

AN ACCURATE REDETERMINATION OF THE ATOMIC
WEIGHT OF CAESIUM

by

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I. INTRODUCTION.

A redetermination of the atomic weight of caesium was undertaken on account of the possibility of finding an isotope. As can be readily seen the present accepted value, 132.81, differs considerably from an integer and yet no isotopes of this metal are known. Other elements, such as chlorine, strontium, ⁽¹⁾mercury and gold, possessing fractional atomic weights, have at least one isotope and yet caesium, also having a fractional atomic weight, possesses none. This may mean one of two things, perhaps both; that either the accepted value of the atomic weight is at fault, or that an isotope, as yet unknown, exists.

In addition to this, the value for the atomic weight of caesium as calculated by chemical and physical methods is not the same. ⁽²⁾Aston in 1921 by making use of the mass spectrograph found caesium to be a simple element, having a mass of $133 \pm .2$. However, the possible error in his early work happens to be as large as the difference between the accepted atomic weight and the mass of the atom, .2 unit; yet there are very few simple elements showing such a great difference between the mass number and the atomic weight. The element

(1) Aston, Phil. Mag., (6) 49, 1191 (1925).
(2) Aston, Phil. Mag., (6) 42, 436 (1921).

caesium possesses a negative packing and when such is the case, the differences between the true weight of the atoms of an element and an integer, are seldom as large as in the case of caesium.

The recent search for element "87" has led to a renewed interest in the atomic weight of caesium. This unknown member, closely related to the latter as it is, has as yet defied discovery; in spite of numerous attempts.⁽¹⁾ Also the "packing effect", as discussed by Aston in a recent paper,⁽²⁾ has thrown much light upon the atomic weight and structure of many elements; caesium included. He has defined the packing fraction as the divergence of the mass of an atom from a whole number, divided by its mass number. By means of the mass-spectra of many elements, he was able to show that the whole number rule, based upon hydrogen as unity, did not hold in all cases. The failure of this law was attributed to the fact, that the protons and electrons in the nucleus were packed so closely together, that their electromagnetic fields interfered, resulting in the loss of a certain fraction of the combined mass. However, outside of the nucleus, owing to the great distances between the charges, nothing such as this, could happen. Therefore, a great loss in energy, corresponding to tight packing of the electrons, would mean great stability and visa versa for a small loss of energy. Caesium is situated in

(1) L.M. Dennis and R.W.G. Wyckoff, Journ. Amer. Chem. Soc., 42,985(1920). Herszfenkiel, Compt.rend., 184,968(1927).

(2) Aston, Proc. Roy.Soc. London, 115A, 487 (1927).

the region of tight packing, since it is only slightly removed from the minimum of Aston's curve. Recently, Millikan and Cameron⁽¹⁾ have concluded, that at one end of this curve the light elements were built up with a loss of mass, corresponding to tight packing of the electrons; and Cabrera⁽²⁾ concludes that the heavy elements, situated at the other end, break down into lighter elements.

On considering all these facts, we saw that a redetermination of the atomic weight of caesium might be of some avail; especially when no work had been done in this field for twenty-four years. (As this work was started in 1927, Richards' and Francon's paper had not been published.) Before continuing I wish to express my sincere thanks to Dr. E.H. Archibald, not only for the loan of the material; but also for his liberal and useful advice, as well as the purification of some of the caesium salts used in the analyses.

II. SYNOPSIS OF EARLIER DETERMINATIONS.

Since the discovery of caesium in 1860 by Bunsen and Kirchhoff, only six investigations as to its atomic weight have been made; two by Bunsen himself and one by each of the following: Johnson and Allan,⁽³⁾ Godeffroy,⁽⁴⁾ Richards and⁽⁵⁾

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- (1) Millikan and Cameron, Science, N.S., 67, 401 (1928).
(2) Cabrera, Compt.rend., 186,228(1928);-186,501(1928).
(3) R. Bunsen, Zeit.anal.chem., 1,137(1862);Pogg.Annal.119,1(1862).
(4) Johnson & Allen, Am.Jour.Sci.& Arts (2), 35,94.
(5) Godeffroy, Liebigs Annal. der Chem., 181,176(1876).

(1) Archibald, Richards and Francon.
(2)

In the following year, 1861, Bunsen published his first determination of the atomic weight. The material used in this investigation was recovered from 150 tons of water, obtained from the mineral spring at Durkeim. The amount of caesium obtained from this large quantity of water was very small indeed, being approximately 12 grams in weight. The satisfactory purification of such a small amount of material is a very difficult procedure and probably accounts for the inaccuracy of the results. Bunsen purified his material by recrystallizing the chlorplatinatate, which is not nearly as soluble as the corresponding rubidium salt. The first value for the atomic weight, as found by Bunsen, was 132.35, which number was soon after rejected by the discoverer himself, since his caesium salt undoubtedly contained traces of rubidium.

In 1862 Johnson and Allen of the Sheffield Scientific School, New Haven, having discovered a much richer source of caesium, began their work on the atomic weight of this element. The mineral lepidolite found in Hebron, Maine, contained about 3 % of caesium oxide and from this they prepared a mixture of lithium, sodium, potassium, rubidium and caesium chlorides. These chlorides were then treated with chlorplatinic acid, whereupon the caesium and rubidium were precipitated as chlorplatinates. In order to separate the rubidium from the caesium,

(1) T.W. Richards and E.H. Archibald, Proc.Amer. Acad.Arts & Sciences, 38, 443,(1903).

(2) W.Richards & M.Francon, Journ.Amer.Chem.Soc.50,2162(1928).

the chlorides were converted through the carbonates into the bitartrates. The acid tartrate of rubidium, being only one-eighth as soluble as the corresponding caesium salt, successive fractional crystallization left the mother liquor nearly free from rubidium. A portion of the salt thus obtained was treated with enough chlorplatinic acid to precipitate all the caesium as the chlorplatinite, which was then washed with water and reduced in a stream of hydrogen. Four determinations of the amount of chlorine in the chloride prepared as above were made for the purpose of finding the atomic weight. Silver nitrate was used to precipitate the chlorine and the resulting precipitate was collected on filter paper. The results ranged from 132.89 to 133.15; the average being 133.04 if oxygen is taken as 16.00 and vacuum corrections applied.

Very shortly after the publication of Johnson and Allen's paper, Bunsen came forward with the results of his second determinations. His method of purification was now very similar to that used by other workers, differing principally in the fact that several recrystallizations of the chlorplatinite were made, with subsequent analysis of each product. Also his method of analysis resembled that of Johnson and Allen. The three results so obtained were 132.949, 133.04 and 132.98, averaging 132.99.

(1)
In 1865, Redtenbacher showed that there was a greater

(1) Redtenbacher, Wiener. Acad. Anzeiger f., 1865, 39.

difference between the solubilities of caesium and rubidium alums, than between the chlorplatينات; hence a better separation of one from the other could be obtained, if the former method was used. Godeffroy made use of Redtenbacher's idea in preparing his pure caesium alums: (a) a caesium alum (pure). (b) caesium alum containing a trace of rubidium. (c) rubidium alum containing a trace of caesium. The latter two were treated with barium chloride and then antimony trichloride. The precipitate, after being washed with hydrochloric acid, was claimed to be free from rubidium. It was now dissolved in water, whereby all the antimony oxychloride separated as a residue. The solution was evaporated and ignited with ammonium chloride, thus removing the last trace of antimony by volatilization and leaving pure caesium chloride as the residue. In 1875 R. Godeffroy⁽¹⁾ showed that the above separation of caesium from rubidium was not satisfactory. The pure caesium alum, (a), was dissolved in hot water and the aluminium precipitated with ammonia. The solution, after filtering, was evaporated to dryness in a platinum dish and the ammonium sulphate driven off by heating. The residue was dissolved in water and the remaining sulphuric acid was precipitated by barium chloride. After filtering off the barium sulphate, the solution was treated repeatedly with ammonia and ammonium carbonate, in order to eliminate all traces of aluminium and barium. The caesium

(1) R. Godeffroy, Journ. Chem. Soc., 28,612 (1875).

chloride, thus obtained, was fused in a platinum dish; thus driving off any ammonium salts that might have been present. This fused mass when dissolved in water was found to be alkaline, but the crystals deposited by evaporation were not hygroscopic. The chlorine was weighed as silver chloride and the four results obtained ranged from 132.50 to 132.71, averaging 132.57. The low result obtained by Godeffroy was probably due to the admixture of sodium salts coming from the apparatus employed in the complicated purification processes. Therefore the salt used in these analyses can hardly be regarded as pure, and no doubt earlier investigators had much purer material.

In 1903 Richards and Archibald, by using an entirely different method of purification, obtained a value, which up to the present has been the accepted atomic weight for caesium.

