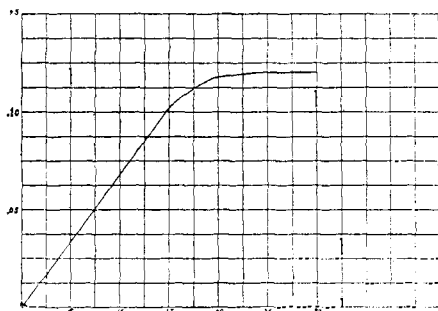


cedure has given an excellent and satisfactory method for the estimation of molybdenum as well as a most gratifying means of separating it from the alkali metals. The conditions were as follows :

No.	MoO ₃ Present in Grams	Dilute Sulphuric Acid (1:10) in cc.	Potassium Sulphate in Grams	Current in Amperes	Volts	Time	MoO ₃ Found
1	0.1200	2	1	5	16	30	0.1197
2	0.1200	2	1	5	16	5	0.0335
3	0.1200	2	1	5	16	9	0.0603
4	0.1200	2	1	5	16	15	0.1026
5	0.1200	2	1	5	16	20	0.1190
6	0.1200	2	1	5	16	25	0.1198

From these data the following curve was drawn :



CURVE II. Rate of deposition of Molybdenum Sesquioxide.

The rapidity with which the oxide separates and the ease with which the determination of molybdenum may be carried out in this way bids fair to render the electrolytic procedure the preferable method with all those who acquaint themselves with it.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE QUANTITATIVE SYNTHESIS OF SILVER NITRATE AND THE ATOMIC WEIGHTS OF NITROGEN AND SILVER.

BY THEODORE WILLIAM RICHARDS AND GEORGE SHANNON FORBES.

Received February 15, 1907.

Introduction

The composition of silver nitrate is one of the questionable premises in the lively argument which has recently taken place concerning the atomic weights of nitrogen and silver.¹ Although Stas's syntheses of this salt were carried out on a large scale, and far more carefully than those of anyone before him, several points concerning the details of the work were not investigated with the care which modern physicochemical

¹ The reader is referred for a convenient résumé to the Report of the International Committee on Atomic Weights, *This Journal*, 28, 1 (1906), and many other places; also to Clarke, *This Journal*, 28, 293 (1905); Gray, *J. Chem. Soc. (London)*, 89, 1173 (1906).

knowledge demands. Accordingly, a repetition of this work of Stas's seemed to be worth the trouble involved; and the following pages contain a brief account of nine months' thought and labor upon it.

The method appears at first sight to be extremely simple, consisting merely in the weighing of pure silver, the dissolving of this silver in nitric acid, and the weighing of the resulting nitrate. The preparation of pure silver having been already solved, the great difficulty consisted in the procuring of satisfactory evidence that the nitrate was free from impurity, and in making sure that none of the silver was lost during the process. The main emphasis of the subsequent discussion will therefore be laid on these points, the other details being often indicated with but few words, because they so closely resemble the details of previous investigations carried out in the Chemical Laboratory of Harvard College.

The research naturally divided itself into four sections, namely, first, the preparation of pure materials; second, the quantitative synthesis; third, the determination of the purity of the product; and fourth, the final result and its relations to the tables of atomic weights. These will be considered in order.

Preparation of Pure Materials

All the substances used in the research were purified with very great care. Nitric acid and silver were the two most important.

Nitric acid was supplied by two firms. Each sample was warranted by the manufacturers to be of a very high grade of purity. Each was redistilled twice just before adding to the silver, using only the middle portion of each distillate. None of the samples left a trace of non-volatile residue on evaporation. No difference could be detected in the results because of the difference of source of the acid, nor was the constancy destroyed when a single distillation only was made. (Experiment 11). Hence little anxiety was felt concerning the purity of this material.

Silver.—The researches of Richards and Wells have shown how to prepare silver of unquestioned purity. Preliminary determinations 1, 2, 3, 4, 5, 7, and 8 were made on a sample (A) left over from the above-mentioned research, crystallized fifteen times with nitric acid, precipitated with formate, and fused on purest charcoal, but not electrolyzed or fused in hydrogen. No. 9 was made with a sample prepared by Professor Baxter for his final work on bromine. It had been through the chloride and formate treatment, electrolyzed, fused in hydrogen, cut with a saw, etched with nitric acid, boiled with water, dried at dull redness in vacuo, and given us ready to weigh. We are much indebted to him for furnishing this check on our silver. The final determinations were made with silver derived from several preparations. The first of these (C) was recrystallized sixteen times as nitrate from water and redistilled nitric acid,

and then precipitated twice in succession with formate. A part of the final formate product was fused on the best lime in carefully purified hydrogen made from aluminum and sodium hydroxide. Sample D had been precipitated as chloride, reduced with best alkaline sugar, washed free from chloride, dissolved in nitric acid, filtered and crystallized as nitrate in platinum six times from nitric acid distilled in a platinum condenser. Centrifugal treatment eliminated the mother liquor. The last crop of crystals was precipitated with formate in a silver dish, washed free from ammonia and fused in a cup of pure lime. Sample F was obtained by the electrolysis of a button of very pure silver from Colorado, which had been fifteen times recrystallized as nitrate, precipitated with formate, and fused on lime. Samples C, D, and F were all cleaned by etching and then purified by electrolysis through a nitrate solution made from some of the same silver and the purest nitric acid. They were then fused separately, on a well-seasoned lime boat, in a new porcelain tube, in an atmosphere of pure electrolytic hydrogen. The Hempel stoppers fitted so well that the pressure could easily be reduced to a fraction of a millimeter by a Geryk oil-pump when desired. The heating was accomplished by a large Heraeus electric furnace which fused the silver without overheating any part of the tube. In all cases the initial fusion was completed in hydrogen at atmospheric pressure, but in half the fusions the tube was evacuated before the temperature was lowered. No spurting or boiling could be observed through the glass window when the pressure was reduced, and the silver thus prepared gave the same combining weight as that cooled under a full atmosphere's pressure of hydrogen. Thus the conclusion of Richards and Wells and of Baxter that silver can not dissolve a weighable amount of hydrogen was confirmed.

