[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF IODINE.

SECOND PAPER.

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VERY RECENTLY, in an investigation upon the atomic weight of iodine,[1] the value 126.975 for this constant was obtained as the average from three closely agreeing ratios. Experiments subsequent to the publication of this research have shown that the results of all three methods were subject to slight errors, and that the atomic weight of iodine is even slightly higher than the above value. Following is a description of these experiments, with details where the processes differed from those previously described. For further information the first paper should be consulted.

THE RATIO OF SILVER IODIDE TO SILVER BROMIDE AND SILVER CHLORIDE.

In the previous investigation the ratio AgI : AgCl was determined by heating silver iodide in a current of chlorine in six experiments which yielded an average result of 126.975, calculated upon the basis of silver 107.93 and chlorine 35.467. The latter value for chlorine was a preliminary one, found in an investigation by Richards and Wells then in progress in this laboratory. Later experiments by these chemists have shown that the atomic weight of chlorine is in reality 35.473,[2] which necessitates a positive correction for the atomic weight of iodine of 0.010. The corrected value, 126.985, agrees very closely with two determinations, made in the course of the earlier investigation, in which silver iodide was heated in a current of carbon dioxide and bromine. Assuming the atomic weight of bromine to be 79.955, the value found by Stas and repeatedly verified by experimenters in this laboratory,[3] these two determinations give the values 126.987 and 126.985. The results obtained by reference both to chlorine and to bromine thus became almost identical. However, in order to confirm these two determinations with bromine, further experi-

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[1] Baxter: *Proc. Am. Acad. of Arts and Sci.*, **40**, 419 (1904); also *Z anorg. Chem.*, **43**, 14; This Journal, **26**, 1577.

[2] Richards and Wells: "Publications of the Carnegie Institution, No. 28 (1905); also This Journal, **27**, 459.

[3] Richards: *Proc. Amer. Phil. Soc.*, **43**, 119.

ments were carried out in the same manner as before, as follows:

Pure silver iodide was prepared as described in the previous paper, by precipitating pure silver nitrate with a considerable excess of the purest ammonium iodide,[1] washing the precipitate with 1 per cent. nitric acid and pure water, and drying the iodide, in an air-bath, and then by fusion in a tared quartz crucible, first in an atmosphere containing free iodine, and finally in air to expel dissolved iodine. Fusion in an atmosphere containing iodine must have completely converted occluded silver nitrate into silver iodide. The iodide was then heated in a current of air and bromine. The air was purified by being conducted successively over beads moistened with silver nitrate solution, sodium carbonate, and finally concentrated sulphuric acid which had been heated to its boiling-point with a small quantity of recrystallized potassium dichromate to eliminate volatile and oxidizable impurities. Four different samples of bromine were employed, each one of which had been thrice distilled from a solution of a bromide, in each distillation the bromide having been made from a portion of the product of the previous distillation. Chlorine must have been completely separated in this way. The presence of iodine in the bromine was of less importance. Nevertheless each sample, while in the form of hydrobromic acid, was freed from iodine by boiling with several small portions of potassium permanganate. The apparatus for purifying the air and saturating the air with bromine was so constructed that the gases came in contact only with glass. The quartz crucibles were always contained in large porcelain crucibles during the heating in bromine, as well as in the initial fusion of the silver iodide with iodine. Volatilization of the silver halides was prevented by heating very gently at first, at a temperature insufficient to fuse the mixture, then, when the greater part of the iodine had been replaced, until the silver bromide barely fused. Furthermore, the crucible was very deep and the current of gases very slow, so that any volatilized silver halides had opportunity to condense upon the cool walls of the crucible. That no loss from volatilization actually took place was certain for two reasons. In the first place, the weight of the bromide in most cases became constant within a few hundredths of a milligram after once being heated, although subsequently the salt was maintained at a temperature slightly above its melting-point,

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[1] The method of purifying the iodine is described briefly on page 879 of this paper.

for at least an hour. In the second place, the perforated cover and hard glass delivery tube for the bromine, when rinsed with ammonia and the solution treated with hydrochloric acid in excess, gave no visible trace of opalescence. Before the salt was allowed to solidify it was maintained above its fusing-point in air for a few minutes to eliminate dissolved bromine.

