The exact figures are given in the following table :

If Ag=107.880, AgNO₃=169.888 and N=**14.008**
If Ag=107.885, AgNO₃=169.893 and N=**14.010**
If Ag=107.890, AgNO₃=169.904 and N=**14.014**
If Ag=107.930, AgNO₃=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.

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.

1848.	Svanberg and Struve (J. pr. Chem., **44**, 320)	32.15
1851.	Struve (Ann., **80**, 203)	31.94
1859.	Dumas (Ann. chim. phys. [3], **55**, 148)	32.00
1860.	Stas[1] (Bull. acad. roy. Belg. [2], **10**, 253, 322)	32.06
1878.	Cooke (Proc. Amer. Acad., **13**, 50)	32.137
	Do	31.980
1891.	Richards (Proc. Amer. Acad., **26**, 268)	32.043
1898.	Leduc (Ann. chim. phys. [7], **15**, 94)	32.056
1899.	D. Berthelot (Jour. de Phys. [3], **8**, 271)	32.050
1904.	Jaquerod and Pintza (Compt. rend., **139**, 129)	32.01
1905.	Guye (Compt. rend., **140**, 1242)	32.065
1905.	Jaquerod and Scheuer (Compt. rend., **140**, 1384)	32.036

The work of the predecessors of Stas is now of historical interest only and does not merit detailed criticism; in recent times the atomic weight of sulphur has rested chiefly upon the experiments of the famous Belgian.

Stas converted silver into its sulphide by heating it in a current of sulphur vapor or hydrogen sulphide; but because he did not know the precautions necessary for preparing perfectly pure silver[2], it is evident that all of his work in which silver was weighed needs revision. Stas also reduced silver sulphate to silver in a current of hydrogen, but in this case he did not take the very important precaution of fusing the sulphate before weighing[3]; and, moreover, the possibility that the reduced silver might contain silver sulphide or sulphate was by no means excluded.

A brief review of subsequent work may not be out of place, although it is of a different order of precision. Cooke reduced silver sulphide in a current of hydrogen, and concluded that the atomic weight of sulphur must lie between the limits 32.14 and 31.98. In summing up his results he stated that "this is equivalent to confirming the accepted value of this constant, so far as any experiments on a scale less extensive than those of Stas can be of value to this end[4]."

The determination of the atomic weight of sulphur by Richards was made incidentally in his work on the atomic weight of copper. The ratio $Na_2CO_3 : Na_2SO_4$ gave as a result $S = 32.075$. If sodium is taken as 23.008 instead of 23.053, the result becomes $S = 32.043$. No very great confidence was placed in these results at the time, as is shown by the following sentence: "The results are hardly capable of deciding the present uncertainty in the atomic weight of sulphur[5]." It is probable that the result is too low, as no proof could be obtained of the thorough desiccation of the sodium carbonate.

[1]Van der Plaats, Ann. chim. phys. [6], **7**, 504, and 526 (1886) pointed out that Stas made an error in calculating his own data. Stas obtained 32.074, but 32.06 is correct.

[2]Dumas, Ann. chim. phys. [5], **14**, 289 (1878); Richards and Wells, Publication Carnegie Inst. No. **28**, p. 66 (1905).

[3]Richards, Pr. Am. Phil. Soc., **42**, 28 (1903).

[4]Cooke, Pr. Am. Acad., **13**, 52 (1878).

[5]Richards, Pr. Am. Acad., **26**, 269 (1891).

Very recently numerous atomic weight determinations have appeared, depending on a purely physical method, based on the assumption that Avogadro's hypothesis and the simple gas law $PV = RT$ is strictly true for gases when indefinitely expanded. Since it is impossible to determine the ratios of the densities of gases with sufficient accuracy at very low pressures, it is necessary to determine this ratio under normal conditions and apply a different correction in each case, depending on the deviation of the gas from the simple gas law. It is probable that the ratio of the densities can be, and in most cases has been, determined with sufficient percentage accuracy. On the other hand, the correction is hypothetical and much less certain; and accordingly, the method has but little value when the correction is large.

According to Leduc[1] the ratio between the densities of sulphur dioxide and oxygen is 2.04835. If no correction is applied for the imperfection of the gases, this value leads to 33.55 for the atomic weight of sulphur. The correction in this case is unusually large and therefore must be known with a high percentage accuracy if the result is to have any value as a determination of atomic weights. The following are the general methods of calculating the correction, but none seems to be of sufficient value for the present case.