The buttons thus obtained were etched to remove lime, and if too large to go into the flask used for the synthesis, were cut with a cold chisel or a jeweler's saw, observing all the precautions recommended by Richards and Wells. The fragments freed from superficial iron were washed and dried, sometimes in the electric oven in air at 150° for an hour, sometimes in a vacuum at dull redness, and sometimes in a reduced pressure of hydrogen. Judging from the constant combining weight, all these methods were equally good.

Water—The water was distilled first with alkaline permanganate through a glass condenser, and then, after the addition of a small drop of dilute sulphuric acid through a carefully cleaned condenser of block tin. Needless to say, dust was excluded as much as possible, and distillations were conducted immediately before the water was needed, in order to avoid absorption of gases or solution of solid matter.

Air.—It will be remembered that Stas allowed his solutions of silver nitrate to evaporate very slowly, the vapors diffusing out through the

neck of his flask and condensing in a suitable receptacle. Under these conditions the evaporation required seventy-two hours of continuous heating—an unnecessarily prolix process. To hasten the escape of aqueous vapor, it was resolved to maintain a gentle current of pure dry air throughout the process. The air for this purpose was delivered from a water pump, which must have removed some of the original impurities. It was passed first through a tall Emmerling tower filled with beads moistened with concentrated sulphuric acid, to which a trace of potassium bichromate had been added, and then through two more towers filled with a concentrated solution of pure potash, being thus freed from ammonia and from acid gases. Next it was passed through a tall drying tower of stick potash, to a hard glass tube containing platinized asbestos heated to dull redness by a Bunsen burner. The hot platinum was intended to destroy organic matter. Hence it passed into a trap designed to catch asbestos shreds, and finally, the air was dried by two towers of broken potash. The whole purifying train was put together without rubber, all the pieces being blown together except the hard glass tube, which was connected with the soft glass on either side with joints so well ground that no lubricant was necessary. The towers were glass-stoppered. Air thus purified and dried contains nothing to injure the silver nitrate except possibly a minute trace of ammonia, which might have come out of the potash solutions.

The Synthesis of Silver Nitrate

The materials having been prepared, the next step was to combine them. This combination must take place in a vessel wholly free from a suspicion of solubility on the one hand, and arranged so as to prevent loss of material on the other hand. At the same time, it was important to be able to evaporate and to weigh the silver nitrate in the same vessel. After a careful consideration of the somewhat conflicting claims of these requirements it was decided to carry out the process in small round-bottomed flasks of fused quartz of from 0.03 to 0.04 liter capacity; with necks 11 cm. in length and 6 to 9 mm. in internal diameter. Collars of platinum wire provided with loops permitted the suspension of these flasks from the hook of the Troemner balance. Before weighing, they were heated in the oven to be presently described to 250° for at least half an hour, a moderate air-current sweeping through them all the time. The coverings were then lifted, and each flask was removed by a hook of platinum wire sealed into a glass rod, and transferred to a large desiccator provided with a suitable support. Two flasks similar in weight and surface were treated in the same way and kept in the same desiccator. After two hours near the balance the first flask was weighed against a tare, its weight being determined by substitution of the first by the second flask and a few small weights. Upon removal from the desiccator both flasks

absorbed moisture from the air, often to the extent of 0.0001 gram, but they soon reached constancy with respect to one another, which was all that was needed. No final weighings were made when the hygrometer in the weighing-room stood above 40, and under these circumstances flasks could be weighed on successive days with variations not exceeding 0.00003 gram.

A new Troemner balance, sensitive to 0.01 mg. was available for the research. The brass weights were carefully standardized at the beginning of the year, and again upon starting the final series; and the rider also was calibrated, and the necessary correction employed. For correction to the vacuum standard 0.000132 was added to each apparent gram of silver nitrate, and 0.000030 was subtracted from each apparent gram of silver. This was on the assumption that the two specific gravities concerned were respectively 4.35 and 10.49, that of the brass weights being 8.3.

The silver was now weighed by substitution, and carefully pushed down the neck of the flask, which was held meanwhile in a horizontal position to avoid breakage. Next the whole was transferred to a large, clean, empty desiccator, whose sides had been moistened; and the flask was laid on a suitable support of glass and platinum tilted 45° from the vertical. A sufficient quantity of purest nitric acid mixed with half its volume of distilled water was poured in from the platinum crucible into which it had just been distilled. The cover of the desiccator was replaced, but its stopper was first removed, and covered with a watchglass and a clean beaker. The apparatus was now kept all night in a warm place, between 40° and 50° ; thus the silver when dissolved remained in solution, though the volume was restricted to 2 cc. of solution per gram of nitrate. In the morning the process was found to be complete. After washing down the neck with a few drops of freshly distilled water, the flask was placed in the oven as before. The desiccator was washed with a little water, the washings being tested for silver in the nephelometer; if any had been found it might have been feared that more had escaped, but as no trace was ever found, it was inferred that the long inclined neck had caught all the spray.