(1)
Wells showed that a very good separation of caesium from rubidium may be obtained by making use of the difference in solubilities of their trihalide salts. Of these, the dichloride, $(CsCl_2I)$, is the best method for not only is the caesium salt from eight to ten times less soluble than the corresponding rubidium one, but also will crystallize below $70^{\circ}C$. in a rhombohedral form, while the other metal gives the corresponding salt in the orthorhombic form only. This property of heteromorphy adds greatly to the efficiency of the separation (3)

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- (1) Wells, Am. Jour. Sci. (3), 43, 17 (1901); Chem. News, 84, 2184, Oct 4
(2) R.W.G. Wyckoff, J. Am. Chem. Soc., 42, 1100 (1920). (1901)
(3) Richards & Archibald, Proc. Amer. Acad. Arts & Sci., 38, 447 (1903)

of the two metals. The greater part of the caesium used in Richards' and Archibald's research was obtained from Pollucite found at Mt. Mica, Paris, Maine. From this material was prepared the dichloriodide, which after several recrystallizations from dilute hydrochloric acid, was spectroscopically pure. The crystals, after being dried, were placed in a porcelain crucible and heated in an electric oven to about 100°C. At this temperature the extra chlorine and iodine are slowly driven off, leaving the chloride as a white porous mass. The chloride, so formed, was placed in a platinum dish and dissolved in a minimum of warm water; after which hydrochloric acid gas, prepared from boiling concentrated aqueous hydrochloric acid, was passed into the solution through a platinum tube. After cooling, the mixture was decanted into another platinum dish; the crystals being washed with a little pure concentrated hydrochloric acid. The salt was redissolved in warm water, precipitated, washed as before and partly dried by suction in a platinum Gooch crucible. A second sample was prepared from the mother liquors from the first, in the same manner as previously described. A third sample was prepared from an impure caesium alum. Barium chloride was used to eliminate the sulphuric acid; the dichloriodide was obtained by adding an excess of aqua regia, followed by an excess of resublimed iodine, to the filtrate. The resulting trihalide salt was recrystallized eight times, after which it was converted into the normal

chloride. The purification process then proceeded in the same manner as Sample I. In order to eliminate all traces of moisture, without decomposition, the caesium halide was fused in an atmosphere of pure nitrogen in the well known "bottling apparatus"⁽¹⁾. Results were obtained with both caesium chloride and bromide; the chlorine and bromine being weighed as silver chloride and bromide respectively. The average atomic weight as determined by twenty-five analyses, which agreed very closely, was 132.81. The reliability of this figure is unquestionable, as there is no doubt as to the superior purity of the salt employed.

In 1928 a redetermination of the atomic weight of caesium was undertaken by Richards and Francon. They felt that there was too great a gap between the atomic weight of that metal, when determined by physical and chemical methods. Their material also consisted of pollucite found in Maine. The ore was first treated with hydrochloric acid; then converted to the sulphate by means of sulphuric acid, where it was recrystallized as alums. The pure caesium alum was treated with barium chloride with the subsequent formation of barium sulphate and caesium chloride. The chloride was now converted into the perchlorate by adding perchloric acid to the above filtrate. The latter was recrystallized and converted back into caesium chloride by heating in a platinum boat to a temperature of

(1) Richards & Parker, *Proc. Amer. Acad. Arts & Sci.*, 32, 55 (1896)
Z. anorg. Chem., 13, 81 (1896).

800°C. This excessive temperature was necessary in order to decompose a trace of caesium chlorplatinat. The residue was filtered and recrystallized, after which it was ready for use. The method of analysis was similar to that used in 1903, with the exception that fusion of the caesium halide was carried out in an atmosphere of nitrogen and hydrogen chloride. The chlorine was weighed up as silver chloride; and from this four values were obtained, which ranged from 132.783 to 132.832, averaging 132.809. As closely as these results agree with the accepted value, nevertheless they can not be classed as reliable. In the first place, the investigators themselves admit the possible presence of sodium in their caesium salt; this would tend to make their values low. Also the alum method of purification is much inferior to the dichloriodide one; and again their caesium chloride may contain traces of extra chlorine, due to the fact that it was fused in an atmosphere of nitrogen and hydrogen chloride. The last item caused us much trouble, especially in the case of the bromide.

From previous determinations, one might expect the atomic weight of caesium to lie somewhere between 133.0 and 132.6; probably nearer the former than the latter value. The value usually selected by Clarke and others, ⁽¹⁾ 132.811, has been in accord with this conclusion and the present investigation shows it to have been fairly accurate.

(1) F.W. Clarke, The Constants of Nature, Vol 54, No 3, Part V, 154(1910)

III. CHEMICAL PROPERTIES OF THE CAESIUM SALTS. ⁽¹⁾

Caesium chloride is a colorless salt, crystallizing in anhydrous cubes, which are very soluble in both hot and cold water. The aqueous vapor pressure of a saturated solution of caesium chloride is slightly greater than that of the air in the average steam heated, American laboratories; hence the crystals are only deliquescent on damp days. The addition of alcohol to its solution precipitates much of the dissolved salt. In addition to this it has no marked tendency to form an acid salt and so is precipitated by hydrochloric acid. But, when the acid concentration is very high a canary yellow precipitate results, which is rendered colorless by fusing. We investigated this colored salt qualitatively and found free chlorine to be present, most likely in the form of a polyhalide of caesium. Caesium chloride fuses to a clear, limpid liquid at 646° C. losing a trace of its chlorine if moisture is present and hydrochloric acid absent. However, the salt shows no traces of alkalinity after being fused in absolutely dry air, especially if it had been recrystallized from hydrochloric acid. In this case, microscopic inclusions of the acid must have been present along with the water and in this way prevented hydrolysis of the salt on fusion. Caesium chloride forms a double salt with antimonious chloride in concentrated hydrochloric acid.

⁽²⁾
Godeffroy made use of this fact in preparing pure

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- (1) L. Moser & E. Ritschel, Zeit. Anal. Chem. 70, 184 (1927).
(2) R. Godeffroy, J. Chem. Soc., 27, 816 (1874): 28, 612 (1875).
(3) C.E. Saunders, J. Chem. Soc., A II, 62, 778 (1892).

caesium salts, but later gave up the idea, since rubidium was found to give an analagous series of double salts. Likewise, the insoluble nature of caesium chlorplatinat has been taken advantage of in preparing pure caesium salts. Caesium also forms an extensive series of alums, which up to the present, has been the commonest method of purification. The rubidium alum is about four times as soluble as the corresponding caesium alum and if this was the only factor involved a very good separation could be obtained. But, both alums have a common crystal form, ⁽¹⁾ which makes complete separation almost impossible. Both caesium and rubidium form an extensive series of trihalide salts, ⁽²⁾ which are relatively unstable towards moderate heat. Of these, the most important are the dichloriodides, which are heteromorphous below 70°C. and differ widely in relation to their solubility in water. Hence a very good separation of caesium from rubidium may be obtained by making use of the above facts.

Caesium bromide greatly resembles the chloride in all respects, both chemical and physical; and also fuses to a colorless, limpid liquid at about 600°C.

(1) C. Setterberg, Journ.Chem.Soc., A,42,464(1882).

(2) H.L. Wells & S.L. Penfield, Journ. Chem. Soc., A ii, 62, 773(1892).

IV. PHYSICAL CONSTANTS USED AS DATA:

Substance	Density (20 ^o C)	M.P.	Vac. Correct	per gm.	At. Wt.
CsBr.	4.380 gms/cc. ⁽¹⁾	600 ^o C.	.00013	" "	-----
CsCl.	3.972 "/ cc. ⁽¹⁾	646 ^o C.	.00016	" "	-----
AgBr.	6.473 " / "	434 ^o C.	.00004	" "	-----
AgCl.	5.560 " / "	455 ^o C.	.00007	" "	-----
Ag.	10.490 " / "	961 ^o C.	-.00003	" "	107.880 (2)
Br.	-----	-----	-----		79.916 (2)
Cl.	-----	-----	-----		35.457 (2)

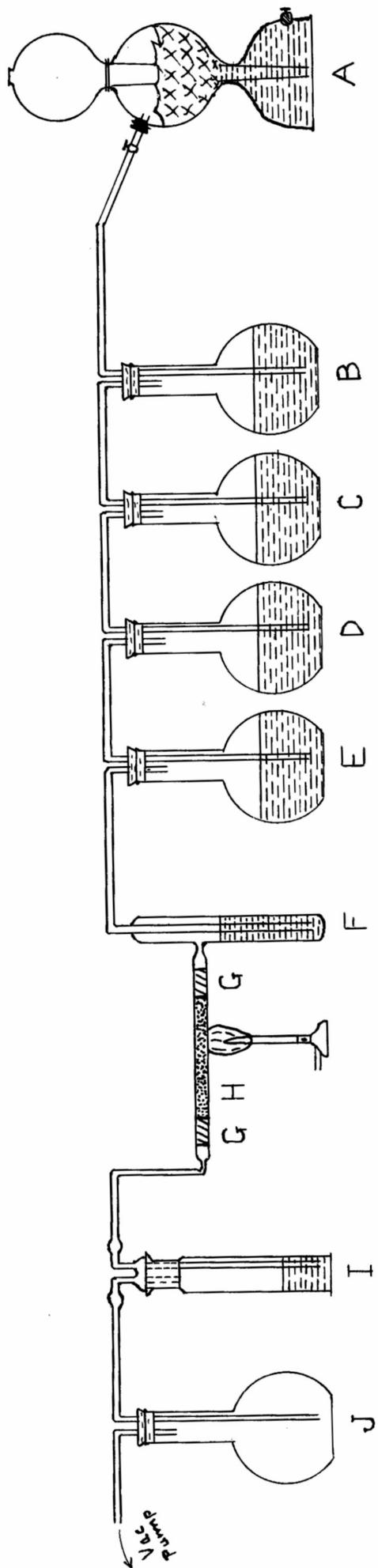
V. PURIFICATION OF CHEMICALS.

Bromine.- A volume of 100 c.c. of "C.P." bromine was twice redistilled from a pyrex flask and each time the first and last 15 c.c. portions were rejected. The purified product was stored in a bottle which had formerly contained bromine.

⁽³⁾
Iodine.- Iodine of the "C.P." variety, was fused under a solution of calcium chloride, potassium iodide and hydrochloric acid. The iodine so obtained was crushed, washed and drained. The resulting crystals were twice sublimed with barium oxide over a water bath and finally resublimed by themselves.

Formic acid.- A volume of 100 c.c. of distilled water was added to 800 c.c. of 75 %, "C.P." formic acid. The resulting mixture was distilled from a quartz still; the first and last 100 c.c. portions were rejected.

