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## A REVISION OF THE ATOMIC WEIGHT OF BROMINE.

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IN numerous investigations in this laboratory upon the atomic weights of certain metals, in which metallic bromides were first titrated against the purest silver, and then the precipitated silver bromide was collected and weighed, the relation between the silver used in the titrations and the silver bromide obtained has yielded

data from which the atomic weight of bromine may be calculated. Furthermore, in all these investigations, as a check upon the purity of the silver and bromine employed, silver bromide was synthesized directly from weighed quantities of silver and an excess of ammonium bromide or hydrobromic acid. Many of these results have already been collected and discussed by Richards;<sup>1</sup> nevertheless they are cited in the following table together with a few more recent determinations.

INDIRECT DETERMINATIONS.

	Bromide analyzed.	Number of experiments.	Analyst.	Reference.	Ratio $\frac{Ag}{AgBr}$
1	BaBr <sub>2</sub>	Last seven	Richards	Pr. Am. Acad., 28, 28	57.444
2	SrBr <sub>2</sub>	Seven	"	Ibid., 30, 389	57.444
3	ZnBr <sub>2</sub>	One	"	Ibid., 31, 178	57.445
4	NiBr <sub>2</sub>	Seven	Cushman	Ibid., 33, 111	57.444
5	CoBr <sub>2</sub>	Last five	Baxter	Ibid., 33, 127	57.446
6	UBr <sub>4</sub>	Three	Merigold	Ibid., 37, 393	57.447
7	CsBr	Three	Archibald	Ibid., 38, 466	57.444
8	FeBr <sub>2</sub>	Two	Baxter	Ibid., 39, 252	57.443
9	CdBr <sub>2</sub>	Eight	Hines	This Journal, 28, 783	57.444
10	MnBr <sub>2</sub>	Thirteen	"	Not yet published	57.444

Average, weighted according to the number of determinations, 57.4443

DIRECT DETERMINATIONS.

11	HBr	Two	Richards	Pr. Am. Acad., 28, 17, 18	57.445
12	NH <sub>4</sub> Br	One	"	Ibid., 30, 380	57.446
13	HBr	Two	"	Ibid., 31, 165	57.444
14	NH <sub>4</sub> Br	One	Cushman	Ibid., 33, 106	57.445
15	NH <sub>4</sub> Br	One	Baxter	Ibid., 33, 122	57.444
16	NH <sub>4</sub> Br	Two	"	Ibid., 34, 353	57.447
17	NH <sub>4</sub> Br	Three	"	Ibid., 39, 250	57.444
18	NH <sub>4</sub> Br	One	Hines	Not yet published	57.443

Average, weighted according to the number of determinations, 57.4447

From the first of these ratios the atomic weight of bromine, referred to silver 107.930, is found to be 79.956, and from the second 79.955.

Very recently, in experiments in which silver iodide was heated first in a current of air and bromine until the iodine was completely displaced, and then in a current of chlorine to displace the bromine, the ratio of silver bromide to silver chloride was determined in six cases. From the results of these experiments the atomic weight of bromine was calculated to be 79.953,<sup>2</sup> if the

<sup>1</sup> Pr. Am. Phil. Soc. 43, 119 (1904).

<sup>2</sup> Baxter: This Journal, 27, 884 (1905).

atomic weight of chlorine is assumed to be 35.473.<sup>1</sup>

These values for bromine are in close agreement with those of Stas.<sup>2</sup> In his experiments weighed quantities of pure silver and bromine were first titrated against each other, and then the precipitate of silver bromide was collected and weighed. Of the four results by the first method, one should be rejected according to his own statements, since the bromine was not thoroughly dried. The remaining three, 79.959, 79.961 and 79.960, give as an average 79.960. From the weight of silver bromide four values were obtained, 79.950, 79.952, 79.955 and 79.957, with an average of 79.954.

Marignac<sup>3</sup> also determined the ratio of silver to silver bromide, with somewhat lower results—79.959, 79.941 and 79.952; average, 79.950.

