

6. The most probable value of the atomic weight of neodymium is found to be 144.27, if silver is taken at 107.88; with silver at 107.87 neodymium becomes 144.26.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

REVISION OF THE ATOMIC WEIGHT OF CALCIUM.

(SECOND PAPER.)

ANALYSIS OF CALCIUM CHLORIDE.

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In an earlier paper concerning the analysis of calcium bromide¹ it was shown that the atomic weight of calcium is probably not far from 40.070, this being in all likelihood the minimum, if silver is taken as 107.88. Two series of analyses containing each six individual experiments, carried out according to two methods, gave this number as their mean. The present paper contains a description of further work upon this constant, involving now the chloride instead of the bromide of calcium.

The importance of carrying out systematic experiments upon more than one compound is evident. The constant errors due to possible unknown impurities, as well as to possible defects in method, so surround any work of this kind that no worker with much experience is inclined to trust a single method, even although a single good method is worth more than any number of bad ones. The exact analysis of the chloride might add either essential confirmation of the work on the bromide or important evidence concerning possible flaws. Five preliminary experiments upon the chloride carried out at Harvard thirteen years ago had indeed yielded a result which almost although not quite agreed with the figure given above²; but this preliminary work was done at a time when considerably less was known about the possible errors in working with chlorides than at present. In any case further work upon the chloride seemed to be imperative.

The present paper concerns the determination of the quantitative relation of metallic silver to pure fused calcium chloride. Both of these substances were weighed with great accuracy, and the end point of the reaction between them was determined in very dilute solution by means of the nephelometer. This method, because of its greater simplicity, is somewhat to be preferred to the weighing of the silver chloride produced from a given amount of calcium chloride. Moreover the preliminary experiments with the chloride had involved this latter process; therefore the comparison with metallic silver would furnish a new ratio, not hitherto investigated.

¹ Richards and Hönigschmid, *THIS JOURNAL*, **32**, 1577 (1910).

² Richards, *Ibid.*, **24**, 374 (1902); *Z. anorg. Chem.*, **31**, 271 (1902).

We are glad to acknowledge the generous support given this investigation by the Carnegie Institution of Washington.

Preparation of Materials.

Calcium Chloride.—Two different specimens of exceedingly pure calcium carbonate remaining from the preparation of the bromide served as the starting point of the work on the chloride. Repetition of the details is unnecessary; the only impurities which could have been present besides moisture were traces of ammonium nitrate included in the precipitate. Each of these specimens was dissolved in specially purified hydrochloric acid, which had been boiled repeatedly with small additions of permanganate, and then distilled twice in succession with the help of a quartz condenser. The calcium carbonate had been heated in a platinum dish to a temperature high enough to free it from water and ammonia, but traces of nitric acid may have remained; accordingly, the carbonate was dissolved in hydrochloric acid, in a quartz dish, and the chloride was evaporated to dryness. Subsequently it was crystallized three times, each time being freed as completely as possible from mother liquor, by means of the platinum centrifuge. Thus two specimens of calcium chloride were obtained and to them were given the designations 1 and 2, corresponding to the designations of the carbonate from which they were made.

The mother liquors from these two chlorides were collected, concentrated and four times recrystallized. The mixture of the two specimens thus obtained having a purity not far different from samples 1 and 2 was designated sample 3, and served for several analyses.

Silver.—Three preparations of silver were used for this work. Of Sample A the preparation has already been described in the previous paper, and Sample B was made in a similar way by Richards and Willard in their work upon the atomic weight of lithium, already cited. The third, Sample C, was prepared by Dr. C. J. Moore and kindly given to us for this work. Silver residues, consisting of the three silver halides, were reduced with zinc. The metal was washed, dissolved in nitric acid, and precipitated as chloride. This was dissolved in ammonia and again precipitated with nitric acid, and once more reduced by means of sugar solution after very thorough washing. The metal thus obtained was melted (by means of the blast lamp on blocks of lime), etched with nitric acid, and then used as an anode in a dilute silver nitrate solution. A pure silver wire served as a cathode; upon this the silver was deposited in beautiful crystals, and these were carefully washed and melted in a stream of hydrogen in the same way as Samples A and B. The boat of pure lime which served to support the metal was so arranged that the buttons were of various sizes. The pure metal was etched with dilute nitric acid, thoroughly washed and dried in a vacuum at 500°. Pure

nitric acid and other substances were prepared with the usual precautions adopted in this laboratory.

Melting and Weighing of the Calcium Chloride.