The silver bromide resulting from each analysis was converted into silver chloride by heating in a current of pure dry chlorine in a similar fashion.[1] Here also constant weight within a very few hundredths of a milligram was easily obtained, and as before the perforated cover and inlet tube were free from weighable amounts of chloride. It has already been shown that silver chloride and silver iodide when fused in an atmosphere of the corresponding halogens and then in air, retain none of the halogen.[2] The quartz crucibles remained almost absolutely constant in weight during these experiments. From the ratio between the original silver iodide and the silver chloride the atomic weight of iodine was calculated.

The following vacuum corrections were applied: silver iodide, +0.000071; silver bromide, +0.000046; silver chloride, +0.000075.[3] The analyses of Series II were obtained through the bromide, those of Series III are the results from the previous paper recalculated from the higher atomic weight of chlorine, with the exception of Analysis 18, which was made subsequently. All completed analyses are recorded in the tables. Several were lost, owing to breaking of the crucibles.

TABLE I.

Series I. AgI : AgBr.

Number of analysis.	Sample of bromine.	Weight of silver iodide in vacuum. Grams.	Weight of silver bromide in vacuum. Grams.	Atomic weight of iodine.
1	A	13.65457	10.92091	126.985
2	A	17.35528	13.88062	126.987
3	B	9.70100	7.75896	126.982
4	B	10.27105	8.21484	126.983
5	B	9.85688	7.88351	126.986
6	C	8.62870	6.90106	126.991
7	D	11.92405	9.53704	126.981
8	D	7.56933	6.05389	126.987
			Average,	126.985

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[1] For preparation and purification of chlorine, see earlier paper.

[2] See previous paper; also Richards and Wells: *Loc. cit.*, p. 59, and Köthner and Aeuer: *Ann. Chem.* (Liebig), **337**, 127.

[3] The value for the specific gravity of silver chloride is assumed to be 5.56, as determined by Richards and Stull in this laboratory. In the previous paper this value was incorrectly taken as 5.62.

Series II. AgI : AgCl.

Number of analysis.	Weight of silver iodide in vacuum. Grams.	Weight of silver chloride in vacuum. Grams.	Atomic weight of iodine.
9	13.65457	8.33538	126.985
10	17.35528	10.59457	126.983
11	10.27105	6.27006	126.980
12	8.62870	5.26735	126.985
13	11.92405	7.27926	126.976
		Average,	126.982

Series III. AgI : AgCl.

Number of analysis.	Weight of silver iodide in vacuum. Grams.	Weight of silver chloride in vacuum. Grams.	Atomic weight of iodine.
14	9.26860	5.65787	126.990
15	6.72061	4.10259	126.984
16	11.31825	6.90912	126.987
17	10.07029	6.14754	126.979
18	13.49229	8.23649	126.980
		Average,	126.984

THE RATIOS BETWEEN SILVER, IODINE, AND SILVER IODIDE.

