[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHTS OF SILVER AND IODINE.

[SECOND PAPER.]

THE RATIO OF SILVER TO IODINE.

BY GREGORY PAUL BAXTER.

Received October 22, 1910.

Introduction.

In a recent investigation upon the atomic weights of silver and iodine, Baxter and Tilley[1] determined the ratio between silver and iodine pentoxide to be 0.646230. Then, the ratio of silver to iodine having previously been found by Baxter[2] to be 0.849943, the per cent. of iodine in the pentoxide was calculated, and thence the atomic weights of iodine and silver. Since the results obtained in this way were unexpectedly low, 126.891 and 107.850 respectively, while several recent investigations, especially that of Richards and Willard[3] on the ratio of lithium chloride to lithium perchlorate, have shown the atomic weight of silver to be not far from 107.871, and since all known possible causes of error in the determination of the ratio of silver to iodine pentoxide were very carefully investigated, it was possible that the final results might have been influenced by an error in the ratio of silver to iodine. This error need be only very slight to explain the discrepancy, because a given percentage error in the ratio of silver to iodine produces one three times as large in the atomic weights of iodine and silver, but in the opposit direction.

In the determination of the ratio of silver to iodine[4] the preparation of silver iodide in every case formed one step in the procedure. The latter substance is, however, difficult to obtain in a pure condition on account of its strong tendency to occlude soluble silver salts. The difficulty was eliminated as far as was possible at the time, either by precipitation of the silver iodide in ammoniacal solution, or by precipitation at high dilution, these precautions having been shown by both Köthner and Aeuer[5] and Baxter[6] to be beneficial. The evidence obtained in the investigation upon iodine pentoxide indicates that even the pains taken in the early work upon the silver-iodine ratio to avoid occlusion by the silver iodide may not have been sufficient entirely to eliminate the difficulty, and hence that the above value of the silver-iodine ratio is too high. Furthermore, it is noticeable that many of the earlier results upon the silver-iodine ratio indicate a perceptibly lower value for the

---

[1] THIS JOURNAL, **31**, 201 (1909).

[2] *Proc. Am. Acad.*, **40**, 419 (1904); **41**, 73 (1905). THIS JOURNAL, **26**, 1577; **27**, 876.

[3] *Pub. Carnegie Inst.*, No. **125** (1910). THIS JOURNAL, **32**, 4.

[4] Baxter, *Loc. cit.*

[5] *Ann.*, **337**, 123 (1904).

[6] *Proc. Am. Acad.*, **41**, 77 (1905). THIS JOURNAL, **27**, 880.

ratio than the one given above, while most of the possible errors would have tended to produce too high a result. Hence new experiments were instituted for the investigation of the silver-iodine ratio.

It seemed highly desirable in these new experiments to carry out the determination of the ratio of silver to iodine in as nearly as possible the same way as in the determination of the ratio of silver to pentoxide, and also to use material which had been purified in as nearly as possible the same way. Thus constant errors which might enter into the determination of the latter ratio would be likely to be compensated by similar errors in the determination of the former ratio.

The method, in brief, was as follows: Weighed quantities of iodine were reduced to hydriodic acid by a solution of hydrazine hydroxide. After considerable dilution the iodine was precipitated as silver iodide by a very dilute solution of silver nitrate containing a few tenths of a milligram excess of silver. The clear supernatant solution was carefully filtered and evaporated to small bulk, and the excess of silver was determined gravimetrically as silver iodide.

Purification of Materials.

Iodine.—Three specimens of iodine were employed. Sample 1 was made from iodic acid remaining from the research upon iodine pentoxide.[1] The iodic acid had been prepared by the action of the purest fuming nitric acid upon very pure iodine, in quartz vessels, and had been crystallized ten times from aqueous solution in a quartz dish.