Scott,<sup>4</sup> in his analyses of ammonium bromide, obtained six values for the same ratio, varying between 79.936 and 79.948, with an average of 79.943. One of his results is here rejected, since the silver used in this experiment was known to be impure.

Dumas,<sup>5</sup> by heating silver bromide in chlorine, found the values 80.06, 79.89 and 79.96.

In computing the atomic weight of bromine from these data, great weight is always given to Stas's determinations, the value 79.955 being usually assumed as the most probable one for the constant in question. Certainly, as pointed out by Richards,<sup>6</sup> the true value must lie between 79.95 and 79.96. Clarke calculates the value 79.949 as the weighted average of the different investigations previous to Scott's.<sup>7</sup>

Considerable uncertainty exists as to the purity of the materials employed in much of the foregoing work. Richards and Wells<sup>8</sup> have already exhaustively investigated the various methods of preparing pure silver, and have found that while it is a comparatively simple matter to free this substance from metallic

<sup>1</sup> Richards and Wells: Publications of the Carnegie Institution, No. 28 (1905); This Journal, 27, 459.

<sup>2</sup> Œuvres Complètes, I, 603.

<sup>3</sup> Ibid. I, 81.

<sup>4</sup> J. Chem. Soc. 79, 147 (1901).

<sup>5</sup> Ann. Chem. Pharm. 113, 20 (1860).

<sup>6</sup> Pr. Am. Phil. Soc. 43, 119 (1904).

<sup>7</sup> "A Recalculation of Atomic Weights," Smith. Misc. Coll., 1897.

<sup>8</sup> Publications of the Carnegie Institution, No. 28, 16; also this Journal, 27, 472 (1905).

impurities, the absence of gaseous impurities is by no means so easy to secure. Oxygen may be eliminated best by fusion in an atmosphere of pure hydrogen gas,<sup>1</sup> or by prolonged fusion in a vacuum, while a lime boat was found to be the most suitable support for the silver during fusion.

In most of the experiments cited on page 202, one of the final steps in the purification of the silver was fusion of electrolytic crystals on lime, in many cases in a vacuum, but without especial care to prolong the fusion. Silver prepared in this way was found by Richards and Wells to contain traces of oxygen, derived from silver nitrate occluded by the electrolytic crystals. In cases 8, 9, 10, 17 and 18, however, the silver was fused in hydrogen. Richards and Wells showed also that Stas's silver contained at least 0.01 per cent. of impurity, since it yielded 0.01 per cent. less silver chloride than their purest silver.<sup>2</sup> Scott's silver in three cases was merely heated, not fused, in hydrogen, and in two of the others was fused before a blowpipe on calcium phosphate. In one experiment only the metal was fused on lime. No details are given as to the purification of the silver used by Marignac.

Bromine also may be freed from impurities only with some difficulty. Experience in this laboratory has shown that chlorine may be eliminated most conveniently by distilling or precipitating the bromine from solution in a bromide. One such distillation is sufficient to remove chlorine completely only when the substance is initially comparatively pure. If, however, the process is repeated by converting a portion of the partially purified product into a bromide, and dissolving the remainder of the bromine in this comparatively pure bromide, the chlorine is eliminated so completely that further repetitions of this process have no apparent effect.<sup>3</sup> The removal of iodine may be easily effected by converting the bromine into hydrobromic acid or a soluble bromide, and boiling the solution with a small quantity of free bromine. Here again it is well to repeat the process several times, since the reaction between free bromine and the iodine ion, like that between free chlorine and the bromine ion, is undoubtedly incomplete.

<sup>1</sup> Baxter : Pr. Am. Acad. Arts Sci. 39, 249 (1903).

<sup>2</sup> Loc. cit., page 62.

<sup>3</sup> Attention has already been called to these points by Richards and Wells : Pr. Am. Acad. Arts Sci., 41, 440 (1906).

The greater part of the experiments cited on page 1323 were made with bromine which had been purified with due observance of these precautions. Of the other investigators, Stas seems to have been the only one to use sufficient pains to secure purity of the bromine. Stas removed iodine by shaking potassium bromide several times with free bromine and carbon disulphide, and in the course of the prolonged purification distilled the bromine twice from solution in a bromide. Marignac's purification consisted solely in crystallization of barium bromate and Scott's in distillation of hydrobromic acid.

