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A REVISION OF THE ATOMIC WEIGHTS OF IODINE AND SILVER.

[PRELIMINARY PAPER].

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The Analysis of Iodine Pentoxide.

For some time it has been apparent that Stas's researches upon the atomic weight of silver, upon which the value now in use depends, are somewhat at fault. The need for a redetermination of the ratio of this constant to the atomic weight of oxygen is especially pressing, since silver has been very frequently used as the basis for exact work upon atomic weights, both directly, and also indirectly through its relation to the atomic weights of the halogens in the analysis of metallic halides.

The problem is made difficult, however, by the fact that the only known definite compounds of silver with oxygen are difficult if not impossible to prepare in a pure state, besides containing so small a percentage of oxygen that the experimental error would be greatly magnified in the calculation. All other methods involve the knowledge of the exact ratio of at least one other atomic weight to that of silver or oxygen, the accuracy of the process diminishing with the number of atoms involved. Among the various classes of compounds the analysis of which may afford the desired information, oxides are of especial interest because the knowledge of the ratio of only one atomic weight to that of silver is involved. The difficulty and uncertainty in analyzing metallic oxides[1] make them unsuited for the purpose. The ratios of the atomic weights of silver and the halogens are known with greater exactness than in the case of most elements, hence to determine the ratio of any one of the halogens to that of oxygen will serve the purpose equally well. The only compound of a halogen and oxygen of considerable stability is iodine pentoxide. This substance is, however, quite stable through a fairly wide range of conditions, and its analysis offered enticing possibilities. To be sure, the percentage of oxygen in the compound is not high, but this disadvantage is in part counterbalanced by the fact that the ratio of the atomic weight of iodine to that of silver is greater than in the case of most elements.

The Preparation of Iodic Acid.—Iodine pentoxide may be readily prepared by dehydration of iodic acid at a comparatively low temperature. Of the various methods for preparing the latter substance, by far the most satisfactory for the present purpose is the oxidation of iodine with fuming nitric acid. The volatile by-products of the reaction, oxides of nitrogen and water, as well as the excess of nitric acid, may be removed by heating, and the acid may be crystallized from aqueous solution.

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[1] Richards and Baxter, *Proc. Amer. Acad.*, **35**, 61 (1899); *Ibid.*, **35**, 253 (1900).

Iodine was purified for most of the preparations by the methods already described by one of us.[1] These consisted usually in a preliminary distillation of commercial iodine from solution in commercial aqueous potassium iodide. The iodine was then twice reduced to hydriodic acid by hydrogen sulphide and water, and the hydriodic acid was subsequently oxidized by recrystallized permanganate, with intermediate boiling of the hydriodic acid solution to eliminate cyanogen as hydrocyanic acid.[2] In this way, since only five-eighths of the iodine is set free from hydriodic acid by permanganate, the iodine was three times distilled from a solution of an iodide, the iodide being of greater purity in each succeeding distillation. It has already been shown that three such distillations are sufficient to remove completely chlorine and bromine,[3] so that there can be no question of the freedom of the resulting iodine from those closely related elements. The final product was once distilled with water into a Jena glass flask cooled with running water, and the resulting solid was washed with the purest water upon a porcelain Gooch crucible containing no mat.

Pure fuming nitric acid was prepared by distilling the best commercial product several times, with rejection of the first and last thirds, until the distillate, after dilution, gave no test for chloride with silver nitrate in a nephelometer.[4] A quartz condensing tube was used in these distillations, and the final product was collected in a quartz vessel. In this way the introduction of silica and alkalies from glass vessels was avoided. Fused quartz vessels have already been shown to be essentially insoluble in acid solutions.[5]

The reaction between iodine and fuming nitric acid proceeds slowly at ordinary temperatures, with the formation of oxides of nitrogen and nitro-iodic acid. Heat hastens the reaction and also breaks up the nitro-iodic acid into nitric oxide, iodine, and iodic acid. If the nitric acid is in large excess the iodine is converted into iodic acid without loss, and the iodic acid remains insoluble in the residual concentrated nitric acid. If the iodine is in excess, the reaction proceeds until the nitric acid is so dilute, owing to the production of water in the reaction, as to be without further effect upon the iodine, although the acid is still so concentrated that the iodic acid remains essentially insoluble. Nitric acid of this concentration dissolves considerable quantities of iodine, however.

Since the largest quartz vessel at first available was a one hundred cubic centimeter transparent fused quartz flask, the most convenient

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[1] Baxter, *Proc. Amer. Acad.*, 40, 421 (1904).

[2] Richards and Singer, *Amer. Chem. J.*, 27, 205 (1902).

[3] Baxter, *Loc. cit*; also *Proc. Amer. Acad.*, 41, 73 (1905).

[4] Richards and Wells, *Amer. Chem. J.*, 31, 235 (1904); 35, 510 (1906).

[5] Mylius and Meusser, *Z. anorg. Chem.*, 44, 221 (1905). Baxter and Hines, THIS JOURNAL, 28, 1565 (1906).

method for making the iodic acid was found to be to treat a large quantity of iodine in the flask with successive portions of fuming nitric acid. After the introduction of the iodine, nitric acid was distilled directly into the flask through the quartz condenser. The flask was then warmed until the nitric acid was spent. The spent acid was removed as completely as possible by drainage, and was replaced by fresh acid, and the process was repeated until the iodine appeared to be completely oxidized. Dissolved iodine was recovered from the spent acid by dilution. After the removal of the last portion of the acid, the iodic acid was dissolved in the smallest possible amount of the purest water and the solution was evaporated to dryness in a dish of fused quartz in order to expel nitric acid and unchanged iodine, for the removal of nitric acid by crystallization is very slow. During this evaporation the dish was placed upon a large watch glass on a sand bath, and was surrounded by a large bottomless beaker. The dish was further protected by being covered with a bottomless flask, through the neck of which a current of pure dry air was introduced in order to hasten evaporation. The air was freed from organic matter by passing over hot copper oxide in a hard glass tube, and was purified and dried by means of a solution of potassium hydroxide and solid caustic potash. The purifying apparatus was constructed wholly of glass.