A second specimen of iodic acid was made from potassium iodate in the following manner: Potassium permanganate was allowed to react with potassium iodide in concentrated hot solution. The products of this reaction are potassium iodate, potassium hydroxide and manganese dioxide. After the precipitated manganese dioxide had been separated from the solution by decantation and filtration, the solution was evaporated to crystallization, and the crystals were carefully separated from the mother liquor by centrifugal drainage. The mother liquor was several times evaporated until the greater part of the iodate had been recovered. A second portion of potassium iodate was made by allowing potassium permanganate to react in concentrated solution with iodine after the addition of a small quantity of potassium hydroxide. The iodine was probably dissolved by the hydroxide with the formation of iodide and iodate, and the iodide was then converted to iodate by the permanganate. At any rate, the products of the reaction were, as in the previous instance, potassium iodate, potassium hydroxide, and manganese dioxide, the hydroxide being formed in smaller proportions than before. The potassium iodate was obtained from the solution by crystallization as described above. Both portions of iodate were combined and purified

---

[1] Baxter and Tilley, *Loc. cit.*

by one recrystallization from aqueous solution, with centrifugal drainage.

From the potassium iodate barium iodate was next prepared by adding to a hot solution of the potassium iodate a hot solution of a nearly equivalent amount of barium hydroxide. The precipitated barium iodate was very carefully washed by decantation with cold water. Very little loss of material takes place during this washing since the barium iodate is only slightly soluble in cold water. The barium iodate, suspended in a comparatively small amount of water, was then converted into barium sulphate and iodic acid by means of an approximately equivalent amount of sulphuric acid at boiling temperature. Since reactions of this sort, which involve the change of one solid into another, progress to completion only with difficulty, the barium sulphate was left in contact with the solution for several days with intermittent heating and shaking. Finally the solution of iodic acid was separated from the barium sulphate by decantation, and was evaporated to small bulk in a platinum dish. Further decantation allowed the removal of traces of barium sulphate which were suspended in the original decantate. The solution was finally evaporated to crystallization in the platinum dish. Somewhat more than a kilogram of iodic acid was prepared in this way.

The final purification of the acid was effected by a long series of crystallizations, as described in the latter part of the paper by Baxter and Tilley.[1] The first mother liquor was found to contain a slight excess of sulphuric acid. This was shown to have been eliminated during the first crystallizations by reducing portions of the mother liquors and testing for sulphate. The barium sulphate, whether dissolved or suspended, was effectually removed during the crystallizations, the solution of acid being occasionally decanted from traces of insoluble material which were present during the first crystallizations. In all, this iodic acid was subjected to eleven crystallizations, the usual process of fractional crystallization being followed in order to avoid too serious loss of material owing to the high solubility of iodic acid, even at ordinary temperatures.

Since chlorides and bromides are not converted to the salts of the oxy-halogen acids by permanganate, it seems probable that the first portion of potassium iodate was free from the corresponding salts of chlorine and bromine. Whether this is true of the second portion, made from iodine, is doubtful, since if the original iodine contained these two elements they would have dissolved in the alkaline solution with the production, to some extent, of chlorate and bromate. Later, however, after the conversion of the iodate to iodic acid, free chloric and possibly bromic acids must have been either vaporized or decomposed during the subsequent treatment.

---

[1] THIS JOURNAL, 31, 216 (1909).

This material differed in its preparation from that used in the earlier determinations of the ratio of silver to iodine pentoxide, and hence a portion of it will soon be used for new determinations of the latter ratio. Iodine made from this iodic acid is designated Sample II.

For comparison with the iodine obtained from the iodine pentoxide, two experiments were made with a third specimen similar to the iodine used in the earlier determinations of the ratio of silver to iodine. This iodine was first distilled from solution in potassium iodide. The product was thus freed from all but traces of chlorine and bromine. Next it was converted into hydriodic acid by suspending the iodine in water and passing hydrogen sulphide through the solution until reduction was complete. The solution of hydriodic acid was boiled to coagulate the sulphur and was filtered. In order to free the hydriodic acid from hydrocyanic acid which might have had its source in iodide of cyanogen contained in the original material, the solution was boiled for several hours until the concentration approached that of the constant-boiling solution. From this hydriodic acid the iodine was set free by the addition of a very nearly equivalent amount of potassium permanganate and distillation into a flask cooled with running water. In this way, since only five-eighths of the iodine is set free by the permanganate, the iodine was a second time distilled from an iodide. The product was distilled once with steam, and after drainage was dried over concentrated sulphuric acid. This specimen is designated Sample III.