In the earlier paper determinations of the ratios of silver to silver iodide and iodine were described. It remained to determine the ratio of iodine to silver iodide. For this purpose iodine was purified as before by thrice converting it into hydriodic acid with hydrogen sulphide, and then heating the hydriodic acid with a slight excess of potassium permanganate which had been freed from chlorine by crystallization. The final product of iodine was distilled once with steam, freed from water by suction upon a porcelain Gooch crucible, and dried as far as possible in a desiccator over concentrated sulphuric acid. It was then sublimed once from porcelain boats in a current of pure, dry air in a hard glass tube, and then a second time from the hard glass tube into the weighing-tube, which was constructed as described in the first paper. This weighing-tube remained constant in weight within a few hundredths of a milligram in each experiment, and lost in weight in all only 0.1 mg. in the eight final analyses. Next, the iodine was dissolved in sulphurous acid, and was then precipitated by adding a solution of a slight excess of pure silver to the solution of hydriodic acid in a precipitating flask. The silver iodide clotted together very rapidly in the presence of the nitric acid and excess of silver, and offered none of the difficulties met when the precipitation is carried out with an excess of iodide, for it may be washed indefinitely with pure cold water without showing the least tendency to pass into colloidal solution. The silver iodide was collected upon a Gooch crucible, dried and weighed. The loss on fusion was determined, and the asbestos shreds in the filtrate were collected. Twelve determinations carried out in this way with solutions varying from tenth- to thirtieth-normal gave results from 126.93 to 126.98. The variations were finally traced to the carrying-down of silver nitrate by the silver iodide, for the more concentrated the solutions during the precipitation and the greater the excess of silver employed, the lower was the observed atomic weight of iodine. The occlusion of silver nitrate by silver halides is well known in the cases of silver bromide and silver chloride, but in these cases it is possible to wash out the occluded salts by oft-repeated treatment with water. The difficulty in removing the silver nitrate in the case of silver iodide is doubtless due to the lesser solubility of this halide. Similar observations have been made by Köthner and Aeuer,[1] who found that with fifth-normal solutions the carrying-down of silver nitrate is very considerable, and that an excess of iodide converts this occluded silver nitrate into silver iodide only very slowly if at all. They found, however, that, if the precipitated silver iodide is washed with ammonia, the greater part of the occluded matter may be eliminated, owing possibly to the slight solubility of silver iodide in ammonia. On account of this newly discovered tendency of silver iodide, it seemed probable that the results of the synthesis of silver iodide from known weights of silver in the early part of this research were somewhat too low, for although the precipitations took place in ammoniacal solution and an excess of iodine was employed, the fact that the solutions were always very nearly as strong as tenth-normal and that the ammonium iodide was poured into the silver nitrate made it probable that occlusion had taken place at least to some extent even here. It is noteworthy that three of these syntheses yielded results as high as 126.985. Similar conclusions are to be drawn concerning the results of the titration of silver and iodine, although in this case precipitation took place in the reverse fashion, *i. e.*, by adding the silver nitrate to the iodide.

Accordingly, experiments were carried out for the redetermination of the ratios of silver to silver iodide and to iodine, as well as the new one of iodine to silver iodide, with special precautions to

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[1] *Ann. Chem.* (Liebig), **337**, 123.

avoid the error of occlusion by using very dilute solutions and no excess of silver. After the iodine had been weighed, very nearly the exact amount of silver to combine with the iodine was weighed out and dissolved in nitric acid with the usual precautions to avoid spattering. The quantity of iodine used in each analysis was between 3 and 4 grams, and the amount of silver consequently about 3 grams. The solutions of both silver and iodine were diluted to a volume of 1 liter each, so that the solutions were about thirtieth-normal, and then the silver nitrate was added very slowly to the solution of hydriodic acid with constant stirring. The flask in which precipitation was carried out was then shaken for some time, and allowed to stand until the supernatant liquid was clear. This liquid was tested for an excess of iodine or silver in a nephelometer,[1] and if a deficiency of either was found it was made up and the solution again shaken, until the point was reached where the extremely faint opalescence produced by both hydriodic acid and silver nitrate was equal in both nephelometer tubes. The excess or deficiency of silver was in no case over 0.1 mg., and in most cases much less.

Several samples of iodine were employed in these analyses, each one of which had been distilled three times from an iodide as previously described. Three different specimens of silver, purified by different methods, were used. Sample A was a portion of the material used in the first investigation. Sample B was prepared from silver nitrate which had been recrystallized seven times from nitric acid, five times from water, and finally precipitated by ammonium formiate.[2] Sample C was precipitated as silver chloride once, electrolyzed once, and finally precipitated with formic acid. All three samples were fused in a current of hydrogen on a lime boat. In order to determine whether an even more gradual addition of silver nitrate would influence the extent of the occlusion, in Analysis 23 the silver was introduced by means of a large funnel provided with a fine spout.