Of the methods employed in these early determinations, that involving the analysis of metallic halides is least suited for the purpose, on account of the danger of occlusion of metallic salts by the precipitated silver bromide. That such an error actually exists to a slight extent is shown by the fact that the average of the "indirect" determinations is slightly larger than the average of the "direct" determinations. Obviously, if silver bromide is precipitated by means of either ammonium bromide or hydrobromic acid, occluded ammonium salts or free acids could be easily expelled by fusion of the bromide. This precaution was observed in most of the determinations recorded on page 202, and is absolutely essential for the complete elimination of water from the salt. Stas and Marignac both fused the silver bromide in their syntheses, but this precaution was omitted by Scott, who dried the bromide at  $180^{\circ}$ . Scott's statement that the loss on fusion of silver bromide which had been dried at  $180^{\circ}$  was due to the presence of asbestos is contradicted by the experiments recorded later in this paper, in which the loss on fusion amounted to about 0.01 per cent. in the case of silver bromide which had been dried in a similar fashion and which was almost entirely free from asbestos.

From this brief discussion of the more important errors which may have influenced previous determinations of the atomic weight of bromine, it is evident that some uncertainty still exists as to the true value of this constant. In the hope of throwing new light upon the subject, experiments were carried out by two of the methods outlined above, with especial precautions to insure purity of materials and to eliminate known possible errors in the experimental methods.

Both the methods chosen—synthesis of silver bromide from a weighed amount of silver, and conversion of silver bromide into

silver chloride—have already been recently tested in this laboratory,<sup>1</sup> and have been found to be at least as satisfactory as any.

#### PURIFICATION OF MATERIALS.

*Bromine.*—In purifying bromine for this research, the principles set forth on page 1325 of this paper were applied, but in some cases the purifying processes were repeated after the product was apparently pure, in order to make certain that further treatment had no effect.

Sample I was first completely dissolved in calcium bromide which had been made from about one-third of the original material by means of lime and ammonia, and was then distilled from the solution. The product was covered with several times its volume of water, and was converted into hydrobromic acid by means of pure hydrogen sulphide which had been generated from ferrous sulphide with dilute sulphuric acid, and which had been thoroughly washed with water. After filtration from the precipitated sulphur and bromide of sulphur, the acid was boiled for some time, with occasional addition of small quantities of recrystallized potassium permanganate to eliminate the iodine. Finally, the residual hydrobromic acid was heated with an equivalent amount of recrystallized permanganate, and the bromine was condensed in a flask cooled with ice.

Sample II was first converted into hydrobromic acid by means of red phosphorus and water, and the hydrobromic acid was then distilled, after having been boiled with an excess of bromine. An equivalent amount of permanganate was added, and the bromine liberated was separated from the solution by distillation. About one-fourth of the product was next transformed into calcium bromide by means of ammonia and lime which was free from chloride, and the remaining three-fourths of the bromine were dissolved in the calcium bromide and distilled. Still a third distillation from a bromide was carried out by reducing the product of the second distillation with hydrogen sulphide and subsequently oxidizing the hydrobromic acid with the purest recrystallized potassium permanganate, after boiling the acid with several small portions of permanganate to eliminate the last traces of iodine.

Sample III was obtained by preparing calcium bromide from a

<sup>1</sup> Baxter: Pr. Am. Acad. Arts Sci. 40, 419; 41, 73. Richards and Wells: Publications of the Carnegie Institution, No. 28; This Journal, 27, 876 (1905).

portion of Sample II and distilling the remainder of Sample II from solution in this bromide.

In the case of Sample IV the processes of reduction to hydrobromic acid with hydrogen sulphide and oxidation of the hydrobromic acid with pure permanganate were four times repeated. After each reduction the hydrobromic acid was boiled with free bromine to remove iodine.

Sample V was three times reduced with hydrogen sulphide and oxidized with permanganate. One-fourth the product was converted into calcium bromide and the remainder was dissolved in this calcium bromide and distilled.

