our guide in interpreting the reactions of carbon chemistry since 1833, is no longer tenable. It must be replaced by the conception of dissociation in its broadest sense. Fundamentally speaking, there are but two classes of carbon compounds—the saturated and the unsaturated. Excluding reactions called ionic, a chemical reaction between two substances always first takes place by their union to form an addition product. The one molecule being unsaturated and partially in an active molecular condition absorbs the second molecule because it is partially split or dissociated into two active portions. The resulting addition product then often dissociates spontaneously, giving two new molecules. The similarity of such reactions to those called ionic is at once apparent, but their relationship can not, in the present state of our knowledge, be clearly understood.

A REVISION OF THE ATOMIC WEIGHT OF IODINE.

BY GREGORY PAUL BAXTER.

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THE atomic weight of iodine has been for some time considered one of the best determined of chemical constants, owing to the extremely concordant results of Stas and Marignac, who both deduced the value 126.85 ($O = 16.000$) from syntheses of silver iodide. Within the last two years, however, two series of determinations, one by Ladenburg and one by Scott, have yielded results over one-tenth of a unit higher than the above. Ladenburg's method consisted in heating silver iodide in a current of chlorine until all the iodine had been displaced, and gave the result 126.96, while Scott, like Stas and Marignac, synthesized silver iodide and obtained in two analyses the values 126.96 and 126.98.[1] The anomaly in the atomic weights of iodine and tellurium has always been of the greatest interest, and has led to a large number of investigations upon the atomic weight of tellurium during the last few years, which have shown conclusively that this value lies in the neighborhood of 127.6. The doubt thrown upon the

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[1] Very recently, since the work described in this paper was completed, Köthner and Aeuer have published a preliminary notice of experiments involving syntheses of silver iodide as well as a repetition of Ladenburg's work, from which they conclude that the atomic weight of iodine cannot be lower than 126,963. Details of their work are not given. See *Ber. d. chem. Ges.*, 37, 2536.

atomic weight of iodine by the work of Ladenburg and Scott makes it imperative to subject iodine to further careful investigation.

PART I.

THE RATIO OF SILVER TO SILVER IODIDE.

In choosing a compound for an atomic weight determination, two of the most important points to be considered are the stability of the substance under various conditions, and the certainty with which the atomic weights are known of those elements, besides the one under examination, which compose it. In the case of iodine, few of its compounds are stable, and the only one which satisfies both the above conditions is silver iodide. Accordingly, synthesis of silver iodide from a weighed amount of silver was selected for the first method of investigation.

Purification of Materials.—The problem of purification of materials was a comparatively simple one. Silver was prepared as follows: To a solution of silver nitrate which had been made strongly acid with nitric acid, there was added a large excess of concentrated hydrochloric acid. After the precipitate had been washed many times wth pure water, it was reduced to metallic silver by means of a solution of sodium hydroxide and invert sugar. The silver was washed well with water and fused with a blowpipe on charcoal. Surface impurities were removed by scrubbing the buttons with sand, and boiling them, first with dilute hydrochloric acid, and then with ammonia. Next, the whole of the process, just described, was repeated, but with reagents which had been purified with the greatest care. Water and acids were freshly distilled, the sodium hydroxide was electrolyzed in a platinum dish until free from iron, and the final fusion was carried out in a porcelain crucible lined with the purest lime. This lining was made by the ignition of a mixture of reprecipitated calcium carbonate and recrystallized calcium nitrate. After the buttons had been cleansed as before, the silver was deposited electrolytically by making one button the cathode, the other buttons in succession the anode, in a cell containing a strong solution of silver nitrate made by dissolving one of the buttons in pure nitric acid. Connection was made with the battery by means of a platinum wire, which, however, did not dip into the solution. The crystals of silver were washed, first with water, then with ammonia, and again several times with water. Finally they were dried and fused in a current of hydrogen on a boat of pure lime contained in a porcelain tube. The hydrogen was generated electrolytically from a cell composed of zinc amalgam, hydrochloric acid, and platinum, and was purified from hydrochloric acid and dried by passing over beads moistened with caustic potash solution and then over solid potassium hydroxide. The silver was cut into fragments weighing from 3 to 5 grams each by means of a clean chisel and anvil, and the iron adhering to the surface was removed by warming the pieces repeatedly with fresh portions of dilute nitric acid, until iron could no longer be detected in the acid. The fragments were washed thoroughly with the purest water, then with ammonia, and again with water as before. They were allowed to dry in the air, and finally the last traces of moisture were eliminated by heating in a vacuum, since silver which is heated to a high temperature in the air has been shown by Stas to absorb considerable oxygen.[1] Silver prepared in a similar fashion by investigators in this laboratory has always been found to be pure,[2] and since two different samples were used in the following work with identical results, there can be no doubt of the purity of that employed here. Furthermore, one synthesis of silver chloride, carried out with a portion of this silver by Wells in the investigation of Richards and Wells upon the atomic weight of chlorine, yielded the value 35.467, which is identical with the average of other similar determinations made with his own silver.