Attention is now called to the apparatus for evaporation.¹ The main feature of this was the combined delivery tube for the air current and hood for the protection of the contents of the flask. This hood *H* with its ingress and egress tubes, *I* and *E*, is shown in the diagram (Figure 1). The dry air used to sweep out the aqueous and nitrous vapors entered from the purifying train at *G*, where connection was made by a well-

¹ In passing it might be noted that one of us used a somewhat similar arrangement for evaporating solutions of sodium sulphate fifteen years ago. (Pr. Am. Acad., 26, 258 (1891).)

ground joint; passing through the tube *I*, it escaped into the body of the flask and out through its neck. A side tube, *E*, was attached to *H* for connection with a water-pump. The flask rested on a triangle of platinum wire attached to a glass tripod, and the whole was placed in a 1.5-

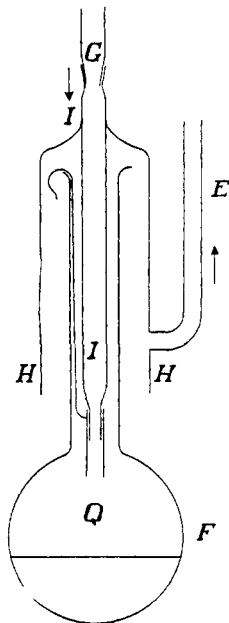


FIGURE 1.

liter beaker which served as the oven. A sand-bath enabled this to be kept at any desired temperature. The cover of the beaker was of sheet copper, pierced with three holes, for the tubes *I* and *E*, and for the thermometer. As no nitrous fumes escaped into the oven, this cover remained intact. In the preliminary trials the extra tube *Q* was lacking, the tube *I* being extended to take its place. The part which had projected into the body of the flask was treated with hot dilute nitric acid and investigated for silver in the nephelometer. Occasionally, some was found, but the corrections required were not large. Nevertheless, the possibility that the fused nitrate had attacked the glass was always disturbing, and the inconvenience and uncertainty of this correction made its elimination desirable. Accordingly, in the final determinations, a section of quartz tubing, *Q*, 3 mm. in diameter and 15 mm. long, was firmly attached to a platinum wire and lowered till it barely projected into the body of the flask. This supporting wire hooked into the collar, so that the quartz tube could be removed while the silver was dissolving. During the evaporation, however, it was in place, and the end of the glass delivery tube was shortened and drawn down to fit into it. The

glass tube was still tested as before, but no silver was ever recovered from it. Hence the flask and the quartz tube must have retained all the silver originally weighed out.

The evaporation of the liquid was easily and quickly conducted in this apparatus. If the flask was not more than half full and the air passed through the drying train no faster than two bubbles per second, it was possible to maintain the temperature of the oven at 125° without risk of ebullition. The vapors drawn out as before described passed first through the U-tube filled with moist glass beads and just sealed with water, afterwards through a tower of caustic alkali to take out nitric acid which might attack the water-pump. When the liquid became coated with a film of crystals the temperature was lowered to 110° ; bubbles of vapor now formed gradually under the crystal layer, and the slight spattering caused by their rupture could be seen on the inside walls of the flask. The oven was now suddenly cooled, so that the vapors from the hot liquid, condensing on the walls of the flask, washed down the crust which had formed during evaporation. Upon continuing the heating, a porous crust was soon formed, under which the formation of steam caused no spattering. Finally, the temperature was raised gradually while the last trace of liquid was disappearing. The solid was dried for a quarter of an hour at 150° in the dark, and then heated to 230° ¹ to insure complete fusion, not only of the main portion, but also of any portions projected on the upper walls of the flask. The temperature was soon lowered to 210° , which sufficed to keep the mass in fusion, and the air current was continued for an hour. Then, in subdued light, the flask was lifted out by a loop of platinum wire passed through its collar, placed on a net-work of platinum wire, and tilted in all directions to cause the nitrate to solidify in a thin layer on the walls. Once this precaution was neglected and the flask was cracked by the contraction of the nitrate on cooling. When the nitrate was wholly solid but still hot, the flask with its contents was transferred to its support of platinum wire in a large, tight desiccator, which was wrapped in a black cloth and left near the balance over night. Then the weight of the flask was determined as before. Thus in the entire cycle of operations nothing but platinum, clean glass, and pure air touched the outside of the flask.

It remains to be proved that no silver was carried out by the air current. This was inferred because no trace of silver was ever found in the U-tube through which all the vapors passed; but more definite evidence was obtained by redissolving two finished determinations, and evaporating them again with the customary precautions.

The first residue in the case of No. 15 was slightly darkened by pro-

¹ This temperature and the others to be recorded later have not been corrected for the exposed stem. They do not indicate the exact melting-point of the salt.

longed heating; still no fixed tendency toward either loss or gain is shown by these figures, and the reliability of the method is demonstrated.

Determination number.	AgNO ₃ once evaporated.	AgNO ₃ twice evaporated.	AgNO ₃ thrice evaporated.	Total gain.
8	10.68933	10.68928	10.68920	-0.00013
15	14.20114	14.20122	14.20127	+0.00013
Average gain or loss.....				±0.00000

Two preliminary experiments were not finished, and one was rejected because of known error. Six preliminary determinations carried out in the way just described gave results varying from 157.483 to 157.475 parts of nitrate from 100.000 parts of silver, in the mean 157.479. This is very nearly the same as the final series, given later, but because of sundry irregularities these determinations are individually much less trustworthy than the latter. One of the preliminary determinations was made with a piece of silver kindly given us by Professor Baxter for the sake of comparison, and for which we are much indebted. It gave a result perhaps higher than the average, but not by an amount greater than the limit of error of the experimentation at that time. It is greatly to be regretted that this piece was not examined after every detail of the process had been perfected, because the comparison would have been interesting, although not at all essential for the completeness of our work.