The residue from the evaporation was dissolved in the purest water and evaporated in the quartz dish with the same precautions as above until a film of solid appeared on the surface of the liquid. This solid is not iodic acid, but is probably a compound having less water, since it was necessary to induce the crystallization of the acid itself by inoculation. If left to itself the acid crystallizes very slowly, some days being necessary for the establishment of equilibrium. It is economical, however, to wait for the establishment of equilibrium, since the solubility of the acid at room temperature is so high, a saturated solution at 20° containing over seventy-five per cent. of acid. The first crop of crystals was drained as completely as possible, usually with centrifugal drainage in a platinum centrifugal machine,[1] and the product was twice recrystallized. On account of the high solubility of the acid and the low temperature coefficient of solubility between 0° and 100° the yields of acid were very small, hence the mother liquors were worked up for several successive yields of crystals. The thrice recrystallized acid was preserved in a desiccator containing solid caustic potash. It was designated Sample I.

The solutions of iodic acid, as well as the solid substance and even iodine pentoxide made from the acid, possessed to a slight degree a peculiar odor which may be described as "aromatic." This odor persisted

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[1] Baxter, THIS JOURNAL, 30, 286 (1908).

through the crystallization although with continual diminution, but was not entirely absent from acid which had been crystallized three times. It was later proved that the odor is not due to the acid itself because after a sufficient number of crystallizations the odor disappears. Furthermore, it was experimentally proved that no appreciable amount of iodine was contained in this vapor, for when a concentrated solution of the acid is boiled no iodine can be detected in the distillate, and when a current of air is conducted over the solid at ordinary temperatures into a solution of sulphur dioxide no iodine can be found in the sulphurous acid solution. Even at high temperatures the pentoxide loses in weight very slowly, ten grams losing only one milligram at 240° in four hours. By far the greater part of this loss is due to decomposition of the pentoxide, for free iodine can be easily detected in the air which has passed over the substance.

The possibility of the presence of metallic impurity in the iodic acid, arising from the action of iodine on the glass of the flask in which it was condensed, was tested by evaporating to dryness the mother liquor of the last crystallization of the original solution and heating the residue in a weighed platinum boat in a current of pure dry air until the pentoxide was completely decomposed. The boat gained in weight only 0.0006 gram, part of this gain being due to the formation of platinous iodide. Faint tests for sodium and calcium only could be obtained with the residue in the spectroscope.

The Preparation of Pure Silver.—Silver was purified by methods already found in this laboratory to be effective for the purpose. A dilute solution of silver nitrate was first precipitated with hydrochloric acid in excess, and the precipitate was thoroughly washed with pure water. The chloride was next reduced by means of invert sugar and an excess of sodium hydroxide, and the metal, after long-continued washing by decantation, was fused upon charcoal. After the buttons had been cleansed by scrubbing with sand and etching with nitric acid, they were dissolved in nitric acid and the silver was precipitated as metal by means of ammonium formate made from redistilled ammonia and formic acid. This precipitate in turn was thoroughly washed and the metal was fused in the flame of a carefully cleaned blast lamp in a crucible of lime made from purified calcium nitrate and carbonate. After being cleansed as before, the buttons were electrolyzed in a cell in which a pile of these buttons served as anode, the cathode being a bar of the purest silver and the electrolyte being a concentrated solution of silver nitrate made from one of the buttons. Next the electrolytic crystals, after being washed and dried, were fused in a current of pure electrolytic hydrogen in an unglazed porcelain boat lined with the purest lime.[1] The resulting

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[1] Fusion in hydrogen (Baxter, *Proc. Amer. Acad.*, 39, 249 (1903)) is probably

buttons were cut into fragments of from three to six grams with a fine jeweler's saw, etched with small portions of dilute nitric acid until the acid used in etching was free from iron, and finally the fragments were washed and thoroughly dried in a vacuum at about 400°. Two different specimens of silver were prepared in essentially the same way, Samples A and B.

The Conversion of Iodic Acid into Iodine Pentoxide.—The conversion of the iodic acid into iodine pentoxide was effected by heating the substance in a current of dry gas. At the beginning of the research the hope was entertained that the final product might be sublimed. In no experiment, however, have we been able to detect the least trace of sublimation, even when the pentoxide was heated to the decomposition point. Iodic acid may be made to lose all its water of composition without fusion, and consequently it was to be expected that under these conditions dehydration could be made nearly if not quite complete. T. W. Richards has already pointed out that a solid which loses water of composition without fusion is left in the form of a skeleton, from the innermost interstices of which the water vapor may escape, while, if fusion takes place during drying, a portion of the original salt may be enclosed within an impervious coating of anhydrous salt so that escape of water is impossible.[1]

It is commonly stated that the dehydration of iodic acid takes place in two stages, two-thirds the water being lost below 130° and the remainder at about 200°.[2] The acid itself, if heated rapidly, melts at 110° with the separation of the solid phase $I_2O_5.HIO_3$, although this second phase shows no indication of melting up to the temperature of the second stage in the dehydration. Our earlier experience was not in accordance with the above statements. The acid, when heated to about 110°, lost *all* its water of composition, at this temperature. This was shown conclusively in one experiment by heating a weighed amount of iodic acid for some time at about 110° and then reweighing. The acid lost the amount of water theoretically necessary for the formation of the pentoxide, and further heating to 300° produced only a negligible diminution in weight. On one later occasion, however, when a comparatively crude specimen of acid was being dehydrated, the second phase unexpectedly appeared, and in all subsequent experiments the same result was obtained, no matter what the source of the iodic acid, or how carefully the apparatus was cleaned before use. This point is additional

safer than fusion in a vacuum, since it eliminates the possibility of the taking up of sulphur by the silver from the rubber ring used in fitting the hollow brass stoppers into the porcelain fusion tube. Richards and Wells (*Pub. Car. Inst.*, No. 28 (1905)) have shown that silver fused in hydrogen is certainly as pure as any other.

[1] *Z. physik. Chem.*, 46, 194 (1903).

[2] For a discussion of this subject see Groschuff, *Z. anorg. Chem.*, 47, 333 (1905).

proof that the second phase is a definite chemical compound. The obvious explanation of the phenomenon is that the laboratory became inoculated with "germs" of the second phase so that its formation was thereafter always induced.

