point is not fixed, the solution being supersaturated with respect to it, but its strength decreases rapidly when the liquid is shaken.

In order to obtain accurate results, the liquid was boiled for five minutes, and as much acid was then added as was necessary to give the first change of the color of the indicator. After boiling, the liquid was cooled to room temperature and the titration was finished, the end-point being taken when the color of the indicator began to change from that given by water. In using dimethylyellow as an indicator, the necessary excess of acid to give a color change amounted to 0.07–0.08 cc. of 0.1 *N* hydrochloric acid in a volume of 200 cc.

In other cases I added to the sodium carbonate solution as much hydrochloric acid as was required in the titration with dimethylyellow as an indicator. The mixture was boiled in Jena flasks for about 20 minutes and cooled, care being taken to prevent absorption of carbon dioxide. Some drops of a freshly prepared phenolphthalein solution in neutral alcohol were added to the cold liquid, and the small excess of acid was titrated back with 0.1 *N* sodium hydroxide solution, added from a microburet divided in 0.01 cc. From blank experiments carried out in the same way with 200 cc. of water it was concluded that the necessary excess of base to give a color change with phenolphthalein was no more than 0.02 cc. of 0.1 *N* sodium hydroxide solution.

In the tables are given the titration values corrected for the necessary excesses of reagent.

¹⁰ Küster, *Z. anorg. allgem. Chem.*, **13**, 127 (1896).

Potassium Iodate.—In the experiments with 0.1 *N* hydrochloric acid 356.6 mg. of iodate was dissolved in 100 cc. of water, and to this solution 0.5 g. of potassium iodide and 3 g. of sodium thiosulfate were added. In the titration with 0.5 *N* acid I used 1.784 g. of iodate, 2 g. of iodide and 13 g. of thiosulfate. In all cases only a small excess of thiosulfate was present at the end of the titration. A large amount of thiosulfate makes the color change less sharp. In the titration with 0.5 *N* hydrochloric acid I always used dimethylyellow as indicator; with 0.1 *N* acid I also used other indicators. In all cases the acid was added while the flask was continuously shaken, since a local excess of the added acid might cause decomposition of the thiosulfate. With dimethylyellow as indicator one has the advantage that the titration may be carried out very quickly; the first color change is permanent for about one to two minutes. The necessary excess of acid required to give a color change with this indicator under the conditions mentioned is about 0.10 to 0.12 cc. of 0.1 *N* hydrochloric acid in 200 cc. of liquid. In the table our titration values are corrected for this amount.

Upon standing for a longer time the excess of acid decomposes the thiosulfate into sulfite and sulfur and the color of the indicator becomes more indefinite.

In the titrations with 0.1 *N* acid I also used methyl orange and bromophenol blue as indicators. However, I prefer the use of dimethylyellow.

Generally, it is better to use methyl red, as the excess of acid required to give a color change with this indicator is negligible. For comparison I used a solution of 0.5 g. of potassium iodide and 0.5 g. of sodium thiosulfate in 200 cc. of water, to which were added 8 drops of a 0.2% methyl red solution. With methyl red as an indicator the titration cannot be carried out very quickly. In the neighborhood of the end-point (within about 2%) the color of the liquid on the addition of more acid is redder than in the comparison liquid. After a few seconds, and just near the end-point after at least three minutes, the color becomes quite stable. More acid is then added, until the liquid remains redder than the solution that is used for comparison. Under the conditions just described (at P_H 5), the velocity of the reaction between the trace of iodate present near the end-point and the iodide is low, that is, the reaction does not proceed instantaneously. At P_H 4 the velocity is much greater, since it is proportional to the square of the hydrogen-ion concentration.

Hence, in using methyl red we have the disadvantage that the titration takes rather more time (about 15 minutes); on the other hand, there is the advantage that no correction has to be applied for the necessary excess of acid.

In the titrations of *borax* with 0.1 *N* hydrochloric acid I used dimethylyellow as well as methyl red as an indicator.

