determined. Values of the same are given for 0°, 25°, and 30°. These values seem to indicate that ferric sulphate begins to be hydrolyzed even at a dilution of a few liters. It is proposed that the hydrolysis occurs in two stages, the first occurring with great rapidity, but not accompanied by any precipitation; the second with measurable speed and being identical with the formation of the "basic salt."

U. S. Geological Survey, Washington, D. C.,
July 8, 1909.

[Contribution from the Laboratories of the Mallinckrodt Chemical Works, St. Louis.]

THE PRESENCE OF IODATE IN COMMERCIAL POTASSIUM IODIDE.—A FALLACY.

By Launcelot W. Andrews.

Received July 13, 1909.

The belief appears to be generally held that commercial potassium iodide frequently contains iodate. Thus, the *Pharmacopoeia* prescribes a test for iodate in the iodides and many procedures have heen published for making the test, differing from one another mainly in the choice of the kind of acid used in acidifying and in the amount of it employed. Now, it is not at all apparent how there can be any iodate present in the salt, since the latter is subjected in the course of manufacture to fusion with charcoal and likewise to reducing agents in solution. The production of a blue coloration when the solution of an iodide is mixed with starch paste and acidified with hydrochloric acid, is by no means to be looked upon as evidence of the presence of iodate, although the non-appearance of such coloration is good evidence of its absence. Most commercial samples of potassium iodide contain traces of iron. This iron is commonly present in one of two conditions, or in both. One form is that found in ordinary dust containing coal smoke or soot, in which condition the metal passes readily into solution as ferric chloride, when acted on by dilute hydrochloric acid. The other form is that of anhydrous ferric oxide in a state of extremely fine subdivision. This form dissolves slowly in the dilute acid, even in the presence of the iodide. It is produced by long boiling of saturated solutions of the iodide with ferric hydroxide. Its state of division is often such that this oxide will pass in part through an ordinary filter paper, but is almost entirely retained by the "toughened" paper of the "Dreverhoff" or "S. and S." brands.

A sample of iodide containing iron, in either form, will of course liberate iodine on acidification with hydrochloric acid, the formation of the iodine following more quickly and with more dilute acid when the iron is in the first, more soluble form. If, however, the solution of the iodide (of potassium) is acidified by the addition of potassium bitartrate and starch paste, no liberation of iodine can be perceived as a result of the presence of iron oxide. The explanation is, simply, that the concentration of hydrogen ions in the solution (limited by the solubility of cream of tartar) is not sufficient to cause the reaction to run in that direction. In other words, the reversible reaction expressed by the symbols

$$2Fe(OH)_3 + 6H^{\bullet} + 6I' \rightleftarrows 2Fe^{\bullet\bullet} + 4I' + I_2 + 6H_2O$$

takes the direction of the lower arrow when the number of $H^{\bullet}$ ions is as small as it is in the case under consideration. The amount of ferrous salt produced and of iodine liberated is too minute to give rise to any visible reaction. If, however, iodate is present, the reaction

$$KIO_3 + 6HI = KI + 3H_2O + 3I_2,$$

being non-reversible, proceeds to completion under the prevailing conditions.

In addition to the iron, commercial samples of potassium iodide very frequently contain minute traces of cuprous iodide. This salt is but slightly ionized in aqueous solution. In a strong solution of an alkali iodide, its ionization is still further set back, to such an extent, in fact, that it is very difficult to remove it and even to detect Cu, without first expelling the iodine. Now, if a solution of an iodide in which such traces of cuprous iodide are dissolved, is slightly acidified, the cuprous salt will be oxidized by dissolved oxygen to cupric, and so by a cycle of operations the iodine will be set free and oxygen taken up, the copper salt in effect acting as a catalyzer, and causing the liberation of much more than an equivalent amount of iodine.