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- (1) Richards & Archibald, Proc. Amer. Acad., 38, 466 (1903); 38, 454 (1903).
 (2) Table of Atomic Weights for 1928.
 (3) G.P. Baxter & L.W. Parsons, Journ. Amer. Chem. Soc., 44, 577 (1922).
 Musset, Journ. Chem. Soc., A., 60, 392 (1891).
 Meineke, Journ. Chem. Soc., Aii, 64, 204 (1893).



Synthesis of Hydrobromic Acid Fig 1

Hydrobromic acid.- The concentrated "C.P." hydrobromic acid was distilled from a pyrex still and the middle fraction collected. The purified acid was stored in a bottle which had formerly contained liquid bromine.

Synthesis of Hydrobromic acid.- Calcium nitrate of the best "C.P." brand and weighing 75 gms. was dissolved in distilled water and the calcium precipitated as calcium carbonate by means of an excess of ammonium carbonate ("C.P.") solution. The precipitate thus formed was thoroughly washed after which it was dissolved in redistilled hydrobromic acid. The resulting solution was evaporated to a volume of 40 c.c. Towards the end of the evaporation process the liquid became dark in color and gave off copious fumes of bromine. About 50 c.c. of doubly distilled bromine were dissolved in this calcium bromide solution, that is, after it had become cold. The resulting solution was diluted to a volume of 200 c.c. and the bromine was distilled off. The still was made of pyrex glass and a bottle, that had previously contained bromine, was used as the receiver. In this way any chlorine present in the pure bromine was left in the still as calcium chloride. Hydrogen, prepared from zinc and dilute "C.P." Sulphuric, in a kipp generator, (A), and purified by being passed successively through wash bottles containing, potassium hydroxide, (B), alkaline potassium permanganate, (C), alkaline pyrogalllic acid, (D), and mercuric chloride, (E), was bubbled through the especially pure bromine,

(F), and then passed over heated platinized asbestos, (H), and finally into distilled water, (I). The apparatus, from the bromine bottle to the wash bottle containing distilled water, was made entirely of glass. The hydrogen was generated at a very moderate rate and was passed over the platinized asbestos, maintained at $350^{\circ}\text{C}.$, (approx.), for eight hours. The asbestos used in the experiment was the very best that could be obtained. Nevertheless it was boiled for 30 min. in 30% hydrobromic acid ("C.P."), after which it was thoroughly washed with hot distilled water. The fibres of asbestos, thus obtained, were ignited for half an hour at white heat, after which they were made into a thick paste with distilled water and into this was sprinkled a liberal amount of platinum black. The resulting mixture, when of a homogeneous appearance, was rammed tightly into a 12" piece of 1/4" glass tubing. At either end of the column of platinized asbestos was a similar one, (G), of pure asbestos 2" long. Drying of the material was accomplished by suction and gentle heat. In fact, so tightly was the asbestos packed that suction had to be applied before the hydrogen could be forced through. At the end of an eight hour run the distilled water was so saturated with hydrogen bromide, that it fumed strongly when exposed to the air. Beyond any doubt, the hydrobromic acid, prepared in this manner, was very pure.

Hydrochloric acid.- The concentrated "C.P." hydrochloric acid was diluted with an equal volume of distilled water to

which was added two crystals of potassium permanganate, which liberated chlorine and so displaced any bromine present in the acid. The volume of this solution was 2000 c.c. The process of distillation was carried on in an all quartz still; the first and last 200 c.c. portions were rejected. The purified acid was kept in a winchester which had formerly contained hydrochloric acid.

Nitric acid.- To 1500 c.c. of the concentrated nitric acid ("C.P.") was added 150 c.c. of distilled water. The resulting mixture was distilled in an all quartz apparatus; the first and last 150 c.c. portions were rejected. The purified acid was tested in a mephelometer for traces of chlorine, but none was found. The resulting acid was kept in a bottle which had formerly contained nitric acid.

Sulphuric acid.- Concentrated sulphuric acid, of "C.P." brand, was distilled from a pyrex still; the first and last fractions were rejected. Any foreign substances which were likely to contaminate our pure sulphuric acid when distilled from a glass apparatus were completely removed by an elaborate system of recrystallization, since our last crop of caesium chloride crystals showed no evidence of containing any impurity.

Ammonium hydroxide.- The concentrated "C.P." ammonium hydroxide was heated in a quartz still and the resulting ammonia gas was bubbled into distilled water in a quartz flask. The middle fraction of ammonium hydroxide obtained in the above

manner was collected.

Barium Hydroxide.- The barium hydroxide, of "C.P." brand, was twice recrystallized from hot distilled water and filtered both times while still hot.

Ethyl alcohol.- A volume of 1200 c.c. of the "C.P." 95 % ethyl alcohol was distilled from a pyrex flask; the first and last 100 c.c. fractions were rejected.

Ammonium formate.- Ammonia gas, obtained by heating our purified ammonium hydroxide in a quartz still, was passed into redistilled formic acid, contained in a quartz flask, until the solution turned into a mass of yellow crystals, which smelled strongly of ammonia. Enough distilled water was added to make a saturated solution of the ammonium formate.

Barium chloride.- Barium chloride, of "C.P." variety, was dissolved in enough water to make an almost saturated solution at 100°C. It was then cooled to about 65°C. and to it was added an equal volume of redistilled water and treated again as above. The second crop of crystals were washed and dried by suction in a Gooch crucible after which they were kept in a tightly corked flask.

Invert Sugar.⁽¹⁾- Pure cane sugar was recrystallized once from distilled water. The crystals so obtained were about 1/4" - 1/2" in diameter and were perfectly transparent and very hard. The sugar was washed and dissolved in a minimum amount of

(1) L.R. Parks and P.G. Bartlett, Journ.Amer. Chem.Soc. 49, 1698(1927).

distilled water. To each litre of solution was added 30 c.c. of redistilled hydrochloric acid and the mixture kept at 50°C. for two hours. In two days the solution, now invert sugar, was ready for use.

Charcoal boat.- The charcoal was made from recrystallized sugar by carefully igniting a ground up portion of the latter in a porcelain boat until no more fumes came off. The carbon thus obtained was ground to a fine powder and made into a paste by adding 5 c.c. of a solution composed of one part of recrystallized sugar to five parts of distilled water. The paste was moulded between two porcelain dishes of slightly different sizes. In this way the boat can be made to any desired thickness. The sides should be at least 1/4" thick. Without removing the inner dish, the mould was transferred to a desiccator, in which it was left until dry. It was then removed and heated very slowly over a gas flame until no more fumes were evolved. After cooling, the inner dish was removed, leaving only the outside one in place. The carbon mould was kept in a desiccator until ready for use. A few small cracks in the boat were of no importance, as the silver, when molten, tended to coalesce into a ball.

Lime boat.- Pure calcium nitrate was recrystallized from distilled water, redissolved and the calcium precipitated as calcium carbonate by means of equal volumes of ethyl alcohol (redistilled) and ammonium carbonate. The resulting crystals

were washed and dried. The calcium carbonate was now made into a thick paste and moulded between two porcelain boats of slightly different sizes. The mould was desiccated and dried, at 100°C for two days, after which the inner boat was removed. The remainder of the mould was heated to redness for half an hour after which it was permanently kept in a desiccator. Since silver was to be fused in this boat, it was therefore necessary to ignite the latter in order to expell any residual nitric acid, which might contaminate the sample of molten silver with oxygen.

(1)

Silver.- Silver nitrate of the "C.P." brand, was twice recrystallized from distilled water to which had been added one c.c. of redistilled nitric acid. The resulting crystals were washed, as before, with 5 c.c. of distilled water, and dissolved in one litre of hot distilled water. To this was added a little at a time, with constant stirring, an equal volume of hot, .6 N., hydrochloric acid solution. The solutions were kept hot and very dilute so as to avoid as far as possible the occlusion of any silver nitrate in the precipitate. The silver chloride was washed first with hot water to avoid contraction of the mass, then with cold distilled water, until no appreciable test for

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- (1) H.V.A. Briscoe, Journ.Chem. Soc., 63,107(1915).
T.W. Richards & R.C.Wells, Journ.Amer.Chem.Soc.,37,459(1905).
G.P. Baxter & L.W. Parsons, Journ.Amer.Chem.Soc.,44,577(1922).
G.P. Baxter, Journ.Amer.Chem.Soc., 44,591(1922).
H. Krepelka, Journ.Amer.Chem.Soc., 42,925(1920).
N.H. Smith, Journ. Amer.Chem.Soc., 49,1642(1927).

chloride could be noticed. The chloride precipitate thus obtained was removed to a large pyrex beaker, to which had been added about one litre of invert sugar solution made alkaline with sodium hydroxide. The mixture was heated to 50°C. and well stirred for 30 min. In this way the silver chloride was reduced to a greyish-brown powder consisting of silver and silver oxide. The supernatant liquid was poured off and the residue when washed with distilled water, was removed. The mixture of the metal and its oxide was dissolved in a slight excess of redistilled nitric acid, to which was then added a quantity of ammonium formate which was sufficient to leave the mixture just acid. On gently warming, the silver nitrate was reduced to a buff colored residue. The silver precipitate was now thoroughly washed and dried; after which it was fused in a charcoal boat before a blast lamp, the nozzle of which was scrupulously cleaned. If the large buttons of silver, so obtained, are not kept hot too long and are cooled in a reducing flame, they are already very pure. Their purity suffices for ordinary work or even atomic weights of usual accuracy. Nevertheless they are not absolutely pure as they must contain about .001% sulphur, traces of carbon from the illuminating gas and oxygen from the air. Therefore when cooled, the silver most likely contains minute cells, enclosing gas. The buttons were now scrubbed

(1) Richards, Proc. Amer. Acad., 29, 65(1893).