Bromocresol blue (green) also is a suitable indicator. In using dimethyl yellow as an indicator the necessary excess of acid amounts to 0.07 cc. of 0.1 *N* hydrochloric acid in a volume of 200 cc. The correction is the same as that for pure water.

In the titrations with 0.5 *N* acid I used only dimethyl yellow as an indicator. In order to detect the end-point accurately, it is necessary to take as a liquid for comparison 200 cc. of a solution, 0.5 *M* in boric acid and 0.25 *M* in sodium chloride. In such a solution the indicator has not the pure yellow color, but has a shade on the orange side. The end-point may be detected with an accuracy of 0.01 to 0.02 cc. acid in 200 cc. of liquid. When we calculate the hydrogen-ion concentration of the comparison mixture with the aid of the dissociation constant of boric acid, we find a value at which dimethyl yellow is completely in the alkaline form. In investigating this point, it appeared to me that practically we cannot speak of a dissociation constant of boric acid. Its so-called "constant" increases rapidly with increasing concentration of boric acid, due to the formation of a stronger complex acid, thus: $4\text{H}_3\text{BO}_3 \rightleftharpoons (\text{H}_3\text{BO}_3)_4$. In a special paper I hope to discuss this question more fully. In the titrations with 0.1 *N* acid I also used methyl red as an indicator. For the comparison I used 200 cc. of a solution, 0.1 *M* in boric acid and 0.05 *M* in sodium chloride, with the same amount of indicator as the liquid to be titrated (8 drops of a 0.2% solution). The "titration exponent" P_H is about 5.0. The accuracy in determining the end-point is about 0.01 to 0.02 cc. of 0.1 *N* acid in 200 cc. of liquid.

TABLE I
TITRATIONS WITH 0.1 *N* HYDROCHLORIC ACID

Standard subs.	G.	Indicator ^a	0.1 <i>N</i> Acid, cc.					Av.	Diff. from Na_2CO_3 value, %
Na_2CO_3	0.5298	D. Y.	99.98	100.01	100.01	99.98	100.01	100.00	...
		P.	100.03	99.99					
KIO_3 , Kahlbaum Comm. ^b	0.3566	M. R.	99.99	100.01	99.97	100.00		99.99	+0.01
		M. R.	99.99					99.99	+ .01
Kahlbaum		D. Y.	100.00	100.03				100.01	- .01
		M. O.	99.99					99.99	+ .01
		B. B.	100.03					100.03	- .03
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, Kahlbaum		M. R.	100.03	100.03	100.02	100.01		100.02	- .02
Other preps.		M. R.	100.02	100.02				100.02	- .02
Kahlbaum		D. Y.	100.04	100.03				100.03	- .03

TITRATIONS WITH 0.5 *N* HYDROCHLORIC ACID AND DIMETHYL YELLOW

Na_2CO_3	2.6490	99.97	99.99	100.02			100.00	...
KIO_3 , Kahlbaum	1.7830	100.00	99.96	100.02			99.99	+0.01
$\text{Na}_4\text{B}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, Kahlbaum			99.97	99.97	99.97		99.97	+ .03
			99.98	100.00			99.99	+ .01

^a D. Y. = dimethyl yellow; P. = phenolphthalein; M. R. = methyl red; M. O. = methyl orange; B. B. = bromophenol blue.

^b Twice recrystallized.

When we titrate to P_H 4.0, the color change is also very sharp without using a solution for comparison. The correction in this case for the necessary excess of acid amounts to 0.1 cc. of 0.1 N hydrochloric acid. In Table I are given the results of the titrations with 0.1 N and 0.5 N hydrochloric acid. We only give the titration values corrected for the necessary excess of acid. In the first column the standard substance used is mentioned; in the second, the indicator; in the third, the *corrected* titration value. In the fourth column are given the mean values from a series carried out in the same way. For the sake of simplicity I recalculated all of the values on a basis of 100.00 cc. as an average of the titrations with sodium carbonate. All the other values are recalculated on this basis.

