

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.

CAMBRIDGE, MASS.

RECEIVED APRIL 18, 1940

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

## A Revision of the Atomic Weight of Cesium

BY GREGORY P. BAXTER AND CHARLES D. HARRINGTON

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.<sup>1</sup> 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<sup>2</sup> 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 potas-

sium 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 alkalis 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).

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

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

TABLE I  
THE ATOMIC WEIGHT OF CESIUM

Anal.	CsCl in vacuum, g.	Ag = 107.880		Cl = 35.457		Atomic wt. of cesium
		Ag in vacuum, g.	Ag added, g.	Ag in vac., cor., g.	Ratio CsCl:Ag	
1	15.73190	10.07971	0.00030	10.08001	1.560703	132.912
2	17.98374	11.52245	.00040	11.52285	1.560702	132.912
3	11.62978	7.45147	.00030	7.45177	1.560674	132.909
4	18.23097	11.68119	.00000	11.68119	1.560712	132.913
5	16.45522	10.54340	.00000	10.54340	1.560713	132.913
6	14.74725	9.44889	.00000	9.44889	1.560739	132.916
7	17.06711	10.93548	.00003	10.93545	1.560714	132.913
8	15.19052	9.73300	.00000	9.73300	1.560723	132.914
9	17.58470	11.26713	.00010	11.26723	1.560694	132.911
10	18.32957	11.74553	.00080	11.74473	1.560663	132.907
11	16.59433	10.63232	.00024	10.63256	1.560709	132.912
12	17.53781	11.23686	.00015	11.23671	1.560760	132.918
				Average	1.560709	132.912(5)

Silver was purified by electrolytic transport four times through a saturated silver nitrate solution.<sup>3</sup> The electrolytic crystals were fused into buttons of suitable size in quartz boats lined with pure lime in slightly moist hydrogen.<sup>3</sup> The fused buttons were etched several times with nitric acid, washed and dried first at 100° in air, then at 400° in a vacuum. Fine adjustment of the weight of silver in the analyses was made with a small quantity of electrolytic crystals which also had been heated to 400° in a vacuum.

Water, nitric acid, perchloric acid and hydrazine were purified by distillation. Electrolytic hydrogen was finally dried with freshly fused potassium hydroxide chilled to -80°. Hydrogen chloride was finally dried with fused calcium chloride also chilled to -80°.

Comparison of the cesium chloride with silver followed conventional lines. The cesium chloride contained in a platinum boat in a quartz tube was fused in a current of dry hydrogen containing from 2 to 30% of hydrogen chloride. After the salt had cooled, the hydrogen and hydrogen chloride were displaced by nitrogen and this in turn by air and the boat was transferred to its weighing bottle by means of the Richards bottling apparatus. When the weight of the cesium chloride was known, as nearly as possible the exact equivalent of the cesium chloride in silver was weighed out. The cesium chloride was dissolved in water, the silver in nitric acid, and, both solutions being between 0.05 and 0.10 normal, the silver solution was added to the chloride in all except analysis 4, where the reverse method of precipitation was used. After standing for at least a week with occasional gentle agitation, the supernatant solution was tested for excess chloride or silver in a nephelometer. If necessary a deficiency of chloride or silver was made up with hundredth normal solutions and the shaking and testing continued

(3) Baxter and Lundstedt, *THIS JOURNAL*, 62, 1829 (1940).

for some months until the end-point was reached and remained constant for some time.

In a few analyses the solution of the salt contained a trace of black insoluble material. Since in analysis 11 this difficulty was far greater than in any other, in this case the solution was filtered on a weighed platinum sponge crucible, and the crucible dried and weighed. The weight of the residue was 0.16 mg., but since after ignition the weight was 0.06 mg., apparently a part of the residue may have been carbon. In no other case was the residue more than a small fraction of this and so it was disregarded. In analysis 11 the weight of cesium chloride was corrected for this material.

One portion of salt fused as in an analysis was tested for acidity, ammonia and hydrazine. After fusion (in 25% hydrogen chloride) it was dissolved in 150 ml. of water. One-half of the solution indicated a pH of 6 with neutralized brom thymol blue. After boiling in a current of pure nitrogen, the addition of 0.1 ml. of 0.01 normal sodium hydroxide gave a pH of 7. Even if this acidity were due to retained hydrogen chloride in the salt, it corresponds to only 0.1 mg. of silver, but it is highly probable that in part at any rate it was due to carbon dioxide. When this same portion of the solution was distilled with sodium carbonate, the distillate gave no indication of ammonia with Nessler solution. To test for hydrazine the other half of the solution was treated with a small amount of iodic acid. No iodine was liberated even on boiling.