(2) Richards and Wells, Journ. Amer. Chem. Soc., 37, 477(1905).

with a brush and carborundum powder then washed with distilled water, etched with redistilled nitric acid, washed again in dilute pure ammonium hydroxide and finally in distilled water. The silver was next subjected to an electrolytic process of purification, in which every conceivable trace of impurity must have been removed, except for about .02 - .05 % of the mother liquor. A button of the metal weighing about 6 gms. was dissolved in a slight excess of pure nitric acid and when diluted to 30 c.c. served as the electrolyte and was contained in a pyrex dish 3/8" deep and 4" in diameter. The silver was electrolyzed between platinum terminals maintained at 6 Volts for six weeks. The silver crystals, some of them .5 in. in length, were removed from time to time and kept beneath distilled water. The electrolyte was finally converted into the chloride to be used for next year's work. The silver crystals were thoroughly washed and in order to free them from all traces of mother liquor were finally melted for 7 min. on a lime boat in an atmosphere of hydrogen within a quartz tube. The hydrogen was prepared from zinc and sulphuric acid and was purified by being passed successively through strong solutions of barium hydroxide, alkaline potassium permanganate, alkaline pyrogallate and mercuric chloride. Lime seems to be a very good substance for a fusion boat, because it is so easily

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- (1) A. Findlay, *Prac. Phy. Measurements*, p.217(1923).
Koscoe & Schorlemmer, *Treatise on Chem. Non-metallic Elements*, Vol.1. p. 693.
H.V.A. Briscoe & H.F.V. Little, *Journ.Chem.Soc.*,105,1310(1914).

obtained pure and is so difficult to reduce, that no metallic calcium could be dissolved by the silver; of course the latter must be saturated with dissolved calcium oxide, but with an amount wholly negligible (less than $.0001\%$ CaO)⁽¹⁾. However, since lime is more or less friable, the buttons may become coated with the former; but due to the high surface tension of silver, the lime remains at the top and can be easily removed. Therefore the silver after fusion must be very pure and Stas states, that the amount of hydrogen dissolved in the silver is not over $.0004\%$. The buttons, so obtained, were filed with a new file, until all the former surface was removed; then washed with distilled water, etched with pure nitric acid, washed with pure dilute ammonium hydroxide and finally with distilled water. If the buttons were not already of the desired size, they were cut into pieces by means of a clean steel chisel before etching. The silver buttons were now placed in a quartz boat in a quartz tube and heated to 400°C . in a vacuum of 10 m.m. Hg. for 15 min., after which they were kept over potassium hydroxide until ready for use.

More silver was needed for the following year and the process of purification was the same as before, with only two minor changes. First: the boat or dish containing the electrolyte was now composed of quartz, instead of pyrex glass.

(1) Richardson and Wells, Journ. Amer. Chem. Soc., 37, 477 (1905).

Second: the hydrogen was carefully dried by means of calcium chloride and phosphorous pentoxide tubes, before passing over the molten metal.

Also another sample of silver, "B", was prepared by recovering the fused silver chloride buttons from our analyses. These were twice reduced by the invert sugar and ammonium formate processes and were not electrolyzed at all. The remainder of their treatment was the same as that given to the other samples.

Purification of caesium chloride.- To begin with, our caesium was in the form of a carbonate, whose original weight was 113 gms. The sample was dissolved in distilled water and the precipitate filtered off. The latter on examination, was found to be only silica. The solution was now made acid with redistilled hydrochloric acid, thereby converting the carbonate into a chloride, which was again filtered to remove the silica, then evaporated to 200 c.c. Enough pure iodine and hydrochloric acid were added to precipitate one half the amount of caesium in the solution; no visible reaction occurred. Chlorine, from an all glass generator with grease free stop-cocks, prepared from potassium permanganate and conc. "C.P." hydrochloric acid, was passed into the solution; thus precipitating the orange red caesium dichloriodide. The supernatant liquid was decanted off and a quantity of pure iodine, sufficient to precipitate one half the remaining caesium, was added. A further precipitate,

of orange red color, was obtained as more chlorine was passed in. When filtered, the mother liquor was evaporated to one quarter of its former volume and the solution again saturated with chlorine, after enough pure iodine had been added to precipitate the remainder of the caesium. The resulting crops of crystals were united, washed, dried by suction and divided into three portions. Each of the above lots was dissolved separately in a minimum amount of hot, distilled water; to which had been added 5 c.c. of pure hydrochloric acid and a few crystals of pure iodine. When cool, the solutions were filtered by suction and the resulting precipitates washed and then united, to give crystals "A". The three filtrates were united and evaporated to 100 c.c., whereby a crop of crystals was obtained.

"Table of Recrystallization of Caesium Dichloriodide."

Precipitate crystals by means of chlorine.

Redissolve these crystals in hot $H_2O(HCl)$ giving:-

Crystals "A" (164 gms.)

Mother liquor ML_1

Evaporate ML_1 to 100 c.c. giving:-

Crystals "B" (35 gms.)

Mother liquor ML_2

Redissolve "A" in hot $H_2O(HCl)$ giving:-

Crystals 1'

Mother liquor ML_3

Evaporate ML_3 to 100 c.c. giving:-

Crystals 1"

Mother liquor ML_4 (Keep 5 c.c. for testing).

Unite crystals 1' and 1" giving (1)

Unite ML_4 and crystals "B" giving:-

Crystals 1 a

Mother liquor ML_5

Redissolve (1) in hot $H_2O(HCl)$ giving:-

Crystals 2'

Mother liquor ML_6

Evaporate ML_6 to 100 c.c. giving:-

Crystals 2"

Mother liquor ML_7

Unite crystals 2' and 2" giving (2)

Unite 1 a and ML_7 giving:-

Crystals 2 a

Mother liquor ML_8

Redissolve (2) in hot $H_2O(HCl)$ giving:-

Crystals 3'

Mother liquor ML_9

Evaporate ML_9 to 100 c.c. giving:-

Crystals 3"

Mother liquor ML_{10}

Unite crystals 3' and 3" giving (3)

Unite crystals 2 a and ML₁₀ giving:-

Crystals 3 a

Mother liquor ML₁₁

Unite (3) and 3 a giving III (126 gms.)

Unite ML₂, ML₅, ML₈, and ML₁₁

Redissolve III in hot H₂O(HCl) giving:-

Crystals 4'

Mother liquor ML₁₂

Evaporate ML₁₂ to 100 c.c. giving:-

Crystals 4"

Mother liquor ML₁₃ (Keep 5 c.c. for testing).

Unite crystals 4' and 4" giving (4).

Redissolve (4) in hot H₂O(HCl) giving:-

Crystals 5'

Mother liquor ML₁₄

Evaporate ML₁₄ to 100 c.c. giving:-

Crystals 5"

Mother liquor ML₁₅

Unite crystals 5' and 5" giving (5)

Unite ML₁₃ and ML₁₅. heat and filter off silica.

Evaporate ML₁₃ and ML₁₅ to dryness giving:-

Crystals 5 a

Unite crystals 5 a and (5) giving (6).

Before subjecting the caesium dichloriodide to recrystallization 5 c.c. of the filtrate, which should contain one quarter of the caesium chloride, was evaporated to dryness and ignited at 200° C. in a quartz boat, until it was a pure white color. On being examined with the spectroscope, the only impurity found was sodium; no trace of potassium, reubidium or lithium could be seen.

Further, on treating 10 c.c. of the combined mother liquors, ML_2 , ML_5 , ML_8 , and ML_{11} , in the same way, sodium was the only impurity found.

Also the 5 c.c. of ML_4 was examined spectroscopically and no impurities were found. Therefore, sodium was eliminated somewhere between ML_2 and ML_4 . The 5 c.c. from ML_{13} also gave negative results, which showed that our caesium dichloriodide was pure as could be prepared.

The crystals of caesium dichloriodide ((6)) were now placed in a large, quartz evaporating dish and gently heated, so as to expell all the iodine. During their heating, they were frequently stirred and once in a while transferred to a mortar and gently ground, in order to facilitate the reaction and to ensure a homogeneous product, which after two days heating, was a pure white color and weighed 61 gms. The caesium chloride thus obtained was dissolved in 30 c.c. of distilled water and filtered to remove silica. Hydrogen chloride, generated by the action of conc. "C.P." sulphuric acid upon

conc. "C.P." hydrochloric acid, in an all glass apparatus, was passed into the solution; whereby caesium chloride was precipitated by the common ion effect.

Recrystallization of Caesium Chloride.

Dissolve crystals A in 30 c.c. hot H_2O giving:-

Solution l_1

Pass HCl into l_1 giving:-

Crystals (1)'

Mother liquor ML_2

Evaporate ML_2 to 20 c.c. and pass in HCl giving:-

Crystals (1)" (yellow)

Mother liquor ML_2 ,

Unite crystals (1)' and (1)" giving (1).

Redissolve crystals (1) in hot H_2O and pass in HCl giving:-

Crystals (2)'

Mother liquor ML_3

Evaporate ML_3 to 100 c.c. giving:-

Crystals (2)" (yellow).

Mother liquor ML_3 ,

Unite crystals (2)' and (2)" giving (2).

Redissolve crystals (2) in hot H_2O and pass in HCl giving:-

Crystals (3)'

Mother liquor ML_4

Evaporate ML_4 to 10 c.c. giving:-

Crystals (3)" (yellow).

Mother liquor $ML_{4'}$

Unite crystals (3)' and (3)" giving (3).