Thus Sample I was twice distilled from a bromide; Sample II was treated three times in the same way; and Samples III, IV and V four times.

Shortly before use each sample was distilled and converted into ammonium bromide by slow addition to an excess of redistilled ammonium hydroxide. The solution was then boiled to expel the excess of ammonia.

*Silver.*—Several different samples of silver were employed, many of which have already been used in atomic weight researches in this laboratory, and have shown evidence of great purity. For details concerning the purification the papers referred to should be consulted.

Sample A was employed in a determination of the atomic weight of iodine.<sup>1</sup> This specimen had been twice precipitated as chloride and once electrolyzed.

Sample B was used in experiments upon the atomic weight of iodine<sup>2</sup> and of manganese.<sup>3</sup> It was precipitated once as chloride, electrolyzed once, and finally precipitated as metal with ammonium formate.

Sample C also was employed in a determination of the atomic weight of manganese, and was purified by recrystallizing silver nitrate, seven times from nitric acid and five times from aqueous solution. Finally, the silver nitrate was reduced by means of ammonium formate.

Sample D was prepared for the determination of the atomic

<sup>1</sup> Baxter: Pr. Am. Acad. Arts Sci. 40, 420 (1904); This Journal, 27, 881 (1905).

<sup>2</sup> Baxter: Pr. Am. Acad. Arts Sci. 41, 79 (1905); This Journal, 27, 881 (1905).

<sup>3</sup> Baxter and Hines: This paper will soon be published.

weights of cadmium<sup>1</sup> and manganese, by one precipitation as chloride, one precipitation with ammonium formate, and one electrolysis.

Sample E was first purified in part by precipitation as chloride, in part by precipitation with ammonium formate. The combined material was then subjected to two electrolyses.

In all cases the electrolytic crystals were fused in a boat of the purest lime, contained in a porcelain tube, in a current of electrolytic hydrogen. After the buttons had been cleansed with dilute nitric acid and dried at 200°, they were cut into fragments of from 4 to 8 grams either by means of a clean chisel and anvil or with a fine jeweler's saw. The latter method was employed in the case of Samples D and E, because it proved easier completely to free the silver from surface contamination with iron by etching the fragments with nitric acid, than when a chisel was used. The cleansing process with nitric acid was repeated until the solution thus obtained, after precipitation with hydrochloric acid and evaporation, proved free from iron. That every trace of iron could be removed by this treatment was proved by testing for iron the evaporated filtrates from several of the analyses subsequently recorded in this paper. Negative results were obtained in all cases.

After thorough washing with water and drying at 100°, the pieces of metal were heated to about 400° in a vacuum, and were preserved over solid potassium hydroxide in a desiccator.

#### THE RATIO OF SILVER TO SILVER BROMIDE.

The ratio of silver to silver bromide was determined as follows: Weighed quantities of silver were dissolved in the purest redistilled nitric acid diluted with an equal volume of water, in a flask provided with a column of bulbs to catch possible splatterings. However, during the solution of the silver the temperature was kept so low that almost no gas was evolved, and hence there was very little danger from this source. Next the acid solution of the silver was diluted with an equal volume of water, and was heated until free from nitrous acid and oxides of nitrogen. After still further dilution, the solution was added slowly with constant agitation to a dilute solution of an excess of ammonium bromide in a glass-stoppered precipitating flask, and the whole was violently

<sup>1</sup> Baxter and Hines : This Journal, 28, 772 (1906).



shaken for some time to promote coagulation. By adding the silver solution to the bromide, occlusion of silver nitrate was almost wholly precluded. In some experiments the solutions were as dilute as twentieth-normal, in others as concentrated as fourth-normal. The final results seemed to be independent of the concentration of the solutions. At the end of about twenty-four hours the flask with its contents was again shaken, and then it was allowed to stand until the supernatant liquid was perfectly clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible, after thorough washing by decantation with water, and was dried in an electric oven, first for several hours at  $130^{\circ}$ , finally for about fourteen hours at  $180^{\circ}$ . Then it was cooled and weighed.