The iodic acid was dehydrated in a platinum boat contained in a hard glass tube heated by a solid aluminum oven. This oven, for the suggestion of which we are indebted to Dr. Arthur Stähler, of the University of Berlin, consisted of two machined aluminum blocks, 15 x 13 x 5 cm., the upper surface of one block and the lower surface of the other being grooved to contain the hard glass tube, when one block was placed upon the other. The blocks were further bored to contain a thermometer in such a way that the bulb was located within a half centimeter of the middle of the hard glass tube. When heated with a small Bunsen flame, this bath could be regulated in temperature to within one or two degrees without the least difficulty, even without the jacket of asbestos paper which was usually employed. Thermometers placed inside the hard glass tube and in the cavity in the blocks registered the same temperature within a degree even when the oven was heated to 300°.

At first the air was purified and dried by passing over hot copper oxide in a hard glass tube, then through two towers containing beads moistened with silver nitrate and caustic potash solutions, respectively, and finally through four towers containing beads moistened with concentrated sulphuric acid to which a small quantity of potassium dichromate had been added in order to prevent any possibility of reduction. The apparatus was constructed wholly of glass with ground or fused joints, rubber and grease being carefully avoided. When heated in a current of air thus purified and dried, even the purest iodine pentoxide became somewhat brown owing possibly to liberation of iodine. The use of electrolytic oxygen in place of air failed to prevent this phenomenon. Finally it was found that if the air was dried more thoroughly, by means of resublimed phosphorus pentoxide, the difficulty could be avoided. The cause of this marked catalytic effect from the minute quantity of moisture which is not absorbed by sulphuric acid was not determined.

The hard glass tube in which the heating was conducted formed part of a bottling apparatus by means of which the boat could be transferred to a weighing bottle, without an instant's exposure to moist air. Similar apparatus was first used for the purpose by Richards[1] and was modified and improved by Richards and Parker.[2] Although these precautions were taken to prevent exposure of the substance to moisture before weighing, little danger was to be feared from this source, for in air ordinarily moist the pentoxide absorbs water very slowly. For instance

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[1] *Proc. Amer. Acad.*, 30, 383 (1894).

[2] *Ibid.*, 32, 59 (1896).

4.4 grams of pentoxide, when exposed in the platinum boat to the air of the laboratory for two hours, gained only 0.0008 gram.

Even when dried under the most favorable conditions the above-mentioned darkening of the pentoxide took place if the temperature rose much over 250°. Accordingly the temperature was not allowed to pass this point in drying the substance for analysis. Furthermore, since it was by no means certain that every trace of water could be expelled from the pentoxide at this temperature, and since it seemed probable that the amount of water retained would vary with the temperature and time of treatment, the conditions in the different experiments were made as nearly as possible identical.

The details of manipulation were as follows: The crystals of iodic acid were powdered in a new smooth agate mortar together with a small quantity, about two per cent. of the weight of the acid, of the phase produced in the first stage in the dehydration, This step was of advantage in catalyzing the first stage in the dehydration, for frequently, when the precaution of thus inoculating the iodic acid was omitted, the temperature reached 130° before dehydration began, whereas when this precaution is taken the water first appears as low as 85°. Since the iodic acid itself melts at 110° when in contact with the phase produced at this temperature, it seemed better to prevent the acid from reaching this temperature until the first stage in the dehydration was past. As a matter of fact, preliminary water determinations in the dried material indicated a slightly larger proportion of water in acid which had not been inoculated with the second phase.

The weighed boat, containing from six to ten grams of the iodic acid, was next heated in a slow current of air at 90°–110° until the first two-thirds of the water of composition had been given off by the iodic acid and had been expelled from the tube by the current of dry air. The temperature was then raised until the second portion of water was given off. Usually the pentoxide began to form at about 220°. There is no evidence of fusion at this point, even if the temperature rises much above 200° before all the remaining water is expelled. After all the water had disappeared the temperature was raised to 240° and maintained at this point for four hours. Then the boat was transferred to the weighing bottle, allowed to stand in the desiccator with the counterpoise for some time, and was weighed.

The Determination of Iodine in Iodine Pentoxide.—The analysis of the iodine pentoxide for iodine was effected by dissolving the substance in water, reducing the iodic acid solution to hydriodic acid with a suitable reducing agent, and titrating the hydriodic acid against a weighed amount of silver.

The operation in detail was as follows: After being weighed, the boat with its contents was placed in a large thick-walled flask and immediately covered with about five hundred cubic centimeters of the purest water, in which it slowly dissolved. Even when the pentoxide was slightly colored the solution was colorless to the eye and absolutely clear. The weighing bottle was rinsed with water and the rinsings were added to the main solution in the flask. In a number of early experiments the reduction was accomplished by slowly pouring the dilute solution of iodic acid into a solution of a slight excess of sulphurous acid. Very nearly the theoretical amount of the purest silver was weighed out and dissolved in redistilled nitric acid diluted with an equal volume of water, in a flask provided with a column of bulbs to collect possible spatterings during the solution of the silver. As a matter of fact, the silver was caused to dissolve so slowly that only a very small quantity of gas was evolved. After the silver was completely dissolved, the solution was diluted with an equal volume of water and heated until free from nitrous acid. This latter precaution was especially necessary, since nitrous acid readily liberates iodine from iodides, while nitric acid has this effect only when hot or rather concentrated. Finally the solution was diluted until at least as dilute as thirtieth normal and was added with constant agitation to the solution of the hydriodic acid which had been diluted to a similar concentration in a large glass-stoppered precipitating bottle. The whole was then thoroughly shaken and allowed to stand until clear. In order to determine whether silver or iodide was in excess, thirty cubic centimeter portions of the solution were tested with silver nitrate and hydriodic acid in the nephelometer. The results of these earlier analyses were extremely unsatisfactory, the end-point changing continuously with time, and an unreasonably large amount of silver was required. This could not have been due to occlusion of silver nitrate by the silver iodide, since it has already been shown by one of us that at concentrations less than thirtieth normal the latter difficulty is too small to have an appreciable effect.[1] The cause of the trouble was finally traced to occlusion of silver sulphate by the silver iodide. Richards and Jones[2] found that silver chloride occludes silver sulphate very markedly and tenaciously, hence it is not in the least surprising to find the same difficulty here. It is to be noted that the concentration of sulphuric acid in these experiments is relatively large, *three molecules* of sulphuric acid being produced in the reduction for every *atom* of iodine. That this difficulty did not appear in the above mentioned researches upon the ratio of iodine to silver, where iodine was reduced with sulphurous acid and the hydriodic acid titrated against silver, is undoubtedly due to the fact that the concentration of sulphuric

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[1] Baxter, *Proc. Amer. Acad.*, 41, 77 (1905).