Silver.—Several samples of silver were used, most of which have been employed in other similar investigations. Sample A was purified by Mr. A. C. Boylston for work upon the analysis of phosphorus tribromide.[1] This material was prepared by first precipitating the silver as chloride from strongly acid solution, with subsequent reduction by means of sodium hydroxide and sugar. The metal was fused upon charcoal before a blowpipe and the surface impurities were removed from the buttons by scrubbing with sea sand and etching with dilute nitric acid. The cleansed buttons were dissolved in nitric acid, and the solution, after neutralization, was precipitated with ammonium formate which had been prepared with distilled materials. The metal was thoroughly washed with water and was again fused with even more care than before in a crucible lined with the purest lime. The resulting buttons were in turn cleansed by etching with dilute nitric acid and were next converted into electrolytic crystals in a cell in which a concentrated, nearly neutral solution of silver nitrate served as electrolyte, and a pile of the buttons served as anode, the cathode being a stick of very pure silver from another preparation. After the crystals had been very thoroughly washed with water, they were fused in a current of hydrogen in a porcelain boat lined with the

---

[1] Not yet published.

purest lime. The boat was provided with cavities so that the buttons of silver varied considerably in size, from 2 to 5 grams. The final product was cleansed from adhering lime by etching with dilute nitric acid and, after being washed with the purest water, it was dried, first in air at 100°, finally in a vacuum at about 500°.

Sample B was prepared in an exactly similar fashion by Dr. H. C. Chapin for work upon the atomic weight of neodymium,[1] except that it was necessary to cut the product into smaller fragments by means of a jeweler's saw. Surface contamination with iron from the saw was removed by etching with successive portions of dilute nitric acid until the acid remained free from iron. Sample C was purified by Mr. Victor Cobb for work upon the analysis of ferrous bromide in a way exactly similar to that used in the purification of Sample A.[2] Sample D was used in an investigation upon the atomic weight of bromine.[3] This material had been precipitated once as silver chloride. The product was reduced with sodium hydroxide and sugar and was twice deposited electrolytically as described above in the case of Sample A.

These methods of purification have already been discussed and shown to be efficient in several papers from this laboratory, especially by Richards and Wells.[4] As will be seen later, the different specimens of silver all gave essentially identical results in this investigation. Several of them have already been compared, with a like outcome.

The Ratio of Silver to Iodine.

In the earlier determination of the ratio of silver to iodine the method employed was as follows: Iodine was sublimed into a weighed tube; next, after being weighed, it was reduced by means of sulphurous acid, and the very dilute solution of iodide was precipitated with a very dilute solution of an equivalent amount of silver nitrate. The end point was then determined in a nephelometer.

In the present instance certain very considerable modifications of the earlier method were made. In the first place, owing to occlusion of silver sulphate by silver iodide, sulphurous acid has been found to be unsuitable as a reducing agent,[5] hence hydrazine hydroxide was substituted. The products of reduction were, therefore, only nitrogen gas and hydriodic acid. In the second place, in the investigation upon the ratio of silver to iodine pentoxide it was found that, even if exactly equivalent amounts of silver and iodine are employed, the end point as determined in a nephelometer is somewhat uncertain, owing to the great dilution

[1] *Proc. Am. Acad.*, **46,** 213 (1910).

[2] This investigation will soon be published.

[3] Baxter, *Proc. Am. Acad.*, **42,** 201 (1906); THIS JOURNAL, **28,** 1322.

[4] *Pub. Carnegie Inst.*, No. **28,** 16 (1905). THIS JOURNAL, **27,** 472.

[5] Baxter and Tilley, THIS JOURNAL, **31,** 208 (1909).

of the mother liquor and, in all probability, to disturbances due to traces of colloidal precipitate.[1] Therefore, as in the investigation upon iodine pentoxide, instead of attempting to determin the end point in this way, a very slight excess of silver was used, and the excess was found by evaporating the mother liquor to very small bulk and then estimating the silver gravimetrically as silver iodide. Owing to the strong tendency of silver iodide permanently to occlude silver nitrate, the excess of silver was very small indeed, as a rule less than 0.2 milligram. Furthermore, both the solution of the iodide and the solution of silver nitrate were made very dilute before precipitation in order to avoid as far as possible the aforesaid occlusion. In the third place, much larger quantities of material were employed so that accidental errors should be of less significance.