The vacuum corrections, —0.000031 for silver and +0.000102 for iodine were applied. The atomic weight of silver is assumed to be 107.930, as before.

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[1] Richards and Wells: *Am. Chem. J.*, **31**, 235.

[2] Richards and Wells: Publications of the Carnegie Institution, No. 28, p. 19.

TABLE II.

Series IV. Ag : I.

Number of analysis.	Sample of silver.	Weight of iodine in vacuum. Grams.	Weight of silver in vacuum. Grams.	Atomic weight of iodine.
19	A	3.29308	2.79897	126.983
20	B	3.70132	3.14584	126.988
21	B	3.75641	3.19258	126.991
22	B	3.24954	2.76186	126.988
23	A	4.12541	3.50639	126.984
24	C	3.53166	3.00165	126.988
25	C	2.99835	2.54842	126.985
26	C	2.00015	1.69991	126.993
			Average,	126.987

In one of the foregoing analyses the attempt was made to determine the ratio between iodine and silver iodide by adding an excess of silver nitrate and weighing the precipitate. Although only 5 mg. excess of silver nitrate were added, and the total volume of the liquid was over 2 liters, the precipitate was 1 mg. heavier than it should have been as calculated from the result of the titration, showing that the occlusion of silver nitrate by the silver iodide may take place even after precipitation. In order to avoid this difficulty, in succeeding analyses the silver iodide was collected without the addition of silver nitrate, after washing with pure water; then the dissolved silver iodide was determined in the filtrate and wash-water, by comparing the precipitates produced by the addition of silver nitrate with those formed in standard solutions of hydriodic acid. As a matter of fact, the filtrates were always found to be practically free from silver iodide, while the wash-waters contained from 0.2 to 0.4 mg. per liter. This difference in solubility of the silver iodide in the filtrate and wash-waters is probably due to colloidal solubility of this salt in pure water. The loss on fusion of the silver iodide and the asbestos shreds were determined as usual. The almost absolute lack of opalescence in the filtrate when treated with silver nitrate or hydriodic acid is a good proof of the complete absence of chlorine and bromine, since both silver bromide and silver chloride are considerably more soluble than the iodide.

TABLE III.

Series V. I : AgI.

Number of analysis.	Weight of iodine in vacuum. Grams.	Corrected weight of silver iodide in vacuum. Grams.	Atomic weight of iodine.
27	3.75641	6.94913	126.987
28	3.24954	6.01137	126.989
29	4.12541	7.63204	126.977
30	3.53166	6.53351	126.979
31	2.99835	5.54682	126.983
		Average,	126.983

Finally, in order to determine the ratio of silver to silver iodide, the filtrate and wash-waters were evaporated to very small bulk, until the greater part of the nitric acid had been expelled, and then the amount of silver in the residue was determined nephelometrically, after dilution to 25 cc., by adding an excess of hydriodic acid and comparing with standard solutions of silver. This quantity, which was never more than 0.1 mg., was subtracted from the original weight of silver, and no correction was applied to the weight of silver iodide for the amount dissolved in the wash-water.

TABLE IV.

Series VI. Ag : AgI.

Number of analysis.	Sample of silver.	Corrected weight of silver in vacuum. Grams.	Corrected weight of silver iodide in vacuum. Grams.	Atomic weight of iodine.
32	B	3.19249	6.94877	126.990
33	B	2.76175	6.01110	126.986
34	C	3.00189	6.53399	126.993
35	C	2.54833	5.54659	126.986
			Average,	126.989

The close agreement of the averages of the different series makes it certain that no constant error of magnitude still remained undetected in any one of the methods.