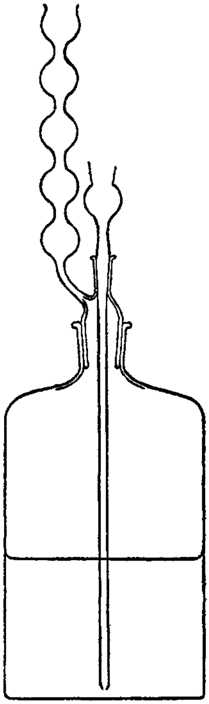
[2] *Pub. Carnegie Institution*, 69, 73 (1907).

acid was relatively much lower, only *one* molecule of sulphuric acid being formed in the reduction of one *molecule* of iodine.

A search for a more satisfactory reducing agent than sulphurous acid failed to reveal any substance more promising than hydrazine, for the reduction of iodic acid with this substance yields only hydriodic acid, nitrogen and water.[1] In order to avoid the introduction of undesirable acids, the hydrazine was used in the form of a solution of the hydroxide instead of as a salt. The hydrazine hydroxide was made by distilling either the chloride or the sulphate with a concentrated solution of a considerable excess of sodium hydroxide in a platinum still. The product was then redistilled in the platinum still to eliminate possible traces of chlorides, and was preserved in a platinum flask. Even when made from the chloride, the doubly distilled product was absolutely free from chlorides. The approximate concentration of the solution was determined shortly before use by titration against a standard solution of iodic acid or potassium permanganate. Preliminary experiments showed that there is no danger of the reduction of the silver salts by a slight excess of hydrazine in nitric acid solution.

Special pains were taken in the reduction of the iodic acid with hydrazine to avoid any possibility of loss of iodine by volatilization. The solution of the iodic acid was transferred to an eight-liter bottle with a carefully ground stopper, and, after the iodic acid had been neutralized with ammonia, very slightly less than the theoretical quantity of hydrazine hydroxide was added. Since in alkaline solution hydrazine is without effect upon iodic acid, the solution was next made acid by slow addition of nitric acid.

As soon as hydriodic acid has begun to be formed, iodine is freed by interaction of the hydriodic acid with the iodic acid. Lest any of this iodine be volatilized from the solution before it could be reduced by the hydrazine the nitric acid was introduced at the bottom of the solution through a long funnel. Thus iodine was sure to be completely reduced before reaching the surface of the solution. A specially devised stopper shown in the accompanying diagram provided for the escape of the nitrogen through a long column of bulbs, which served to catch spatterings


Apparatus for Reduction of Iodic Acid

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[1] Brown and Shetterly have shown that no hydronitric acid is formed by the action of hydrazine on iodates or iodine. THIS JOURNAL, 30, 53 (1908).

or soluble vapors, if any reached this point. As a further precaution against the escape of iodine a small quantity of sulphurous acid was poured into the bottle through the train of bulbs. This sulphurous acid served also to complete the reduction of the iodic acid. The amount of sulphuric acid formed in this way was not sufficient, however, to produce appreciable occlusion of silver sulphate.

After the reduction and subsequent dilution of the solution to a concentration between thirtieth and fiftieth normal, the hydriodic acid was precipitated with a dilute solution of a weighed amount of silver as before described. On account of the large bulk of the mother liquor, six to seven liters, the end-point as determined in the nephelometer was somewhat uncertain, especially since it seemed to be complicated by a minute trace of silver iodide held in suspension. Hence instead of attempting to use exactly the theoretical quantity of silver, an amount was employed a few tenths of a milligram in excess of the required quantity. Then this excess was determined by evaporating the supernatant liquid to a very small bulk, precipitating the excess of silver as silver iodide and determining the silver iodide either gravimetrically upon a Gooch-Munroe-Neubauer crucible, or nephelometrically by comparison with dilute standard solutions of silver. Before evaporation, the supernatant solution was carefully filtered through the Neubauer crucible and the precipitate of silver iodide was washed by decantation several times with pure water to remove any adsorbed silver nitrate. That washing was able to remove any adsorbed silver nitrate was shown by treating a very carefully washed precipitate of silver iodide resulting from one of the analyses with a solution of silver containing a few tenths of a milligram of silver in six liters. After thorough agitation with the precipitate the solution was filtered and evaporated as in the analyses, after washing of the precipitate. Practically all this silver was found in the evaporated solution. Although the silver determined in this way includes the silver iodide *dissolved* in the mother liquor, the error introduced is very small, the solubility of silver iodide being probably at least as low as 0.0000035 gram per liter.[1] The platinum boat was not appreciably changed in weight.

The Determination of Moisture in Iodine Pentoxide.—The determination of the water content of the iodine pentoxide when dried under the conditions used in the analyses for iodine, was fully as difficult as the iodine determination, and it was in preliminary attempts to determine the water content that evidence was obtained which led to the adoption of the above precautions for reducing the water content to a constant low value. The method of operation consisted in brief in completely decomposing the pentoxide into iodine and oxygen by heating in a current of dry air, and, after removing the iodine as far as possible by condensation

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[1] Kohlrausch, *Z. physik. Chem.*, 50, 355 (1904).

and finally by a layer of hot silver, collecting the water in a weighed phosphorus pentoxide tube. Great pains were taken that the iodine pentoxide should be prepared for the water determinations exactly as for iodine determinations. In order to avoid absorption of water between the heating and the decomposition, the decomposition of the pentoxide took place immediately upon the completion of the heating without interruption of the experiment, the weighing of the pentoxide, which need not be very accurate on account of the low per cent. of water, having taken place before the long heating at 240°.

The iodic acid used in the water determinations was not made from either purified iodine or purified nitric acid, and most of it was prepared in glass vessels. However it was very carefully purified by repeated crystallization from aqueous solution in platinum vessels with centrifugal drainage of the crystals in each case, and gave every outward evidence of great purity. Not only were the final crystals pure white, but the final mother liquor was colorless. The crystals gave a perfectly clear solution in water and left no appreciable residue when decomposed in the platinum boat.