In all but the last three experiments the tube in which the iodine was weighed was of glass, about 18 centimeters long and 1.8 centimeters in external diameter. The ends of the tube were constricted and were provided with well fitting ground-glass caps in order to avoid vaporization of the iodine during the weighing of the tube and the subsequent manipulation.

The iodine was prepared for weighing by first dehydrating a suitable quantity of iodic acid in a platinum boat in a current of pure dry air, as described in the paper upon the analysis of iodine pentoxide. The air was purified by being passed over hot copper gauze, and then through a system of towers containing in succession glass beads moistened with silver nitrate solution, a solution of potassium hydroxide containing potassium permanganate, and concentrated sulphuric acid containing a small amount of potassium dichromate. The final drying of the air was effected with phosphorus pentoxide which had been freshly sublimed in a current of oxygen. The apparatus was constructed wholly of glass with fused joints. The boat containing the iodic acid was placed in a hard glass tube through which the current of air was passed, the tube being heated by means of the solid aluminium oven which has been described elsewhere.[2] The first stage of the dehydration of iodic acid takes place rapidly at 100° if it has been previously ground with a small percentage of the substance produced in the first stage of the dehydration, $HIO_3.I_2O_5$. Inoculation with this phase not only reduces the temperature at which the dehydration begins, but also diminishes the proportion of moisture finally retained by the pentoxide.[3] As soon as water ceased to be given off, the temperature was raised until the second and final stage in the dehydration began, at about 220°. Finally the pentoxide was

---

[1] Baxter and Tilley, THIS JOURNAL, **31**, 210 (1909).

[2] Baxter and Coffin, *Proc. Am. Acad.*, 44, 184 (1909). THIS JOURNAL, **31**, 206.

[3] Baxter and Tilley, THIS JOURNAL, **31**, 212 (1909).

heated for one hour at 240°. Iodine pentoxide which has been dried in this way has been found to contain only a little over 0.002 per cent. of residual moisture.[1] The water formed during the dehydration was, of course, carefully expelled by heating the hard glass tube.

Next the iodine pentoxide was converted into iodine and oxygen by heating the section of the tube containing the boat to about 350°. The iodine was allowed to condense in the cooler portions of the tube beyond the boat, although, of course, a slight loss of iodine took place. During this decomposition it seems certain that the trace of residual moisture in the pentoxide must have been eliminated. Nevertheless, for the sake of certainty, before the iodine was sublimed into the weighing tube, it was heated slightly above its melting point, 114°, in the current of dry air. The weighing tube was then placed in position, with the constricted end of the hard glass tube inserted for a short distance into one end of the weighing tube, the weighing tube being supported upon a glass stand. The iodine was slowly sublimed into the weighing tube by gently warming the hard glass tube. Finally the iodine in the weighing tube was heated to fusion and allowed to solidify. The caps were placed on the weighing tube, which was allowed to stand near the balance case, under a bell jar containing concentrated sulphuric acid, for several hours. During the manipulation the weighing tube was handled only with clean, cork-tipped forceps.

Since during the sublimation of the iodine the hard glass tube must have been slightly attacked, and since it is possible that alkali iodides thus formed could have been carried into the weighing tube with the iodine, a quartz tube was substituted for the hard glass tube after the first five experiments. This tube was provided with several constrictions beyond the section in which the boat was placed, which served the purpose first of preventing to a considerable extent the conduction of heat along the tube, and second, of preventing back diffusion of iodine. Since a small amount of undecomposed pentoxide was carried along by the rather rapid current of oxygen evolved during the decomposition, the first constriction in the quartz tube was loosely filled with a roll of platinum gauze which was heated to redness, so that any pentoxide which reached this constriction must have been completely converted to iodine and oxygen. As a matter of fact, neither of these changes produced any perceptible effect upon the results.