In the last column are given the difference in the titer found with the other standard substances as related to the value obtained with sodium carbonate.

Discussion of the Results

When we consider the results given in the table, we see that there is a close agreement between the titers found with sodium carbonate, borax and potassium iodate as standard substance. The difference is never larger than 0.03%. As the uncertainty in the results is about 0.02%, we may state that the three standard substances give the same results.

Moreover, we may conclude from the results that potassium iodate is an excellent substance for the standardization of hydrochloric acid. The titration gives the calculated results. When the determination is made with dimethylyellow as indicator, no waiting is necessary near the end-point.

Sodium carbonate is the least suitable standard substance, as it attracts water during the preliminary weighings. Special precautions must be taken to avoid this trouble. Moreover, the detection of the end-point is difficult. When dimethylyellow is used as an indicator, the liquid must be boiled at the point where the indicator just begins to change its color. After the boiling the cold liquid is titrated to the end-point.

The substance most to be recommended as a standard is borax.¹¹ By recrystallization from water and drying in a desiccator of a 60% relative humidity ($\text{NaBr}\cdot 2\text{H}_2\text{O}$ -sat. sol.) it is obtained in a pure state. It has the advantage of the large equivalent weight of 190.61. A small error in the weighing has much less influence on the result than with the use of the other standard substances. By using methyl red as an indicator with the proper liquid for comparison, one can titrate exactly to the equivalent

¹¹ Borax is recommended by different authors as a standard substance. Rimbach [*Ber.*, 26, 171 (1893)] applied the titration method with borax for the determination of the atomic weight of boron. From his results he derives a value of 10.91 for the atomic weight; I have calculated from his data a rational equivalent weight of borax of 190.79.

However, it is not quite certain whether Rimbach corrected in all cases for the buoyancy of the air.

point; therefore, no correction has to be applied for a necessary excess of acid. In the titration of 0.1 *N* solutions the Sørensen value (*P_H*) at the end-point is about 5.0.

Dimethylyellow, methyl orange and indicators with similar range of Sørensen values for their intervals may also be used.

I wish to thank Professor School for his great interest shown in the course of this investigation.

Summary

1. An application is made of the reaction: $6\text{H}^+ + \text{IO}_3^- + 5\text{I}^- \rightleftharpoons 3\text{I}_2 + 3\text{H}_2\text{O}$ for the standardization of strong acids with pure potassium iodate in the presence of a slight excess of thiosulfate.

2. When the right conditions are employed, sodium carbonate, borax and potassium iodate as standard substances give the same respective titers for 0.1 *N* and 0.5 *N* hydrochloric acid solutions.

3. As sodium carbonate is hygroscopic, and the color change of dimethylyellow at the end-point can be observed accurately only when the excess of carbon dioxide is removed, this salt cannot be recommended as a standard substance.

4. The most favorable standard substance for acids is *borax*. It has a high equivalent weight, and the color change with indicators such as methyl red and dimethylyellow can be observed very accurately.

5. From the determination of the water content of borax and from the results of the titrations we find good confirmation of the internationally accepted atomic weight of boron (10.82).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CATALYTIC OXIDATION OF CARBON MONOXIDE. II. THE ADSORPTION OF CARBON DIOXIDE, CARBON MONOXIDE, AND OXYGEN BY THE CATALYSTS, MANGANESE DIOXIDE, CUPRIC OXIDE, AND MIXTURES OF THESE OXIDES

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In the present paper are presented the results of experiments, completed in 1922, on the adsorption of carbon dioxide, oxygen and carbon monoxide by the catalysts, investigated by Almquist and Bray,¹ the compositions of which with respect to cupric oxide, MnO_x (where *x* is less than 2), water and carbon monoxide are given in the first paper. The results of Almquist and Bray (see the last column of Table I below) showed that in three related series of catalysts, in which the composition varied between

¹ Almquist and Bray, *THIS JOURNAL*, **45**, 2305 (1923). This article contains references to earlier work on the catalytic oxidation of carbon monoxide.