The first, called the "method of corresponding states" was developed for this purpose by Leduc[2]. It depends on the assumption of van der Waals that two gases are in corresponding states and deviate equally from the hypothetical perfect gas if their temperatures and pressures are equal multiples or sub-multiples of their critical temperatures and pressures, respectively. In calculating the correcting factor, the compressibility and critical constants are used. Leduc[3] by this method obtained 64.056 as the molecular weight of sulphur dioxide, and 34.071 as the molecular weight of hydrogen sulphide, and hence from both $S = 32.056$.

The second method is the "method of critical constants" as developed by Guye[4]. The correction is calculated by the use of van der Waals's equation, the quantities a and b being calculated from the critical constants of the gases under consideration. In a complicated manner Guye applied a correction to the quantities a and b of van der Waals's equation, because they appear to vary slightly with the temperature and the pressure[5]; in this way was obtained the value 64.065 as the molecular weight of sulphur dioxide; hence $S = 32.065$.

The third method is called the "method of limiting density." It was

[1] Leduc, Compt. rend., 117, 219 (1894).

[2] Leduc, Ann. chim. phys. [7], 15, 5 (1898).

[3] Ibid, 94 (1898).

[4] Guye, Compt. rend., 138, 1215 (1904); Bull. soc. chim. [3], 5 Août (1905); J. chim. phys., 3, 321 (1905).

[5] Guye, Bull. soc. chim. [3], 5 Août, p. XII (1905).

originated by Daniel Berthelot in 1898[1] and has been used by Rayleigh[2] and Jaquerod[3]. It depends on the experimental determination of the compressibilities of gases at pressures in the neighborhood of one atmosphere. By an extrapolation, the "limiting ratio" of the densities at very low pressures can be calculated. This method has reached its greatest perfection in the hands of Lord Rayleigh, who has shown that for the permanent gases the deviation from Boyle's law only varies slightly with the pressure and therefore the extrapolation is fairly safe. This physical method has been applied with the greatest success to the cases of hydrogen, carbon, and, especially, nitrogen, because in these cases the correction is comparatively small. Here also, however, the application to sulphur is far less satisfactory. It is to be regretted that Lord Rayleigh's work did not include compounds of this element.

Jaquerod and Pintza determined the density of sulphur dioxide at 760 mm., 570 mm. and 380 mm. pressure, and from these results calculated the compressibility. The results were extrapolated to zero pressure on the assumption that the deviations from Boyle's law diminish as the pressure is lowered. They obtained 32.01 as the atomic weight of sulphur. Afterwards Jaquerod and Scheuer determined the compressibility of sulphur dioxide through the ranges 400 to 800 mm. and 200 to 400 mm. by a method similar to Lord Rayleigh's. They found, as was to be expected, that the deviation from Boyle's law was smaller at the lower pressure. Nevertheless, in calculating the molecular weight of sulphur dioxide, they assumed that the deviation from Boyle's law per centimeter of pressure between 0 and 760 mm. was the same as between 400 and 800 mm. They obtained 64.036 for sulphur dioxide and hence $S = 32.036$. If their measurement of the compressibility through the range 200 to 400 mm. is used, the result becomes 32.052, and it seems probable that yet a higher value is the true outcome of their experiments. These different conclusions emphasize the uncertainty of the method.

Probably the adsorption of sulphurous oxide and hydrogen sulphide on the glass of the containing globes introduces an error in both the density and compressibility determinations, and hence in facts to which the assumption above mentioned are applied. This possibility of adsorption seems to have been not sufficiently heeded by any of the experimenters on sulphur compounds. It adds yet another uncertainty to the results.

The upshot of these considerations is the conclusion that none of the

[1] Berthelot, Compt. rend., **126**, 954, 1030, 1415, 1501 (1898); Jour. de Phys. [3], **8**, 263 (1899).

[2] Rayleigh, Phil. Trans. A., **204**, 352 (1905); A., **196**, 205 (1901), and A., **198**, 417 (1902).

[3] Jaquerod and Pintza, Compt. rend., **139**, 129 (1904); Jaquerod and Scheuer, Compt. rend., **140**, 1384 (1905).

2

work heretofore done upon the atomic weight of sulphur decides its value. Hence further investigation is imperative. The problem, for complete solution, must be approached from many sides, and the work must involve many compounds of sulphur. The following contribution describes one section of a comprehensive program by which it is hoped the question may be answered.