The crystallized chloride, like the bromide, cannot be conveniently dehydrated by heating the hydrated crystals, because a crust forms over the liquefied mass. This greatly hinders the evaporation, which is almost invariably accompanied with projection or spattering of drops. On the other hand, as in the case of the bromide, if calcium chloride is placed in a vacuum desiccator at a temperature below its transition point, 29° , the water leaves the salt with considerable rapidity and the dried skeleton of the crystal can then be heated to 200 or 300° without danger of loss. In the present case a fortnight's standing in a vacuum desiccator over lime in the best vacuum obtainable by means of a Geryk pump was quite enough for preliminary treatment.

The thoroughly effloresced material was further dehydrated and finally fused in an apparatus essentially like that used for the melting of the bromide and almost exactly similar to that used by Richards and Willard for the melting of lithium chloride.¹ The calcium chloride was contained in a platinum boat enclosed in a wide quartz tube connected with the familiar Harvard "bottling apparatus," and in this position was gradually brought by means of electrical heating to the temperature of 400° , in a current of nitrogen. After an hour the air in the tube had been displaced, and the salt was almost wholly free from water. Turning the 3-way cock then admitted dry hydrochloric acid gas; and as soon as all the nitrogen had been displaced the temperature of the chloride was raised to its melting point, about 800° . For fifteen minutes the fusion was maintained in the current of acid gas; then this gas was displaced by nitrogen, and the fusion was continued until the greater part of the hydrogen chloride had been given out by the inert element. The product was then allowed to cool rapidly in nitrogen.

During the cooling a hitherto unnoticed phenomenon was observed. As the temperature decreased, the perfectly clear glassy solid, which was at first formed in the boat, was flecked with small white spots. These were caused by the shattering of the glassy chloride as it crystallized, sometimes almost explosively, at the lower temperature; and they gradually spread over the whole surface. Occasionally some particles of the salt were thrown out of the boat during this process. The effort was made to prevent the change by cooling as quickly as possible. This device was unsuccessful, but we found that the transition could be prevented by heating the salt for a long time in nitrogen. From this fact the conclusion may be drawn either that traces of hydrochloric acid are dissolved by the fused salt, and that these traces hasten the crystallization, or else that

¹ Richards and Willard, *THIS JOURNAL*, 32, 25 (1910).

the traces of alkali formed by long ignition in nitrogen retard the crystallization. The transition phenomenon is accompanied by considerable increase in volume; in one case, indeed, a thin platinum boat was so much increased in diameter by the expanding salt as to make it incapable of admission into its weighing glass—a mishap which naturally caused the loss of that experiment.

After the chloride had been completely cooled and the apparatus again filled with pure dry air, the boat and its contents were pushed into the weighing bottle and allowed to stand at least six hours in a desiccator in the neighborhood of the balance. It was then weighed in the usual fashion by substitution.

The platinum boat was attacked somewhat more strongly by hydrochloric acid than by hydrobromic acid. Nevertheless, since the average loss was only 0.08 milligram in a single experiment, and since any platinum which had been dissolved probably reverted to the condition of metal in the salt during its fusion in a neutral atmosphere, this complication may be left entirely out of account. The original weight of the boat was taken in each case as the true one.

The experiments with the bromide had already shown us that with a salt as easily decomposed as calcium chloride, it is by no means easy to obtain an exactly neutral product. Accordingly each specimen of fused calcium chloride was dissolved in a small amount of water and then titrated with $\frac{1}{100}$ normal nitric acid or caustic potash, using methyl red as an indicator. The departures from neutrality were so slight that they scarcely could have been observed and could not have been accurately estimated without comparison with a standard solution of calcium chloride known to be neutral. This latter was prepared by crystallizing moderately pure calcium chloride, faintly acid, four times from the purest water with thorough centrifugal treatment and all precautions. An equal quantity of this certainly neutral salt was dissolved in precisely the same amount of water as was used for the sample to be tested, and to each was added the same quantity of methyl red. In most cases the solution of the melted chloride was thus found to be slightly acid, and only when the product had been fused in dry nitrogen for some time did an alkaline reaction appear. Whether the lack of chlorine evidenced by the alkaline reaction was caused by traces of oxygen or water in the nitrogen or by a reduction to subchloride cannot be absolutely proved; but the former is by far the most likely assumption, therefore it was made in calculation of the results. In this way it was found that the eighth, tenth, and eleventh specimens were precisely neutral, as nearly as this testing could show it. The sixth, seventh, and ninth were slightly acid, requiring 0.10, 0.30 and 0.20 milliliters of $\frac{1}{100}$ alkali respectively, whereas the twelfth sample of calcium chloride was alkaline, needing 0.70 ml.

of $\frac{1}{100}$ normal acid for its neutralization. In order to correct for these slight deviations from neutrality a small correction was added to or subtracted from the weight of the calcium chloride according as the calcium was lacking (in slightly acid specimens) or calcium oxide was present as an impurity (in the alkaline specimen). The actual amounts of the corrections in analyses 6, 7, 9 and 12 amounted respectively to + 0.00002, + 0.00006, + 0.00004 and - 0.00020 gram.