The operations of precipitation and filtration were performed in a large cupboard lighted with red light, and if the flask was taken out of this cupboard it was enveloped in several thicknesses of black cloth.

Even after the prolonged drying, traces of moisture were retained by the salt, and could be expelled only by fusion. This was done by transferring the bulk of the silver bromide, freed as completely as possible from asbestos, to a small porcelain crucible which was weighed with its cover. The silver bromide was then fused by heating the small crucible, contained in a large crucible to prevent direct contact with the flame of the burner. A temperature much above the fusing point of silver bromide was avoided so that volatilization of the salt could not take place. This treatment must have eliminated occluded ammonium salts as well as water. Finally, in order to convert any occluded silver nitrate, metallic silver, or silver sub-bromide into silver bromide, the salt was again fused in a current of dry air containing bromine vapor. This treatment seldom produced any measurable effect either upon the weight or the appearance of the salt, which was perfectly transparent and of a light yellow color even after the first fusion in air.

A few shreds of asbestos displaced from the crucible, together with an occasional trace of silver bromide which escaped the crucible, were collected upon a tiny filter-paper which was then ignited in a porcelain crucible. Before being weighed the ash was either treated with a drop of nitric and hydrobromic acids

and again heated, or else was heated for some minutes in a current of air and bromine.

The filtrate and washings were evaporated to small bulk. The precipitating flask and all other glass vessels used in the analysis were rinsed with ammonia and the rinsings were added to the evaporated filtrate and wash-waters. The whole was then tested in a nephelometer for silver and the quantity found was estimated by comparison with standard silver solutions. In most cases the correction thus obtained was less than 0.1 mg.

The asbestos which formed the felt in the Gooch crucible, after having been shredded, was digested for some hours with aqua regia and was then thoroughly washed with water. Before the empty crucible was weighed, the felt was ignited with a Bunsen burner. Crucibles thus treated and then heated to 180° after being moistened with water did not change in weight.

In the following table are cited all the analyses which were completed without accident. Vacuum corrections of  $-0.000031$  for every apparent gram of silver and of  $+0.000041$  for every apparent gram of silver bromide are applied.<sup>1</sup> The atomic weight of silver is assumed to be 107.930.

The platinum plated brass weights were standardized from time to time and were found to retain their original values within a very few hundredths of a milligram in all cases.

#### THE RATIO OF SILVER BROMIDE TO SILVER CHLORIDE.

The ratio of silver bromide to silver chloride was determined much as described in previous papers upon the atomic weight of iodine.<sup>2</sup> Pure silver bromide was prepared by precipitation of silver nitrate with an excess of ammonium bromide. The silver employed was purified either by precipitation as chloride and reduction with invert sugar, or by electrolysis, or by precipitation with ammonium formate. The metal was then fused before a blowpipe upon a crucible of the purest lime, and the buttons were thoroughly cleansed with nitric acid. No further purifica-

<sup>1</sup> The specific gravity of the weights was determined to be 8.3. The specific gravity of silver has been found to be 10.49. Richards and Wells: Publications of the Carnegie Institution, No. 28, 11. The specific gravity of fused silver bromide has been found to be 6.473. Baxter and Hines: *Am. Ch. J.* 31, 224.

<sup>2</sup> Baxter: *Pr. Am. Acad. Arts Sci.* 40, 432 (1904); 41, 75 (1905); *This Journal*, 27, 876 (1905).

TABLE I.—THE ATOMIC WEIGHT OF BROMINE. SERIES I.