Preliminary Experiments

The sulphate of silver was selected as the most suitable starting-point for the present investigation, because it seemed probable that this salt could be prepared in a pure condition and accurately analyzed. A further reason for studying silver sulphate lies in the possibility of later combining the results with some ratio involving the sulphide and thus furnishing evidence on the even more important question as to the atomic weight of silver. Balanced against the advantages is the disadvantage that only about 10 per cent. of its weight is sulphur, causing the experimental errors to be greatly multiplied in the calculations; but the advantages more than outweigh the disadvantage.

A tentative preliminary plan of operations was to fuse silver sulphate in a platinum crucible, dissolve it, precipitate as chloride, and collect and weigh the precipitate. This plan was thwarted by numerous obstacles. It was found that the sulphate decomposes slightly when fused, a difficulty which was later overcome. Again the quantitative solution of the silver sulphate was a very tedious process. Eight grams fused in a platinum crucible and placed in 1.5 liters of water required six weeks for its complete solution, even with frequent agitation. The action on the glass during this long time, the danger of the access of gaseous impurity, and the loss of valuable time all made this difficulty a serious one.

Silver sulphate can be readily dissolved by placing twice its weight of concentrated sulphuric acid in the crucible and heating at about 300°; on cooling, the acid sulphate of silver crystallizes out[1]. Upon adding water to this acid sulphate the normal sulphate is formed as a fine powder, which can readily be washed into the precipitating flask and dissolved. The large excess of sulphuric acid thus introduced was far from desirable, however, for it tends to cause considerable occlusion of silver sulphate in the precipitated chloride. In order to test this question, a solution, prepared as described above, and containing 7.4 grams of silver sulphate, was precipitated with hydrochloric acid. The precipitate was washed by decanting eleven times with very dilute hydrochloric acid and then dissolved in ammonia and diluted. The silver chloride was then reprecipitated with hydrochloric acid; the solution should contain all the sulphate previously occluded. After settling, this mixture was filtered, and the perfectly clear solution was evaporated in a platinum dish over an alcohol lamp

[1] Schultz, Pogg. Ann., 133, 145 (1868).

until ammonium chloride crystallized out on cooling, the volume being then about 0.1 liter. To this were added about 10 grams of barium chloride. An undoubted precipitate of barium sulphate was produced, which proved that there is considerable occlusion of sulphate by silver chloride precipitated from solutions containing a large excess of sulphuric acid.

For the sake of comparison, approximately the same amount of silver chloride prepared from nitrate was dissolved in ammonia, and 3.5 mg. of sulphate added. The solution was treated exactly like the preceding operations, and yielded about the same amount of precipitate. This experiment gives an approximate idea of the extent of the occlusion.

In searching for a means of wholly eliminating the sulphate it was found that a small proportion of silver sulphate in silver chloride could be completely converted into chloride by fusion in a current of hydrochloric acid gas. This observation led to the development of a new process in which the entire reaction was carried out in this manner, fused silver sulphate being wholly converted into chloride without the need of dissolving in water. Thus the operation was greatly simplified, and the chances of error diminished.

The method of preparing the materials, the shape and nature of the apparatus, and many of the precautions and details of manipulation were adopted only after numerous preliminary experiments. A detailed account of this tentative work is, however, unnecessary, since the important results are implied in the description of the method which was finally adopted.

The Preparation of Pure Materials

Sulphuric Acid.—The best commercial "chemically pure" acid was twice fractionally distilled, using a quartz condenser and a platinum dish as receiver. Only the middle fractions were used; 17 grams left no visible or weighable residue on evaporation.

Silver Sulphate.—Pure silver chloride residues from previous atomic weight investigations in this laboratory were reduced with invert sugar and sodium hydroxide. The reduced silver was thoroughly washed, and dissolved in nitric acid, and the nitrate was diluted and filtered. It was evaporated on the steam-bath until saturated, and crystallized by adding an equal volume of concentrated nitric acid and cooling. The crystals were drained centrifugally as usual[1]. The crystallization from pure concentrated nitric acid and centrifugal draining was repeated five times, using Jena-glass vessels. It was finally recrystallized once more, using a platinum dish and redistilled nitric acid. This silver nitrate was dissolved in a small amount of water in a platinum dish, and an excess of the purest sulphuric acid, diluted with an equal volume of pure water, was poured into it. The precipitated silver sulphate was drained in the centrifugal

[1] Richards, This Journal, **27**, 104 (1905).