Redissolve crystals (3) in hot H_2O and pass in HCl
giving:-

Crystals (4)'

Mother liquor ML_5

Evaporate ML_5 to 10 c.c. giving:-

Crystals (4)" (yellow). (Set aside for testing).

Mother liquor $ML_{5'}$

Redissolve crystals (4)' in hot H_2O giving:-

Crystals (5)

Mother liquor ML_6

Redissolve crystals (5) in hot H_2O giving:-

Crystals (6)

Mother liquor ML_7

The crystals (6) were dried by suction and kept in a desiccator over calcium chloride.

The canary yellow crystals viz. (4)" were tested, without result, for iodine and iron. We now suspected the presence of an acid salt and took steps to verify our suspicion.

Analysis:

Weight of oxalic acid = .1502 gms.
Weight of sodium hydroxide = 1.500 gms.
17.5 c.c. of xN. Sodium hydroxide = .1502 gms oxalic acid.

. . Normality of sodium hydroxide = .1363 N.

Weight of caesium chloride = .1645 gms.

But .1 c.c. of .1363 N. sodium hydroxide are necessary for neutralization.

This shows that no acid salt was present; but just a trace of residual hydrochloric acid. However, on heating the yellow salt the color disappears and does not return on cooling. Further, when the latter were tested with starch potassium iodide solution, we obtained a positive test for the presence of free chlorine. It now seems probable that some chlorine was actually in feeble combination with the caesium chloride molecule and the formula for the salt will be of the nature of $CsCl_2Cl$ cf. $(CsCl_2I)$.

An Examination of the Yellow Caesium Chloride.- The yellow colored caesium chloride previously mentioned and prepared by passing hydrogen chloride into a solution of caesium chloride was now investigated in larger quantities. About a gram of this salt was placed in a clean porcelain boat within the fusion tube of the "bottling apparatus". After reassembling the apparatus, the salt was heated so as to just fuse in an atmosphere of pure, dry nitrogen and hydrochloric acid. The

chloride was kept in a molten condition for about 2 min., after which time the hydrochloric acid bottle was cut out, leaving only a stream of pure nitrogen passing through the apparatus. The salt was still maintained at its melting point in the atmosphere of nitrogen for an additional 3 min., after which it was allowed to cool. This fusion process was performed in the same manner and with the same care as was given to any atomic weight analysis. However, subsequent chloride analyses did not employ an atmosphere of both nitrogen and hydrochloric acid; but only the former. When cool, the boat was removed and its contents inspected. The original canary yellow color of the caesium chloride had not completely vanished, as the salt near the middle of the boat was still of a faint yellow tinge. As a result the boat and its contents were replaced in the fusion tube and melted again for 10 min. When cooled, the now colorless salt was dissolved in 20 c.c. of redistilled water and the resulting solution was found to be absolutely neutral. Therefore no error could be introduced into an atomic weight determination by using the yellow, instead of the pure white, caesium chloride.

Recovery of Caesium Chloride and its Conversion into Bromide.-

The caesium, after the analysis, is in the form of nitrate, being contained in the filtrate along with some silver nitrate. The latter is almost completely removed by the addition of a small quantity of pure hydrochloric acid and subsequent filtration.

However, the solution is not free from silver as silver chloride is slightly soluble in a salt solution and quite soluble in strong hydrochloric acid or brine solution.

The combined filtrates were evaporated to a small volume, diluted to 250 c.c. and left over night. On examination, a large mass of long, white, silky, needle-like crystals were found to have been deposited. The supernatant liquid was decanted off and treated with pure hydrochloric acid; whereby, a white precipitate of silver chloride formed. Some of the above mentioned crystals were kept for examination, the remainder dissolved in water. The rate of solution of these crystals was very slow, even in 250 c.c. of water. The decanted liquid and the above mentioned solution were saturated separately with hydrogen sulphide. The latter was made from iron pyrites and dilute "C.P." hydrochloric acid and before being passed into the solution was thoroughly washed with water, in order to remove any soluble impurities contained in the gas. The solutions were filtered free from silver sulphide and again saturated with the gas; but with no result. The filtrates were now united and evaporated to 75 c.c. Upon cooling, the same needle-like white crystals were deposited, similar to those mentioned before. 13 c.c. of conc., redistilled sulphuric acid were added and the mixture evaporated, until the white fumes of sulphur trioxide were evolved. The resulting compact, crystalline, mass was dissolved in water, containing 1 c.c. of

pure sulphuric acid and again evaporated as above and the process repeated. The crystals so obtained were dissolved in 500 c.c. of distilled water and heated to 80° C., whereupon a hot solution of recrystallized barium chloride was added, until no further precipitate formed. The solution was filtered and to the filtrate was added a dilute solution of pure sulphuric acid, until precipitation ceased. The solution, containing caesium chloride and sulphate; but no barium salt in dissolved form, was filtered; then evaporated to dryness. The salt was covered and placed under a bell-jar for the summer months. We now decided to work with the bromide instead of the chloride, as we had done last year; hence our conversion from chloride to bromide. The caesium chloride was dissolved in distilled water and added to the mother liquors of last years chloride purifications, viz. Ml III, IV, and V, which contain nothing but the chloride and dichloriodide of caesium. In this way no foreign impurity was annexed. To the resulting solution 19 c.c. of conc. pure sulphuric acid were added and evaporation continued, until white fumes were evolved. The crystals were dissolved in 400 c.c. of distilled water at 80° C. and to this was added an excess of a hot solution of recrystallized barium chloride. After filtering, the solution was treated with a slight excess of pure sulphuric acid and again filtered. The solution was made acid with hydrobromic (conc. and redistilled) with an excess of 15 c.c.; filtered and evaporated as below.

Recrystallization of Caesium Bromide.

Evaporate the original solution of CsBr giving:-

Crystals 1

Mother liquor ML_1 (10 c.c.)

Dissolve crystals 1 in hot $H_2O(H Br)$; filter and evaporate giving:-

Crystals 2

Mother liquor ML_2 (7 c.c.)

Dissolve crystals 2 in hot $H_2O(H Br)$; evaporate to dryness; heat to $120^{\circ} C.$ for 4 hrs; dissolve in H_2O and filter off silica; add 10 c.c. of HBr and evaporate giving:-

Crystals 3

Mother liquor ML_3 (5 c.c.)

Dissolve crystals 3 in hot H_2O and evaporate giving:-

Crystals 4

Mother liquor ML_4 (5 c.c.)

Dissolve crystals 4 in hot H_2O and evaporate giving:-

Crystals 5

Mother liquor ML_5 (5 c.c.)

Dry crystals 5 in a desiccator over phosphorous pentoxide. The drying process lasted about 3 weeks, during which time many peculiar things took place. The caesium bromide first turned a

yellowish red around the edges and the crystalline mass a mauve color. A few days later a brown crust⁽¹⁾ formed over the surface, covering a pure white interior and when the lid to the desiccator was removed, dense clouds of hydrogen bromide were liberated. Seeing the possibility of an acid salt, a further crop of crystals was obtained by evaporating Ml_2 to 3 c.c., at which volume the solution became a beautiful, light purple color. The solution was cooled, filtered by suction and dried in this manner for one hour; the crystals were a pure white color. A portion of the crystals, weighing .2014 gms., was neutralized by .3 c.c. of .1363 N. sodium hydroxide; thus eliminating the possibility of any acid salt. Since the bromide had lost hydrobromic acid, even after being twice recrystallized from water, we suspected that the brown portion might be alkaline. However, on titration, this portion was found to possess the same degree of acidity, as the sample previously mentioned. But when a small amount of the brown residue was dissolved in water a transparent sandy precipitate was left behind. This meant one of two things, either silica was present or phosphorous had combined with the caesium to give a phosphide. The latter is decomposed by water, liberating small amounts of phosphine and hydrogen and depositing a hydride of phosphorous. The solution was immediately tested for the latter; but with no result. The

(1) H.L. Wells and S.L. Penfield, Journ. Chem. Soc., A II 62, 773(1892).

whole sample of caesium bromide was now heated in an oven at 125°C. for 2 hours, after which it was dissolved in distilled water and filtered. The residue was at first a brown color, but in 5 minutes became colorless, evidently, having lost bromine. The filtrate became a milky color when diluted and hence was again filtered; further dilution produced no precipitate. The solution was evaporated to a small volume giving:-

Crystals 6

Mother liquor Ml_6

The caesium bromide was filtered and dried by suction for an hour; the so formed crystals were perfectly white. The latter were removed to a vacuum desiccator and kept at a very low pressure for two days.

Repurification of Caesium Bromide.- The repurification process for caesium bromide was, in most respects, very similar to the procedure used in its purification. During the process, whenever we saw the possibility of an objectional chloride or sulphate of caesium being present a recrystallization was made. In this way we made sure, beyond any doubt, that our final product was absolutely pure. Also great care was taken to purify all the chemicals used in the procedure from chlorides and sulphates.