When it appeared impossible to improve upon the details of the experimentation, a final series of six consecutive determinations was carried out with all possible care. In each case, except Nos. 14 and 15, the silver nitrate was maintained for an hour in a fused condition while dry air swept over it. In No. 14 only one-quarter of an hour was allowed, whereas in No. 15 the fusion was prolonged for three hours. Sample D of silver was used in syntheses 10, 11 and 12, and sample F in the other three.

THE SYNTHESIS OF SILVER NITRATE.

No. of synthesis	Weight of fused silver (in vacuum). Grams.	Weight of fused silver nitrate (in vacuum). Grams.	Weight of silver nitrate made from 100.000 parts of silver.
10	6.14837	9.68249	157.481
11	4.60825	7.25706	157.480
12	4.97925	7.84131	157.480
13	9.07101	14.28303	157.480
14	9.13702	14.38903	157.481
15	9.01782	14.20123	157.480
Average.....			157.480

For this ratio just found to be 100.000:157.480, Stas obtained an average of 100.000:157.475 from nine determinations, which ranged from 157.463 to 157.488.

¹The probable error of this average, computed from the results when carried to the next decimal place, is only 0.0001, a wholly negligible quantity. Hence repetition of the process was unnecessary.

Better agreement than that exhibited by the above table could hardly be desired or expected, as the greatest deviation corresponded to less than 0.1 mg. in the weight of the silver nitrate. This series demonstrated that it is not necessary to use very large amounts of material in order to attain a very high order of precision, if only the details of experimentation are fittingly arranged.

Satisfactory as this series of results appears to be, it is by no means to be accepted without further question as representing the true weight of silver nitrate to be obtained from pure silver. Even in this fused salt, prepared under such favorable conditions, several impurities might exist; and because in each case the method of treatment was the same, these impurities might be constant in amount and therefore not perceivable in the results. Accordingly, attention was now directed to the search for these impurities; and this part of the investigation was found to be the most arduous and time-consuming part of it. The following section discusses this matter.

The Purity of the Fused Silver Nitrate

The first impurity for which search was made was air. While crystals obtained from solution, although always containing solvent, may be supposed to be free from air, the fused material can not without question be assumed to be free from this impurity. The only manner of approaching this question seems to be to fuse the salt a second time in a vacuum, in order to detect a possible loss of weight. This Stas did in a single case with a negative result. Nevertheless, a single experiment, even of Stas's, does not carry with it much weight; therefore the test deserves repetition.

This was carried out in the present case without great difficulty on five of the preliminary determinations. The flasks containing the silver nitrate which had been fused for an hour in air were lowered into manimoth test-tubes—long tubes of soft glass 4.5 cm. in diameter—sealed at the lower end and scrupulously clean. A hood was placed over the mouth of the flask to prevent fragments of glass from entering, and the tube was drawn down in two large converging blast flames. A glass tube was fused on and connected with an efficient mechanical hand pump; several exhaustions, followed by admission of dry air, excluded all moisture. Finally, the system was reduced to 2 mm. and sealed, and heated to 210°. After having been maintained in a state of fusion in the dark for half an hour, the salt was cooled in the usual cautious fashion, and air was admitted very slowly. The flask was placed in a desiccator over night and weighed. The product was always slightly discolored, indicating decomposition, but showed no serious loss in weight.

Forty-five grams of salt lost in all 0.00035 gram. This is less than 1 part in 100,000, and may safely be referred to the trace of decomposition

indicated by the pale brownish coloration. Not only is it reasonable to suppose that but little air is dissolved (for according to the law of Henry

THE EFFECT OF FUSION IN VACUUM.

Determination number.	Original weight. Grams.	Weight after fusion. Grams.	Change.
1	8.04489	8.04477	-0.00012
2	8.75813	8.75810	-0.00003
3	8.54170	8.54170	±0.00000
4	9.87850	9.87837	-0.00013
9	10.76381	10.76374	-0.00007

nearly all of it should have been expelled by this treatment) but also one is led to infer that very little water remains to be expelled. This matter is not, however, so simply settled; the final testing of it cost much labor.

It has been ordinarily assumed that water is entirely expelled from crystallized or evaporated salts upon fusion. This is in all probability the case with sodium and potassium chlorides, and other salts which fuse at high temperatures and show little affinity for water. Whether or not this was the case with silver nitrate, which at 210° is miscible with water in all proportions, was a question which required experimental investigation.

Besides the conservation of weight on fusion in a vacuum, another argument may be adduced to show that most of the water has been driven out. The combining weight of silver nitrate seems to be nearly independent of the time of its fusion in a current of dry air, as is shown by the following table :

Determination	Time kept in fusion	Weight of AgNO ₃ formed from 100 parts Ag
14	15 minutes	157.481
9, 10, 11, 12, 13	1 hour	157.480
15	3 hours	157.480

It should be stated that the last residue was slightly discolored, and increased 0.00008 gram upon a subsequent evaporation with water and nitric acid; hence, a real loss of weight during the extra period of fusion is indicated; but this was probably due to decomposition of the salt, rather than to escape of water; therefore the table bears out the contention stated above. In any case this loss amounts to much less than a unit in the last decimal place.