machine. It was then dissolved in hot concentrated sulpharic acid in a platinum dish, and the solution was boiled for several minutes to expel nitric acid. On cooling, the acid sulphate crystallized in large crystals. This acid sulphate was very thoroughly whirled, placed in a platinum dish, and treated with purest water. Heat was evolved and the normal sulphate crystallized out as a fine powder. This powder was washed by decantation with the purest water until the wash-waters were no longer acid[1]. All the water used in this work was purified in the manner described in previous communications. During this washing the action of light on the wet silver sulphate produces a slight violet color. This, however, does no harm, as any slight decomposition is remedied during the subsequent fusion. It was then dried as much as possible in the centrifugal machine, and the drying was completed in an air-bath at 110°. These operations were carried out as much as possible under the protection of a very large inverted funnel, and the dish was kept covered with a large watch glass, to avoid the introduction of dust. This sample was called A and was used in the preliminary series and in experiments 4 and 5 of the final series of quantitative experiments.

Sample A was dissolved in concentrated sulphuric acid, boiled, crystallized as acid sulphate by cooling, centrifugally drained, converted into the normal sulphate by adding water, washed, and dried as before. This sample was called sample B. Since the mean of the results with this sample is the same as the mean of experiments 4 and 5, in which sample A was used, it is evident that the boiling of the sulphuric acid solution followed by a crystallization in two different crystalline forms did not affect the result; therefore further purification seemed unnecessary.

Hydrochloric Acid.—Hydrochloric acid, which was only used as a gas, was made from two sources. In experiments 5 and 6 the hydrochloric acid was made by dropping pure sulphuric acid on pure ammonium chloride. In the other experiments the best commercial concentrated hydrochloric acid was used. Richards and Wells[2] have shown that this acid contained no other halogen or arsenic; it was therefore suitable for our purpose.

The Fusion of Silver Sulphate

Much thought was expended on the devising of a piece of apparatus which should be suitable not only for the fusion of silver sulphate, but also for the quantitative conversion of the sulphate into the chloride. Finally the simple symmetrical tube shown in the diagram was found to be best. It was the outcome of several trials and suggestions, and consisted of a thin cylindrical tube of fused quartz with smaller quartz tubes

[1] Unless this precaution is taken the silver sulphate can not be dried thoroughly in the air-bath; in which case it would be impossible to clean properly the receiving end of the tube into which it was afterwards introduced. (See p. 833).

[2] Richards and Wells, loc. cit.

fused upon the ends[1]. The tube was very light, weighing less than 6 grams. A very fine platinum wire was wrapped many times around the constricted portion of the tube (A); by pulling this, the tube could be readily rotated. It was hung on the balance in a horizontal position by means of a platinum wire. The same tube was used throughout the research, the cylindrical shape giving it sufficient strength to withstand all the strains to which it was subjected.

The tube remained remarkably constant in weight in spite of the very vigorous treatment it received. During the entire fifteen experiments the loss in weight was only 0.41 mg., and during the twelve experiments of the final series the loss was only 0.16 mg. This slight loss is probably accounted for by a slight solubility of the quartz in the concentrated ammonia or potassium cyanide solution used to remove the silver chloride after each determination.

The sulphate of silver prepared as described above must have contained a little included water and excess of sulphuric acid, since it had
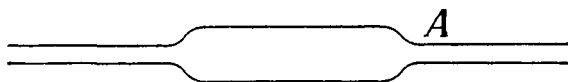

FIGURE 1.

been crystallized from an acid solution[2]. The only certain method of removing mother liquor included within crystals is to fuse the salt. This part of the problem caused considerable difficulty; for it was found that silver sulphate decomposes slightly when fused in air, becoming yellowish brown in color. In order to decrease this thermal dissociation, the experiment was made of fusing the salt in a current of dilute sulphuric oxide, with complete success. The salt is then pure white in color.

The small crystals of silver sulphate were pushed into the tube with a platinum rod, and the narrow ends were freed from loosely adhering silver sulphate by means of a clean feather tip, which had been previously washed with alcohol and·ether to free it from grease. The tube was supported, on hooks of hard glass, in front of the apparatus for delivering sulphur trioxide. The very fine platinum wire needed for rotating it had been wound around the tube in the first place.

The apparatus for delivering a current of pure dry air or sulphur trioxide or hydrogen chloride is shown diagrammatically in figure 2. A cur-

[1] We are greatly indebted to Professor Baxter for his kindness in making this apparatus from a fine quartz tube and a quartz test-tube. To Mr. F. B. Coffin also we are indebted for a suggestion which led to a modification of the original shape of the tube.