The platinum boat, containing about twenty-five grams of acid which had been inoculated with the second phase, was freed from water by heating at 100° and then at 220°+ in the usual way. It was then bottled and weighed. Next the boat was transferred to a long hard glass tube very carefully ground into the socket of the bottling apparatus and was heated to 240° for four hours in a current of dry air. Toward the end of the heating all of the apparatus beyond the phosphorus pentoxide drying tube was gently heated with a Bunsen flame in order to dislodge any adsorbed water from the inside surface of the glass. Although by far the greater part of the iodine formed in the decomposition condensed in the hard glass tube, a small quantity of iodine vapor was always carried along by the current of gases.[1] For the absorption of this iodine vapor a small hard glass tube containing small electrolytic crystals of silver which had been dried by heating to about 400° in a vacuum, was carefully ground on the end of the hard glass tube. This tube was attached to the hard glass tube during the decomposition of the pentoxide and was heated to very dull redness. The column of metallic silver was several inches in length, and although considerable silver iodide was produced at the end of the column nearest the decomposition tube, the silver at the other end of the column remained perfectly bright through all the determinations, showing the absorption of iodine to have been complete.

The U-tubes for the absorption of water were provided with glass stopcocks and were filled with phosphorus pentoxide which had been freshly

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[1] Baxter, Hickey and Holmes, "The Vapor Pressure of Iodine," THIS JOURNAL, **29**, 127 (1907).

sublimed in a current of oxygen. They were weighed by substitution, with the use of a similar tube as counterpoise. Before being weighed, the tubes were wiped with a damp cloth and were allowed to stand near the balance case for at least an hour. The tubes were weighed with one stopcock open. The balance was provided with a few milligrams of radium bromide of radioactivity 10000 to dispel electrical charges. Under these conditions no difficulty was experienced in weighing the tubes within a few hundredths of a milligram, since they quickly came to constancy in the balance case and retained their weights unchanged for days at a time. Two phosphorus pentoxide tubes were used in the first experiments, but since the gain in weight of the second tube was found to be negligible in all cases where it was used, the second tube was omitted in the later experiments. Still another phosphorus pentoxide tube was placed beyond the weighed tubes as a protection against the back diffusion of moisture. Blank experiments were usually run after the collection of the water resulting from the decomposition. Frequently no gain in weight of the tube in these blank experiments could be detected and in no case did the gain in weight amount to more than one-tenth of a milligram.

The decomposition of the iodine pentoxide was effected by removing the aluminum oven and heating the tube to the temperature of decomposition of the pentoxide, about 350°, with a Bunsen burner. Decomposition was conducted as evenly as possible so as to avoid an unduly rapid current of oxygen from the apparatus with consequent incomplete absorption of the water. When decomposition was complete the condensed iodine was heated above its melting point to set free traces of absorbed moisture. Then the decomposition tube was swept out with a current of dry air and the absorption tube was weighed. In four experiments carried out as above the following results were obtained:

No. of analysis.	Weight of I_2O_5. Grams.	Weight of H_2O. Gram.	Per cent. of H_2O.
1	25.0	0.00060	0.0024
2	20.7	0.00032	0.0016
3	26.1	0.00067	0.0026
4	24.6	0.00060	0.0024
		Average,	0.0023

In addition, several experiments were performed in order to determine the effect of varying the conditions of treatment. In Analysis 5 the heating at 240° lasted only one hour, and in Analysis 6 the iodine pentoxide was heated for four hours at 260°. In Analysis 7 to 11 only a very small quantity of the second phase was used to inoculate the pentoxide, in Analyses 7 and 8 the substance was powdered to the same degree of fineness as in the first set of experiments, in Analysis 9 the material was very finely powdered and in Analyses 10 and 11 the material was rather coarsely powdered.

No. of analysis.	Weight of I_2O_5. Grams.	Weight of H_2O. Gram.	Per cent. of H_2O.
5	25.5	0.00066	0.0026
6	25.3	0.00062	0.0025
7	24.9	0.00113	0.0045
8	26.8	0.00100	0.0037
9	18.9	0.00077	0.0041
10	21.3	0.00133	0.0062
11	25.0	0.00155	0.0062

The differences in composition of the pentoxide actually observed, even with very widely differing methods of treatment, are so small that there can be no doubt that the slight variations in treatment likely to occur in the course of an analysis could not have had an appreciable effect.

The Specific Gravity of Iodine Pentoxide.—In order to find out exactly the buoyant effect of air upon the weight of the pentoxide an accurate knowledge of the specific gravity of the substance was necessary. The density was determined by displacement of kerosene of known specific gravity, by pentoxide which had been prepared as previously described by heating in a small platinum boat. The boat was weighed in a small weighing bottle, and immediately after the weighing the boat was covered with kerosene in the bottle. The bottle was placed in a small vacuum desiccator and the desiccator was kept exhausted with continual jarring until apparently every trace of air had been displaced from the powder. A special pycnometer stopper[1] was next inserted in the bottle and the pycnometer was set while immersed in a water bath at 25° C.

THE SPECIFIC GRAVITY OF IODINE PENTOXIDE.

Specific Gravity of Kerosene = 0.7655.

Weight of I_2O_5 in vacuum. Grams.	Weight of displaced kerosene in vacuum. Gram.	Specific gravity of I_2O_5. $25^\circ/4^\circ$.
5.5136	0.8811	4.790
5.2704	0.8393	4.807
	Average,	4.799[2]

The vacuum correction for one apparent gram of iodine pentoxide calculated from the above value for the density is +0.000106 gram, the

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[1] For details of pycnometer and setting see Baxter and Hines, *Amer. Chem. J.*, **31**, 220 (1904).

[2] At 0° Ditte obtained the value 4.487. At 9° Kammerer obtained the value 4.799. Filhol found the density to be 4.250. Dammer, *Handb. der anorg. Chem.*, **1**, 560.

weights being assumed to have the density 8.3.[1] Silver has been found to have the density 10.49,[2] hence its vacuum correction is —0.000031.

