ART. XV.—*Contributions from the Sheffield Laboratory of Yale College.*—V. *On the Equivalent and Spectrum of Cæsium*; by S. W. JOHNSON and O. D. ALLEN.

IN the last vol. of this Journal a method is described of separating cæsium from rubidium by fractional crystallization of the bitartrates of these metals.¹ The analyses of the bitartrate of cæsium there given, while perfectly according with each other as regards carbon, disagree with the numbers deduced from Bunsen's equivalent to such an extent that we have undertaken to ascertain whether the salt was impure or Bunsen's equivalent incorrect.

From the great care used in preparing the bitartrate and especially from the fact that its spectrum remained unaltered though the salt was repeatedly recrystallized, we were inclined to suppose that Bunsen had not operated with a pure substance.

This might easily happen on account of the small quantity of material at his disposal without at all detracting from the merit of this distinguished chemist.

A quantity of bitartrate of cæsium purified by concentrating its solution and recrystallization as described in the paper referred to, and containing no foreign matters recognizable by the spectroscope, except an inevitable trace of sodium and (to judge from a certain red line,) perhaps some lithium, was treated directly with bichlorid of platinum in quantity sufficient for complete precipitation. This platinchlorid of cæsium after thorough washing was reduced in hydrogen, the chlorid of cæsium dissolved from the platinum and evaporated to dryness with addition of a little hydrochloric acid.

We thus obtained an amorphous mass of a pure white color

¹ Observations on Cæsium and Rubidium, by O. D. Allen, vol. xxxiv, pp. 367-373.

which, unlike Bunsen's chlorid was *not perceptibly deliquescent* even in a very moist atmosphere. The spectrum of the chlorid thus prepared was identical with that of the original bitartrate. Both salts gave a red line nearly coincident with the α line of lithium. In order to determine whether this line was due to a trace of lithium or belongs to the spectrum of cæsium, a portion of chlorid was again precipitated with a relatively small quantity of bichlorid of platinum, the precipitate was most thoroughly washed and from it a new sample of chlorid of cæsium was prepared. The red line was no less apparent in this than in the former preparations. The same process of partial precipitation was repeated to the third time without altering the spectrum.

Again, from a hot dilute solution of 15 grms. of chlorid of cæsium, about 1 gm. of cæsium was thrown down as platinchlorid; the product thus procured gave a spectrum identical with that from the original bitartrate.

We concluded from these experiments that our chlorid of cæsium was free from lithium and as pure as it is well possible to obtain any substance without the most extraordinary and for most purposes unreasonable precautions.

As to the properties of the chlorid of cæsium, we observed that not only is it not deliquescent, but it is hardly hygroscopic. The unfused and porous salt may be weighed in moist air with as much accuracy as chlorid of sodium. After it has been fused it does not alter in weight during 24 hours' exposure to the air in cold dry weather. It may be fused in a platinum capsule over the gas flame when the air is dry, without acquiring an alkaline reaction. In a damp atmosphere it is apt to lose chlorine during fusion. The residue after the reduction of platinchlorid of cæsium by hydrogen at a gentle heat, is alkaline. It is hardly possible to fuse chlorid of cæsium without loss, by volatilization. Hence our first estimations of cæsium in this form were too low by 4 to 7 tenths of one per cent.

For determining the equivalent of cæsium we have made four chlorine estimations. Two of these, I and II, were made in the chlorid obtained as already described. Their details and results are given below. The filtrates from these analyses containing nitrates of cæsium and silver, after the latter had been removed, were added to a solution of several grammes of the original chlorid and the whole was partially precipitated with bichlorid of platinum and a second portion of chlorid of cæsium procured, on which determination III. was made. Finally the nitrate of cæsium from this analysis was mingled with repeatedly purified chlorid obtained in the previous study of the spectrum, about half the cæsium was again thrown down as platinchlorid, and with this product another estimation of chlorine, IV, was made.

The determination of chlorine was conducted in the usual manner by precipitation with nitrate of silver and filtration. Washed Swedish filters were employed which gave each an ash weighing $\frac{1}{10}$ ths of a milligramme. The weighings were taken on a balance by Becker and Sons of Brooklyn, N. Y., which with an ordinary load indicates $\frac{1}{20}$ th of a milligramme with great decision and perfect constancy.

The data of our determinations are as follows :

I.	1.8371 grms. Cs Cl	gave 1.5634 Ag. Cl	= 386598 Cl	and 1.4505 Cs.
II.	2.1295 " " "	1.8111 " "	= 447848 " "	1.68165 "
III.	2.7018 " " "	2.2992 " "	= 56853 " "	2.13327 "
IV.	1.56165 " " "	1.3302 " "	= 32893 " "	1.23272 "

The percentage composition of chlorid of cæsium and the equivalents deduced from the above figures are as follows; silver being considered = 107.94 and chlorine = 35.46, Stas :

	Per cent of		Equiv. of Cs.	
	Cl	Cs		
1.	21.044	78.956	133.050	Allen.
2.	21.031	78.969	133.150	Johnson.
3.	21.043	78.957	133.054	Johnson.
4.	21.063	78.937	132.892	Allen
Average,	21.045	78.955	133.036	

We may accordingly assume the round number, 133, as the equivalent of cæsium.

