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A Revision of the Atomic Weight of Iodine. The Ratio of Silver Iodide to Silver Chloride

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The atomic weight of iodine is of especial interest at the present time, for, since iodine is apparently a simple element, a comparison of the physical and chemical scales may be made through this constant with less uncertainty than in the case of a complex element.

In two recent investigations Hönigschmid and Striebel[1] by the conversion of silver iodide into silver chloride found a value for the atomic weight of iodine, 126.917, which is appreciably lower than that in general use at the time, 126.932. The latter value depended chiefly on the quantitative comparison of silver with iodine by one of us. We have therefore endeavored to discover the cause of this discrepancy, first by repeating a part of the experimental work of the German chemists.

Although slightly lower than theirs the result of our work is in close accord with that of Hönigschmid and Striebel. However, silver iodide above its melting point seems to be somewhat unstable in air and even in nitrogen, so that some slight uncertainty exists as to the exact composition of the fused material of which the analyses were made.

We used the method, which has been employed not only by Hönigschmid and Striebel, but also earlier by Ladenburg, Köthner and Aeuer, and Baxter, of heating weighed quantities of silver iodide in a current of chlorine until no further loss in weight occurred.

Purification of Materials

Our silver iodide was prepared by precipitation, using purified silver and iodine as the starting points. Silver nitrate was obtained from mother liquors of the crystallization of a sample of silver nitrate which had been made from partially purified silver. This silver nitrate was recrystallized ten times more with the addition of nitric acid to lower the solubility. Centrifugal drainage and rinsing of the crystals was employed. Part of this sample was combined with a second specimen of silver nitrate which had been prepared from commercial silver nitrate by ten recrystallizations. All the material was next reduced with ammonium formate and the metal was fused on a pure lime boat in hydrogen. After etching with nitric acid to remove lime the buttons were dissolved in nitric acid as needed. This material is designated as Sample A.

A second sample (Sample B) consisted of material which had been precipitated as chloride, as metal with ammonium formate, and as metal by electrolytic transport with dissolving anode. This was fused in hydrogen and etched as described above.

Several samples of iodine also were prepared. The purification of Sample I consisted in (a) distillation from aqueous potassium iodide, (b) reduction to hydriodic acid with hydrogen sulfide, (c) removal of hydrocyanic acid by boiling the aqueous solution of hydriodic acid, (d) partial oxidation with permanganate and distillation of the iodine, (e) conversion of 25% of the iodine to potassium iodate with permanganate, then to potassium iodide and distillation of the remaining iodine from solution in this iodide, (f) three sublimations in quartz in a current of air over red hot platinum wire.[2]

Sample II was purified by Dr. L. D. Frizzell in a very similar fashion.

Sample III was obtained from pure iodic acid remaining from previous investigations involving this substance.[3] It was carefully dehydrated and decomposed in a quartz tube, and the resulting iodine sublimed as with Samples I and II.

The silver iodide was made by adding silver nitrate solution to a solution of hydriodic acid. Since the silver iodide was eventually fused in an atmosphere of iodine the occlusion of either silver or iodide by the precipitate should cause no difficulty. Nevertheless dilute (0.05 *N*) solutions were employed.

To prepare hydriodic acid iodine was dissolved in distilled hydrazine. After dilution of the hydriodic acid solution, silver iodide was precipitated by adding a solution of an approximately equivalent quantity of silver nitrate. If silver buttons were used they were dissolved in an excess of nitric acid. Coagulation of the precipitate was hastened by the addition of nitric acid and after standing for some time the precipitate of silver iodide was washed by decantation with very dilute nitric acid followed by water and collected on platinum sponge crucibles (on sintered glass in one preparation). To dry the precipitate it was transferred to a quartz vessel while moist and dried in a porcelain oven.

Silver nitrate in excess was used in precipitating Samples I and III of silver iodide, hydriodic acid in excess in preparing Samples II and IV.