A nearly new No. 10 Troemner balance was used in all the weighings. It was readily sensitive to one-fiftieth of a milligram. The weights were carefully standardized to hundredths of a milligram by the method described by Richards.[3]

The Adsorption of Air by Iodine Pentoxide.—Since the pentoxide is formed by a process of double efflorescence, it must be extremely porous, with consequently an unusually large surface with relation to its weight. Hence it might be supposed that such a substance could adsorb appreciable amounts of gases, possibly even air. Stas, in the case of sublimed ammonium chloride, found that this substance does in fact adsorb air, and hence he weighed the chloride contained in an exhausted vessel.[4] This question was investigated with iodine pentoxide by determining the difference in weight of the substance in a vacuum and in air.

Two weighing bottles were constructed with long very well ground stoppers which terminated in stopcocks through which the tubes could be exhausted. These tubes were very closely of the same weight and of very nearly the same internal capacity. The tubes were first exhausted and compared in weight by substitution. Next they were filled with dry air and again weighed, the weighings being carried out with the stopcocks open. Both steps were then repeated with essentially the same results.

Into one of the tubes was introduced about twenty-five grams of carefully dried pentoxide and both tubes were completely exhausted. When the tube containing the pentoxide was warmed to about 150° no perceptible quantity of gas was evolved. After the difference in weight of the exhausted tubes had been determined, they were again filled with dry air and weighed, and the process of exhausting the tubes and filling them with air was repeated. In all the weighings the tubes were treated as described in the case of the phosphorus pentoxide tubes.

		Gram.
I.	Difference in weight of exhausted tubes	0.01405
I.	Difference in weight of tubes filled with air	0.01395
I.	Difference in air content of tubes	0.00010
II.	Difference in weight of exhausted tubes	0.01415
II.	Difference in weight of tubes filled with air	0.01397
II.	Difference in air content of tubes	0.00018
	Average difference in air content of tubes	0.00014

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[1] Baxter, *Proc. Amer. Acad.*, **42**, 209 (1906).

[2] Richards and Wells, *Pub. Carnegie Institution*, **28**, 11 (1905).

[3] THIS JOURNAL, **22**, 144 (1900).

[4] *Untersuchungen* (Aronstein's translation), p. 56 (1867).

		Grams.
	Weight of tube with iodine pentoxide	58.6353
	Weight of tube	32.7966
	Weight of iodine pentoxide	25.8387
I.	Difference in weight of exhausted tubes, one containing iodine pentoxide	25.85120
I.	Difference in weight of tubes filled with air at 19° C. and 758 mm	25.84473
	Difference	0.00647
	Average difference in air content of empty tubes	0.00014
	Air displaced by I_2O_5 at 19° and 758 mm	0.00633
II.	Difference in weight of exhausted tubes, one containing iodine pentoxide	25.85091
II.	Difference in weight of tubes filled with air at 20° C. and 768 mm	25.84430
	Difference	0.00661
	Average difference in weight of empty tubes	0.00014
	Air displaced by I_2O_5 at 20° and 768 mm	0.00647
	The same corrected to 19° and 758 mm	0.00641
	Average weight of air displaced by I_2O_5 at 19° and 758 mm.	0.00637
	Weight of air displaced by I_2O_5 at 19° and 758 mm. calculated from the density 4.799	0.00649

The agreement in the air displaced as determined experimentally and as calculated from the observed density is as close as could be expected, showing that the vacuum correction determined on page 213 is correct. It is to be noted that if air is adsorbed by the powder the observed weight of air displaced would be less than that calculated from the density. This seems to be actually the case to a very slight degree.

THE RATIO OF SILVER TO IODINE PENTOXIDE. SERIES I.

BY G. S. TILLEY.

Sample I of Iodic Acid and Sample B of Silver were Used.

No. of analysis.	Corrected weight of I_2O_5 in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Weight of AgI. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio $2Ag:I_2O_5$.
1[1]	6.06570 9.48035	3.92046 6.12703	0.00042 0.00200	3.92027 6.12611	0.646234
2	7.73052	4.99599	0.00077	4.99564	0.646223
3	12.63909	8.16804	0.00058	8.16777	0.646231
4	9.49913	6.13884	0.00094	6.13841	0.646208
5	8.34369	5.39206	0.00008	5.39202	0.646239
6	8.83155	5.70748	0.00071	5.70715	0.646223
7	6.77487	4.37836	0.00071	4.37803	0.646216
				Average,	0.646225

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[1] The first two analyses were inadvertently mixed, and hence are combined in the table.

The atomic weights of iodine and silver calculated from the ratio of silver to pentoxide depend of course upon the ratio of the atomic weights of silver and iodine. The latter ratio has recently been subjected to careful revision by one of us,[1] and has been found to have the value 0.848843. Using this ratio the atomic weight of silver calculated from the above data is 107.847.

This value is highly sensitive to changes in the ratio of silver to iodine, a negative error of one one-hundredth of a per cent. producing a negative error of three-hundredths of a per cent. in the atomic weight of silver. Hence if the above value of the atomic weight of silver is too low, it might be expected that the ratio of silver to iodine also is too low. From the work of both Köthner and Aeuer[2] and Baxter, however, it seems certain that the ratio of silver to iodine is at any rate no higher than the value used in our calculations.

The result of the experiments which have been described is unexpected. For although several recent investigations have shown that the atomic weight of silver may be possibly as low as 107.87, referred to oxygen 16.000, no evidence has yet been published which indicated a value as low as the foregoing. Accordingly a new series of experiments was undertaken, similar to the early one, with even greater pains to avoid possible sources of error.

Two new specimens of iodic acid were prepared. In order to determine whether crystallization of the iodic acid alone was sufficient purification, Sample II was made from iodine which had been purified by only a single distillation from solution in an iodide, and then by one from water, while the nitric acid was once distilled through a quartz condenser with no special attempt to remove chlorine. A portion of the iodic acid was prepared in the transparent fused quartz flask as already described. The remainder was made in a large opaque fused-quartz dish nearly one liter in capacity. The inside of this dish had been abraded with sand to break the edges of the bubbles, and had been digested for hours with acid solutions to remove soluble impurities. The combined specimens of acid were crystallized at least ten times in dishes of transparent fused quartz, with centrifugal drainage, until free from the organic odor previously mentioned. In the preparation of this sample the solutions were always heated and evaporated upon an electric stove under a large Victor Meyer funnel, instead of in the special evaporating apparatus previously described.