Ordinarily, in the past, the investigator has been satisfied with such an outcome and has gone no further. But in this case we were anxious to leave no stone unturned; and accordingly a drastic method of treatment was adopted, which permitted no trace of water to escape being weighed. This was to decompose completely the silver nitrate by heat, and to pass the gaseous product of the decomposition through a weighed tube containing phosphoric oxide.

A hard glass combustion tube was bent and drawn out in the manner shown in figure 2, the space between C and D being packed, with glass wool. Into the space between B and C was then introduced about 50 grams of silver nitrate which had been crystallized from nitric acid, barely fused in porcelain, cooled, and pounded in a mortar. The tube was heated to 220° in an air-bath for an hour in a stream of dry air passed in through A. The silver nitrate should now be in a condition somewhat comparable to that of the quantitative determination. Finally, a weighed pentoxide tube was attached at D, and the temperature raised to 500° . Yellow oxides of nitrogen came over, also a fine gray dust caused presumably by the bursting of bubbles of decomposing salt. After an hour, the pentoxide tube was removed, swept out with air, and weighed again. A trace of the gray dust had been carried in, and suggested a slight gain in weight, but by no means enough to account for the great increase of weight, 0.012 gram. This was finally traced to the adsorption of nitrous fumes by the pentoxide, 2 mg. being lost upon passing dry air over the tube for an hour, and the rest giving a very strong test for nitrous acid after being dissolved in water.

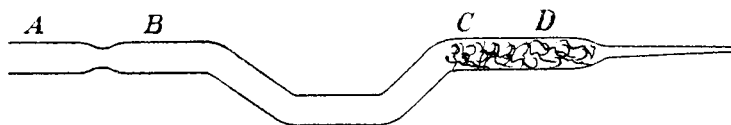


FIGURE 2.

In the effort to eliminate this seriously disturbing effect, recourse was next had to spirals of copper gauze heated in a combustion tube, in order to abstract the oxygen from the nitric oxide, leaving only nitrogen. It is well known that metallic copper adsorbs hydrogen; hence the spirals were first superficially oxidized in a stream of dry air, and then reduced by pure dry carbon monoxide. This was generated by heating the purest oxalic and sulphuric acids of commerce together, the carbon dioxide being absorbed by a generous train of pure concentrated potash solution, and the monoxide dried first by a tower of concentrated sulphuric acid, with beads, and finally by two towers of pounded potash. The resulting copper should be above the suspicion of containing any considerable amount of hydrogen or moisture. The silver nitrate was treated as before and the decomposition was continued until traces of yellow fumes were noted coming past the copper. This meant that nitric oxide had been coming over for some time, since the last part of oxygen is harder to detach than the first. When swept out with air, the gas in the pentoxide tube turned yellow, but it was not then supposed that much nitric oxide could be absorbed by the pentoxide in so short a time. Nevertheless, nitrous acid was found upon solution, even though the gain in weight was only a third as great as before.

Efforts were now made to reduce accidental water from rubber, etc. All joints were made to overlap, so that the rubber surfaces exposed to nitric oxide might be small, and the large asbestos screens kept them from being overheated by the adjacent furnaces. Fresh sublimed pentoxide was used in the weighing-tube, which was carefully imitated as to volume and surface by a similar tube, to be used as a counterpoise in weighing; both were opened after coming to the temperature of the balance-room, wiped with a clean, slightly damp cloth, and weighed by substitution. A substantial plug of glass wool in the decomposition tube strained the gases before passing over the copper; it had been heated in the dry air to remove moisture.

To eliminate the possibility of water in the copper gauze and to test the apparatus, a blank run was made, removing the decomposition tube, and oxidizing the copper with dry air. Here the pentoxide tube lost 0.0004 gram, a result which indicated no error in that part of the process.

It is not worth while to record the individual experiments by which the gradual improvements in apparatus and manipulation were tested, tiresome and time-consuming as these were in execution. By the time seven experiments had been performed, it was clear that the fused silver nitrate could not contain over 0.004 per cent. of water. Even of this small amount a part was undoubtedly due to nitric peroxide; for the copper gauze was not enough to effect a complete decomposition of the gases. Passing carbon monoxide through the apparatus while the decomposition was in progress lengthened the effective life of the reduced copper, but introduced other complications; and the addition of a second tube of hot gauze, a meter long, was still inadequate.

The next step was to secure a copper surface so large that all the nitrogen oxide resulting from the complete decomposition of 50 grams of silver nitrate could be removed, and this without increasing the complications of the apparatus. Powdered copper oxide looked promising as a source of this metal, but it must be made from pure materials to avoid the presence of detrimental impurities. Pure electrolytic copper (Merck) was dissolved in nitric acid, evaporated to dryness in porcelain, and very gradually ignited, with constant stirring, to powdery oxide. A hard glass tube 30 cm. long and 3 cm. internal diameter was used to contain it; the ends were drawn down conveniently and the oxide was reduced at a very moderate heat with carbon monoxide, prepared as usual, except that it was finally dried with pentoxide. Nearly 300 grams of copper oxide were present; therefore the process was very tedious, since the gas had to pass through its purifying train at a moderate rate of speed. With this large mass of finely divided copper the glass wool (from C to D in the diagram) was no longer necessary, therefore it was no longer used. No trace of powdered nitrate ever appeared beyond the copper.