When iodine from Sample III was employed, it was sublimed from a platinum boat into the quartz tube and once again from one portion of the tube to another before the final sublimation into the weighing tube.

In order to reduce the iodine to hydriodic acid, it was next dissolved in a solution of an excess of hydrazine hydroxide. A thick-walled flask

---

[1] Baxter and Tilley, This Journal, 31, 212 (1909).

of Jena glass holding nearly two liters was provided with a column of bulbs carefully ground into the neck. In the flask was placed a quantity of a solution of hydrazine hydroxide considerably more than sufficient to combine with the iodine. The hydrazine was made from the sulphate by distillation in a platinum still with an excess of sodium hydroxide, and was redistilled before use. The weighing tube containing the iodine was carefully introduced into the flask, the stoppers being removed in the process, and the column of bulbs was put in place immediately after the introduction of the iodine tube. In this manipulation a small quantity of iodine vapor may have escaped from the tube during the very short time in which it was exposed to the air. However, since the total amount of iodine vapor contained by the tube at 20° was not greater than 0.03 milligram,[1] and since certainly only a small fraction of the total vapor could have escaped into the air outside the flask, and especially since the interior of the flask and the column of bulbs had been moistened with hydrazine solution shortly before the iodine tube was introduced so that any iodine vapor in the flask must have been quickly absorbed, the error from this source must have been very small. The solution of the iodine in hydrazine progresses too rapidly if the iodine has not been previously fused, for crystals of iodine, on account of their large surface, reduce so rapidly that the current of nitrogen issuing from the flask might possibly carry with it traces of iodine vapor. Since acid is produced in this reaction, it was found advantageous to keep the solution nearly neutral by the occasional addition of redistilled ammonia. This had two advantages: first it accelerates the rather slow solution of the fused iodine; secondly, it prevents the possible escape of hydriodic acid vapor from the flask. Several tests in which the nitrogen evolved in the reduction was caused to pass from the top of the column of bulbs through a trap sealed with water showed that in fact no iodine was lost in this way.

After the dilution of the iodide solution to a volume of about one and one-half liters, it was transferred for precipitation to an 8-liter bottle with a carefully ground stopper. Whether or not the solution was ammoniacal at this point, about 25 cc. of constant boiling nitric acid were introduced, after the acid had been diluted to a volume of one liter and boiled to destroy nitrous acid; for unless the nitric acid is free from nitrous acid, iodine is set free. The bottle was immediately stoppered after the addition of the nitric acid, and was allowed to stand for some time after any liberated iodine had been reduced by the excess of hydrazine. In all but the earlier experiments the acid was introduced through a long

---

[1] The vapor pressure of iodine at 20° is 0.2 mm. Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907). The interior volume of the tube was less than ten cubic centimeters.

thistle tube at the bottom of the bottle, so that iodine could not reach the surface of the solution until after the bottle was closed. The amount of iodine set free in this way was, however, in no case large enough to have caused appreciable loss by evaporation. If the solution did not at this point have a total volume of nearly four liters, it was next diluted to this volume.