All the unused caesium bromide was added to the solution of caesium nitrate, containing a small amount of dissolved silver bromide, obtained from the previous unsuccessful bromide

analyses. The resulting solution was evaporated to 100 c.c., during which the liquid assumed a dark red color and gave off abundant fumes of bromine and hydrogen bromide. The solution became a pale yellow color as its volume approached 100 c.c.. It was then diluted to 250 c.c. and saturated with hydrogen sulphide prepared from iron pyrites and dilute "C.P." hydrochloric acid in a Kipp generator, Before being passed into the caesium solution the gas was twice washed with water. The scanty greyish precipitate formed was filtered off and the filtrate again saturated with the gas, but with no result. A volume of 30 c.c. of concentrated, redistilled sulphuric acid was added and the solution evaporated until the white fumes of sulphur trioxide were evolved for at least five minutes. This process was repeated three times and each time an additional 2 c.c. of the concentrated acid was added to compensate for that which was lost during the evaporating process. The last evaporation was continued for an hour after the first white fumes made their appearance. When cool, the viscous solution was diluted with 10 c.c. of distilled water; immediately a white precipitate formed. The mother liquor, containing any undecomposed caesium chloride, was drained off. The resulting crystals, crystals "A", were dissolved in 600 c.c. of hot distilled water, to which was then added a solution of twice recrystallized barium hydroxide, until no further precipitate formed. The barium sulphate thus formed was filtered off and to

the filtrate was added a dilute solution of pure sulphuric acid, until the latter was present in a slight excess. The solution was then filtered and evaporated in a large platinum dish to a volume of 125 c.c. During the evaporation a white crystalline precipitate was deposited, presumably barium sulphate. After the solution of caesium hydroxide had cooled, a few c.c.^s of pure barium hydroxide were added to get rid of the slight excess of sulphuric acid. There was no danger of having added too much of the former, as much of the caesium hydroxide had been converted into the carbonate during the evaporation, and by virtue of this took care of an excess of the latter, precipitating it as barium carbonate. The solution was filtered and to the filtrate at 40°C., was added enough doubly distilled bromine to leave the solution highly colored. A white crystalline precipitate, probably caesium bromate, was formed which dissolved when the solution was heated. Evaporation was continued until the solution reached a volume of 50 c.c.; it was then cooled and to it was added five drops of bromine. The resulting mother liquor was poured off and along with it went any trace of barium bromide or sulphate that might have been present, leaving the crystals, "B", as pure caesium bromate, bromide and hypobromite along with some silica. The above mentioned crystals were placed in a porcelain evaporating dish and heated to a temperature of 350°C. for 20 min., after which they were fused for 5 min. The fused mass was of a clear color and no fumes of

bromine or hydrogen bromide were given off. The resulting product was known as crystals "B",. These were dissolved in distilled water and the silica filtered out. The filtrate was acidified with 2 c.c. of synthesized hydrobromic acid of our own preparation and a crop of crystals obtained.

Table of the Recrystallization of Caesium Bromide.

From conc. H_2SO_4 obtain:-

Crystals "A"

Mother liquor ML_A (10 c.c.)

Dissolve crystals "A" in H_2O convert to bromide and evaporate giving:-

Crystals "B"

Mother liquor ML_B (7 c.c.)

Heat crystals "B" to $350^{\circ}C$. for 20 min.; fuse for 5 min. giving:-

Crystals " B_1 "

Dissolve crystals "B" in H_2O and filter: add 2 c.c. HBr; evap. giving:-

Crystals 1

Mother liquor ML_1 (7 c.c.)

Dissolve crystals 1 in H_2O (2 c.c. HBr) giving:-

Crystals 2

Mother liquor ML_2 (5 c.c.)

Dissolve crystals 2 in H_2O giving:-

Crystals 3

Mother liquor ML_3 (5 c.c.)

Dissolve crystals 3 in H_2O giving:-

Crystals 4

Mother liquor ML_4 (15 c.c.).

Crystals 4 were filtered by suction for an hour in a Gooch crucible, after which they were kept over sodium hydroxide sticks until ready for use.

However, when a few drops of ML_4 were treated with a dilute solution of pure barium chloride, a white precipitate was formed, which dissolved when the solution was acidified with several drops of concentrated nitric acid. The above mentioned precipitate was evidently barium sulphate and not barium carbonate, since no gas was evolved as the former dissolved. Further, when crystals 4 were treated in a similar manner only a very faint turbidity was produced, which showed that the removal of the sulphate by the process of recrystallization was somewhat slow.

A few crystals of our first sample of caesium bromide were now tested by means of a solution of pure barium chloride and were found to contain a large amount of sulphate, which, no doubt, accounted for the poor results obtained in the atomic weight determinations.

Having discovered our real trouble we now proceeded in

the following manner:

Dissolve crystals 4 in H_2O giving:-

Crystals 5 (containing a trace of SO_4).

Mother liquor ML_5 (7 c.c.).

Unite mother liquors ML
1, 2, 3, 4, 5.

Enough pure barium bromide was added to the combined mother liquors to precipitate three quarters of the sulphate present, after which the solution was filtered and evaporated giving:-

Crystals 6

Mother liquor ML_6 (15 c.c.).

Unite crystals 5 and 6 dissolve in H_2O giving:-

Crystals 7.

Mother liquor ML_7 (10 c.c.).

Crystals 7 were found to be sulphate free and hence were kept over solid sodium hydroxide until ready to be used.

The caesium bromide after being repurified was unquestionably pure; not the slightest trace of any impurity could be found. The possibility of the presence of any trace of chloride or sulphate was nil; since great care had been taken to eliminate these at every possible point. As a result the fusion of the caesium bromide could now be performed in a platinum boat without the decomposition of the former nor the corrosion of the latter.

Sample No. I of caesium chloride was obtained from the British Drug Houses, London; and prepared as previously described.

Sample No. II of caesium chloride was obtained from Buckfield, Maine. This portion was purified by Dr. Archibald in a similar manner to first. However, after the dichloriodide treatment, this salt was twelve times recrystallized as the chloride from water; the last mother liquor was water white in color.

Analysis of U.B.C. Distilled Water 9/24/27.

Amt. Distilled = 1000 c.c.

Wt. of Pt. dish = 49.8326 gms.

" " " " + residue = 49.8338 gms.

∴ Wt. of residue = .0012 gms.

Analysis of U.B.C. Distilled Water 2/2/28.

Amt. distilled = 2000 c.c.

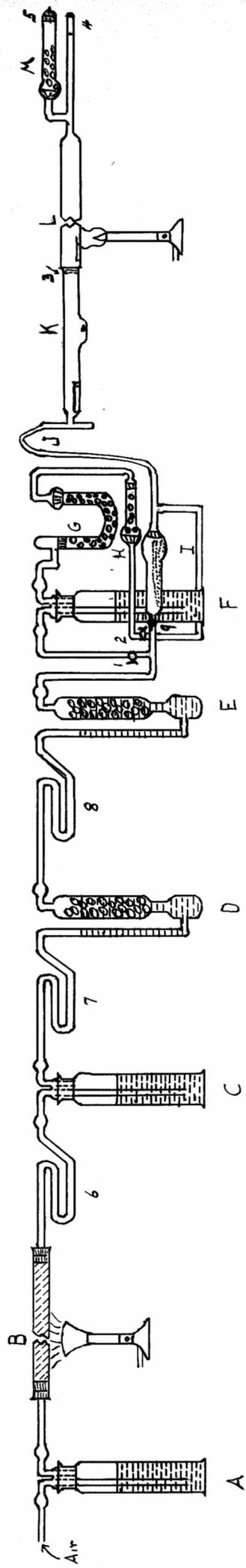
Wt. of Pt. dish = 78.90549 gms.

" " " " + residue = 78.90750 gms.

∴ Wt. of Residue = .002 gms.

∴ " " " per litre = .001 gms.

Specific conductivity = 4.3×10^{-6} ohms.



Purification Train for Gases and "Botting Apparatus"

Fig 2

VI. DESCRIPTION OF APPARATUS.

- A. Wash bottle containing some of our purified concentrated ammonium hydroxide. When pure dry air is required, in place of nitrogen, this unit is removed.
- B. Pyrex tube two feet in length packed with fine threads of pure copper. Heat is applied at the centre so that the rubber corks at either ends are not effected.
- 6-7-8 These glass coils are inserted so as to take up any strain to which the apparatus may be subjected.
- C. Wash bottle containing a dilute solution of redistilled sulphuric acid, which will remove any trace of ammonia that has not been decomposed in B.
- D. Tower of beads soaked in a concentrated solution of potassium hydroxide, for the purpose of absorbing any sulphur gases.
- E. Tower of beads moistened with redistilled concentrated sulphuric acid for drying purposes.
- F. Wash bottle partly filled with redistilled hydrobromic acid.
- G. U tube filled with recently reheated, anhydrous calcium bromide.
- H. Drying tube packed with the same material as G.
- I. Large drying tube filled with phosphorous pentoxide.
- J. Fine glass tubing arranged in a spring-like fashion, thus permitting "bottling apparatus" to be twisted one quarter turn.

- K. Bottling chamber of soft glass containing weighing bottle and stopper in position.
- L. Hard glass fusion tube containing platinum boat.
- 3. One inch ground glass joint connecting K and L.
- M. Drying tube filled with calcium chloride (anhydrous).
- 4,5. ground glass stoppers.
- 1. Stop cock lubricated with concentrated sulphuric acid.
- 2-9 Stop cocks lubricated by means of a paste of phosphorous pentoxide.

Note. 1 and 2 are kept closed, except when fusing caesium bromide in the bottling apparatus, (KLM).

VII. ANALYSIS OF THE CHLORIDE.

The water used throughout the analysis was made from redistilled laboratory distilled water, to which had been added two crystals of potassium permanganate and .5 c.c. of .1 N sodium hydroxide. The still and condenser were made of fused "milky" quartz - the receiver of clear fused silica. The water thus obtained ⁽¹⁾ was stored in pyrex flasks, which had contained distilled water for the last 10 years. In this way we were sure that all soluble substances in the glass had long since been removed. Nephelometer tests failed to show the presence of chlorine, not only in our pure product, but also in the ordinary distilled water.

(1) Specific Conductivity = 1.43×10^{-6} Ohms.