The second specimen of acid was prepared from iodine resulting from the decomposition of the iodine pentoxide in the water determinations. It was first dissolved in pure sulphurous acid and then set free from solution by distillation with recrystallized potassium permanganate, a

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[1] Baxter, *Proc. Amer. Acad.*, 41, 73 (1905).

[2] Liebig's *Ann.*, 337, 123 (1904).

little less permanganate than was necessary to set free all the iodine being employed. The product was thus distilled once from a dilute solution of an iodide. Finally the iodine was once distilled from pure water. The nitric acid for this preparation was carefully freed from chlorine by double distillation with a quartz condenser as previously described. The iodine was converted into iodic acid by treatment with the nitric acid in the large opaque quartz dish used for the preparation of Sample **II**. Before the crystallization of the iodic acid was commenced, the powder resulting from the treatment of the iodine with nitric acid was drained and heated on the electric stove until apparently all nitric acid had been expelled. Then it was heated to 300° in a current of pure dry air in small portions in a platinum boat. The resulting iodine pentoxide was dissolved in water and at least ten times recrystallized in quartz dishes from solution in the purest water, with centrifugal drainage in platinum Gooch crucibles. In spite of the drastic treatment to which the iodine had been subjected before conversion into iodic acid, the mother liquors of the first crystallization were by no means free from the organic odor previously observed, although nitric acid seemed to have been completely removed. This odor disappeared gradually during crystallization as before, and the final product was free from odor. This specimen is designated Sample III.

Two new specimens of silver were employed. A portion of one had already been used in an investigation upon the atomic weight of lead.[1] This sample was precipitated once as silver chloride, once as metal by ammonium formate, and was finally electrolyzed. This specimen is designated Sample C. Sample D was employed in an investigation upon the atomic weight of bromine.[2] It was first purified in part by precipitation as chloride, in part by precipitation with ammonium formate. The combined material was then subjected to two electrolyses. Both specimens were finally fused in a current of pure hydrogen.

The acid was converted into pentoxide exactly as in the first series. Then, after weighing, it was dissolved and reduced with a slight excess of hydrazine as before, and precipitated with a slight excess of silver. After filtration and evaporation of the filtrate the excess of silver was determined gravimetrically as silver iodide in a Gooch-Munroe-Neubauer crucible.

Essentially no change was made in the method of analysis in Analyses 8 and 9 except that a slight excess of hydrazine was employed. At this point a tube 50 cm. in length filled with glass pearls was substituted for the column of bulbs in the reduction apparatus, since it was feared that traces of the spray produced by the effervescence during reduction might

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[1] Baxter and Wilson, *Proc. Amer. Acad.*, 43, 365 (1907).

[2] Baxter, *Ibid.*, 42, 201 (1906).

have been carried through the bulbs by the current of nitrogen disengaged. The pearls were moistened with sulphurous acid before reduction was commenced. This change in the apparatus was without effect, the succeeding five analyses giving results identical with previous ones. In Analyses 15 to 17 the method of precipitation was reversed by pouring the iodide solution into the silver nitrate solution. This change also was without effect, hence it is reasonably certain that the dilution of the solutions during precipitation was sufficient to prevent occlusion of perceptible amounts of either iodide or silver nitrate. It is worth pointing out that occlusion of iodide would lower the observed atomic weight of silver, while occlusion of silver nitrate would produce the opposite effect. The occlusion of ammonium nitrate by the silver iodide would of course be without influence upon the final result.

In one analysis which is not recorded in the table about one-quarter of the iodic acid was reduced by means of sulphurous acid, the ratio of silver to iodine in this experiment being slightly higher than in the other cases, owing doubtless to the occlusion of silver sulphate. In another analysis the attempt was made to precipitate the silver iodide from ammoniacal solution by adding the silver nitrate solution to the slightly ammoniacal solution of the iodide. Köthner and Aeuer[1] and Baxter have shown that silver iodide formed in ammoniacal solution is freer from occluded matter than when formed in acid solution. This experiment was a failure, for silver was reduced to the metallic state owing to the slight excess of hydrazine.

The question of adsorption of silver nitrate by the precipitate was further tested in several instances by evaporating the wash waters of the silver iodide separately from the filtrate. In every such case only a mere trace of silver could be detected, even when the precipitate was allowed to stand in contact with the wash waters for several hours.

No experiments were performed to test for complete reduction of the iodic acid to hydriodic acid, since evidence upon this point is already available. Sammet[2] has recently determined the equilibrium constant for the reaction of iodides upon iodates in acid solution to be as follows:

$$\frac{(H^+)^6.(IO_3^-).(I^-)^5}{(I_2)^3} = 2.8 \;.\; 10^{-47}.$$

$$i.\ e.,\ IO_3^- = \frac{(I_2)^3}{(H^+)^6.(I^-)^5}. \;.\; 2.8 \;.\; 10^{-47}.$$

Since after reduction by the hydrazine the concentration of the free iodine approximates zero, and since the concentrations of the hydrogen and iodide ions are fairly large, and since the constant itself is extremely

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[1] *Loc. cit.*

[2] *Z. physik. Chem.*, 53, 640 (1905).

small, it is evident that the concentration of residual iodate must have been vanishingly small.

A few analyses which met with known accidents are omitted from the following table.

THE RATIO OF SILVER TO IODINE PENTOXIDE. SERIES II.

BY G. P. BAXTER.