Number of analysis.	Sample of silver.	Sample of bromine.	Ag : AgBr.			Ag = 107.930			Corrected wt. of silver bromide. Grams.	Ag Ratio ——— AgBr	Atomic weight of bromine.
			Weight of silver in vacuum. Grams.	Weight of silver bromide in vacuum. Grams.	Loss on fusion in bromine. Grams.	Weight of asbestos. Grams.	Dissolved silver bromide. Grams.				
1	A	II	4.71853	8.21362	0.00027	0.00007	0.00021	8.21363	57.4476	79.946	
2	B	II	5.01725	8.73387	0.00020	0.00019	0.00007	8.73393	57.4455	79.952	
3	A	II	5.96818	10.38799	0.00023	0.00034	0.00122	10.38932	57.4453	79.953	
4	C	II	5.62992	9.80000	0.00017	0.00039	0.00017	9.80039	57.4459	79.951	
								Average,	57.4461	79.950	
5	A	IV	8.13612	14.16265	0.00002	0.00047	0.00024	14.16334	57.4449	79.954	
6	C	IV	5.07238	8.82932	0.00013	0.00043	0.00035	8.82997	57.4451	79.954	
7	B	IV	4.80711	8.36838	0.00015 <sup>1</sup>	0.00000	0.00004	8.36827	57.4445	79.956	
								Average,	57.4448	79.955	
8	C	V	4.27279	7.43771	0.00010 <sup>1</sup>	0.00009	0.00007	7.43776	57.4473	79.947	
9	A	V	5.86115	10.20299	0.00007 <sup>1</sup>	0.00004	0.00003	10.20299	57.4454	79.953	
10	B	V	7.91425	13.77735	0.00010	0.00010	0.00001	13.77736	57.4439	79.958	
11	D	V	6.40765	11.15461	0.00000	0.00006	0.00001	11.15468	57.4436	79.959	
12	D	V	6.38180	11.10942	0.00025	0.00012	0.00001	11.10930	57.4456	79.952	
13	D	V	6.23696	10.85722	0.00005	0.00004	0.00001	10.85722	57.4453	79.953	
								Average,	57.4452	79.953	
14	E	I	9.18778	15.99383	0.00014	0.00019	0.00004	15.99392	57.4455	79.953	
15	E	I	8.01261	13.94828	0.00018	0.00009	0.00007	13.94826	57.4452	79.953	
16	E	I	10.48638	18.25467	0.00025 <sup>1</sup>	0.00007	0.00001	18.25452	57.4454	79.953	
								Average,	57.4454	79.953	
17	E	III	8.59260	14.95790	0.00014	0.00016	0.00005	14.95797	57.4450	79.954	
18	E	III	8.97307	15.62013	0.00004	0.00007	0.00006	15.62022	57.4452	79.953	
								Average,	57.4451	79.954	
			Total,	121.67653				211.81305	57.4452	79.953	
								Average of all 18 determinations,	57.4453	79.953	
								Average of last 7 determinations,	57.4453	79.953	

<sup>1</sup> Fusion in bromine lost, after the salt had been fused in air.

tion was considered necessary, since the weight of the metal was of no consequence.

After the silver bromide had been washed by decantation with water, in some cases it was collected in a Gooch crucible in which a disk of filter-paper was employed instead of asbestos, and after drying at  $100^{\circ}$  it was carefully separated from the filter-paper. In other cases the precipitate was transferred to a platinum dish, and was drained with a platinum reverse filter<sup>1</sup> with a disk of filter-paper. In still others a platinum Gooch crucible with small holes was found to be sufficiently effective as a filtering medium without the use of either asbestos or filter-paper.

Before being weighed the silver bromide was fused in a current of air saturated with bromine in a weighed quartz crucible. The air was purified by passing successively over beads moistened with silver nitrate solution, over sodium carbonate, and finally over 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. The air was then passed through dry bromine in a small bulb. This apparatus was constructed entirely of glass with ground joints. The tube which conducted the gases into the crucible passed through a Rose crucible cover of glazed porcelain in all experiments except analyses 28 to 31, in which a quartz cover was employed. The quartz crucibles were always contained in large porcelain crucibles while being heated. They remained almost absolutely constant in weight during the experiments. The bromine was in each case a portion of the sample from which the silver bromide had been made.

Next the bromide was heated barely to fusion in a slow current of chlorine, generated by the action of hydrochloric acid upon manganese dioxide, and dried by means of concentrated sulphuric acid. The apparatus for this purpose also was constructed wholly of glass. When the bromine was apparently completely displaced, the silver chloride was heated in the air for a few minutes to expel dissolved chlorine, and then was cooled and weighed. A repetition of the heating in chlorine seldom affected the weight of the salt more than a few hundredths of a milligram, although occasionally a third heating was necessary to effect this result.