In Series I, II and III, the three chief possible errors have been considered and shown to have no effect. Occluded silver nitrate in the silver iodide was eliminated by fusion in iodine, and it was proved both that no volatilization of the halides actually took place and that no halogen was retained by the solidified salt. In Series IV, V and VI, the chief possible error, that of occlusion of silver nitrate by silver iodide, was avoided by sufficiently diluting the solutions before precipitation. That the dilution was sufficient was evident from the agreement of the results of the experiments with the larger and smaller quantities of material, the total volume of the solutions being the same in all cases. Furthermore, the weight of the silver iodide obtained in the analyses recorded in Series V was in every case very nearly equal to the sum of the weights of silver and iodine employed (Series IV), which could not have been the case if silver nitrate had been retained by the iodide. One is forced, then, to conclude that the average of all six series, 126.985, represents the atomic weight of iodine within a very few thousandths of a unit, and that the results of the syntheses of silver iodide described in the first paper are slightly too low, owing to occlusion of silver nitrate by the silver iodide. Furthermore, the agreement of the results from silver bromide with those of the other series is an indication that the assumed atomic weight of bromine, 79.955, is very nearly correct. However, from the weights of silver bromide and silver chloride produced in the same analyses, the atomic weight of bromine may be computed.

TABLE V.

Series VII. $AgBr : AgCl$.

Sample of bromine.	Weight of silver bromide in vacuum. Grams.	Weight of silver chloride in vacuum. Grams.	Atomic weight of bromine.
A	10.92091	8.33538	79.955
A	13.88062	10.59457	79.951
B	8.21484	6.27006	79.952
B	7.87887	6.01352	79.956
C	6.90106	5.26735	79.951
D	9.53704	7.27926	79.952
		Average,	79.953

Stas's value and the value obtained in this laboratory[1] are thus confirmed. A repetition of these experiments with precipitated fused silver bromide is now under way.

Shortly after the publication of my first paper upon the atomic weight of iodine there appeared the complete paper of Köthner and Aeuer upon the same subject.[2] These chemists, by determining the ratio $AgI : AgCl$, obtained the value 126.936 ($Cl = 35.45$; $Ag = 107.93$) as the average of eight closely agreeing analyses. One synthesis, by precipitating a weighed amount of silver with hydriodic acid, gave the value 126.978, and from one synthesis by

[1] Richards: *Loc. cit.*

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

heating a weighed amount of silver in iodine the result 126.963 was obtained. A second paper[1] by the same authors contains a recalculation of their results from the higher value of chlorine, 35.467, and a critical discussion of their own, Ladenburg's[2] and my work. In this second paper two main criticisms of my investigation are made. One of these concerns the validity of the conclusion that ordinary iodine does not contain an undiscovered halogen element. This criticism is founded upon a mistaken understanding, however. My experiments were directed to prove the existence or non-existence of an element of *higher* atomic weight than iodine, which, if its properties were those to be expected from the properties of the other members of the halogen family, would have been set free from solutions of its compounds by iodine, and hence would have accumulated in the first fraction of the fractional separation (see page 1580 of the first paper). The existence of an unknown halogen of lower atomic weight than iodine was not considered.

Although Köthner assumes the possibility that such an element exists, it is obviously improbable that any halogen of lower atomic weight could have remained in the purified samples of iodine which were employed in my experiments; since those specimens which received even the least purification were thrice distilled from an iodide, the iodide having been made in each distillation from nearly one-half the iodine from the previous distillation.

In the second place, it is maintained that volatilization of silver halides takes place when silver iodide is heated in a current of chlorine. This is undoubtedly true, unless precautions are taken to prevent the volatilization. Silver iodide is much more volatile at its fusing temperature than silver chloride; and if the original silver iodide is fused before the current of chlorine or bromide is begun, a loss may take place by volatilization or possibly by *spattering*. In my own work, however, fusion of the salt was always avoided until the greater part of the change had taken place. Proof that no volatilization of silver halides actually occurred in my experiments has already been given (page 877). It may be added that the close agreement of the results of Series I and II is additional evidence in the same direction; for any loss of silver bromide, which is the most volatile of the three halides, would

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[1] *Ann. Chem.* (Liebig), **337**, 362 (1904).