A quantity of silver, a very few tenths of a milligram, in excess of the amount necessary to combine with the iodine, was weighed out, the greater part being in buttons weighing several grams each, the final adjustment of the weight being made with tiny ignited electrolytic crystals. This silver was dissolved in redistilled nitric acid which had been diluted with an equal volume of water, in a flask provided with a column of bulbs to catch possible spatterings. The silver was dissolved so slowly, however, that very little effervescence took place, nitrous acid rather than nitric oxide being formed. The solution was then further diluted and heated until free from nitrous acid. Next the silver nitrate solution was diluted to a total volume of nearly four liters and then was slowly added to the solution of hydriodic acid in the precipitating bottle, with continual agitation during the precipitation. The precipitating bottle was shaken violently for a short time, and was allowed to stand for at least one week with occasional shaking until the supernatant liquid seemed to be absolutely clear. The clear liquid was then filtered through a Gooch-Munroe-Neubauer crucible with a very dense mat of platinum sponge, so that, although the filtration proceeded slowly, there seemed to be certainty that every particle of suspended silver iodide was removed during the filtration. The filtered solution was evaporated to a very small bulk, until the greater part of the free nitric acid had been expelled. Toward the end of the evaporation small quantities of silicic acid separated out. Consequently, before the precipitation of the silver in the evaporated filtrate, it was filtered a second time through the Neubauer crucible. The total volume of the solution, after the second filtration, was not more than 100 cc. and frequently was as small as 50 cc. To this solution was added a quantity of a solution of pure hydriodic acid large enough completely to precipitate the silver. Several days' standing were usually necessary to insure sufficient coagulation of the opalescent silver iodide for filtration. Then the precipitate was collected upon a small weighed Neubauer crucible, and, after being heated to about 200°, it was weighed. In order to show that no silver iodide was lost in this filtration, in several instances the filtrate was evaporated to small bulk and tested nephelometrically for silver, always with essentially negative results. The quantity of silver used in each experiment was so carefully adjusted before precipitation that the silver content of the filtrate seldom amounted to more than 0.5 milligram, and in all but two of the later experiments it was less than 0.2 milligram.

During every experiment the glass tube in which the iodine was weighed lost slightly in weight. In a few cases the loss amounted to as much as 0.3 milligram, although in many it was hardly more than 0.1 milligram. This loss in weight was probably due in part to the action of the iodine on the glass with the formation of soluble iodides. Since these iodides would have dissolved during the reduction of the iodine, the error from this source must have been considerably less than the loss in weight of the tube. Furthermore, it is very probable that the loss in weight of the weighing tube was caused in part by the solvent action of the ammoniacal hydrazine solution and possibly to mechanical abrasion of the ground surfaces during the manipulation.

In the last three experiments the glass weighing tube was replaced by a similar quartz tube with glass caps. Although the loss in weight was somewhat diminished by this change, it was not wholly prevented, the losses in the first two of the three experiments being 0.00010 and 0.00020 gram, respectively. In these three experiments it is more probable that the difficulty was due to the solvent action of the hydrazine solution and to abrasion than to action of the iodine on the quartz. If this is the case, the results would not be at all affected by the loss in weight of the tube.

One of the chief dangers in these experiments lies in the occlusion of silver nitrate by the silver iodide. For this reason the solutions were made as dilute as possible before precipitation. In the first ten analyses the volumes of the two solutions before precipitation were nearly four liters, while in the last three analyses the volumes were between seven and eight liters. Hence the concentrations varied between eightieth normal in analysis 5 and thirtieth normal in analysis 2. The fact that the results seem to be independent of the concentrations is strong evidence that the occlusion could not have been very serious. The attempt was made, however, to secure further evidence that this occlusion was negligible by conducting the precipitation in two analyses (9 and 10) in reverse fashion, *i. e.*, by pouring the hydriodic acid solution into the silver nitrate solution. Although the opportunity for occlusion of silver nitrate was evidently very much greater in these two experiments than in the others, the results of analyses 9 and 10 agree so well with those of the others that very little doubt can exist that the occlusion of silver nitrate had been prevented. Similar evidence was obtained in the analysis of iodine pentoxide.[1]

The solubility of silver iodide has been found by Kohlrausch[2] to be only

---

[1] THIS JOURNAL, **31**, 218.

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

0.0000035 gram per liter at 21°. In 8 liters of mother liquor there would be dissolved then only 0.00003 gram of silver iodide while the wash waters would contain a trace more. The correction for the equivalent amount of silver or iodine would not amount to more than 0.0002 per cent. in any one of the first ten analyses. In the last three analyses the volume of the mother liquor was at least 16 liters. Hence the dissolved silver iodide amounted to 0.00006 gram. However, since larger quantities of material were used in the last three experiments, the percentage correction due to solubility is no greater.

Evidence that the Neubauer crucible was an effective filtering medium is to be found in the fact that in many of the analyses the quantity of silver iodide obtained from the filtrate was not much greater than the amount which should have been dissolved. Furthermore, in one analysis, the only one completed which is not recorded in the following table, the filtrate was found to contain only a mere trace of silver. The crucible which was employed in all the analyses, with a water pump vacuum, allowed from one to two liters of solution to pass per hour.