It is interesting to note that the sum of all these corrections is a negligible quantity. Their effect is only to improve slightly the agreement of the results. Thus, on the average, the calcium chloride was neutral. This is especially important in its bearing upon other cases, because occasionally, for example in the case of zinc bromide,¹ indicators give results so unsatisfactory that no clue can be gained as to the neutrality of the fused salt after it has been dissolved. Evidently the amount of acid gas dissolved by the fused salt at a bright red heat is almost negligible, even when the acid gas is present under a full atmosphere's pressure.

The weighings were made upon the same balance and in the same way as has been already described. For the determination of the correction to vacuum of the calcium chloride, it was necessary to determine the weight of air displaced by a given weight of this substance.

The density of fused calcium chloride was determined in the pycnometer devised by Baxter² for salts of this kind. Toluene having a specific gravity 0.8630 at 25°, compared with water at 25° (that is to say, weighing 0.8605 gram per cubic centimeter), was used as the liquid to be displaced. Two pairs of experiments were made. In the first pair 4.8462 grams in vacuum of fused calcium chloride displaced 1.9417 grams in vacuum of toluene, and in another pair 4.1223 grams of calcium chloride displaced 1.6447 grams of toluene, the temperature being 25° as before. These two results correspond respectively to values for the density of calcium chloride of 2.148 and 2.156, the mean being 2.152. This value is used in calculating the corrections of the vacuum standard. Because the specific gravity of the gilded brass weights was 8.3, the following vacuum corrections per gram were applied.

	Density.	Vacuum correction.
Silver.....	10.49	-0.000030
Silver chloride.....	5.56	+0.000071
Calcium chloride.....	2.15	+0.000415

Precipitation and Gravimetric Titration.

The weight of silver supposed to be exactly equivalent to each fused and weighed portion of calcium chloride was dissolved with all ordinary precautions in nitric acid. After dilution the liquid was heated, in order

¹ Richards and Rogers, *Proceedings Am. Acad.*, 31, 158 (1895).

² Baxter and Hines, *Am. Chem. J.*, 31, 221 (1904).

to expel nitrous vapors, and then diluted further to a liter. The chloride solution also, after being tested for its neutrality, was diluted to a liter in the three-liter Erlenmeyer flask which had served originally for its dissolving. The silver solution was added little by little to the chloride solution in the dark room; and the flask was then closed and the mixture shaken for a short time in order to mix thoroughly the two solutions. Violent shaking was not practised, because this causes the precipitate to cohere, and prevents the washing out of included chloride or silver. On the following morning the mixture was shaken energetically for about fifteen minutes, and then packed in ice in order to diminish the solubility of silver chloride by lowering the temperature and thus to increase the accuracy of the determination of the end point. The question as to whether silver or chloride was in excess in the supernatant liquid was then determined by means of the nephelometer in precisely the same way as had been used in the already often quoted work on the atomic weight of lithium, where the details are to be found. The test was made only after the chloride solution had remained for twenty-four hours in the cooling bath. Seven determinations gave the following results:

RATIO OF CALCIUM BROMIDE TO SILVER—FINAL CALCULATIONS.

No. of exp.	Sample of calcium chloride.	Sample of silver.	Corrected weight of calcium chloride in vacuum.	Weight of silver in vacuum.	$\frac{2\text{Ag}}{100} : \text{CaCl}_2 =$ 100: x.	Atomic weight of calcium.
VI	I	A	4.60350	8.94908	0.514410	40.075
VII	II	B	4.82401	9.37780	0.514407	40.074
VIII	II	C	4.81846	9.36688	0.514415	40.076
IX	II	C	5.29799	10.29911	0.514412	40.076
X	III	C	5.40550	10.50832	0.514402	40.073
XI	III	C	5.24539	10.19715	0.514398	40.073
XII	III	C	5.34110	10.38328	0.514394	40.072
			35.53595	69.08162	0.5144054	40.074

It is to be noticed that the three samples of silver gave results essentially identical, and that the three specimens of calcium chloride were also practically alike, within the limit of error in experimentation. The quantity of material used, although not differing greatly in the individual experiments, seems to have produced no noticeable effect on the results. It is worthy of remark that the series of determinations was an uninterrupted one, no experiments having been rejected from it.

