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

BY GREGORY P. BAXTER AND OSCAR W. LUNDSTEDT

Since the synthesis of silver iodide from metallic silver is a more direct method of finding the relation of the atomic weights of silver and iodine than that of finding the relation of silver iodide to silver chloride, we have carried out new syntheses of silver iodide and incidentally new determinations of the ratio of silver iodide to silver chloride. These experiments together with other evidence seem to indicate an atomic weight of iodine not far from 126.915.

I. The Ratio of Silver to Silver Iodide

Purification of Silver.—Several specimens of silver were purified by us, entirely by electrolysis with a dissolving anode. Silver of purity 99.85% was fused on charcoal into large buttons which were cleaned with nitric acid. A portion was dissolved in nitric acid, the solution was evaporated and the resulting silver nitrate was fused. A saturated solution of the salt was filtered through sintered glass into the electrolytic cell. The anode consisted of a pile of the buttons contained in a sintered glass crucible to collect anode dust while the cathode was a bar of previously purified silver. Contacts were made with platinum wires which, however, did not dip into the solution. Slow electrolysis with 0.1± ampere followed. The crystalline product was occasionally removed and the anode supply replenished. Second and third electrolyses in a similar fashion followed. The product of each preceding electrolysis was fused with a clean blast lamp in a porcelain crucible lined with pure lime made from recrystallized calcium nitrate, and the buttons were several times etched with nitric acid to remove adhering lime. A portion was dissolved in nitric acid and converted to neutral silver nitrate for the preparation of electrolyte. One button served as cathode, the remainder as anode.

The anode dust from the first electrolysis contained gold and platinum. The first electrolyte was nearly freed from silver by means of ammonium formate and after the filtrate had been evaporated to dryness, the ammonium salts were expelled from the residue. Spectroscopic examination showed lead, copper, tin, zinc, magnesium and calcium (doubtless in part from the glass dishes). Similar treatment of the second and third electrolytes showed that the above impurities disappeared progressively but the residue from the third electrolysis still contained traces of copper. Even the twice electrolyzed silver when directly examined spectroscopically seemed to be very pure and the spectrum of silver which had been electrolyzed three times was identical so far as could be determined with those of pure samples previously tested by Baxter.[1] This material is designated as Sample A.

Sample B consisted of a portion of Sample A which had been once more electrolyzed. The residual electrolyte even here showed a trace of copper. Sample C received still a fifth electrolysis.

Sample D was originally prepared under the direction of the late Professor T. W. Richards by Drs. Wadsworth,[2] and Sameshima.[3] This specimen had been purified by crystallization of silver nitrate and precipitation with ammonium formate. The metal powder was fused by us on pure lime in a clean flame and subjected to one electrolytic transport.

Sample E remained from an investigation by Baxter,[4] on the atomic weight of bromine. Its purification included precipitation as chloride, as metal by ammonium formate, and electrolytic transport, followed by fusion in hydrogen on lime in a porcelain tube.

All the samples were finally fused in boats lined with pure lime in a current of pure hydrogen. This operation had been carried on, in the case of samples prepared earlier in this Laboratory, in porcelain tubes closed with water-cooled brass stoppers. When we attempted to do this with a new lot of porcelain tubes the resulting silver showed traces of lead, although the original silver crystals were free from this element. After considerable investigation we came to the conclusion that the source of this lead was the glaze of the porcelain. The adoption of quartz boats (lined with lime) and quartz tubes for the fusion eliminated the difficulty entirely. On the other hand, the proportion of calcium taken up by the metal from the lining of the boats was several times as large as that found in samples fused by the old method (0.00004%, Ref. 1). This was ultimately traced to the more complete removal of moisture from the fusion tube before the fusion, owing to the smaller diameter and the absence of the water-cooled stopper. When the hydrogen was slightly moist (2± mm. aqueous pressure) the calcium lines were scarcely detectable in the spectrum, but under dry conditions of fusion the percentage of calcium was markedly higher. In order to discover the proportion of calcium contained in silver which had been fused in dry hydrogen, 27.9 g. of silver was dissolved in nitric acid and the silver removed as chloride. The residual solution after evaporation in platinum yielded a precipitate with ammonium oxalate weighing 0.07 mg. after ignition which became 0.14 mg. after conversion to sulfate. This represents 0.00017% of calcium impurity.