The chief impurities in commercial iodine are halogens of lower atomic weight and iodide of cyanogen. These were removed by dissolving iodine in a strong solution of half its weight of potassium iodide, and distilling the greater portion of the iodine from a retort into a flask cooled with cold water. The iodine thus obtained was next converted into hydriodic acid by covering it with considerable water and passing through the solution a stream of hydrogen sulphide. This gas was generated by the action of dilute sulphuric acid upon ferrous sulphide, and was purified by bubbling through three gas washing-bottles containing water and through two towers filled with beads moistened with water. The reaction between the hydrogen sulphide and the iodine results

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[1] *Œuvres Complètes*, 3, 125.

[2] *Proc. Am. Acad.*, **28**, 22; **29**, 46; **31**, 173; **39**, 249.

chiefly in the formation of hydriodic acid and the precipitation of sulphur, although a small quantity of sulphuric acid is always produced. Iodide of cyanogen with hydrogen sulphide yields hydrocyanic acid, hydriodic acid, and sulphur.[1] The solution was first boiled for a short time until the sulphur had clotted together, and the sulphur was removed by filtration. The clear solution was then boiled for several hours in order to eliminate the hydrocyanic acid.[2] Finally the hydriodic acid was partially converted into iodine by distilling the solution with potassium permanganate. This permanganate must also have had the effect of oxidizing any organic impurities. Since in the reaction three-eighths of the iodine remains in the form of iodides, the resulting iodine was thus subjected to a second distillation from an iodide. The product was again converted into hydriodic acid by means of hydrogen sulphide, and this again into iodine by recrystallized potassium permanganate which was free from even a trace of chlorine. Since in the case of bromine it has already been shown that two distillations from a pure bromide are sufficient to free this element from chlorine,[3] three distillations of iodine from a solution of an iodide should insure complete elimination of chlorine and bromine, even if the original substance were very impure. The purified iodine was again converted into hydriodic acid by hydrogen sulphide, and this into ammonium iodide by an excess of freshly distilled ammonia. This material was used in the analyses made with Sample I.

It was suggested by Professor T. W. Richards that an undiscovered element resembling the halogens, but of a higher atomic weight, might exist, and an attempt to detect the existence of such an element was carried out as follows: One pound of iodine was purified as described above, but the process of converting the iodine into hydriodic acid by hydrogen sulphide, and the hydriodic acid into iodine by potassium permanganate, was repeated four times. The iodine obtained in the last distillation with permanganate, amounting in all to about 50 grams, was set free in four fractions by introducing the permanganate in portions of about 2 grams each. An element belonging to the halogen family, and of higher atomic weight than iodine, should be more easily

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[1] Dammer: *Handb. d. anorg. Chem.*, II, 1, 432.

[2] Richards and Singer: *Am. Chem. J.*, **27**, 205.

[3] *Proc. Am. Acad.*, **28**, 17; **31**, 165; **37**, 106; **39**, 249.

set free than iodine, hence the first of the four fractions should have contained nearly all of such an element which occurred in the pound of iodine. Each one of the fractions was once distilled with pure water, and was then converted into ammonium iodide, as in the case of Sample I. The first fraction was Fraction 1 of Sample II, the fourth was Fraction 4 of Sample II. No difference in appearance between these samples and Sample I or even the original crude iodine could be detected.

All reagents used in the course of the purification or in the analyses were carefully purified. Acids and ammonia were redistilled, usually with the use of a platinum condenser. The water was distilled twice, once from alkaline permanganate, once from a solution containing a trace of sulphuric acid. In both distillations block-tin condensers were used.

Method of Analysis.—In order to convert a known weight of silver into silver iodide the following method was employed. The silver was dissolved in nitric acid in an Erlenmeyer flask, into the neck of which a column of glass bulbs was ground.[1] The acid consisted of the constant boiling distillate diluted with an equal volume of water. Solution was effected by warming so gently that almost no gas was evolved. When the silver was completely dissolved, the solution was diluted with an equal volume of water and was heated until all nitrous acid was destroyed and all oxides of nitrogen were expelled. It was then transferred to one of the precipitating flasks. These were Erlenmeyer flasks of 1 and 2 liters capacity, into the necks of which glass stoppers had been carefully ground.[2] Into the solution of silver nitrate, which had been diluted until not more than 1 gram of silver was contained in 100 cc., and to which an excess of ammonia had been added, a slight excess of the solution of pure ammonium iodide, which also had been diluted until it was not stronger than 1 per cent., was poured. The flask was stoppered and shaken for some time and allowed to stand for about a day. Then a very slight excess of nitric acid was introduced, the flask again shaken for some time, and allowed to stand for one or two days until the solution above the precipitate seemed perfectly clear. The precipitate was washed by decantation with 1 per cent. nitric acid at least eight times, and transferred with water to a

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[1] Richards: *Proc. Am. Acad.*, **25**, 198.