A clean pentoxide tube, with glass stopcocks, was refilled with resublimed pentoxide and glass wool; dry air was passed through for ten minutes to assure constancy. A duplicate tube was also prepared for a counterpoise, and extraordinary precautions were taken in protecting and weighing these tubes. As another precaution it seemed also expedient to prepare silver nitrate nearly as pure as that used in the determinations for fear of hygroscopic nitrates, silicic acid, and ammonium salts, which would yield water when decomposed. A moderately pure salt was recrystallized from nitric acid, filtered, precipitated with formate, washed free from ammonium salts, and fused on lime in the blast. The buttons were etched and dissolved in freshly distilled nitric acid in Jena glass, and the salt was crystallized with ample protection against ammonia, dried centrifugally and kept in a clean, tight desiccator. There was no ammonia in this product. Before using, it was fused in platinum.

In the first determination of this series the silver nitrate was heated too hot (520°) and the gases came over so fast that the reduced copper was only superficially attacked; even so it was vastly more efficient than the gauze. Because, however, some nitric peroxide still escaped, this experiment also had to be rejected, a part of the 0.004 per cent. impurity which it indicated being undoubtedly due to nitrous fumes.

The apparatus was now improved by sealing off the end (*A*) of the tube after the silver nitrate had been fused for a long time in a current of dry air. Moreover, the last trace of rubber exposed to nitrous fumes was eliminated by providing an accurately ground joint between the decomposition tube and the copper oxide. The process was conducted so slowly at 490° that the silver nitrate could be entirely decomposed to pure spongy silver without exhausting all the copper. Care was taken to have the very pure silver nitrate in a state comparable to that used in the determinations. The salt after its preliminary treatment in platinum still contained a few crystals of unfused nitrate; accordingly in the tube it was heated evenly at 220° with shaking to dislodge steam bubbles, exactly as the determinations had been. Under these conditions reliable results were obtained. In No. 25, a second weighed pentoxide tube placed in tandem with the first showed no gain in weight; hence the first tube caught all the water vapor. The remaining nitrogen was driven out by pure dry air before weighing. That water vapor was

WATER OBTAINED BY DECOMPOSITION OF SILVER NITRATE.			
Experiment number.	Weight of Ag No. ₂ Gram	Gain in weight of drying tubes. Gram	Percentage of water found. Per cent
25	53	0.0015	0.0028
26	52	0.0011	0.0020
27	44	0.0014	0.0033
---	---	---	---
Average.....50.....		0.0013.....	0.0027

actually present was shown by the "melting" of phosphoric pentoxide in the first tube.

Thus it is clear that less than 0.003 per cent. of water was held by the silver nitrate after fusion. There was only one other source from which this milligram or so of water might have come, namely, from the copper used for the reduction of the nitrous fumes. Less than 0.0002 gram of hydrogen retained by 300 grams of copper, or less than one part in a million, would have been enough to cause this effect, hence it seemed rash to assume that the water did not come from this source. As much hydrogen as this might have come from a trace of moisture in the hundred liters of carbon monoxide used for the reduction of the copper.

The question thus raised was capable of being investigated. For this purpose the mass of copper, reduced just as it would have been for one of the preceding experiments, was twice oxidized by a very large volume of pure ignited air dried with the usual potash towers and finally with phosphoric pentoxide. This air, having been already passed over red-hot cupric oxide in a hard glass tube and thoroughly dried by pentoxide, could hardly bring with it any water which could be taken up by the following tube of the same material. On one of these occasions, 0.0009 gram of water was found, and on another 0.0007 gram. Possibly some of this may have come from the atmosphere during the manipulation of the tubes; but a similar amount must be supposed to have been taken during each of the previous determinations. Hence it seems to be permissible to subtract the average 0.0008 gram from the average result of experiments 25, 26 and 27, namely, 0.0013 gram. This leaves only 0.0005 gram as the maximum amount of water held by 50 grams of carefully fused silver nitrate, introducing an error of only 1 part in 100,000. As the average of the final series led to a value a trifle over 157.480 grams as the weight of nitrate obtainable from 100.000 grams of silver, the correction to be applied for water reduces the result only to 157.479. Possibly not even as much water as this was present in the quantitatively made silver nitrate, because the relative surface exposed for drying was not so great in the long, narrow tube just used as it was in the quartz flask employed for experiments 10 to 15.

This unimportant change in the synthetic result from 157.480 to 157.479 was the only apparent outcome of these tedious and often exasperating experiments on the decomposition of the nitrate; but in reality more was shown by them. The experience furnished to the experimenters a striking example of the essential importance of taking as much care in determining a small correction as in determining the quantity to be corrected. It moreover confirmed the impression that except in cases like the chloride of zinc, when water acts chemically upon the substance, little or no water is retained by most fused salts. If silver nitrate, which

at 200° is miscible with water in all proportions, sets free so nearly all that it possesses in a current of dry air at this temperature, it is much more likely that other salts, fusing at a higher temperature and possessing a less attraction for water, should be free from it after fusion. This is a reassuring conviction, well worth the trouble spent upon the point.

Attention was now directed to other foreign substances besides water and air which might be present in the synthetic silver nitrate. Further careful investigation was needed to show that all the silver was combined as nitrate and that no other impurities were concealed in the salt. The pure, pearly whiteness of the cold fused material precluded the possibility of there having been a trace of reduction to metallic silver. The salt was soluble in pure water without residue or turbidity, and maintained its clearness when diluted to half or quarter normal; hence oxide and halogen salts must have been absent. The only other likely impurity seemed to be ammonium salts, nitrite, and excess of nitric acid. Of these possibilities, Stas thought only of the likelihood of the presence of free acid; but each was carefully considered in the present work.