That no loss of silver chloride by volatilization took place is

<sup>1</sup> Cooke: *Pr. Am. Acad. Arts Sci.* 12, 121.

certain for two reasons. In the first place the cover of the crucible and the delivery tube for the bromine when rinsed with ammonia and the solution treated with a slight excess of hydrochloric acid gave no visible opalescence in the nephelometer. In the second place the weight of the chloride became constant without difficulty. It has already been shown that silver chloride which has been fused in chlorine, if subsequently heated in air, retains no excess of chlorine.<sup>1</sup>

The following vacuum corrections were applied: Silver bromide, +0.000041; silver chloride, +0.000071.<sup>2</sup> The atomic weight of chlorine referred to silver 107.930 is assumed to be 35.473.

Aside from the close agreement of all the results of Series I, the fact is to be emphasized that of the last seven analyses, which were consecutive, only two differ from the average of the series, 79.953, by as much as one one-thousandth of a unit. Furthermore, there is no evidence of any dissimilarity in the different preparations of bromine. Material which has received only two distillations from a bromide gives values no lower than bromine which has been thus treated four times. The various specimens of silver also show no difference in purity.

In the case of Series II, the extreme variation of the results is only four-thousandths of a unit, and only one of the thirteen experiments yielded a value which differs from the average by more than one one-thousandth of a unit.

Finally, the difference between the averages of Series I and II is only seven ten-thousandths of a unit. It is extremely unlikely that constant errors could have affected both series equally, so that this striking agreement is strong proof that both series are free from such errors.

It has already been pointed out that the average of Stas's syntheses, 79.954, probably represents with considerable accuracy the atomic weight of bromine, and that certainly his determinations are more accurate than those of later experimenters. His syntheses are few in number, however, and differ among themselves by several thousandths of a unit, so that they do not define within this amount the constant in question. Their average,

<sup>1</sup> Baxter: *Pr. Am. Acad. Arts Sci.* 40, 432 (1904); *This Journal*, 26, 1591 (1904); Richards and Wells: *Publications of the Carnegie Institution*, No. 28, page 59.

<sup>2</sup> Richards and Stull have found the density of fused silver chloride to be 5.56.

however, confirms the value obtained in this paper. From all the experiments here described the number 79.953 seems to be the most probable value for the atomic weight of bromine if the atomic weight of silver is assumed to be 107.930.

TABLE II.—THE ATOMIC WEIGHT OF BROMINE. SERIES II.

AgBr : AgCl.					
Ag = 107.930			Cl = 35.473.		
Number of analysis.	Sample of bromine.	Weight of silver bromide in vacuum. Grams.	Weight of silver chloride in vacuum. Grams.	Ratio $\frac{\text{AgBr}}{\text{AgCl}}$ .	Atomic weight of bromine.
19	II	8.03979	6.13642	131.0176	79.953
20	II	8.57738	6.54677	131.0170	79.952
21	II	13.15698	10.04221	131.0168	79.952
Average,				131.0171	79.952
22	IV	12.71403	9.70413	131.0167	79.952
23	IV	13.96784	10.66116	131.0162	79.951
Average,				131.0164	78.952
24	V	13.08168	9.98469	131.0174	76.953
25	V	12.52604	9.56059	131.0175	79.953
26	V	11.11984	8.48733	131.0170	79.952
27	V	8.82272	6.73402	131.0172	79.953
Average,				131.0173	79.953
28	I	11.93192	9.10721	131.0162	79.951
29	I	12.53547	9.56767	131.0190	79.955
Average,				131.0176	79.953
30	III	17.15021	13.09009	131.0167	79.952
31	III	10.31852	7.87572	131.0168	79.952
Average,				131.0168	79.952
Total,		153.94242	117.49801	131.0170	79.952
Average of all 13 experiments,				131.0171	79.952
Average of Series I and II,					79.953

In conclusion, attention may be called to the fact that a diminution in the atomic weight of bromine raises slightly all atomic weights resulting from the analysis of metallic bromides by precipitation with silver.

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