Further evidence of the purity of the silver samples was obtained by synthesizing silver chloride from weighed quantities of silver. The silver was dissolved in nitric acid and after precipitation of the chloride the precipitates were collected on weighed platinum sponge crucibles, dried at 350° and weighed. The bulk of the silver chloride was

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(1) Baxter, THIS JOURNAL, **44**, 577, 591 (1922).

(2) *Ibid.*, **38**, 2616 (1916).

(3) *Ibid.*, **42**, 928 (1920).

(4) Baxter, *ibid.*, **38**, 1322 (1916).

TABLE I

THE RATIO OF SILVER TO SILVER CHLORIDE

Sample of Ag	Ag in vacuum, g.	AgCl in vacuum, g.	Change in wt. on fusion, g.	AgI from filtrate, g.	Cor. wt. of AgCl in vacuum, g.	Ag:AgCl	Atomic wt. of Cl
A	9.00350	11.96250	+0.00004	0.00016	11.96264	0.752635	35.457
B	10.40823	13.82892	− .00012	0.00121	13.82954	0.752609	35.461
D	8.99809	11.95543	− .00021	0.00045	11.95549	0.752632	35.457

then fused in chlorine in a quartz crucible and the change in weight determined. Dissolved silver chloride was found by evaporating the filtrates and precipitating the silver as iodide, which was collected and weighed.

Since with international atomic weights for silver and chlorine the expected ratio of silver to silver chloride is 0.752632, there seems every reason to believe that the various samples of silver were of uniform purity and that the electrolytic method of purification is as satisfactory as any, as well as being less laborious.

It was unfortunate that this discovery that in a dry hydrogen atmosphere lime may be perceptibly reduced (owing presumably to solution in the silver) was not made until after our work was completed. However, the effect of 0.00017% of calcium in our silver would be to lower the atomic weight of iodine by only 0.0004 unit.

Purification of Iodine.—Two samples of iodine were prepared by widely different methods. The purification of Sample I consisted largely in repeated distillation from potassium iodide solution of increasing purity. Commercial iodine was dissolved in portions in a concentrated solution of one-half kilogram of commercial potassium iodide and then was distilled from the solution into a receiver. About a kilogram of iodine was thus treated. The product was then redistilled with steam.

About one-fifth of the product was next converted to potassium iodate by addition to a hot slightly alkaline solution of recrystallized potassium permanganate. Potassium iodate was recovered from the resulting solution by crystallization and converted to iodide by thermal decomposition. The remaining four-fifths of the iodine in portions was dissolved and distilled from a solution of this iodide. The process was then repeated. Thus all the iodine received three distillations from iodide of increasing purity.

The removal of organic matter was effected by sublimation in a current of oxygen[5] over platinum at ±700°. This was done in a quartz tube divided into three compartments by constrictions. The constrictions were partly filled with platinum wire and were heated to redness while the iodine was transported in a dry oxygen stream from the first to the second and from the second to the third compartment. The iodine in the last compartment was melted and poured into cold water, centrifugally drained and partially dried over sulfuric acid.

The source of Sample II was sodium iodate resulting from the neutralization of pure iodic acid with pure sodium carbonate.[6] Iodine which had been prepared originally by Baxter and Butler,[7] much as with Sample I, was converted by them to iodic acid through potassium iodate and barium iodate, and the iodic acid was fractionally crystallized. The iodic acid was further fractionated by Baxter and Hale. To convert the sodium iodate to iodine somewhat more than five parts of sodium iodate were converted to iodide by thermal decomposition and dissolved in water together with one part of sodium iodate. Iodine was liberated with sulfuric acid in excess and distilled from the solution. Redistillation with steam followed.