No. of analysis.	Sample of I_2O_5.	Sample of Ag.	Corrected weight of I_2O_5 in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Weight of AgI from filtrate Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio $2Ag:I_2O_5$.
8	II	B	12.09036	7.81397	0.00167	7.81320	0.646234
9	II	B + C	6.29744	4.07015	0.00127	4.06957	0.646226
10	II	A	10.89880	7.04362	0.00092[1]	7.04309	0.646226
11	II	D	9.33895	6.03554	0.00106	6.03505	0.646222
12	II	A	10.15370	6.56194	0.00055	6.56169	0.646236
13	III	D	11.00453	7.11201	0.00130	7.11141	0.646226
14	III	A	7.01649	4.53456	0.00055	4.53431	0.646236
15	III	D	9.33573	6.03362	0.00125	6.03304	0.646231
16	III	D	8.72163	5.63666	0.00103	5.63619	0.646231
17	III	D	9.01524	5.82603	0.00025	5.82591	0.646229
						Average,	0.646230

The average of this series is higher than that of Series I by less than one one-thousandth of a per cent., the atomic weight of silver calculated from the ratio of silver to pentoxide being 107.850. While it is true that impurity in the iodic acid not containing halogens would tend to lower the observed atomic weight of silver, the close agreement of the two series carried out with material of fairly diverse nature practically eliminates impurity in the iodic acid or silver as the cause of the low resulting value for the atomic weight of silver. . Sample I of iodic acid was crystallized only three times from aqueous solution, while Samples II and III were both crystallized at least ten times. It is improbable that any impurity could have passed through the additional crystallizations without appreciable diminution in quantity. It has already been shown that mineral impurities were surely absent even before the crystallization of the acid. Nitric acid could hardly have survived the prolonged heating at 240°, even if it had not been completely removed by the many crystallizations of the iodic acid.

With regard to impurities containing halogens other than iodine, it may be pointed out that Samples I and III were prepared from iodine and nitric acid which had been very thoroughly freed from chlorine and bromine while even in the case of Sample II only traces of chlorine could have been present. Aside from these facts it is decidedly improbable that an oxygen acid of either chlorine or bromine could have been formed and then have accompanied the iodic acid during its purification, for

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[1] AgBr.

during the heating of the acid both before and after crystallization such impurities would have been either volatilized or destroyed. Impurity of chlorine would probably tend to lower the observed atomic weight of silver on account of the relatively high solubility of silver chloride. For the same reason a trace of chlorine in either the hydrazine or the nitric acid employed in the analysis would have had no injurious effect. Impurity of bromine would produce the reverse effect if present in the form of a compound analogous to iodine pentoxide.

The presence of a halogen of higher atomic weight than iodine, forming an insoluble silver salt, if present as pentoxide would lower the observed atomic weight of silver. The existence of such an element is purely hypothetical, however, and what evidence exists is contrary to such an hypothesis. One of us has recently searched for such an element in vain.[1]

Two other possible contingencies must be considered, the presence of either free iodine or oxides of iodine higher than the pentoxide. Free iodine might result from reduction of the pentoxide during the heating. Such reduction or decomposition actually does take place to an extremely slight extent when the pentoxide is heated to 240°, for traces of free iodine can be detected in air that has been passed over iodine pentoxide at that temperature. That no appreciable quantity of iodine could remain in the pentoxide was shown by the fact that the solutions of the pentoxide were always absolutely colorless even when concentrated. Furthermore it was found by experiment that a mere trace of iodine could be detected by its color in such a solution. About one one-hundredth of a per cent. of iodine in the pentoxide would be necessary to raise the observed atomic weight of silver by one one-hundredth of a unit.

Iodine heptoxide might result from either the presence of periodic acid in the iodic acid or from auto-oxidation of the pentoxide during the heating. Both possibilities are wanting in plausibility, for it is not at all probable in the light of the known instability of the heptoxide that the latter substance could have withstood the high temperature of heating. Twenty-five thousandths of a per cent. of heptoxide in the iodic acid would be necessary to lower the observed atomic weight of silver by one one-hundredth of a unit.

Although it is intended to pursue the study of iodic acid farther in this laboratory, and the results presented in this paper are published subject to revision, it is of interest to consider the bearing of these results upon other recent investigations. Noyes and Weber[2] have found the atomic weight of chlorine, referred to oxygen 16.000, to be 35.452. Assuming the ratio of silver to chlorine found by Richards and Wells, 3.04260, the atomic weight of silver calculated from Noyes and Weber's results is 107.866.

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[1] Baxter, *Proc. Amer. Acad.*, 40, 422 (1904).

[2] THIS JOURNAL, 30, 13 (1908). Morley's value for hydrogen is used.

On the other hand Edgar[1] finds chlorine to be 35.461 referred to oxygen 16.000, whence silver is 107.893. Richards and Forbes[2] have found the per cent. of silver in silver nitrate to be 63.5005. Upon this basis, if the atomic weight of silver is assumed to be 107.850, the atomic weight of nitrogen is 13.991. The results of this research certainly confirm the belief that Stas's values for the atomic weights of silver and nitrogen are much too high.

We are very greatly indebted to the Carnegie Institution of Washington for pecuniary assistance which has done much to aid the progress of this research; also to the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

The results of this research may be briefly summed up as follows:

1. The preparation of pure iodic acid is described.
2. The existence of the compound $I_2O_5.HIO_3$ is confirmed.
3. It is shown that while iodic acid may be almost completely converted to pentoxide by heating at 240°, a small proportion of water remains, which is constant for definite conditions of heating.
4. It is shown that silver iodide occludes silver sulphate and that sulphur dioxide may not be used as a reducing agent if the iodine is to be precipitated by means of silver.
5. Hydrazine salts are found to be suitable reducing agents.
6. The specific gravity of iodine pentoxide at 25° referred to water at 4° is found to be 4.80.
7. It is shown that iodine pentoxide does not adsorb appreciable amounts of air.
8. The ratio of silver to iodine pentoxide is found to be 0.646230.
9. Upon this basis, if oxygen is assumed to be 16.000, the atomic weight of silver is 107.850 and that of iodine is 126.891.

CAMBRIDGE, MASS., November 24, 1908.

ON THE OXIDATION OF HYDRAZINE. III.

BY A. W. BROWNE AND F. F. SHETTERLY.

Received November 24, 1908.

The present article contains the description of a series of experiments upon the behavior of hydrazine sulphate in aqueous solution toward the following oxidizing agents: potassium persulphate, potassium permanganate, hydrogen peroxide, potassium perchlorate, sodium periodate, lead dioxide, red lead and manganese dioxide. The experiments have been performed primarily for the purpose of investigating the possible formation of hydronitric acid and ammonia as products of the reaction between these oxidizing agents and hydrazine sulphate, and for the pur-

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[1] *Chem. News*, 98, 97 (1908).

[2] *Pub. Car. Inst.*, 69, 47 (1907).