[2] Richards: *Ibid.*, **28**, 24.

weighed Gooch crucible through which the washings had been poured. Finally the crucible was heated in an electric air-bath for several hours, first at 100° to 110°, then at 200° C.

Although silver iodide is very slightly sensitive to diffused daylight, the operations of precipitation and filtration were performed in a large cupboard lighted wth orange light. When taken out of the dark room, the flask was enveloped in several thicknesses of black cloth.

The tendency of precipitated silver iodide to pass into a milky condition when washed with pure water is very marked. It has been found by Stas and others that if the water is previously heated to about 60° C., and plenty of time is allowed for the precipitate to settle at that temperature, this tendency can be overcome. When washed with warm water, however, silver iodide adheres to the flask to such an extent that it is impossible entirely to remove the precipitate, even by vigorous rubbing. The conditions which were found most favorable for preserving the precipitate in such a state that it could be easily and rapidly manipulated were as follows: In the first place precipitation was carried out in ammoniacal solution, because the silver iodide clotted together much more rapidly than in acid solution, owing probably to the greater solubility of silver iodide in the alkaline solution. A large excess of nitric acid also coagulated the precipitate, but since the acid caused the separation of a large amount of iodine, it could not be employed in the present case. Dilute nitric acid, on the other hand, proved to be a satisfactory medium for washing the silver iodide, for it was found that the precipitate could be washed indefinitely with even 1 per cent. nitric acid wihout passing into the colloidal state. The washings obtained in this way, when treated with an iodide, gave no trace of opalescence even on long standing, showing that silver iodide is insoluble in the dilute acid. When silver iodide which has been washed with nitric acid only is dried at a high temperature, a loss of iodine takes place, owing to action on the silver iodide by the nitric acid. This was evident from the dark color of the iodide. In order to avoid this difficulty, the precipitate was finally transferred to the Gooch crucible with pure water, sometimes after one rinsing with water. The nitric acid was so completely displaced by this means that the precipitate did not darken even on fusion. Unfortunately, even this slight washing with water in most cases caused some of the precipitate to pass through the crucible in a colloidal condition; consequently, these last washings were collected separately. In the earlier analyses the silver iodide in this colloidal solution was determined by first boiling the solution with a small quantity of ammonium iodide until the silver iodide was coagulated, and then collecting the precipitate upon a small filter-paper, together with the asbestos shreds and any silver iodide which were contained in the remainder of the filtrate and washings. As a rule, this operation was performed only after the wash waters had stood for two or three days, in order that insoluble matter might have time to settle. The bottom of each flask was rubbed gently with a rubber-tipped stirring rod to detach adhering particles. Finally the filter-paper was burned in a weighed porcelain crucible at as low a temperature as possible, for if a high temperature is employed, a loss of silver iodide by volatilization occurs. The ash was treated with a drop of nitric acid, and, after warming, a drop of ammonium iodide solution was added. The excess of acid and ammonium salt was driven off and the crucible was weighed.

In these earlier analyses it was found necessary to detach small particles of adhering silver iodide from the neck of the precipitating flask by rubbing with a rubber-tipped rod. Later a better method was devised for collecting this small amount of precipitate, together with that contained in the colloidal washings. First the flask was rinsed with a small quantity of a solution of potassium cyanide, and this solution was poured into the colloidal washings. Then the solution was evaporated to small bulk and electrolyzed in a weighed platinum crucible, which was heated to 130° in an electric oven, and was finally reweighed. The film was dissolved in dilute nitric acid and the solution precipitated with an excess of ammonium iodide. This precipitate of silver iodide, if over 0.0005 gram in weight, was collected on a small weighed Gooch crucible, and the filtrate, together with the original filtrate and wash waters, was passed through a small filter repeatedly until clear. If the precipitate weighed less than the above quantity, it was collected wholly upon a filter. These filters were, of course, ignited and treated as before. The weight of the silver iodide and asbestos was used in computing the results, the weight of electrolyzed silver serving merely as a check upon the weight of silver iodide.

In order to drive off the last traces of moisture from the silver iodide it was fused in a porcelain crucible. The bulk of the precipitate, freed as completely as possible from asbestos, was transferred to a clean crucible, which was then weighed with its cover. The crucible and cover were placed inside a large porcelain crucible, and were heated until fusion took place. A temperature much above the melting-point of silver iodide was avoided, since this substance is distinctly volatile at higher temperatures. The loss in weight was then determined. The fused salt, when cold, was light yellow in color, with no trace of darkening, showing that no appreciable loss of iodine had taken place.