Method of Synthesis.—A weighed amount of pure silver was dissolved in 8 N nitric acid in a flask protected with a spray trap, and after removal of nitrous acid and nitrogen oxides the solution was diluted till about 0.2 N. An excess of iodine was converted to iodide with redistilled hydrazine hydrate and enough ammonium hydroxide nearly to neutralize the hydriodic acid produced. For precipitation the iodide solution was diluted to 0.2 N. In all except some preliminary experiments the silver and iodide solutions were made ammoniacal and the iodide solution was added to the silver solution in a flask with smooth neck. After standing for some time, the solution was made acid with nitric acid and the precipitate was allowed to stand for some days. This method has already been found to produce a more manageable precipitate than if precipitation takes place in acid solution.[8] Silver iodide precipitated from solutions of so high a concentration is known to coprecipitate silver and probably iodide but this difficulty is provided for in the subsequent treatment by fusion in an atmosphere containing iodine.

The silver iodide was washed with 1% nitric acid,[9] collected on a weighed platinum sponge crucible, dried at 275–300° for from six to eighteen hours, and weighed. In order to expel residual ammonium salts and water and at the same time convert occluded silver nitrate to iodide the silver iodide was fused in an atmosphere containing iodine. Because of the volatility of silver iodide at the fusion point, this was carried on in the quartz fusion tube described in the preceding paper (page 1826), which was constructed especially to avoid this difficulty. The silver iodide was removed from the platinum crucible, rapidly crushed in an agate mortar and placed in the fusion tube. After the tube and contents had been weighed, in a few cases it was heated to 130–285° and reweighed. Since no appreciable change in weight was produced during the heating it seems safe to assume that during the transfer no absorption of water took place.

A few crystals of dry iodine were now placed in the inlet tube and with a slow current of dry nitrogen (99.98%) flowing the fusion tube was slowly heated until finally the silver iodide was barely fused. At the same time the iodine was gently heated so that the iodine concentration in the gas was fairly high. The current of gas was continued some time after the iodine had volatilized and disappeared from the fusion chamber. After cooling and solidification in a thin layer to prevent fracture of the fusion tube the

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(5) Baxter, THIS JOURNAL, **32**, 1591 (1910); Baxter and Parsons, *ibid.*, **44**, 580 (1922).

(6) Baxter and Hale, *ibid.*, **56**, 615 (1934).

(7) Baxter and Butler, *ibid.*, **53**, 968 (1931).

(8) Baxter, *ibid.*, **26**, 1581 (1904).

(9) Baxter, *ibid.*, **26**, 1581 (1904).

system was reweighed. The fusion in iodine was repeated until the weight became constant within 0.05 mg. Because at the end of a fusion the tube was not filled with air, after analysis 14 the tube was placed in a vacuum desiccator, exhausted and then pure dry air was admitted before weighing took place. In several instances, however, where the tube was weighed before and after this procedure no change in weight could be detected, showing that during the handling of the tube before weighing sufficient diffusion had occurred. During this fusion in iodine four changes may be expected to occur. Moisture not expelled during the drying should be eliminated. Occluded silver nitrate should be converted to silver iodide and the other products of the reaction should be expelled. Reduced silver iodide should be re-formed from the reduction product (silver). Occluded iodide (ammonium iodide and hydriodic acid) should be expelled. The net effect of this fusion was a considerable gain in weight. When necessary correction was made for the small difference between the total weight of silver iodide and that actually fused. The silver iodide prepared in this way was lemon yellow. Prolonged heating in nitrogen, however, caused discoloration (reduction) and loss in weight, which could be largely but not wholly remedied by refusion in iodine. This is in accord with the experience of Baxter and Titus set forth in the preceding paper. The slight permanent loss in weight may be attributed to loss of silver iodide as smoke owing to evaporation, although no such loss was experienced when silver iodide was repeatedly heated in an atmosphere containing iodine, followed by a comparatively short period in nitrogen alone.

TABLE Ia

Ag added, mg.	AgI recovered, mg.	AgI calculated, mg.
0.15	0.11	0.33
.15	.31	.33
.15	.34	.33
.50	1.04	1.09

An attempt was made to detect such lost material by fusing silver iodide in a gas current in a glass tube terminating in a fine sintered glass filter. When this tube was rinsed with ammonia, no silver could be found in the rinsings.