It is therefore clear that in this case also, assuming the correctness of the theory, no iodine will be set free on acidification, provided free oxygen be rigorously excluded and as before the conditions be made such that the ferric oxide will not react. These requirements may be met in various ways. For practical purposes the following technique has been found sufficient and convenient. A small flask with a round bottom (70 to 100 cc.) is half filled with a ten per cent. solution of the iodide. The flask is closed with a very perfectly fitting soft rubber stopper, slightly lubricated with lanolin. Through the stopper is passed a narrow glass tube, bent twice at right angles. This tube must, of course, fit the stopper faultlessly, the joint being lubricated. Over the outer end of the tube is drawn a piece of good black rubber tubing, about two inches long and not too thin in the wall and which can be closed by a pinchcock. This connection is likewise lubricated and the rubber bound to the glass. The free end of the tubing is immersed in about 75 cc. of distilled water contained in a small beaker, the whole arrangement being firmly supported by a ring-stand. In the water is placed about one gram of the purest potassium acid tartrate and a little starch paste. Both the flask and the beaker are heated, the contents of the former being kept in gentle ebullition till about half the liquid is boiled off, the delivery tube being always near the bottom of the beaker, so that the escaping steam passes through the cream of tartar solution. In this manner, the dissolved oxygen is expelled from both solutions. Now, the flame is removed from the flask and simultaneously the pinchcock is applied to the rubber tube, while the solution in the beaker is still maintained at the boiling point by a small flame. When the flask has begun to cool a little, the cock is opened so as to allow half or more of the liquid in the beaker to flow into the flask and then closed. The flask is cooled to room temperature or lower. If the solution becomes blue, the presence of iodate is indicated, if not, it is certainly absent. Iron oxide or cuprous iodide will not give the reaction.

These observations were first made by me more than five years ago. Since that time I have had occasion to examine many samples of domestic and foreign potassium and sodium iodides and have not as yet detected the presence of iodate in a single sample.

The following tests were carried out to determine how small an amount of iodate can be detected under the conditions of this test. A solution of potassium iodide was made up to contain 100 grams per liter. The salt used was specially purified. No copper or iron could be detected in it. When to 25 cc. of this solution, one cc. of double normal hydrochloric acid was added, the liquid exhibited no color after standing half an hour, either with or without starch paste. It could, consequently, be regarded as free, within the limits of sensitiveness of the test, from iodate, copper and iron or other catalyzers or iodine liberators. Also a solution was made of 36 milligrams of potassium iodate in a liter of water.

Four portions of the potassium iodide solution were measured out of about 50 cc. each. To the first, 2 cc. of the iodate solution were added, to the second 4 cc., to the third 8 cc., and to the fourth 16 cc. Each portion was then examined for iodate in the apparatus and manner described above. The first showed no coloration, the second a distinct violet-rose, and the others were bluish violet. As the second portion contained 5 grams of iodide and 0.144 mg. of iodate, it appears that the limit of sensitiveness is greater than one part of iodate in 35000 of iodide. A repetition of the test between a narrower range showed that the limit is in fact 3.9 cc. of the millinormal iodate solution, corresponding to about one part of iodate in 47,000 of iodide, roughly 20 parts per million. By using a more concentrated solution of the iodide (1:1), in which case the color is pink, not blue, this sensitiveness may be somewhat enhanced, but not by any means proportionally, as is further elucidated below.

The conclusion is, that the received opinion, that commercial iodides often contain iodate, is not supported by the evidence and that, if any iodate is present, it must be in a proportion less than 20 parts in a million.