In the following table are given the results of all the analyses which were completed, with the exception of the one mentioned above in which no silver was found in the filtrate. The silver used in this experiment, if it was exactly equivalent to the iodine, yielded a ratio of silver to iodine very close to the other analyses, 0.849916, but on account of the uncertainty as to whether the silver was sufficient to combine with the iodine, and because the analysis met with a slight accident, it has been considered wiser to omit this result in computing the average.

The weights of the silver and the iodine are corrected to the vacuum standard by subtracting 0.000031 gram for each apparent gram of silver and adding 0.000099 for each apparent gram of iodine.[1] The weights were carefully standardized by the method described by Richards.[2]

Results and Discussion.

A careful examination of the following table shows that neither the variations in the specimens of silver and iodine employed, nor those in the methods of analysis produced appreciable effects upon the results. The extreme difference in the ratio of silver to iodine is 0.007 per cent.; but all except three of the results agree within 0.003 per cent. and the last ten analyses within 0.005 per cent. The final average is 0.005 per cent. lower than the result previously obtained, 0.849943, while no one of the thirteen analyses yielded a result as high as the above figure. This outcome confirms the suspicion previously expressed on page 1591

---

[1] Calculated from the following specific gravities: Weights, 8.3; silver, 10.49; iodine, 4.93; air, 0.0012.

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

that the silver iodide obtained in the earlier determinations of the silver-iodine ratio was contaminated by occluded impurities.

The Ratio of Silver to Iodine.

No. of analysis.	Sample of silver.	Sample of iodine.	Weight of silver. in vacuum. Grams.	Weight of iodine in vacuum. Grams.	Weight of silver iodide corrected for solubility. Gram.	Corrected weight of silver in vacuum. Grams.	Ratio Ag : I.
1	A	I	7.65478	9.00628	0.00022	7.65468	0.849927
2	A	I	11.43208	13.45067	0.00062	11.43179	0.849905
3	A	I	10.08602	11.86648	0.00067	10.08571	0.849933
4	A	II	7.24530	8.52461	0.00070	7.24498	0.849890
5	A	II	5.46366	6.42840	0.00033	5.46351	0.849902
6	B	II	7.05651	8.30266	0.00022	7.05641	0.849897
7	B	III	8.45918	9.95288	0.00030	8.45904	0.849909
8	A	II	5.92510	6.97131	0.00042	5.92591	0.849899
9	A	II	7.97952	9.38852	0.00055	7.97927	0.849897
10	C	II	5.58238	6.56811	0.00015	5.58231	0.849911
11	A	III	16.03919	18.87136	0.00036	16.03902	0.849913
12	A	II	15.16312	17.84091	0.00136	15.16249	0.849872
13	D	II	12.71182	14.95666	0.00027	12.71170	0.849902
						Average,	0.849906

When the average ratio is combined with that of silver to iodine pentoxide, 0.646230, the atomic weights of silver and iodine are found to be 107.864 and 126.913, respectively. On the basis of 107.864 for the atomic weight of silver, the older value of the silver-iodine ratio yields 126.907 as the atomic weight of iodine, *i. e.*, the newer value raises the apparent atomic weight of iodine referred to silver by 0.006 unit. It is of interest to note that a positive error of 0.0003 per cent. in the ratio of silver to iodine is necessary to lower the apparent atomic weight of silver by one one-thousandth of a unit, while a negative error of 0.0002 per cent. in the ratio of silver to iodine pentoxide produces the same effect. The agreement of the final value for the atomic weight of silver with that recently found by Richards and Willard, 107.871, is as satisfactory as could be expected from consideration of the widely different methods employed in the two researches. There seems to be little doubt that the atomic weight of silver lies nearer 107.87 than 107.88, the commonly accepted value. Further evidence upon the ratio of silver to iodine is desirable, and it is intended to pursue the investigation by new determinations of the ratio of silver to silver iodide and of silver chloride to silver iodide.

I am very greatly indebted to both the Carnegie Institution of Washington and the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum and quartz apparatus.

Cambridge, Mass.