It is known that copper dissolving in nitric acid forms perceptible quantities of ammonium nitrate. Apparently, no similar reaction has been noted with silver, and from an electrochemical standpoint it seemed unlikely; moreover, ammonium nitrate if present would probably be for the most part decomposed by the hour's fusion of the silver salt. Nevertheless, thoroughness demanded evidence on this point. Nessler solution is the most convenient for this test, but silver must first be precipitated from solution in the dark. Light generates chlorine, which interferes with the test.

In order to prepare for this search for ammonia, the synthetic nitrate of silver resulting from several experiments was shaken with a slight excess of standard pure sodium chloride until the supernatant liquid was clear: the latter was decanted, made up to 50 cc., and placed in a comparison cylinder. The sodium chloride gave no test with Nessler solution.

The cylinder full of liquid prepared from the silver nitrate was finally tested by comparison with other cylinders containing known traces of ammonium nitrate mixed with sodium nitrate in concentration equal to that existing in the actual determination. The sodium nitrate had been several times recrystallized with centrifugal draining, and was shown to be free from ammonia. In this way the following results were attained: Synthesis 12 was found to contain 0.05 mg. of ammonium nitrate, synthesis 13, 0.06 mg., and synthesis 14, 0.05 mg.; in all, 36.5 grams of silver nitrate were proved to contain no more than 0.00016 gram of ammonium nitrate,—less than one two-thousandth of 1 per cent. The source of this ammonia was not determined; it might have come from

the reduction of nitric acid or from the large volume of air used in evaporating the silver nitrate. The only possible place where it could have entered with the reagents used in the test was in the sodium chloride solution; this was indeed tested, with negative results; but Nessler's reagent is not very sensitive in the presence of chloride, and a trace of ammonia might have eluded detection. If the amount found had been larger, more time would have been spent upon the matter, and a sample of the silver nitrate often recrystallized in an atmosphere free from ammonia would have been used in a blank experiment for comparison; but with such a small trace of impurity this was not worth while.

In summing up the results of the test for ammonia, the amount should be calculated for the quantity of silver nitrate produced from 100.000 grams of silver. Thus it is found that 157.480 grams of fused silver nitrate could not have contained over 0.0007 gram of ammonium nitrate.

The next impurity to be studied, nitrous acid, was sought by means of sulphanic acid and naphthylamine hydrochloride. These were proved with a standard nitrite solution of which 1 liter contained 0.1 gram of nitrogen. To insure parallel conditions in testing by comparison, pure silver nitrate was prepared with some care. It was thrice recrystallized from nitric acid with centrifugal treatment, fused in porcelain, then recrystallized three times more from the purest water in platinum, with centrifugal drainage as before. The specimens of fused silver nitrate resulting from quantitative determinations were dissolved in known amounts of water, and comparison solutions of equal concentration prepared. The crystallized silver nitrate gave no trace of pink color with the reagents. A fresh solution, to which 0.1 cc. of nitrite solution (0.01 mg.) had been added, gave a pronounced color, while determinations 2, 3, and 11 all gave a much fainter, barely visible color; hence it was permissible to conclude that the loss of oxygen from the nitrate on fusion could not have exceeded 0.00005 gram, a wholly negligible quantity.

In seeking for the next impurity, free nitric acid, Stas tested aqueous solutions of his fused silver nitrate with "tournesol" and found them alkaline rather than acid. This alkali may have come from his glass vessels. We used methyl orange, a more sensitive indicator, and noted that the purest crystallized neutral specimens and the fused salt alike gave equally pronounced acid reactions in solution. The color was not modified by the addition of half a milligram of nitric acid; therefore the equality in color does not disprove the presence of free acid in our fused product. Dilute sodium hydroxide freed from carbonate by barium hydroxide threw down a precipitate without changing the pink color. Hence the indicator was discarded and the investigation continued with the nephelometer.

The test for acid with the help of this instrument was conducted by adding a very dilute standard caustic alkaline solution to the solution to be tested and by observing if this addition caused a permanent cloud.

Preliminary trials were necessary in the first place in order to determine the conditions best suited for accuracy. It was found that a concentration of nitrate no stronger than 4 grams in 0.025 liter was best adapted to the work, as silver hydroxide is distinctly soluble in double this concentration of silver nitrate. On the other hand, silver hydroxide precipitated by somewhat concentrated alkali does not quickly redissolve in an equivalent quantity of nitric acid mixed with the dilute silver solution. It was found that even the precipitate caused by 0.1 cc. of a two-hundredth normal solution may produce a fairly permanent cloud in spite of the presence of an excess of 0.00003 gram of nitric acid, enough to dissolve it. Still more dilute solutions behaved much more satisfactorily, however. A milliliter of a two-thousandth normal caustic solution (equivalent to 0.00003 gram of nitric acid) added with constant stirring to the pure standard silver nitrate formed a cloud easily seen in the nephelometer. In case 0.00003 gram of nitric acid had been introduced before adding alkali, no precipitate was formed under the same conditions. Hence under these circumstances the test attained a degree of sensitiveness suited to the case in hand.

In this way it was found that the silver nitrate remaining from synthesis 11 gave a distinct opalescence with the addition of 0.00002 gram of sodium hydroxide, and an obvious cloud with 0.00003 gram. Hence it was concluded that silver nitrate fused in a stream of pure air for one hour contains no weighable excess of nitric acid.