The density of pure silver iodide was found by displacement of water. Three determinations were made with material which had been fused in a porcelain crucible and cooled by pouring the fused mass upon a cold tile. The solidified salt was broken into small fragments and was introduced into a weighed pycnometer for solids, which was then reweighed. Water sufficient to cover the salt was introduced into the pycnometer and the system was placed in a vacuum desiccator which was kept exhausted until it seemed probable that all air had been extracted from the solid. Then the pycnometer was immersed in a bath at 25° C. and exactly filled with water. Finally the system was weighed. Two more determinations were carried out with material which had been cast into sticks by pouring the fused salt into a porcelain boat. These sticks were used in an elongated form of pycnometer for solids.[1] The average of the last two experiments is undoubtedly more accurate than that of the first three, since it was extremely difficult to pump out the air from the more porous material used in the first experiments.

The vacuum correction for silver iodide, when weighed with brass weights, calculated from this value for its specific gravity, is + 0.000071 gram for every apparent gram of salt. A vacuum correction of — 0.000031 gram was applied to every apparent gram of silver.

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[1] Baxter and Hines: *Am. Chem. J.*, **31**, 222.

Weight of silver iodide in vacuum. Grams.	Weight of water displaced in vacuum. Grams.		Density of silver iodide. 25°/4°.
15.5871	2.7590		5.650
14.5141	2.5652		5.658
16.3685	2.8853		5.673
		Average,	5.660
21.5876	3.8017		5.678
16.7274	2.9505		5.669
		Average,	5.674[1]

The platinum-plated brass weights were twice carefully standardized to hundredths of a milligram, and the two sets of corrections agreed to within 0.02 mg. in every case. Two short-armed Troemner balances. sensitive to a fiftieth of a milligram with a load of 50 grams, were used in the work. All weighings were made by substitution. In the case of the Gooch crucible a platinum tare, and in the case of the porcelain crucibles, porcelain tares were used.

In the following table are given the results of all the syntheses which were completed without accident. The atomic weight of silver is assumed to be 107.930 in the calculations.

THE ATOMIC WEIGHT OF IODINE.

Preliminary Series. Ag : AgI.

No. of analysis.	Sample of iodine.	Weight of silver in vacuum. Grams.	Weight of silver iodide in vacuum. Grams.	Loss on fusion. Gram.	Weight of silver from filtrate. Gram.	Weight of silver iodide and asbestos from filtrate. Gram.	Corrected weight of silver iodide in vacuum. Grams.	Atomic weight of iodine.
1	I	5.23123	11.38079	0.00030	......	0.00482	11.38531	126.970
2	I	3.57039	7.77026	not fused.	......	0.00007	7.77033	126.961
3	I	4.60798	10.02751	0.00047	......	0.00100	10.02804	126.951
4	I	4.52467	9.84838	0.00036	......	0.00020	9.84822	126.986
5	I	4.66256	10.14605	0.00062	......	0.00048	10.14591	126.930
Average								126.960

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[1] The values for the density of silver iodide found by other experimenters are as follows:

Boullay : *Ann. chim. phys.* (2) **43**, 266 (1830)	5.614
Karsten : *J. Chem. Phys.*, **65**, 417 (1832)	5.026
Filhol : *Ann. chim. phys.* (3) **21**, 417 (1847)	5.500
Schiff : *Ann. Chem. Pharm.*, **108**, 21 (1858)	5.35
H. St. Clair Deville : *Compt. Rend.*, **64**, 325 (1867)	5.687 at 0°
Schroeder : *Ann. Chem. Pharm.*, **192**, 295 (1878)	5.650 to 5.718

Final Series. Ag : AgI.

No. of analysis.	Sample of iodine.	Weight of silver in vacuum.	Weight of silver iodide in vacuum.	Loss on fusion.	Weight of silver from filtrate.	Weight of silver iodide and asbestos from filtrate.	Corrected weight of silver iodide in vacuum.	Atomic weight of iodine.
6	I	4.77244	10.38668	0.00020	0.00033	0.00050	10.38698	126.975
7	I	4.82882	10.50876	0.00035	0.00053	0.00140	10.50981	126.977
8	II,1	4.04262	8.79718	0.00058	......	0.00095	8.79755	126.947
9	II,1	1.64711	3.58503	0.00020	0.00015	0.00032	3.58515	126.994
10	II,2	4.86054	10.57440	0.00122	0.0025	lost.	10.57318	126.972
11	II,2	4.83482	10.52213	0.00044	0.00032	0.00072	10.52241	126.967
12	II,3	4.97120	10.81696	0.00025	0.00052	0.00129	10.81800	126.940
13	II,3	3.53858	7.70139	0.00038	0.00017	0.00035	7.70136	126.969
14	II,3	3.89693	8.48181	0.00026	0.00012	0.00032	8.48187	126.985
15	II,4	5.33031	11.59785	0.00034	0.00185	0.00360	11.60111	126.973
16	II,4	5.08748	11.07231	0.00035	0.00017	0.00063	11.07259	126.973