These analyses thus lead to the number 40.074 for the atomic weight of calcium, if silver is taken as 107.88 and chlorine as 35.457. The probable error of this series of results is smaller than that of either of the two series with bromide, being only 0.0004. The maximum deviation from the mean is only 0.002 in the atomic weight of calcium, which corresponds to about 1 part of calcium chloride in 55,000. The agreement is there-

fore as good as could be expected in work of this kind. The reason for the improvement over the previous series is undoubtedly to be found in the increase of experience with which this last problem was attacked. The knowledge gained in earlier work was of great service in the later determinations.

The Atomic Weight of Calcium.

Four series of determinations concerning the atomic weight of calcium have been carried out in the Harvard laboratory. The first series, executed in 1897 and 1898, claimed to be nothing more than a preliminary treatment of the subject, and was undoubtedly subject to several minor possibilities of error which modern knowledge could have eliminated. The present authors in their recent paper on the analysis of calcium bromide contributed the next two series, and the analysis which has just been described completes the list. The results of these four series with their respective "probable errors" are entered in the following table:

From the ratio 2AgCl:CaCl ₂	Ca = 40.085(±0.0011)
From the ratio 2AgBr:CaBr ₂	Ca = 40.070(±0.0007)
From the ratio 2Ag:CaBr ₂	Ca = 40.070(±0.0007)
From the ratio 2Ag:CaCl ₂	Ca = 40.074(±0.0004)

Average for the atomic weight of calcium. . Ca = 40.075

This average, 40.075, is almost exactly identical with the last of the four series, and may be taken as the atomic weight of calcium, if silver = 107.88 and chlorine = 35.457. Possibly silver is really as low as 107.87; if this is the case, the atomic weight of calcium would become 40.072. It would appear that Hinrichsen's value, 40.142,¹ is in all likelihood distinctly too high. A repetition of the first, slightly divergent series, given in the above table, has already been begun; but the work has been interrupted by the necessary departure of one of us for Europe. It will be continued in the near future.

Summary.

The most important results recounted in the present paper are as follows:

Pure calcium chloride was prepared by dissolving very pure carbonate in very pure hydrochloric acid by crystallization of the product. Three samples gave consistent results, showing the material to have been pure.

Fused calcium chloride was found to suffer transition into a more bulky form on cooling, if traces of hydrochloric acid are present. The glassy fused salt, obtained by the fusion of a neutral or slightly alkaline salt, was found to have the density 2.15 at 25°.

By gravimetric titration 35.53595 grams of fused neutral calcium chloride were found to require 69.08162 grams of silver in seven consecutive ex-

¹ *Z. physik. Chem.*, 39, 311 (1901).

periments, corresponding to an atomic weight for calcium of 40.074, if silver is 107.88.

This value equals almost exactly the average of all the Harvard work upon the subject, 40.075, and may be taken for the present as the most probable atomic weight of calcium.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

A DETERMINATION OF THE RATIO BETWEEN CHLORINE AND BROMINE AND SODIUM.

BY JACOB S. GOLDBAUM.

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Introduction.

Before the National Academy of Sciences, Wolcott Gibbs, in 1880, first suggested the use of mercury as cathode in electro-analysis. His experiments, although purely qualitative, were sufficient to indicate the correctness of the principle involved. The subsequent development of the mercury cathode cell in metal determinations furnishes an important chapter in the history of analytical chemistry, but it is to its extension into the domain of anion estimation that especial attention is now directed.

Vortmann¹ and later Specketer² had published brief accounts of halogen fixation, but the activities of Edgar F. Smith and his students in the use of an attackable silver anode with a mercury cathode, made for sure and steady advance in this phase of our science. Within the last decade much has been published of results obtained in this laboratory in the analysis of alkali and alkaline earth salts, with particular emphasis upon the halides of these metals. The advent of the "double cup" as devised by Hildebrand was important and timely. By its use many analyses and separations of decided interest have been effected, as is evident by reference to the work of Hildebrand,³ McCutcheon,⁴ McCutcheon and Smith,⁵ Lukens and Smith,⁶ Kollock and Smith,⁷ and Goldbaum and Smith.⁸

Extreme accuracy has always been a feature of the values obtained in the papers mentioned above. It seems, however, that in the hands of other investigators, difficulty in duplicating results is being encountered

¹ *Elektrochem. Z.*, 1, 137.

² *Z. für Elektrochem.*, 4, 539.

³ THIS JOURNAL, 29, 447.

⁴ *Ibid.*, 29, 1445.

⁵ *Ibid.*, 29, 1460.

⁶ *Ibid.*, 29, 1455.

⁷ *Proc. Am. Philos. Soc.*, 46, 341.

⁸ THIS JOURNAL, 30, 1705; 31, 900; and 32, 1468.