The various suspected impurities having thus been duly sought, it is instructive and interesting to tabulate the results. These are as follows:

	Grams
Weight of fused AgNO_3 from 100.000 grams Ag.....	157.480
Correction for weight of--	
Dissolved air.....	0.000
Retained water	-0.0016
Retained ammonium nitrate	-0.0007
Nitrite	0.000
Free acid.....	0.000
	<hr/>
Corrected weight of silver nitrate obtainable from	
100.000 grams of pure silver.....	157.478

As the subtractive corrections given in the above tables are maximum values, the weight of argentic nitrate in question can hardly be lower than this value, 157.478. On the other hand, it can hardly be higher than the uncorrected value, 157.480. Thus two limits are set, very near together, between which the true value must lie. Obviously, for the

present, one can not go very far astray in accepting the mean value, 157.479; and this value will be used in the following discussion.

The Final Result and Its Relations to the Values of Atomic Weights of Nitrogen and Silver

The conclusion reached by the foregoing series of experiments is that 100.000 parts of silver yield very nearly 157.479 parts of silver nitrate. Among other experimenters, Penny found 157.442; Marignac found 157.424; Stas found 157.474 in one series of seven determinations and 157.486 in another of two, and Hardin found 157.484. From these older figures, by an interesting coincidence Clarke calculated exactly the value found in the present research.¹ This coincidence is to be attributed not so much to the efficacy of the method of calculation as to the fact that in this case the impurities in the silver happened to balance exactly the impurities in the silver nitrate. At first sight it is incomprehensible how Stas, working with slightly impure silver, could have obtained any results higher than the true value; but it must be remembered that his nitrate was fused in a glass vessel, which must have been attacked by the strongly acid nitrate at 220°. Constancy in the weight of the vessel would be no evidence of absence of action, for silver might partly take in the glass the place of the sodium taken from it. Thus a gain in weight due to sodium nitrate might be accompanied with no considerable loss of weight of the vessel. In favor of this hypothesis is the fact that Stas's results steadily decreased in each series, as he proceeded with the work; the flask seems to have been less and less susceptible to attack, as is reasonable. If the last two determinations of the first series are taken as the most nearly free from this cause of error, the number 157.466 obtained from them should furnish by comparison with our number, some clue to the amount of gaseous impurity in Stas's silver. Thus it appears that his silver must have contained nearly 0.01 per cent. of impurity—probably more if it is considered that the flask was still not wholly resistant—a conclusion not very different from that reached by Richards and Wells.

Speculations of this kind concerning older work are rather a thankless task, however; there is usually too much that is doubtful to allow them to serve a very valuable purpose. The only object in pursuing the review at all is in order to assure one's self that no real inconsistency exists in the data.

Attention is now directed to a more important matter, namely, the effect of the new experimental result upon the table of atomic weights. This is quickly stated: The newly advocated low atomic weight of nitrogen is incompatible with the ratio 100.000; 157.479, if silver is taken as 107.930. If, on the other hand, the new atomic weight of nitrogen is the true one, silver must have a much lower value than this.

¹ Recalculation of the Atomic Weights (1897), p. 64.

The exact figures are given in the following table :

If Ag=107.880,	AgNO ₃ =169.888	and N=14.008
If Ag=107.883,	AgNO ₃ =169.893	and N=14.010
If Ag=107.890,	AgNO ₃ =169.904	and N=14.014
If Ag=107.930,	AgNO ₃ =169.967	and N=14.037

This series of conditional statements contains in a nutshell the result of the present investigation. In order to decide between the alternatives, other compounds must be further studied, especially the chlorates and the ammonium salts. Investigations in both of these directions have already been begun in the Chemical Laboratory of Harvard College.

Summary

Silver nitrate was made from pure silver, and the gain in weight was carefully noted.

In the course of the work, a new and convenient apparatus for quantitative evaporation was devised. Quartz flasks were used as a part of it.

The silver nitrate was fused until constant in weight: it was carefully tested for dissolved air, retained water and ammonia, and nitric and nitrous acids. Only the second and third of these impurities could be detected by tests proved to be adequate, and these only in mere traces, less than 0.002 per cent in all.

The outcome was that 100,000 parts of pure silver produced 157,479 parts of silver nitrate. If, then, silver is taken as 107.93, nitrogen must be 14.037; or if silver is taken as 107.880, nitrogen must be 14.008, oxygen being 16.000.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE]

THE MOLECULAR WEIGHT OF SILVER SULPHATE AND THE ATOMIC WEIGHT OF SULPHUR.

BY THEODORE WILLIAM RICHARDS AND GRINNELL JONES.

Received February 15, 1906.

Introduction

The atomic weight of sulphur has been investigated by many experimenters; but, as will be seen, the results are far from concordant. A brief review of these investigations forms the most appropriate introduction to the present one. The values in the following list have been recalculated with modern figures for the other atomic weights involved:¹

1814.	Berzelius (Phil. Trans., 104, 20).....	32.00
1826.	Berzelius (Pogg. Ann., 8, 15).....	32.08
1833.	Turner (Phil. Trans., 123, 539).....	32.
	Do.....	32.06
1836.	Thomson (J. pr. Chem., 8, 370).....	32.
1844.	Erdmann and Marchand (J. pr. Chem., 31, 396).....	31.99
1845.	Berzelius (Lehrbuch, 5th ed., 3, 1187).....	32.04
	Do.....	32.16

¹ Ag = 107.93; Cl = 35.473; Pb = 206.9; Hg = 200.0; Na = 23.008; C = 12.002.