[2] Richards, Pr. Am. Phil. Soc., **42**, 28 (1903).

rent of air was first driven over red-hot copper oxide (A) to remove organic matter, and subsequently through an Emmerling tower (B) containing beads moistened with a strong caustic potash solution. This tower was closed by a rubber stopper at the top, which introduced no impurity, since nothing but pure air passed over it. From this point, however, the apparatus contained no rubber connections or stoppers. All stopcocks were lubricated with phosphoric or sulphuric acid.

The air was dried by passing through two Emmerling towers (C and D) containing beads moistened with concentrated sulphuric acid. The current of air could then be either used in a pure dry state by passing through L or F, or else charged with sulphur trioxide by bubbling twice through fuming sulphuric acid in the bottle E. This acid was kept saturated by an excess of solid sulphur trioxide. A current of air mixed with any desired proportion of sulphur trioxide was thus delivered through G into the quartz tube H. The delivery tube (G) and the quartz tube (H) touched each other, but no attempt was made to secure a tight joint.
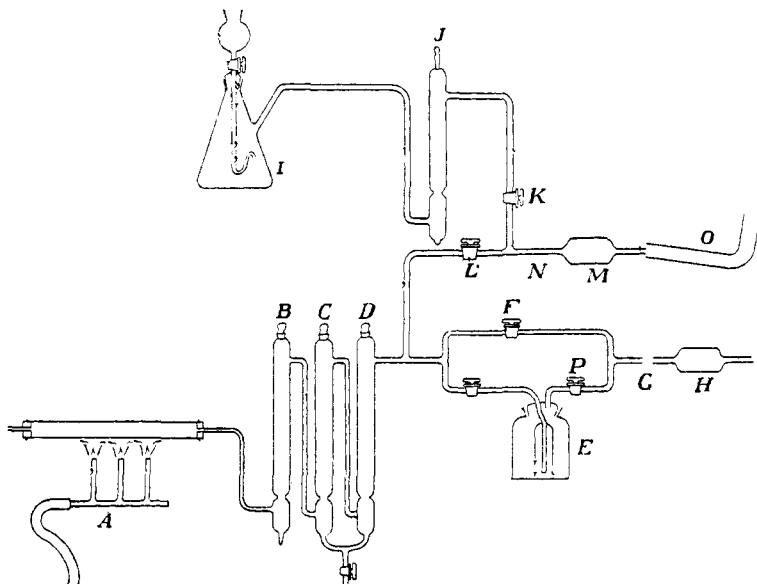

FIGURE 2.

The silver sulphate contained in the quartz tube was then fused with a fish-tail Bunsen burner held in the hand. A red heat is required. When all of the sulphate was fused, the stopcock (P) delivering sulphur trioxide was closed and a rapid current of air was admitted through F. As soon as the fumes of sulphuric acid could no longer be seen escaping from the end of the quartz tube, the flame was removed and the tube was slowly rotated by drawing out the platinum wire wrapped around one end.

This causes the silver sulphate to solidify in a thin sheet around the tube. Unless care is taken to keep the salt at least 1 cm. distant from either of the end tubes, difficulty is experienced during the conversion into chloride.

The final solidification in the current of pure dry air was carried out very rapidly, in order to avoid decomposition and obtain a perfectly white sample. If the silver sulphate was kept fused 10 or 15 seconds too long after the sulphur trioxide current was stopped, a yellowish brown product was obtained. This indicates that the salt contained either metallic silver or silver sulphide. Richards, Wells, and Forbes[1] have shown that a slight discoloration of a fused silver salt is a very delicate test for impurity. The loss of weight due to this discoloration was very slight, as will be shown on page 836.

The entire tube was later heated in a current of pure air at a temperature above the boiling-point of sulphuric acid for about 5 minutes, in order to drive out any possible accidental trace of acid in the tube. While still warm it was placed in a desiccator, and later weighed. The tube was kept horizontal until the end of the experiment, to avoid any chance of mechanical loss.

The device of spreading the salt in a thin layer around the tube by rotating the tube during the cooling had four very important advantages: First, the chance of breaking the very fragile quartz tube during the solidification and cooling was greatly reduced by the more even distribution of the strain; secondly, the salt was agitated and spread out in a thin layer while still fused in a current of pure air, thus facilitating the escape of any possible trace of dissolved sulphur trioxide; thirdly, the cooling was made more uniform and rapid, so that the silver sulphate had no time to decompose before it had solidified; and fourthly, a much larger surface was exposed to the later action of the hydrochloric acid.