[2] *Ber. chem. Ges.*, **35**, 2275.

have tended to raise the results of Series II above those of Series I, whereas such slight difference as exists is in the opposite direction.

Köthner's average result in the series AgI : AgCl, when recalculated upon the basis of chlorine 35.473, becomes 126.974. The slight difference between this value and the final result of the research described in this paper may be explained in several possible ways. A perusal of Köthner's paper does not make clear whether or not fusion of the silver iodide took place at the beginning of his experiments, so that it is uncertain whether the gain in weight of the coil of glass tubing, which was attached to the reaction tube, was due to volatilized silver halides or to attacking of the glass by the hot halogens. At any rate, it is hard to believe that a meter and a half of glass tubing subjected to the long-continued action of mixed chlorine and iodine at 150° should not have altered its weight somewhat. Furthermore, Köthner himself showed that the tube in which the reaction took place was slightly attacked by the fused silver chloride, but the nature of the correction for this attacking of the glass is uncertain. Finally, although the precaution was taken of fusing the silver iodide before the initial weighing, so that the salt must have been free from moisture, it was not fused in an atmosphere of iodine. Hence it is possible that the iodide still contained traces of occluded silver nitrate (or metallic silver). This deficiency in iodine, as well as the possible gain in weight of the apparatus during the experiment, would have lowered the atomic weight of iodine.

As far as Köthner's syntheses of silver iodide from weighed amounts of silver are concerned, it need only be said that, even assuming that occlusion was avoided in the synthesis in the wet way, and that in the synthesis in the dry way a single precipitation of the iodine from solution in an iodide had completely removed such impurities as chlorine and bromine, which would have accumulated in the silver iodide during the experiment, the fact that Richards and Wells[1] have shown that silver fused in the air or with borax and saltpeter, according to Stas, must contain oxygen, makes it certain that the results of Köthner's syntheses are too low.

I am indebted to the Cyrus M. Warren Fund for Research in Harvard University for platinum vessels, quartz crucibles and balance.

[1] Publications of the Carnegie Institution, No. 28, p. 62.

SUMMARY.

The results of this investigation are, then, as follows:

(1) The atomic weight of iodine is found to be 126.985 (Ag = 107.930), one one-hundredth of a unit higher than the value previously obtained. If silver is assumed to be 107.920 and oxygen 16.000, iodine becomes 126.973.

(2) The observation of Köthner and Aeuer that under certain conditions silver iodide occludes silver nitrate, and that this occluded salt cannot be removed by washing with water, is confirmed.

(3) Richards and Wells's value for the atomic weight of chlorine, 35.473, is substantiated.

(4) Stas's value for the atomic weight of bromine, 79.955, is shown to be very nearly correct.

CHEMICAL LABORATORY OF HARVARD COLLEGE,
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[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

THE OPTICAL PROPERTIES OF CASTOR OIL, COD-LIVER OIL, NEAT'S-FOOT OIL, AND A FEW ESSENTIAL OILS.

BY HERMANN C. LYTHGOE.

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I. CASTOR OIL.

Castor oil is "a fixed oil expressed from the seeds of *Ricinus communis*. A pale yellowish or almost colorless, transparent, viscid liquid, having a faint, mild odor, and a bland, afterwards slightly acrid, and generally offensive taste; Sp. gr., 0.950 to 0.970 at 15° C.," U. S. Pharmacopoeia.

Several authorities state that castor oil rotates the plane of polarized light, although Allen claims that all the samples examined by him were inactive[1]. Deering and Redwood report that twenty-three samples of Indian castor oil, polarized in a 200 mm. tube in a Laurent instrument, gave readings from + 7.6° to + 9.7°[1]. This corresponds to from 21.9° to 28.0° Ventzke.

During the routine examination of drugs in this laboratory, there has been occasion to examine a large number of samples of

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[1] Lewkowitsch: "Oils, Fats and Waxes," p. 420.