The sensitiveness of the test for iodate corresponds closely with the sensitiveness of the iodine-starch reaction. It is well known that this sensitiveness is strongly influenced by temperature, but I am not aware that the influence of the potassium iodide has been studied, except for more dilute solutions.[1] It therefore seems to be worth while to record my observations on this point. A thousandth normal solution of iodine was used, containing in each liter 127 milligrams of iodine and 166 milligrams of potassium iodide. Solutions of pure, neutral potassium iodide of various concentrations received an addition of two cc. of freshly made starch paste of two per cent. starch and were then titrated with the iodine solution till a perceptible permanent color appeared. This color was blue when little or no iodide was present, violet in the presence of a larger amount and rose-red in more concentrated solutions of iodide. It was soon apparent that a point of maximum sensitiveness exists for a certain iodide concentration. If to 50 cc. of water two cc. of starch paste be added and then 0.4 cc. of the iodine solution, the mixture will show no color or a scarcely visible trace. If now a little potassium iodide (about 1/10 gram) is added, the liquid becomes very distinctly blue. On the gradual addition of more iodide, the color at first exhibits no change, then becomes paler and disappears entirely. More iodine must now be added to restore the color, which can be destroyed again by addition of more iodide. The quantitative relations are given in the following table. Column 1 gives the number of cc. of N/1000 iodine required to impart permanent color, column 2 the amount of potassium iodide added (in addition to that contained in the iodine solution), column 3 the volume of the water (not that of the solution) present after the addition of all the reagents, that is at the equilibrium point. The iodide concentration corresponding to the maximum sensitiveness was not determined, but merely the fact that it is much less than one gram per 100 cc. The temperature was at nearly 25° in every case.

1. Iodine.	2. KI. Grams.	3. Volume. cc.	4. Iodine sol. calculated.	5. Iodine detectable, parts per million.
0.5	0.0	50.0	0.5	...
0.4	0.0	50.0	0.5	...
1.1	0.0	100.0	1.0	...
0.9	0.0	100.0	1.0	...
0.25	0.06	50.0	...	...
1.0	1.0	51.0	0.99	127
3.0	5.0	53.0	2.95	76
12.5	25.0	62.5	12.72	64
12.55	25.0	27.5	12.37	...

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[1] Meineke, *Chem. Ztg.*, 17, 157 (1894).

These results demonstrate that, apart from lower iodide concentrations, the addition of each gram of potassium iodide diminishes the sensitiveness of the starch reaction as much as the addition of 50 cc. more water. The observations are well reproduced by the formula, $z = 0.01\ v + 0.484\ w$, in which z = cc. of iodine sol. required, v is the volume in cc. of water present, and w is the weight in grams of potassium iodide. Column 4 shows the volumes of iodine solution as calculated by this formula. The latter does not correctly present the results of the observations on solutions more dilute as to iodide but only those on solutions which contain two per cent. or more of this salt. The somewhat curious conclusion is, that by increasing the amount of iodide tested from one gram to twenty-five grams, the sensitiveness of the test for free iodine or for iodate is only doubled. By increasing the amount taken from 5 grams to 25, the sensitiveness is only enhanced by about twenty per cent. This relation is exhibited by the figures of column 5, which are the number of parts of free iodine in one million parts of potassium iodide which must be present to be just detectable by the reaction as described.

Meineke[1] in a careful study of the starch-iodine reaction found a maximum sensitiveness in solutions containing about 25 mg. of potassium iodide per 100 cc. of $10^6 \times 2.6$ normal iodine, which is of the same order as the limit found by me, $10^6 \times 5.0$ normal. Eckstädt[2] found the limit to be $10^5 \times 2.5$. Meineke expressly states that potato starch is considerably more sensitive than starch from the cereals. In the experiments described in the present paper, maize starch was used. Meineke records no observation in solutions containing over ten per cent. of potassium iodide, and in that case the diminution of sensitiveness, as compared with the maximum, was much less than was shown by my observations. I have found no explanation for this discrepancy and was compelled, therefore, to content myself with establishing the correctness of the formula as given above by repeated observations with different starch paste preparations made from washed maize starch. It is impossible to fix very precisely the concentration of iodide which corresponds to the maximum sensitiveness, since, as is well shown in the table of Meineke, the curve is too flat, but it is possible to say that it is less than N/150.

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[1] *Loc. cit.*

[2] *Z. anorg. Chem.*, **29**, 55 (1901); compare also Pinnoff, *Z. anal. Chem.*, **41**, 485 (1902).