SUMMARY.

Statements of earlier writers are fully confirmed, that silica cannot be rendered wholly insoluble by a single or any number of evaporations with hydrochloric acid when followed by a single filtration, no matter what temperature may be employed, but that two or more evaporations alternating with filtrations are necessary to secure satisfactory results.

It is shown that the generally accepted view that any silica passing into the filtrate is wholly thrown down by ammonia or sodium acetate in presence of much aluminum or iron is incorrect. Also that silica is appreciably soluble in melted potassium pyrosulphate and that consequently when siliceous oxides of iron and aluminum obtained in analysis are then fused their silica contents are only in small part left undissolved when the fused mass is taken up with water or acid. Both these sources of error are avoided by separating all silica at the start as above.

The need of blast ignition in order to get the correct weight of silica obtained in analysis is proved. The opposite conclusion of Lunge and Millberg, being based on what seems to be a different behavior of the silica derived from silicon tetrafluoride, is therefore not justified.

LABORATORY U. S. GEOLOGICAL SURVEY,
December, 1901.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REDETERMINATION OF THE ATOMIC WEIGHT OF CALCIUM—PRELIMINARY PAPER.

BY THEODORE WILLIAM RICHARDS.

Received February 16, 1902.

DURING the years 1897 to 1899 an investigation upon the atomic weight of calcium was conducted in the Chemical Laboratory of Harvard College. This investigation was more carefully conducted, and in some respects more elaborate than any previous research of a similar kind conducted in this laboratory. The details are so many that time has not yet been found for a verbal presentation of them, but a brief report of the results was made to the American Association for the Advancement of Science in August, 1899, of which a notice is published in the journal.[1]

---

[1] This Journal, **22**, 72 (1900).

Very recently there has appeared the account of a careful investigation of calcium carbonate made by Hinrichsen under the direction of Landolt.[1] Since this investigation confirms the outcome of the Harvard research, a brief preliminary account of this may be interesting. It is hoped that later the details may be presented in full.

In spite of the common occurrence of the element calcium, its atomic weight had been investigated only in a partial and incomplete manner. The chief work upon the subject has consisted of the quantitative ignition of calcium carbonate, and it seemed important to obtain also data of a radically different kind. Because of the peculiar properties of the halides of silver, most of the accurately determined atomic weights of other metals have been found by the analysis of their respective halides, and it would evidently be worth while to include calcium in this series. The old work of Dumas is, of course, of no importance, because of his faulty comprehension of the method of Gay-Lussac.

Accordingly the present series of determinations consisted of the analysis of calcium chloride, the silver chloride obtained from a known weight of the anhydrous salt being collected and weighed with care.

The first problem to be solved was the preparation of pure calcium chloride. Preliminary experiments showed that calcium nitrate is the best salt to use for recrystallization, because of its rapid variation of solubility with the temperature, and because of the fact that the corresponding salts of magnesium, strontium, and barium do not crystallize out with it. Two portions of marble were used as the starting-point, one came from Rutland, Vermont, U. S. A., while the other was a specimen of the purest Italian marble taken from a ship which had just arrived at the port of Boston. The Rutland marble was converted into the nitrate, and from this specimen, after preliminary purification with lime, etc., two samples were prepared, one having been carefully recrystallized ten times, and the other twenty times.[2]

The single specimen of pure nitrate from the Italian marble was recrystallized fifteen times, thus being comparable with the

---

[1] *Ztschr. phys. Chem.*, **39**, 311 (1901).

[2] The process of recrystallization was kindly conducted by M. J. B. Churchill, who also made the preliminary experiments, showing the degree of purity to be obtained in this way.

average of the American samples, in case any difference between them might exist.

The metal in each of these specimens was precipitated as carbonate by the purest ammonium carbonate, and then converted into chloride. After four recrystallizations the chloride was dried, ignited in a porcelain tube in a stream of hydrochloric acid gas to render a possible trace of silica insoluble, dissolved, filtered, and crystallized twice more. Of course platinum vessels were used throughout, and every precaution was taken to insure a close approach to that perfect purity which is unattainable.

The three samples of material which had been thus made ready were dried for analysis by prolonged ignition and final fusion at a bright red heat in a porcelain tube. The hydrochloric acid gas, which had been added to the nitrogen in the tube to prevent loss of chlorine, was then wholly displaced by the inert gas, and when the apparatus was nearly cold this was driven out by dry air. After having been transferred to the stoppered weighing-bottle by means of the convenient automatic bottling apparatus so much used at Harvard, it was weighed and analyzed. The correction for the solubility of the silver chloride was determined much as in the case of barium chloride, several years ago.

The results show that the three samples of calcium chloride (which were wholly neutral to methyl orange) were essentially identical. Hence neither a change in the source of the material nor repeated fractionation causes any variation in the atomic weight. The following table contains the weights of material, reduced to the vacuum standard, and the calculated results.

THE ATOMIC WEIGHT OF CALCIUM.

O = 16.000; Cl = 35.455.

No.	Weight of $CaCl_2$ in vacuum.	Weight of AgCl in vacuum.	Atomic weight of calcium.
1	1.56454	4.0409	40.121
2	3.57630	9.2361	40.130
3	3.59281	9.2788	40.129
4	5.00880	12.9364	40.124
5	9.00246	23.2506	40.125
		Average,	40.126

American (10 crystallizations), Nos. 2, 5	40.127
American (20 crystallizations), No. 4	40.124
Italian (15 crystallizations), Nos. 1, 3	40.125

The results thus agree closely with the value 40.142 since obtained by Hinrichsen, who was not cognizant of my work. A further investigation is now being undertaken at Harvard to show whether other methods, executed with great care, support or discountenance this high value.

COMMERCIAL AQUA AMMONIA, ITS EFFECT UPON IRON, ITS IMPURITIES, AND METHODS FOR DETERMINING THEM.

By J. D. Pennock and D A. Morton.

Received January 10, 1902.

THE very extensive development of refrigerating plants, large and small, throughout the country during the last decade has greatly increased the manufacture of aqua ammonia.

Formerly aqua ammonia of 26° Bé., or 29.0 per cent. NH_3, was shipped in carboys. The shipments of aqua soon became so large that it was no longer practicable to transport in such cumbersome and fragile receptacles, and recourse to metal carriers was had. But ammonia was known to attack most metals seriously. W. R. Hodgkinson and N. E. Bellairs[1] found that all metals which form soluble double salts with ammonium salts are most acted upon by ammonia solution. Zinc, nickel, and cobalt are, after copper, most rapidly attacked. Lead dissolves more slowly, and iron, aluminum, and magnesium do not appear to dissolve at all.

Lunge says[2] that aqua ammonia in contact with iron, "gives rise to red precipitates of iron oxides."

Lunge's opinion was evidently held by European ammonia manufacturers, for in one of the larger works that the writer visited in Belgium in 1897, the absorber for the ammonia gas was a lead-lined vessel, and the aqua produced was shipped in carboys.

The opinion was held by certain manufacturers that aqua made from the distillation of sulphate of ammonia with lime would not attack iron, but that aqua made from crude ammonia liquor would.

To ascertain the effect of ammonia on iron and determine if an iron absorber could be used in place of a lead one, and if aqua could be shipped in iron drums and iron cars, various experiments

---

[1] *Proc. Chem. Soc.*, 9, 146 (1895).

[2] "Coal-Tar and Ammonia," p. 685.