Although the solubility of silver iodide is almost negligible, dissolved silver iodide was determined together with any precipitate adhering to the walls of the precipitating flask. The filtrate and wash waters were evaporated to small bulk. The precipitating flask was rinsed with concentrated ammonia and after expulsion of the greater part of the ammonia the rinsing was added to the evaporated filtrate. Evaporation of the combined solution was then continued until much of the ammonium salt (nitrate) had been decomposed. After solution in ammonia a slight residue was removed by filtration, the solution was acidified and its silver content precipitated with iodide. The trace of silver iodide was collected on a small platinum sponge crucible and weighed.

The insoluble residue removed from the evaporated filtrate was found to be free from silver by treatment with cyanide and acidification.

Because of the surprisingly small amount of silver iodide recovered in this way, blank experiments were performed to test the recovery of silver from ammonium nitrate solutions. In these experiments known amounts of silver as nitrate were added to ammonium nitrate solutions similar to those obtained from the filtrates and the silver was precipitated as iodide, collected on a very fine platinum sponge crucible and weighed. No serious uncertainty appears in Table Ia

TABLE II
THE ATOMIC WEIGHT OF IODINE
I:Ag

Anal. no.	Sample of Ag	Sample of I	Ag in vacuum, g.	AgI in vacuum, g.	Gain on fusion, g.	AgI from filtrate, g.	Cor. AgI in vacuum, g.	Ratio I:Ag	Atomic wt. of I
1	A	I	9.11927	19.84592	0.00143	0.00003	19.84738	1.176422	126.9124
2	A	I	10.48742	22.82288	.00218	.00002	22.82508	1.176425	126.9127
3	A	II	10.14331	22.07333	.00253	.00003	22.07589	1.176399	126.9099
4	A	II	9.00775	19.60274	.00206	.00003	19.60483	1.176440	126.9143
5	D	II	9.53995	20.76117	.00212	.00004	20.76333	1.176461	126.9166
6	D	I	9.78621	21.29650	.00246	.00017	21.29919	1.176449	126.9153
7	B	II	9.04011	19.67303	.00204	.00003	19.67510	1.176423	126.9125
8	B	I	9.99801	21.75765	.00242	.00001	21.76008	1.176441	126.9144
9	A	II	9.14163	19.89496	.00105	.00000	19.89601	1.176418	126.9120
10	B	II	10.00740	21.77565	.00459	.00000	21.78024	1.176413	126.9114
11	D	I	10.47710	22.80163	.00122	.00003	22.80288	1.176450	126.9154
12	B	I	9.52800	20.73659	.00048	.00006	20.73713	1.176441	126.9144
13	C	I	9.89577	21.53156	.00587	.00001	21.53744	1.176429	126.9132
14	C	I	10.47841	22.79437	.00971	.00134	22.80542	1.176420	126.9122
15	C	I	10.44012	22.71293	.00913	.00020	22.72226	1.176437	126.9140
16	E	I	8.47813	18.44768	.00451	.00008	18.45227	1.176455	126.9160
								1.176433	126.9135

TABLE III

Iodine	Silver A	B	C	D	E	Average
I	126.9126	126.9144	126.9131	126.9154	126.9160	126.9140
II	126.9121	126.9120		126.9166		126.9128
Average	126.9123	126.9132	126.9131	126.9158	126.9160	

A comparison of the different samples of iodine and silver is given in Table III.

It is probable that such differences as appear in Table III are of a purely fortuitous nature. The low value obtained in analysis 3 is almost entirely responsible for the difference between the averages of samples I and II of iodine. Without this analysis the average for sample II is 126.9138. Furthermore, without analysis 3 the average value with sample A of silver becomes 126.9129. It is only fair to point out that the three samples of silver purified by electrolysis only, A, B and C, give somewhat lower values than the other two. It is unfortunate that the limited quantity of Samples D and E of silver did not permit further investigation of this difference. It also should be pointed out, however, that after the third electrolysis (Sample A), a fourth and fifth similar purification were without effect. It is difficult to believe that any important proportion of impurity could have shown no change under these conditions. Furthermore, spectrographic examination indicated identity of all the samples.