The Method of Analysis

The reaction tube was made of quartz of the shape indicated in the figure. The main body of the tube was provided with a constriction to minimize loss by vaporization and spattering of the silver halides when fused in the bottom. The loosely fitting bent quartz tube served for in-

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(1) Hönigschmid and Striebel, *Z. physik. Chem.*, Bodenstein-Festband, 283 (1931); *Z. anorg. allgem. Chem.*, **208**, 53 (1932).

(2) For further details see Baxter, THIS JOURNAL, **26**, 1589 (1904); **32**, 1597 (1910); Baxter and Butler, *ibid.*, **53**, 969 (1931).

(3) Baxter and Butler, note (1); Baxter and Hale, THIS JOURNAL, **56**, 615 (1934).

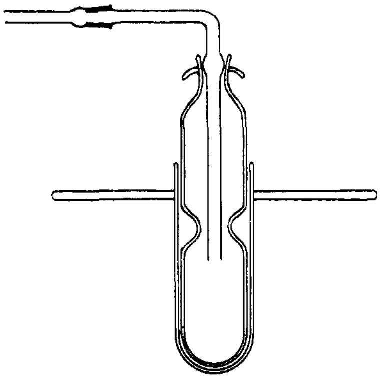
troduction of gases. In order to avoid heating the reaction tube directly it was surrounded with a second quartz tube supported on trunnions. When weighed it was always compared by substitution with a quartz counterpoise of essentially the same shape and weight.

The dried silver iodide was coarsely crushed in an agate mortar and introduced through a funnel. A small amount of pure dry iodine was placed in the tube through which dry air was supplied and this tube was connected to the quartz inlet of the reaction tube. While the iodine was being slowly evaporated into the air current the silver iodide was gradually brought to fusion and maintained at this temperature for some time after the iodine had completely evaporated. In order to avoid fracture of the tube the fused iodide was rolled around the inside walls of the reaction tube during solidification. The cooled material was clear and lemon yellow. Less complete iodination, however, is likely to result in material of noticeably darker color.

During the greater part of the chlorination of the iodide the reaction tube was placed in an electrically heated beaker furnace heated to 200°. Chlorine from a partially emptied cylinder was passed over aqueous sodium hypochlorite, concentrated sulfuric acid and phosphorus pentoxide and then into the reaction tube at 200° until the conversion was nearly completed. While surrounded with the quartz protection tube the reaction tube was then gradually heated to the melting point of the silver chloride and maintained at this temperature for two hours after visible evidence of iodine in the escaping gases had disappeared. With the silver chloride still fused the chlorine was displaced by air and the chloride caused to solidify in a thin layer as in the case of the iodide. In most cases a second treatment with chlorine failed to alter the weight of the chloride by more than a few hundredths of a milligram, but in two cases a slightly larger loss was observed. In these cases a third treatment did not alter the result appreciably.

In two analyses the silver iodide was first converted to bromide by heating the iodide in a current of air laden with pure bromine and after the bromide had been weighed this in turn was converted to chloride.

The chief difficulty which we experienced was with the silver iodide. If this substance was heated for some time and finally fused in an atmosphere rich in iodine, and then was maintained in a fused condition in air for twenty to forty minutes a maximum weight was obtained which was not appreciably altered by further heating to 330°, *i. e.*, below its melting point. If, however, the heating of the *melted* material in air is continued, a slow loss in weight takes place. This loss in weight is accompanied by a darkening of the cold product and is apparently due in part to dissociation and loss of iodine. That this loss of iodine actually takes place is shown by the fact that when the fusion in air was conducted in a closed quartz receptacle so that the resulting air could be passed into a potassium iodide–starch solution a blue color was developed. The liberation of iodine was much accelerated by raising the temperature still higher. A similar effect was observed but to a far less degree when pure nitrogen was used instead of air. Furthermore, when slightly decomposed silver iodide was again heated in iodine the original color was regained and the weight increased. On the other hand, the weight of the reiodinated product was always less than the original weight by a few tenths of a milligram. This *permanent* loss in weight was probably due to vaporization of silver iodide and loss, possibly as smoke. The *temporary* loss in weight, that is the gain in weight on reiodination after prolonged fusion in air, in three of the experiments was found to be 0.168, 0.264, 0.150, av. 0.192 mg. per hour with 23 ± g. of silver iodide. In only a few of our experiments was the silver iodide after the final iodination fused in air for longer than one hour, so that the maximum uncertainty in the weight of the silver iodide is apparently no greater than 0.2 mg. Actually the error must have been less than this since the complete removal of iodine from the fused silver iodide undoubtedly required some time and it is by no means certain that the dissociation of the silver iodide starts promptly.