Average 126.970

Average, rejecting analysis 12 .... 126.973

Average of analyses with Sample I 126.976

Average of analyses with Sample II, Fraction 1 ..... 126.971

" " " " " " " 2 ..... 126.970

" " " " " " " 3 ..... 126.977

" " " " " " " 4 ..... 126.973

The results tabulated in the preliminary series were undoubtedly less accurate than those of the final series, since it was in these analyses that experience in handling silver iodide was gained. Hence these analyses are collected by themselves. In the final series the rejection of Analysis 12 seems justifiable, since two other analyses made with the same material yielded results in close agreement and considerably higher than that of Analysis 12.

From an examination of this table two important deductions may be drawn. First, there can be little doubt of the identity of the different samples of iodine, for the extreme averages of the results from the various samples differ by only 0.007 of a unit. The variation in the values from the analysis of Sample II, Fraction 1, was undoubtedly due in the case of Analysis 8 to lack of experience in manipulating silver iodide, for this analysis was the first one to be completed in the final series, and in the case of Analysis 9, to the small quantity of available material. One may conclude without hesitation that, in the material examined in this investigation at least, no new halogen existed.

The second important deduction is that the atomic weight of iodine is evidently very slightly greater than 126.973, for most of the experimental errors, such as loss of silver iodide, or loss of iodine by the silver iodide, would have caused the result to be too low.

PART II.

THE RATIO OF SILVER TO IODINE.

The ratio of silver to iodine was next investigated. The problem of obtaining iodine in a *dry* state presented most difficulties in this portion of the research, and was finally solved as follows: Iodine which had been prepared in the same way as Sample I, was first freed from the greater part of the water which it contained by exposure to concentrated sulphuric acid, which had been boiled to remove every trace of hydrochloric acid. It was then sublimed from a crystallizing dish to the bottom of a glass dish half filled with water, which covered the crystallizing dish. In this way the greater part of the "included" moisture must have been eliminated. The sublimed crystals were finally again sublimed in a current of pure dry air from a porcelain boat contained in a hard glass tube into the weighing-tube. This weighing-tube was about 10 cm. long and 15 mm. in diameter, and was drawn down to less than half this diameter at both ends. Glass stoppers were ground into both ends of the tube. The air was purified and dried by passing over beads moistened with a solution of silver nitrate, then over sodium carbonate, and finally over three feet of beads moistened with concentrated sulphuric acid, all in an apparatus made entirely of glass and connected with the sublimation tube by means of a ground glass joint. During the final sublimation of the iodine, the end of the hard glass tube, which had been drawn down to small diameter, was inserted into one end of the weighing-tube. After the weighing-tube had been filled, the glass stoppers were inserted, the tube was carefully wiped with a slightly damp "chemically clean" cloth, and was allowed to stand in a desiccator for some time. It was then weighed. Needless to say the weighing-tube had been originally treated as above before being weighed empty. Both weighings were made with a counterpoise exactly similar to the weighing-tube.

In all but one of the experiments the weighing-tube was broken during the solution of the iodine, so that it was impossible to weigh the tube after the experiment, and determine how much the glass was attacked by the warm iodine. In one experiment, however, a loss in weight of 0.00032 gram was found. Whether or not this change was accompanied by the evolution of a gas, the loss in weight must have been at least partially due to combination of the iodine with the alkaline metals of the glass, with the formation of soluble iodides which were dissolved by the solution of sulphurous acid. Hence the error must have been considerably less than 0.3 mg., if, as was necessarily the case owing to breakage of the tubes, the first weight of the tube was used in determining the weight of the iodine.

Immediately after being weighed, in order to avoid loss by volatilization, the iodine was converted into hydriodic acid by means of pure sulphurous acid. This acid was made by heating sulphuric acid with metallic copper and collecting the sulphurous oxide in water, and then distilling the sulphurous oxide from the solution into the purest water. During this distillation any trace of halogen acid which might have had its source in either copper or sulphuric acid must have been completely eliminated, for it must have been almost wholly in the ionized condition.