Before starting the analyses, a platinum boat was thoroughly cleaned in several portions of nitric acid followed by hydrochloric; thus removing all traces of iron. It was then dried, weighed and in it was placed a known weight of our caesium chloride; after which the boat and contents were placed in a clean pyrex tube and heated until the chloride just fused. On cooling, the platinum vessel was found not to have adhered to the glass, nor was it in any way attacked by the caesium chloride. Therefore no error could be introduced in this way.

The balance, used in all determinations, was of the short arm type, manufactured by Henry Troemner and had been used only once before by Dr. Archibald for a previous atomic weight determination. When not in use it was kept in an air-tight box; hence isolated from all fumes. Before using, the instrument was inspected and thoroughly cleaned. A new set of gold plated brass weights of the best make were carefully standardized, according to a method devised by Richards.⁽¹⁾ The weights were again standardized at the completion of the work and no difference in their value was noted.

For the dissolving of silver the following apparatus was found to be the most efficient: a 10 c.c. pipette was ground into the neck of a florence flask in such a way that the tip of the former reached almost to the bottom of the latter. To the neck of the flask was attached a U-tube which could be partly

(1) T.W. Richards, Journ.Amer.Chem.Soc., 22, 144(1900);
Z. Phys.Chem. 33, 605(1900).

filled with dilute nitric acid and in this way the loss of any silver nitrate in the spray was prevented. During the experiment, the pipette was removed only twice; therefore minimizing the danger of falling glass from the ground joint.

(1)
Pure nitrogen was prepared from ammonia by passing air through a concentrated solution of ammonium hydroxide; the ammonia being oxidized to nitrogen as it passed over heated copper turnings; the nitrogen then passed through successive purification columns containing, dilute sulphuric acid, concentrated potassium hydroxide, concentrated sulphuric acid, phosphorous pentoxide and then into the "bottling apparatus."

Procedure:

A small button of pure silver was weighed on tared watch glasses, allowances being made for the differences in densities of silver and the brass weights. Vacuum correction for silver is $-.000031$ gms. per gm. of metal. The weighed sample was now dissolved in the solution flask, by means of pure nitric acid and the silver nitrate, thus formed, was diluted to a volume of 600 c.c.

The caesium chloride was placed in a clean platinum boat within the heavier of two tared weighing bottles. The weight of the salt was adjusted, so that when the reaction was over, there would be a small excess of silver nitrate. One analysis

(1) T. W. Richards & E. P. R. Sacrens, Journ. Amer. Chem. Soc., 46, 939 (1924)
H. C. Kremers & C. W. Blake, Journ. Amer. Chem. Soc., 40, 601 (1918).

was tried with an excess of caesium chloride; but due to the fact, that both caesium and silver chlorides were present in the filtrate, our colorometric analysis was a failure, although the gravimetric part was unaffected. The above sample was now transferred to the "bottling apparatus", through which had been running a stream of pure, dry nitrogen for the last 15 minutes. The glass stopper, belonging to the weighing bottle, was first pushed into its hiding place; the bottle itself being left at the extreme end of the cooling chamber. The platinum boat containing the salt was then placed in the fusion chamber. The apparatus, having been reassembled, was left for 20 minutes; so that the nitrogen, which had been running uninterruptedly, might sweep out any air that had entered during the bottling process. Heat was applied to the fusion tube, so that the chloride just fused and no more than fused. The tube and contents were cooled for 20 minutes in a stream of nitrogen gas and when thoroughly cool, the latter was shut off and a stream of pure, dry air was forced through the apparatus for about 20 minutes. The platinum boat was then pushed into its weighing bottle by means of a long glass rod; then the stopper was rolled out of its niche and rammed firmly into the glass bottle. The air, which had been running all the time, was turned off; the apparatus taken apart and the weighing bottle removed to a desiccator for 30 minutes. The caesium chloride was now very accurately weighed; deductions being made for the boat, weighing bottles and

vacuum correction, (.00016 gms. per gm. of salt). The chloride was now washed from the boat into a large, glass-stoppered erlenmeyer flask and the solution diluted to 700 c.c. The flask used in the procedure was covered with two layers of black, glazed paper, which covering served to protect the silver chloride from the light, when filtering.

The precipitating process took place in a dark room illuminated by a single red light. The silver nitrate solution was added very slowly to the chloride, meanwhile stirring continuously. The vessel, containing the former, was thoroughly rinsed with several portions of water, which were also added to the chloride solution. The addition of the one solution to the other required from 75 to 90 minutes. The solutions were mixed slowly and in dilute form, to avoid any occlusion of silver nitrate. The precipitated mixture was given a final shake and left in the dark room over night. Before filtering, the flask was again shaken. Filtration was carried on in new, cleaned, platinum crucibles provided with a porous mat, composed of a platinum iridium alloy. Before being used, they were washed with several portions of hot nitric acid, hydrochloric acid, water, ammonium hydroxide and finally water (redistilled). They were then heated to 150°C. for 1 hour, desiccated for an equal time and carefully weighed; one being used as a tare for the other. The heavier one was now placed in the suction flask ready for use. A platinum lid to the crucible protected the

chloride precipitate from the action of light. Before removing the precipitate to the crucible, the supernatant liquid was poured off through the suction filter and the former shaken for 30 minutes with two, separate, 50 c.c. portions of water, which were then added to the original filtrate. The precipitate was now soaked for 1 hour in 200 c.c. of water, after which it was completely washed out into the crucible. The black paper was now removed from the flask, so as to make sure every speck of silver chloride had been removed to the platinum crucible. This last portion of water, consisting of more than 200 c.c., was classed as wash water and was kept separate from the filtrate. The precipitate was then washed with two portions of water (50 c.c.), so as to remove all silver nitrate from the residue, which would otherwise seriously impair our results.

The crucible and precipitate, now covered with the platinum lid, were removed to an oven, and maintained at a temperature of 150°C ., for 2 hours; after which they were desiccated for an hour. The crucible was now tared and carefully weighed; with due allowance being made for the vacuum correction of silver chloride, amounting to .00007 gms. per gram of the chloride.

In order to expell the last trace of moisture the dried button was removed from the platinum crucible to a previously cleaned, ignited and desiccated porcelain one, which was tared by another porcelain crucible, similarly treated. After being carefully weighed it was heated, so that the contents were just

fused, after which it was desiccated for an hour and the loss in weight determined by weighing. However, as silver chloride is slightly soluble in water, the above weight does not represent the total mass of chloride that was precipitated: an appreciable amount being contained in the wash water.

Wash Water.- In order to estimate the amount of chloride dissolved in the wash water, a standard solution of silver nitrate was required for comparison. A known weight of pure silver was dissolved in a minimum of pure nitric acid, contained in the previously described apparatus. The silver nitrate solution, thus obtained, was diluted to exactly 2000 c.c. by means of a recently standardized volumetric flask; calibrated to deliver 1000 c.c. of redistilled water, when drained for 30 seconds. The wash water will contain dissolved silver chloride, which can be precipitated with silver nitrate by the common ion effect and hence, determined colorometrically. When a few drops of acidified, concentrated silver nitrate solution were added to a known volume of the former, a turbid solution was formed; which, on being diluted to 100 c.c., was compared with a definite volume of our standard solution, diluted to an equal volume and precipitated by hydrochloric acid. Both solutions were precipitated at the same time and diluted to exactly 100 c.c. in two long tubes of the same size and material. Then, since the volume of our wash water had been accurately measured, we were therefore able to calculate the total weight of dissolved silver^{chloride.}

However, some difficulty was experienced in producing two precipitates of the same color. With equal quantities of

the same solution we were able to produce precipitates, ranging all the way from a very light grey to an almost azure blue color. We found, that if the concentration of the nitric acid was the same in both solutions and both precipitations made at the same time, that the resulting turbid solutions were of the same shade. It then appeared that the acid concentration must determine the size of the individual particles and their rate of aggregation. Also,,since the solubility of a sparcely soluble salt varies with the degree of dispersion of its particles, we can assume that the nitric acid diminished the solubility. Moreover, on observing the fresh turbid solution for a few minutes, we could notice the color gradually change from a bluish to a greyish tinge and remain so for several hours. The color change was fairly rapid, progressing at a constant rate and at no time showing any evidence of a decided increase or decrease in speed. A variable solubility of this nature may be due to one of two causes: the precipitate may be capable of existing in several allotropic forms, of which the most unstable appears at first: or the size of the individual particles may be gradually increasing. The work of Oswald⁽¹⁾ and Hulett⁽²⁾ has shown how greatly a difference in size of the grains may effect the solubility, especially of a salt only slightly soluble.

Filtrate.- The volume of the filtrate was carefully measured and its silver nitrate content colorometrically estimated.

(1) Oswald, Ztschr.Phy.Chem., 22,307(1897)
(2) Oswald, Ibid., 34, 495(1900).
(3) Hulett, Ibid., 37,385(1901); 47,357(1904).

This showed us just how much silver was actually required to react with all the caesium chloride and so gave us a second method to determine the atomic weight.

Analysis No. 5:

Weight of Silver	2.74335	gms.
Vac. Correct	<u>-0.00008</u>	"
. . Weight of silver	2.74327	"
Weight of CsCl after fusion	4.27543	gms.
Vac. Correct.	<u>0.00068</u>	"
. . Weight of CsCl	4.27611	"
Weight of AgCl	3.93234	Gms.
Vac. Correct.	<u>0.00026</u>	"
	3.93260	"
Loss in fusion	<u>0.00044</u>	"
	3.93216	"
Dissolved AgCl	<u>0.00176</u>	"
	3.93392	"
Wt. of crucible	<u>0.29480</u>	"
. . Weight of AgCl	3.63912	" .

Colorometric Analysis:

Standard solution contain .00958 gms. Ag./2000 c.c.

Wash Water:

Volume = 830 c.c.