The Conversion of Silver Iodide to Silver Chloride.—Since there was no reason to suppose that the fused silver iodide obtained in the synthesis experiments was not pure, it was used in later experiments for quantitative conversion to silver chloride as in the preceding investigation by Baxter and Titus. The empty fusion tube was carefully weighed at the start in order to find the precise weight of the fused silver iodide. Slow conversion of the silver iodide to silver chloride in a current of dry chlorine at gradually increasing temperatures up to the fusion temperature was followed by expulsion of dissolved chlorine in a current of nitrogen. No difficulty was experienced in securing constant weight on refusion in chlorine and nitrogen.

TABLE IV

THE ATOMIC WEIGHT OF IODINE

AgI:AgCl

Anal. no.	AgI in vacuum, g.	AgCl in vacuum, g.	Ratio AgI:AgCl	Atomic wt. of I
6a	21.24430	12.96904	1.638078	126.917
8a	21.70430	13.24993	1.638069	126.916
9a	19.80231	12.08877	1.638075	126.917
10a	21.61515	13.19557	1.638061	126.915
11a	22.69504	13.85480	1.638063	126.915
12a	20.61686	12.58599	1.638080	126.917
13a	21.28690	12.99508	1.638073	126.916
14a	22.65326	13.82927	1.638066	126.915
15a	22.47202	13.71853	1.638078	126.917
16a	18.19991	11.11055	1.638075	126.917
		Average	1.638071	126.916

It is apparent from the foregoing results together with those given in the preceding paper by Baxter and Titus that the method of converting silver iodide to chloride in our hands yields a slightly higher value for iodine than the synthesis of silver iodide. The average of all the experiments of the former sort by both Baxter and Titus and ourselves is 126.915(6), while the synthesis of silver iodide yields 126.913(5). Both these results are slightly lower than that found recently by Hönigschmid and Striebel, 126.917. All values obtained with silver iodide are subject to some uncertainty owing to the slight instability of silver iodide. Of the two methods under discussion the conversion method is subject to the possibility of loss of silver iodide from the conversion tube, although neither Hönigschmid nor ourselves could detect such loss. The synthesis method is subject to the possibility of loss of silver iodide at some stage of the collection and weighing of the precipitate. Since these errors are of opposite sign, to average the foregoing values seems on the whole the safest course. This average is 126.914(6). This value is dependent upon the atomic weight of silver assumed. Since the latter value is open to some slight uncertainty, the above value is subject to uncertainty in the same proportion.

Several ratios determined in recent years permit the calculation of the atomic weight of iodine, directly with the assumption of certain atomic weights, and by indirect processes not involving the assumption of any atomic weight except that of oxygen. By the latter methods the effect of experimental error is considerably magnified in the calculations.

Since 1900 the following ratios have been investigated.

TABLE V

	Ag:AgI		At. wt. I
1902	Scott		126.91
1904	Baxter		126.914
1904	Köthner and Aeuer	wet	126.919
		dry	126.905
1905	Baxter		126.930
	Ag:I		
1904	Baxter		126.920
1905	Baxter		126.928
1910	Baxter		126.932
	AgI:AgCl		
1902	Ladenburg		126.940
1904	Baxter		126.926
1904	Köthner and Aeuer		126.917
1905	Baxter		126.925
	Baxter (AgI:AgBr)		126.924

TABLE V (*Concluded*)

	AgI:AgCl	At. wt. I
1931	Hönigschmid and Striebel	126.917
1932	Hönigschmid and Striebel	126.917
	$2Ag:I_2O_5$	
1909	Baxter and Tilley	126.936
	$I_2O_5:I_2$	
1916	Guichard	126.91
1931	Baxter and Butler	126.905

With the exception of the work of Hönigschmid and Striebel, the conversion of silver iodide to silver chloride was conducted in crucibles with Rose covers. It seems probable that vaporization and loss of silver iodide from the crucible was responsible for the higher results of most of these earlier experiments.