Calculated by this equivalent the formula of bitartrate of cæsium corresponds well with the results of experiment. As mentioned in the paper referred to, the analyses of this salt furnished the following data:

- I. 0.4718 grm. gave { 0.0786 grm. water, and
0.294 " carbonic acid.
- II. 0.5966 grm. gave { 0.101 grm. water, and
0.372 " carbonic acid.
- III. 1.3086 grm. gave 0.7708 grm. chlorid of cæsium.

In two other estimations since made—

- IV. 2.0347 grm. gave 1.206 grm. chlorid of cæsium.
- V. 1.8271 " 1.0857 " " "

Calculated.						Found.				
Cs=123.35			Cs=133.			I.	II.	III.	IV.	V.
C ₈	48.00	17.62	C ₈	48.	17.02	16.99	17.02			
H ₅	5.00	1.83	H ₅	5.	1.77	1.85	1.88			
O ₁₁	88.00	32.31	O ₁₁	88.	31.21					
CsO	131.35	48.24	CsO	141.	50.00			49.30	49.61	49.73
	272.35	100.00		282.	100.00					

The equivalent number 133, brings cæsium into a triad with rubidium and potassium. We have then two alkali triads, viz: lithium, (eq. 7), sodium (eq. 23) and potassium (eq. 39·1),

$$\frac{7+39}{2}=23$$

and potassium, rubidium (eq. 85·36) and cæsium.

$$\frac{39+133}{2}=86$$

The correction of the equivalent of cæsium implies a revision of its spectrum, since the data given by Kirchhoff and Bunsen with reference to both, were obtained from the same impure material.

The cæsium spectrum, as we have procured it, is, perhaps, from the number, color and definition of its lines, the most beautiful to be observed among all the alkali and earthy metals. Kirchhoff and Bunsen, in the figure given by them (*Pogg. Ann.*, 1861, and *Fres. Zeitschrift für Analyt. Chemie*, Heft, 1, 1862), represent 11 lines. We find without difficulty 7 more lines, and observe further that some of those figured by K. & B., are not mapped in their correct positions. To enable other chemists to compare their cæsium preparations with ours, we will attempt to describe the cæsium spectrum as seen in our instrument, which has a single flint glass prism.

Beginning at the left or red extremity of the spectrum, we will indicate the lines in the order of their occurrence by Roman numerals; I. is a red line of medium brightness nearly equidistant between the Fraunhofer lines α and B; II. is a bright line partly coincident with, but slightly to the left of and narrower than the α line of lithium; III. is a faint line nearly approaching Fraunhofer's line C; IV. is the faintest of the red lines; V. is a faint line midway between the α and β lines of lithium; VI. is a bright red line midway between the sodium line and α lithium; VII. is an orange-red line of medium intensity directly to the right of the α strontium line; VIII. is a fine yellow line just to the right of and close upon the sodium line. The position of the green lines it is difficult to describe. First comes a group of three, IX, X. and XI, which are separated by very narrow spaces, and which are represented well in the spectrum plate of Kirchhoff and Bunsen, though placed a trifle too far to the right. Then, after an interval scarcely wider than the lines themselves, come XII. and XIII, which are very near each other. After another space as broad as these lines we encounter XIV. Midway between XIV. and XVI. is XV. The latter, XV, coincides with the dark line E. Finally, the two pale blue lines, XVII. and XVIII, complete the list.

For the convenience of those who may use spectroscopes of the same construction as ours, we will mention the degrees on the scale of our instrument, which correspond to the cæsium lines. In our observations we have brought the degree 100 (10 on the scale) into the sodium line. Then the blue of strontium is at 156° , the violet of potassium 257° , the red of potassium at $65-6^{\circ}$; the red of lithium at $80-1^{\circ}$. With this adjustment the cæsium lines are as follows, beginning with the red: I 75° , II 80° , III $82-3^{\circ}$, IV 85° , V $87-8^{\circ}$, VI 91° , VII $97-8^{\circ}$, VIII 101° , IX 106° , X $107-8^{\circ}$, XI 109° , XII 111° , XIII $112-13^{\circ}$, XIV $114-15^{\circ}$, XV 118° , XVI 121° , XVII $157-58^{\circ}$, XVIII 160° .

The position of the cæsium lines on the scale figured at the top of the spectrum plate in Fresenius' Zeitschrift, is approximatively given in the accompanying diagram, by help of which our results may be directly compared with those of Kirchhoff and Bunsen.

The order of brilliancy in the lines of what we suppose to be the spectrum of pure cæsium, with but the minutest trace of sodium, is for the red lines as follows: VI, II, VII, I, V, III, IV. The line IV is only made out under the most favorable conditions. II, nearly coincident with α lithium of Kirchhoff and Bunsen, and not figured by them, is as bright as their γ cæsium, our VI(?). Among the yellow and green lines to the right of the sodium line, the order of brilliancy is the following: VIII, IX, XI, XII, XIV, XIII, XV, X. The yellow line VIII, is hardly less characteristic of the spectrum of *pure* cæsium than the two blue lines. It also is nearly as distinct as any of the green lines when sodium is not present in too large quantity, and is much more readily made out than the extreme red line δ of rubidium.

To sum up, we find 4 red lines to the left of those given by Kirchhoff and Bunsen, one of which is as bright as any of the red lines in the cæsium spectrum. Further, the red lines of K. & B. are not figured in their true positions, being too near each other and too far to the right. Finally, we observe a fine yellow line and two unimportant green lines not mapped by K. & B. The lines which we have supplemented to those of K. & B. are not characteristic except in the absence of foreign matters. For this very reason however they become important to those who are engaged in the study of the new elements.

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