On adding a conc. solution of AgNO_3 to wash water:
5 c.c. Standard soln. = 15 c.c. of wash water,
Corresponding to .00176 gms. AgCl in 830 c.c.

Filtrate:

Volume = 1480 c.c.

On adding HCl to the filtrate:

15 c.c. of Standard soln. = 24 c.c. of filtrate,
Corresponding to .00443 gms. Ag . in 1480 c.c.

∴ Actual amount of silver required = $2.74327 - .00443$
= 2.73884 gms.

Calculations:

$$\text{Mol. Wt. of CsCl} = \frac{3.63912}{4.27611} = \frac{143.338}{X}$$

$$\therefore X (\text{CsCl}) = 168.427 \quad (\text{at. wt. of Cl} = 35.457).$$

$$\therefore \text{At. Wt. of Cs} = 132.970$$

$$\text{Mol. Wt. of CsCl} = \frac{2.73884}{4.27611} = \frac{107.880}{X}$$

$$\therefore X (\text{CsCl}) = 168.431 \quad \therefore \text{At. Wt. of Cs.} = 132.975$$

VIII. ANALYSIS OF THE BROMIDE.

On first sight, due to the extremely insoluble nature of the silver bromide, this analysis would appear to be much easier than that of the chloride; but as a matter of fact it was much more troublesome than the former. In the first three analyses we met with difficulties from start to finish. The procedure followed was almost identical with that of the chloride, with the exception of slight variations of minor importance. The

WEIGHTS - RATIOS - ATOMIC WEIGHTS OF CAESIUM.

		Cl = 35.457									
No. of analysis:	Sam-ple of CsCl :	Weight of CsCl in a. vacuum.	Weight of AgCl in a. vacuum.	Weight of Ag in a. vacuum.	Ratio of AgCl: CsCl=100:x:	Ratio of Ag: CsCl=100:x:	Atomic weight of caesium gravimetrically.	Atomic weight of caesium colorometrically.			
		3.73344	3.17745	2.39124	117.498	156.131	132.961	132.976			
1	I	3.73344	3.17745	2.39124	117.498	156.131	132.961	132.976			
2	I	3.66651	3.11997	2.34860	117.517	156.114	132.989	132.960			
3	I	3.10787	2.64511	—	117.495	—	132.957	—			
4	I	3.92746	3.34251	2.51555	117.501	156.127	132.965	132.973			
5	I	4.27611	3.63912	2.73884	117.504	156.130	132.970	132.975			
6	I	4.50248	3.83195	2.88407	117.498	156.117	132.961	132.965			
		Average (a).....			117.502	156.124	132.967	132.970			
7	II	2.78213	2.36770	1.78200	117.503	156.124	132.967	132.970			
8	II	.94854	.80720	.60752	117.510	156.134	132.978	132.980			
		Average (b).....			117.507	156.129	132.973	132.975			

fusion chamber of the apparatus was thoroughly washed and dried before being used for the bromide. The fusion was still carried out in an atmosphere of pure dry nitrogen.

The first sample was fused in a platinum boat, but the salt on melting turned a dark, reddish-brown color; it was therefore kept in a molten condition for five minutes, during which time the salt became much lighter in color and gave off abundant fumes of hydrogenbromide and bromine. The bromide was bottled in the usual manner and upon examination was found to be a dirty, greyish-black color. When brought into solution with water a very fine, black precipitate settled out; but the solution, on being tested with indicators, was neither acid nor alkaline. However, the platinum boat had lost .00283 grams during the process. Since it was impossible for us to use a platinum boat we then chose a quartz one. As was expected, the bromide still turned a dark brown color, but upon five minutes further heating was absolutely colorless. Caesium bromide, just like the chloride, contracts considerably upon cooling and as a result our quartz was badly fractured; in fact it was recovered by filtration, followed by ignition and weighing. The salt, when cooled, was a beautiful, white, crystalline mass. As a last resort a porcelain boat, placed on a piece of platinum foil, was used for the fusion, and served the purpose splendidly; for it was neither cracked nor attacked by the molten salt.

Since our platinum boat was badly corroded by the molten salt and since the latter, when dissolved in water, was neutral to indicators; we came to the conclusion, that the caesium bromide contained a considerable amount of extra bromine in combination. The peculiar behavior of the salt when drying over phosphorous pentoxide also supports our conclusions as to its composition. One would expect the salt to become alkaline upon loosing any of its constitutional bromine; but since the fused salt was neutral, then the bromine liberated must have been extra or added bromine. Fusion appears to be the one and only way to get rid of this additional bromine, as we had tried nearly every other way and failed.

The fused salt was now weighed and was found to have lost twenty milligrams during the fusion. No doubt the greatest part of this was caused by the loss of some of the bromide by sublimation, as a white coating was noticed on the inside of the fusion tube. Precipitation was accomplished in the dark room and the resulting mixture allowed to stand overnight, as had been done in the case of the chloride. The solution was then decanted through a platinum crucible provided with a filtering mat of platinum and iridium. The silver bromide was shaken for an hour with 75 c.c. of redistilled water, after which it was decanted off and added to the first solution. The operation was again repeated, after which the bromide was assumed to have been thoroughly freed from any excess silver or caesium nitrate. The pretty, canary yellow silver bromide was treated from here just

exactly as was the chloride.

The precipitate of silver bromide is of a fine, granulated nature and does not coagulate as does that of silver chloride. As a result, in our second analysis, some very fine particles of the bromide were noticed to be passing through the platinum-iridium filtering mat. However, the filtrate on examination appeared to be perfectly clear; yet the platinum crucible, when dried on a watch glass, deposited a thin, yellow ring of the bromide. This showed conclusively that the silver precipitate was being lost; and in order to counteract this, two layers of filter paper were placed upon the mat before filtering. This latter procedure proved to be very effective. An equal amount of filter paper must be added to the tare crucible in order to obtain accurate weighings.

The results from four analyses proved to be somewhat discouraging as they fell somewhere between 135.522 and 135.538. As far out as the values were, yet nevertheless they agreed remarkably well among themselves. Since all possible precautions had been taken this shows that some constant error was present in all four determinations. We could not say for sure what this was, but thought that it might possibly be a trace of chlorine. The only place at which the latter could be introduced would be along with the hydrobromic acid, which had been previously distilled in order to eliminate any trace of chlorine. The only way out of our difficulty was to repurify the caesium bromide

which we did with the utmost care. The purpose of purification was twofold; first, to eliminate any impurity, chlorine included; second, to obtain the bromide in such a condition that platinum and not porcelain vessels could be used for the fusion.

The process of analysis for the repurified bromide was, with the exception of the fusion, exactly the same as that which had been used previously. The fusion of the caesium salt was now made in an atmosphere of nitrogen and hydrobromic acid; the latter being used to prevent any possible decomposition of the molten salt. ⁽¹⁾ The exact procedure used was as follows: the caesium bromide, contained in a platinum boat, was placed in the pyrex fusion tube; after which the remainder of the apparatus was assembled in the customary way. A current of pure nitrogen, bubbled through concentrated redistilled hydrobromic acid, and dried by means of freshly fused calcium bromide, was then passed through the apparatus for 20 min., When all the air had been swept out of the latter, the caesium bromide was heated to about 150°C. for an additional 20 min., after which time the temperature was increased so that the caesium bromide just fused in the atmosphere of nitrogen and hydrobromic acid. While the bromide was still molten, the hydrobromic acid bottle was cut out; thus allowing a stream of pure, dry nitrogen to pass over the salt, which was kept fused for 5 min. before it was allowed to cool. The purpose of the last step was to prevent the hydrobromic

(1) T.W. Richards & E.H. Archibald, Proc. Amer. Acad., 38, 465 (1903).

acid from combining with the caesium bromide resulting in the formation of a polybromide of the metal. After the tube and its contents had cooled to room temperature a stream of pure, dry air was passed through the apparatus for another 20 min., after which the caesium bromide was bottled in the usual manner. This time the caesium salt fused to a clear, limpid liquid without showing any signs of decomposition and when dissolved in water gave a clear solution.

IX. SUMMARY.

The two salts of caesium have been prepared in a very pure form and the amount of chlorine and bromine combined with the former has been determined by a series of accurate analyses. The values obtained are as follows:

From chloride analyses 1 to 6	132.9685
" " " 7 " 8	132.9740
" bromide " 1 " 4	<u>132.9705</u>
Mean value	132.9710

Therefore 132.971 represents the atomic weight of caesium as determined by analysis of the chloride and bromide of the metal.

WEIGHTS - RATIOS - ATOMIC WEIGHTS.

No. of Analysis	Sample of CsBr	Weight of AgBr in a vacuum.		Weight of Ag in a vacuum.		Ratio of AgBr:CsBr=100:x		Ratio of Ag:CsBr=100:x		Atomic weight of caesium gravimetrically.	
		Weight of AgBr in a vacuum.	Weight of CsBr in a vacuum.	Weight of Ag in a vacuum.	Weight of CsBr in a vacuum.	Ratio of AgBr:CsBr=100:x	Ratio of Ag:CsBr=100:x	Atomic weight of caesium gravimetrically.	Atomic weight of caesium gravimetrically.		
1	I	2.14919	2.14919	1.08906	1.08906	197.343	197.343	132.978	132.978		
2	I	3.36959	3.36959	1.70760	1.70760	197.331	197.331	132.962	132.963		
3	I	2.47584	2.47584	1.25456	1.25456	197.346	197.346	132.964	132.982		
4	I	2.05580	2.05580	1.04178 ⁺	1.04178 ⁺	197.335	197.335	132.979	132.969		
Average (c)			113.360	113.360	197.339	197.339	132.968	132.973		

Ag = 107.880

Br. = 79.916

+ Sample of silver, "B".

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