Of the more recent determinations the highest results of all were found by Baxter and Tilley, and Baxter, by comparing silver with iodine pentoxide and iodine, respectively. In order to avoid coprecipitation the reacting solutions were made very dilute, 0.03 N or less, because of the strong tendency of silver iodide to carry down foreign substances. It appears now from the result of these comparisons that the silver iodide retained more iodide ion than silver ion in spite of the fact that in these experiments silver ion was always in slight excess at the end. In both comparisons, however, the conditions of precipitation were very closely the same so that errors of nearly the same sort and magnitude might reasonably be expected. While neither series of experiments appears to have been correct by itself, if the two are combined the errors should compensate to a large extent. Baxter and Tilley[10] found $2Ag/I_2O_5 = 0.646236$, (corrected, using the density 4.98 for I_2O_5[11]) while Baxter[12] found $Ag/I = 0.849904$. (In the original paper the average is incorrectly given as 0.849906.) If the first is divided by the second, $I_2/I_2O_5 = 0.760364$ and $I = 126.920$. In this calculation an error in either ratio of 0.001% affects the atomic weight of iodine by 0.004 unit.

Baxter and Shaefer[13] compared arsenic trichloride with iodine pentoxide by quantitative oxidation of the former by the latter in solution, and obtained the value 3.25818 for the ratio $6AsCl_3/I_2O_5$ (density $I_2O_5 = 4.98$), while Baxter and Frizzell[14] obtained the ratio $AsCl_3/I_2 = 0.714191$ in a similar way (Series III). Combining these ratios $I_2/I_2O_5 = 0.760343$ and $I = 126.905$. This method is as sensitive to experimental error as the one above. Combination of the two ratios involving $AsCl_3$ with that for $AsCl_3/3Ag$ obtained by Baxter, Shaefer, Dorcas and Scripture (Series 6 and 7 of their experiments), 0.560128, gives $2Ag/I_2O_5 = 0.646317$ and $I = 126.915$, and $Ag/I = 0.850033$ and $I = 126.913$ ($Ag = 107.880$), respectively.

Baxter and Hale[15] compared by neutralization iodine pentoxide and sodium carbonate and found $I_2O_5/Na_2CO_3 = 3.14950$. This ratio can be combined with the ratio $2Ag/Na_2CO_3$, determined by Richards and Hoover[16] to be 2.03556, to give $2Ag/I_2O_5 = 0.646312$ and $I = 126.916$.

The average of these five indirect methods is 126.914. Of these the first two are independent of the atomic weight of silver, the last three assume this value, 107.880. In all five the method of calculation multiplies the experimental error many times in the final result, so that the above average is confirmatory rather than definitive.

It is generally agreed by mass spectroscopists that iodine is essentially a simple element. Aston's early estimate[17] of the packing fraction of iodine is -5.3×10^{-4} but later evidence indicates a considerably lower value for this constant. From Dempster's[18] recent packing fraction curve the value for iodine may with some difficulty be interpolated to be -4.2×10^{-4}, while the estimate of Hahn, Flügge and Mattauch[19] is -4.4×10^{-4}. With the conversion factor 1.000275 the last two values of the packing fraction give 126.912 and 126.909, respectively, for the atomic weight of iodine. While the small discrepancy between these values and that found by chemical means may be due to analytical error, it seems probable that it may in part be due either to an incorrect value for the atomic weight of silver or to error in the assumed values of the packing fraction. With conventional assumptions our experimental value for the atomic weight of iodine, 126.915, corresponds to the packing fraction -3.9×10^{-4} while Hönigschmid and Striebel's recent value for iodine, 126.917, gives -3.8×10^{-4}. Since no direct measurement of the packing fraction of iodine has been made for some time, too much weight should not be laid on the interpolated

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(10) Baxter and Tilley, THIS JOURNAL, **31**, 201 (1909).

(11) Baxter and Kelley, *ibid.*, **62**, 1824 (1940).

(12) Baxter, *ibid.*, **32**, 1591 (1910).

(13) Baxter and Shaefer, *ibid.*, **55**, 1957 (1933).

(14) Baxter and Frizzell, *ibid.*, **57**, 851 (1935).

(15) Baxter and Hale, *ibid.*, **58**, 510 (1936).

(16) Richards and Hoover, *ibid.*, **37**, 95 (1915).

(17) Aston, *Proc. Roy. Soc.* (London), **A115**, 510 (1927).

(18) Dempster, *Phys. Rev.*, **53**, 869 (1938).

(19) Hahn, Flügge and Mattauch, *Ber.*, **73A**, 1 (1940).

physical values of the packing fraction given above.