It would have been preferable to fuse the silver iodide finally in nitrogen rather than air, since the difficulty was markedly less in nitrogen than in air. Unfortunately the full appreciation of the situation came too late for remedy. The uncertainty, however, amounts at the worst to only 0.001% of the weight of silver iodide, or 0.001 unit in the atomic weight of iodine.

Aside from a few preliminary experiments in which quartz Rose crucibles were employed, all the experiments undertaken were completed and are recorded in Table I.

In referring the weights to the vacuum standard

TABLE I

THE ATOMIC WEIGHT OF IODINE

Ag = 107.880 Br = 79.916 Cl = 35.457

AgI:AgCl

Anal.	Sample of Ag	Sample of I_2	Time of fusion in air, min.	AgI in vacuum, g.	AgCl in vacuum, g.	Ratio AgI:AgCl	Atomic wt. of iodine
1	B	I	30	19.29812	11.78127	1.638033	126.911
2	B	I	40	18.56636	11.33416	1.638089	126.919
3	B	I	30	17.61333	10.75259	1.638055	126.914
4	B	I	40	17.28888	10.55452	1.638055	126.914
5	A	II	80	24.77025	15.12167	1.638063	126.915
6	A	II	60	26.53177	16.19680	1.638087	126.918
7	A	III	60	27.13226	16.56361	1.638064	126.915
8	A	III	70	26.72367	16.31365	1.638117	126.923
9	A	III	100	23.26211	14.20115	1.638044	126.912
10	A	III	60	24.35477	14.86829	1.638034	126.911
11	A	III	40	23.82804	14.54653	1.638057	126.914
12	A	III	40	23.54677	14.37480	1.638059	126.914
					Average	1.638062	126.915

AgI:AgBr

	AgI in vacuum, g.	AgBr in vacuum, g.	Ratio AgI:AgBr	
5a	24.77025	19.81186	1.250274	126.916
6a	26.53177	21.22030	1.250301	126.922

AgBr:AgCl

	AgBr in vacuum, g.	AgCl in vacuum, g.	Ratio AgBr:AgCl	Atomic wt. of bromine
5b	19.81186	15.12167	1.310163	79.915
6b	21.22030	16.19680	1.310154	79.914

the density of the air at the time of weighing was calculated from conditions at the time. The following densities were assumed:

Air (0° and 760 mm.)	1.293	AgBr	6.473
Weights	8.3	AgCl	5.553
AgI	5.675		

Because of the high densities of the salts the vacuum corrections per gram were always small and near the following values

AgI	+0.067 mg.
AgBr	+0.041 mg.
AgCl	+0.071 mg.

A comparison of the different samples of silver and iodine gives no indication of variation in the purity of the materials, since the averages of values obtained with the two silver samples are both 126.915 and those with the three samples of iodine are 126.915, 126.917 and 126.915, respectively.

A discussion of this result is reserved for the following paper, which includes a description of a repetition of these experiments, together with further evidence.

Summary

By converting weighed quantities of silver iodide to silver chloride the atomic weight of iodine is found to be 126.915. This result is slightly lower than that found by Hönigschmid and Striebel. Silver iodide is found to be somewhat unstable above its melting point.

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