The following densities were used in computing the vacuum corrections: air (0°, 760 mm.), 1.293; silver, 10.49; cesium chloride, 3.97.

The average of the twelve analyses is slightly higher than that found by Baxter and Thomas. This may be in part due to removal of rubidium and potassium from the material used by them.

With the conversion factor 1.000275 our new value for cesium yields  $-3.79 \times 10^{-4}$  for the packing fraction of cesium. Interpolation from Dempster's<sup>4</sup> packing fraction curve gives  $-3.8 \times 10^{-4}$ , while from the curve of Hahn, Flügge and Mattauch<sup>5</sup> the value for cesium is  $-4.0 \times 10^{-4}$ . Aston<sup>6</sup> found the packing fraction of cesium to be  $0.3 \times 10^{-4}$  smaller than that of xenon. Using the recent value for xenon,  $-4.1 \times 10^{-4}$ , as calculated by Hahn, Flügge and Mattauch,<sup>5</sup> and Aston's difference, the packing fraction of cesium is  $-3.8 \times 10^{-4}$ . This close agreement together

(4) Dempster, *Phys. Rev.*, **53**, 870 (1939).

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

(6) Aston, *Proc. Roy. Soc. (London)*, **A134**, 573 (1932).

with similar agreement in the case of iodine<sup>7</sup> is reassuring in its indication that in this region the chemical and physical scales are not far apart. It should be pointed out, however, that no recent direct determination of the packing fraction of cesium has been made and that the atomic weight of silver, to which cesium is referred chemically, is subject to slight uncertainty.

### Summary

1. By comparison of cesium chloride with silver the atomic weight of cesium is found to be 132.913 ( $Ag = 107.880$ ).

2. The packing fraction of cesium is calculated to be  $-3.8 \times 10^{-4}$ , in close agreement with recent values.

(7) Baxter and Lundstedt, *THIS JOURNAL*, **62**, 1829 (1940).

CAMBRIDGE, MASS.

RECEIVED MAY 13, 1940

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

## A Revision of the Atomic Weight of Potassium

BY GREGORY P. BAXTER AND CHARLES D. HARRINGTON

As a check on the analytical procedure of the analysis of cesium chloride described in the preceding paper a few analyses of potassium chloride were made. The results fall between those of Richards and Staehler,<sup>1</sup> Richards and Mueller,<sup>2</sup> Baxter and MacNevin,<sup>3</sup> Baxter and Alter,<sup>4</sup> and Hönigschmid and Sachtleben,<sup>5</sup> and that of Johnson.<sup>6</sup>

Potassium chlorate which gave no evidence spectroscopically of containing cesium or rubidium was crystallized three times from aqueous solution. The chlorate was converted to perchlorate by heating barely to fusion in platinum, and the perchlorate was separated from the chloride by crystallization. After two more crystallizations of the perchlorate it was converted to chloride in platinum. The chloride was dissolved, the solution filtered through platinum sponge and the salt recovered by crystallization from concentrated hydrochloric acid solution. Four more

(1) Richards and Staehler, *THIS JOURNAL*, **29**, 623 (1907), 39.096.

(2) Richards and Mueller, *ibid.*, **29**, 639 (1907), 39.096.

(3) Baxter and MacNevin, *ibid.*, **55**, 2185 (1933), 39.094.

(4) Baxter and Alter, *ibid.*, **55**, 3270 (1933), 39.096.

(5) Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **213**, 365 (1933), 39.094, 39.097.

(6) Johnson, *J. Phys. Chem.*, **39**, 781 (1933), 39.100.

crystallizations from hydrochloric acid and one from water, all in platinum, followed (Sample A). No cesium or rubidium could be detected spectroscopically.

A second sample of chloride which had been similarly purified by Baxter and MacNevin was used in one analysis (Sample B).

The details of the method of preparing potassium chloride for analysis and of the analytical method are essentially like those described for cesium chloride in the preceding paper. In analyses 1, 2 and 5 the fusion atmosphere was hydrogen plus a few per cent. of hydrogen chloride. In analysis 3 the salt was fused first as above, then in hydrogen alone, and in analysis 4 first in nitrogen, then in hydrogen plus hydrogen chloride.

The following densities were used in computing vacuum corrections: air ( $0^\circ$ , 760 mm.), 1.293; KCl, 1.988; Ag, 10.49.

From Dempster's<sup>7</sup> curve the packing fraction of potassium is  $-7 \times 10^{-4}$ , while Hahn, Flügge and Mattauch<sup>8</sup> give  $-6 \times 10^{-4}$ . Brewer<sup>9</sup> finds the

(7) Dempster, *Phys. Rev.*, **53**, 870 (1939).

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

(9) Brewer, *THIS JOURNAL*, **58**, 365, 370 (1938).