Summary

The atomic weight of iodine found by synthesis of silver iodide from silver and by converting silver iodide to silver chloride, together with the results obtained by Baxter and Titus by the latter method, described in the preceding paper, is 126.915. This value is between that found by Hönigschmid and Striebel, 126.917, and the best mass spectrographic value.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY, HARVARD UNIVERSITY]

A Revision of the Atomic Weight of Cesium

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Together with iodine, cesium furnishes an exceptional opportunity for the comparison of the chemical and physical mass scales. Because of simplicity no uncertainty due to abundance ratios of isotopes exists. Both elements may be purified more readily than most, the compounds suitable for analysis are definite in composition and methods of analysis which have been thoroughly tested may be applied. The investigation of iodine has been recently described.[1] In the present paper the investigation of cesium by analysis of cesium chloride is considered. Although the analysis of this compound was carried out not long ago by Baxter and Thomas[2] the precision of the final result, 132.91, did not extend beyond the second decimal place in the atomic weight, whereas there seemed to be good reason to expect that the third decimal was within reach.

Purification of Cesium Salt

Originally cesium nitrate was obtained by decomposition of pollucite from Andover, Maine, with nitric acid. Nearly four kilograms of this salt was fractionally crystallized through seventeen series. Of the fourteen fractions in the seventeenth series, the three least soluble were set aside, the next two, which had been combined, were divided into two portions, the sixth and seventh which also had been combined, were divided into two portions and the eighth and ninth were combined in one portion. The total quantity of material in the five nearly equal original fractions was practically 2500 g. Fractional crystallization was then continued. When the least soluble fraction had been crystallized six times it was set aside to be combined later with the next fraction when it had received eight crystallizations and the third when it had received ten crystallizations. In none of the original fractions nor in those selected as above could rubidium or potassium be detected when they were examined spectrographically on copper electrodes. In the small most soluble fraction of the seventh series (10 fractions) traces of both rubidium and potassium were found. This fraction was set aside and the fractionation was continued. The most soluble fraction was similarly removed and similarly tested through nine additional series of fractionations. The proportion of rubidium and potassium gradually decreased until in the most soluble fraction of the twentieth series these elements were hardly detectable. The sensitiveness of the spectroscopic test for rubidium is diminished by the continuous spectrum of the alkalies in the blue region. With our instrument it was possible to detect beyond any question 0.005% of rubidium added to one of our purest fractions. This proportion would lower the observed atomic weight of cesium by 0.002 unit but it is certain that the material used in our experiments was much purer than this.

The three purest fractions of nitrate were combined and dissolved in water. After filtration through platinum sponge the solution was poured into a slight excess of redistilled perchloric acid, and the resulting perchlorate was centrifugally drained and washed. The residual solution gave no spectroscopic test for rubidium. Next the perchlorate was three times crystallized from aqueous solution in platinum vessels, with centrifugal drainage. Then it was converted to chloride by thermal decomposition in platinum. Since the resulting chloride contained platinum owing to attack of the platinum still in which the decomposition took place, it was dissolved and the solution filtered through platinum sponge. Purification of the chloride by crystallization from saturated hydrogen chloride at low temperature in platinum resulted in the attack of the platinum. The various fractions of chloride were therefore treated with a small quantity of distilled hydrazine, heated to precipitate platinum, and the solutions were filtered through platinum sponge. Fractional crystallization by cooling from hot solution was continued, care being taken always to have a small quantity of hydrazine in the solutions. In this way, so far as we could tell, attack of the platinum vessels was prevented. Nevertheless, the solutions were occasionally filtered through platinum sponge. Because of the high solubility of cesium chloride, the extreme crystal fraction was removed for analysis as soon as it became too small to warrant further treatment, and the fractionation continued. All the material used for analysis received at least four crystallizations or their equivalent. The crystallized chloride was not entirely free from hydrazine, but this disappears in the final fusion of the chloride (see page 1835).

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(1) Baxter and Titus, THIS JOURNAL, **62**, 1826 (1940); Baxter and Lundstedt, *ibid.*, **62**, 1829 (1940).

(2) Baxter and Thomas, *ibid.*, **56**, 1108 (1934).