A considerable quantity of this sulphurous acid was poured into one of the precipitating flasks, and the weighing-tube, containing the iodine, was introduced, after the lower stopper had been allowed to drop out of the tube into the flask. The sulphurous acid immediately sealed the open end of the tube so that no iodine vapor could escape. The other stopper was then removed by means of a platinum wire, the wire rinsed into the flask, and the flask quickly closed by means of its glass stopper. Solution of the iodine in the sulphurous acid was hastened by gently agitating the flask. Any iodine vapor which escaped from the tube must have been instantly converted into hydriodic acid. After sufficient time had been allowed for every trace of this hydriodic acid to be absorbed by the solution, the flask was opened and the solution transferred to another precipitating flask, and a slight excess of the purest ammonia added. When iodine is dissolved in a large excess of sulphurous acid the solution becomes colored yellow, owing to the formation of an iodide of sulphur,[1] and, upon standing, this solution may deposit sulphur. Since the solution was made alkaline with ammonia as soon as the iodine was dissolved, with the complete disappear-

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[1] Dammer: *Handb. d. anorg. Chem.*, 1, 557.

ance of the color and without the formation of the slightest trace of a precipitate, no danger was to be feared from this source.

From the weight of the iodine, the weight of silver necessary exactly to combine with it was calculated. This silver was weighed out and dissolved in nitric acid, as described previously in this paper. The solution was diluted until not stronger than 1 per cent. and was added slowly to the already dilute solution of ammonium iodide in the precipitating flask. The flask was shaken for some time, and was then made acid with a considerable excess of nitric acid. Long-continued shaking, followed by several days' standing, yielded a clear supernatant solution. Twenty-five cc. portions of this solution were pipetted into nephelometer tubes and were tested with cubic centimeter portions of hundredth-normal silver nitrate and hydriodic acid solutions in a nephelometer.[1] If an excess of either iodine or silver was present, the deficiency of the other was made up in the remaining solution by addition of standard silver nitrate or hydriodic acid until the exact end-point was reached. It was never necessary to add more than 0.1 mg. of either iodine or silver, so that the liquid removed from the flask for the tests could be neglected. This end-point is very sharp in the case of silver and pure iodine, for so little silver iodide is dissolved that the two nephelometer tubes remain almost absolutely clear. An excess of a 0.1 mg. of silver in a liter of solution is easily detected. This almost complete lack of opalescence in the nephelometer tubes is strong evidence of the absence of even a trace of either chlorine or bromine in the iodine, for silver chloride or bromide, on account of their greater solubility, would have produced much more marked precipitates.

The specific gravity of solid iodine was assumed to be 4.933;[2] hence a vacuum correction of +0.000102 was applied to every apparent gram of iodine.

THE ATOMIC WEIGHT OF IODINE.

Ag : I.

Number of analysis.	Weight of silver in vacuum. Grams.	Weight of iodine. in vacuum. Grams.	Atomic weight of iodine.
17	5.54444	6.52288	126.977
18	6.27838	7.38647	126.979
19	4.57992	5.38814	126.976
		Average,	126.977

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

[2] Ladenburg: *Ber. d. chem. Ges.*, **35**, 1256.

As was to be expected, the average of this series is slightly higher than that of the previous one, and undoubtedly represents very closely the true value of the atomic weight of iodine. Nevertheless, the investigation was not allowed to rest at this point.

PART III.

THE RATIO OF SILVER IODIDE TO SILVER CHLORIDE.

In any atomic weight investigation it is extremely desirable to obtain the value sought by reference to as many different well-known atomic weights as possible. The method of heating silver iodide in a current of chlorine, which has already been used by Berzelius and Dumas, as well as by Ladenburg, furnishes the ratio between iodine and chlorine, and seemed capable of yielding trustworthy results, for since the silver halides fuse at a comparatively low temperature, there is no possibility of inclusion of silver iodide by the silver chloride formed in the reaction, and hence there is certainty that the reaction will be complete.

First, silver iodide was prepared by precipitating an ammoniacal solution of the purest ammonium iodide (Sample I) with a solution of recrystallized silver nitrate. In this operation a slight excess of ammonium iodide was used. The precipitate was well washed with 1 per cent. nitric acid, rinsed with water, and was collected on a Gooch crucible with the use of a disk of filter-paper instead of an asbestos mat. In this way contamination of the precipitate with asbestos shreds was avoided. The silver iodide was finally dried in an air-bath at about 100° C. for at least eight hours. After removal of the filter-paper, those portions of the precipitate which had come in contact with the filter-paper were cut away with a clean knife. Next the substance was fused in a weighed crucible protected from the flame by a very large crucible. While the silver iodide was fused, a small quantity of the purest iodine was placed upon the lower side of a second crucible cover, and this cover was substituted for the one which had been weighed with the crucible. The iodine immediately vaporized and the silver iodide was thus fused in an atmosphere contaning iodine vapor. Finally the cover was removed, so that the uncombined iodine escaped from the crucible, and the salt was kept fused, covered with the original crucible cover, until it was certain that all excess of iodine had been eliminated. That no excess of iodine was retained by the silver iodide was readily shown in one experiment with 18 grams of salt by reheating the salt to its fusing-point and reweighing. A loss in weight of only 0.00003 gram resulted.

After the silver iodide had been weighed it was heated in a current of chlorine. This gas was generated by dropping concentrated hydrochloric acid upon manganese dioxide, and it was purified and dried by bubbling through water and passing through a three-foot tube filled with beads moistened with concentrated sulphuric acid. Traces of bromine or iodine in the chlorine would have been no disadvantage, and it is inconceivable that it should have contained fluorine. In order to prevent spattering of the fused salt from the crucible, a perforated porcelain disk, which fitted the crucible half-way between the bottom and the top, was placed in the crucible. This disk was always weighed with the crucible. The chlorine was conducted into the crucible by means of a small hard glass tube. which passed just through the perforated cover of a Rose crucible. The apparatus for generating chlorine was constructed wholly of glass with the exception of the joint between this hard glass tube and the drying tube. The chlorine did not come in contact with the rubber tube used in making the connection tight, however, for the hard glass tube telescoped into the drying tube for some distance and the joint was sealed with concentrated sulphuric acid. In order to avoid volatilization of the silver salts, the heat applied was very gentle and only sufficient to fuse the silver chloride. Even at this temperature the iodine was rapidly replaced. Heating in chlorine was continued some time after the color of the iodine vapor had ceased to be visible. Then the Rose cover was replaced by the ordinary cover and the silver chloride was kept fused for several minutes, with occasional lifting of the cover, so as to drive off any chlorine which might have been dissolved by the fused salt. Although fused silver chloride, when cooled in chlorine. dissolves this gas very appreciably, no evidence was found that any remained in the solidified salt when it was heated for a short time in air. In one experiment, 18 grams of the chloride, after the usual treatment, were re-fused in air with a loss in weight of only 0.00002 gram. The same chloride, when fused and cooled in chlorine, gained 5 mg.

It was soon discovered that a porcelain crucible, when used for the conversion of silver iodide into silver chloride, gradually gained in weight. In the first experiment this gain was over 3 mg., and in several subsequent experiments with the same crucible amounted to slightly less than a milligram in each case. This gain did not take place to the slightest extent when the crucible was heated alone in chlorine, nor after the reaction was complete, for the weight of the crucible and silver chloride very soon became constant. Probably it was due partially to solution of the silver salt in the glaze, as was shown by slight discoloration on the bottom of the crucible. Possibly, however, it was caused by the attacking of the glaze by the "nascent" chlorine and iodine set free in the process, perhaps with evolution of oxygen. At any rate too great an uncertainty existed as to the weight of the crucible at the end of the experiment. Accordingly, quartz crucibles were next employed for the same purpose. These crucibles behaved in an ideal fashion, for they remained practically constant in weight through the process. It was only necessary to rotate the crucibles during the solidification of the fused salts in order that the salt might solidify in a thin layer on the sides of the crucible. Neglect to do this almost invariably resulted in the cracking of the crucible.

After the first weighing of the crucible it was again heated in chlorine for an hour, and again cooled and weighed. In no case did a loss in weight of more than 0.1 mg. take place, showing both that the iodine was completely replaced, and that no silver chloride had volatilized.

Four determinations (Analyses 20 to 23) were completed with quartz crucibles in the manner described. Two more determinations (Analyses 24 and 25) were made by heating silver iodide first in a current of carbon dioxide and bromine, and then in chlorine. The weight of the silver bromide was obtained, but, although the results for the atomic weight of iodine calculated from the weight of the bromide agreed closely with those obtained by the other methods, on account of some uncertainty as to the purity of the bromine, these results are withheld until the experiments can be repeated. The only possible impurity in the bromine, chlorine, would not affect the final weight of the silver chloride.

At the time these experiments were performed the atomic weight of chlorine was thought to be 35.456. The atomic weight of iodine calculated from the ratio between silver iodide and silver chloride, using this value for chlorine, was very close to 126.96 in every case, which is considerably lower than the results obtained from the other two methods. At about this time, however, Richards and Wells, working upon the atomic weight of sodium in this laboratory, found that the atomic weight of chlorine is in reality 35.467.[1] In the following table the results are calculated upon this basis.

The specific gravity of silver chloride was assumed to be 5.56 as recently determined by Richards and Stull in this laboratory, and accordingly a vacuum correction of +0.000075 was applied to every apparent gram of salt.

THE ATOMIC WEIGHT OF IODINE.

AgI : AgCl.

Ag = 107.930 Cl = 35.467

Number of analysis.	Weight of silver iodine in vacuum. Grams.	Weight of silver chloride in vacuum. Grams.	Atomic weight of iodine.
20	9.26860	5.65787	126.980
21	6.72061	4.10259	126.974
22	11.31825	6.90912	126.977
23	10.07029	6.14754	126.969
24	13.65457	8.33538	126.975
25	17.35528	10.59457	126.973

Average	126.975
From ratio Ag : AgI	126.973
From ratio Ag : I	126.977
Average from all three ratios	126.975

The close agreement of the average of the last series with the averages of the first two series leaves no doubt that the atomic weight of iodine is very close to the final average of all three series, 126.975. Incidentally this agreement is additional evidence in favor of Richards and Wells's new value for the atomic weight of chlorine, 35.467. Further work is under way upon the atomic weight of iodine, with the purpose of determining the ratio between iodine and silver iodide, and the ratio between all the halogens, as described upon page 1592 of this paper.

In discussing the bearing of this investigation upon the results of earlier work by other chemists, the experiments of Millon upon

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[1] This investigation will soon be published.

silver and potassium iodates,[1] and of Berzelius[2] and Dumas,[3] who converted silver iodide into silver chloride, may be disregarded, since at the time the analyses were made quantitative analysis was in its infancy. Marignac's value for the atomic weight of iodine, 126.85, obtained from the titration of weighed amounts of silver with potassium iodide,[4] and from syntheses of silver iodide from weighed quantities of silver, may be accounted for by the supposition that the iodine used in the experiments was not pure. To explain Stas's[5] low value, 126.85, is a difficult matter. His iodine was purified by two different methods, *i. e.*, by once precipitating or distilling the iodine from a strong solution of potassium iodide, and by precipitation of nitrogen iodide. A third sample was purified by both methods. Since the material purified by each of the two methods gave identical results with that purified by both methods, it is inconceivable that either method of purification should not have been effective. Impurity in the silver or loss of silver iodide are improbable causes of the discrepancy, for the weight of the silver iodide produced was equal to the sum of the weights of the silver and iodine employed. Richards and Wells have recently shown, however, that Stas was not infallible, and, in fact, was capable of making serious mistakes, such that his value for the atomic weight of sodium was 0.2 per cent. too high, and that for the atomic weight of chlorine 0.03 per cent. too low, so that it is not at all surprising to find that here also his work was faulty in some undiscovered particular.

Ladenburg's result,[6] when calculated from the true value of the atomic weight of chlorine, becomes 126.978, which agrees very closely with the value deduced in this paper. His determinations were affected by several small errors, so that the close agreement is somewhat the result of chance. In the first place, porcelain crucibles, as has been pointed out before, gain in weight when used for the conversion of silver iodide into silver chloride, so that the weight of the silver chloride is somewhat uncertain. Furthermore, Ladenburg did not fuse the silver iodide before weighing it. Although Stas states that silver iodide may be

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[1] *Ann. chim. phys.* (3), **9**, 400 (1843).

[2] *Ibid.*, (2) **40**, 430 (1829).

[3] *Ann. Chem. Pharm.*, **113**, 28 (1860).

[4] Berzelius' "Lehrbuch," 5th ed., **3**, 1196.

[5] *Œuvres Complètes*, **1**, 548.

[6] *Ber. d. chem. Ges.*, **35**, 2275.

completely dried without fusion, his experiments show a loss in weight on fusion of 0.002 per cent., while the average loss on fusion, as given on pages 1585 and 1586 is about 0.004 per cent. Moreover, Ladenburg's method of purifying silver iodide, by washing the precipitated salt with ammonia, could hardly be expected to remove last traces of silver chloride and silver cyanide "included" by the precipitate. These errors are all so small that they would not affect the second place of decimals. However, Ladenburg's, Scott's,[1] and Köthner and Aeuer's work all afford confirmation that the atomic weight of iodine is undoubtedly much higher than has been usually supposed.

The results of the research are, then, as follows:

(1) The atomic weight of iodine is found to be 126.975 (O = 16.000).

(2) Richards and Wells's value for the atomic weight of chlorine, 35.467, is confirmed.

(3) The existence of an element of the halogen family of higher atomic weight than iodine is shown to be improbable.

(4) The specific gravity of pure fused silver iodide is found to be 5.674 at 25° referred to water at 4°.

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CHEMICAL LABORATORY OF HARVARD COLLEGE,
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THE USE OF THE ROTATING ANODE IN ELECTRO-ANALYSIS.

BY EDGAR F. SMITH.

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THE results obtained by Exner, in this laboratory, with a rotating anode in the electrolytic precipitation of metals led to further study along the same line. Thus, Ashbrook succeeded in effecting a number of separations reducing the time factor, in every instance, very considerably. Ingham exhaustively investigated the precipitation of zinc from various electrolytes, show-

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[1] *Proc. Chem. Soc.*, 18, 112.