The possibility just mentioned that the colorless silver sulphate might contain an excess of sulphur trioxide needed careful consideration. Unfortunately a direct test for acid seemed to be impracticable, owing to the slight solubility of silver sulphate, hence light upon the question was sought in several distinct ways.

Weber[2] has found that in order to prepare a compound $Ag_2S_2O_7$ silver sulphate must be heated with sulphur trioxide under pressure in a sealed tube. This, together with the fact that silver sulphate decomposes so easily when fused, indicates that it does not have a great tendency to retain sulphuric oxide, and that the vapor pressure of the trioxide in the disulphate is far above that maintained in the present experiments. In order to obtain quantitative evidence, the pure white sulphate in six of the final

[1] Richards and Wells, Carnegie Inst. Pub. **28**, 31 (1905); Richards and Forbes, the preceding paper, p. 816.

[2] Weber, Ber., **17**, 2503 (1884).

experiments, after being weighed, was fused again for about 10 to 15 seconds in order to decompose it slightly. This gave a slight but unmistakable dark color to the salt. The resulting losses of weight are tabulated below.

THE LOSS OF WEIGHT CAUSED BY SLIGHT DECOMPOSITION.

No. of experiment	White Ag_2SO_4.	Darkened Ag_2SO_4.	Difference.
9	5.27714	5.27709	0.00005
10	5.16313	5.16302	0.00011
11	5.08585	5.08577	0.00006
12	5.13372	5.13367	0.00005
13	5.16148	5.16138	0.00010
15	5.37436	5.37425	0.00011
Average			0.00008

The loss in weight was thus on the average only 0.08 mg. or 0.0015 per cent. It seems certain that at least part of this loss in weight was due to a deficiency of either oxygen or sulphur trioxide in the darkened sulphate, and not to the loss of an illegitimate excess of the latter substance. Therefore, although it may be a debatable question as to whether it is safer to take the weight of the white or darkened samples as the true weight, it seems probable that the weight of the white sample was more trustworthy. Even at the worst the uncertainty can not have been greater than 0.001 per cent. This result agrees with the earlier conclusions already cited concerning the obvious effect of very slight decomposition on the color of silver salts. It appears that in the present case, as in the others, the slight stability of these compounds is a real assistance in the production of a typical compound, instead of a hindrance to precise quantitative work.

For weighing the silver sulphate, and of course the chloride also, the Troemner balance which had served in many similar researches was used[1]. The Sartorius platinized brass weights were standardized by the usual Harvard method[2].

As usual, all weighings were made by substitution, a make-weight being placed on the right-hand balance pan. In order to avoid as far as possible any error due to changing meteorological conditions, a substituting counterpoise of the same material and approximately the same surface and weight was used. Every weighing was repeated, and the successive values seldom differed more than 0.03 mg. No difficulty was experienced from hygroscopic adsorption of water by either silver sulphate or silver chloride, except on a few days when the air was unusually humid. In these cases the tube was heated to about 330° and allowed to remain in a desiccator until the conditions were more favorable. The tube was always allowed to remain at least three hours in a desiccator near the balance

[1]Richards, Pr. Am. Acad. **26**, 242 (1891).
[2]Richards, This Journal, **22**, 144 (1900).

before making a weighing and during this time was covered by a black cloth to protect the sensitive salts from the light.

In order to correct the weights to the vacuum standard, the specific gravity of silver sulphate is needed. Following are the published results concerning this datum:

Density of Silver Sulphate

5.341. Karsten, Schweigger's J., **65**, 419 (1832).
5.322. Playfair and Joule, Mem. Chem. Soc., **2**, 430 (1845).
5.410. Filhol, Ann. chim. Phys. [3], **21**, 417, (1847).
5.425. Schröder, Pogg. Ann., **106**, 245 (1859).
5.49. } Petterson, Upsala, Nova Acta [3], **9**, 35 (1874).
5.54. }

After a study of the original papers, the value 5.45 was provisionally adopted as the most probable value; but, as there was some doubt about its accuracy, this was verified by experiment.

The density of the toluene to be displaced by the salt was determined by means of an Ostwald pycnometer at 29.2° to be 0.8566 (the mean of 3 concordant determinations); 6.067 grams of previously fused silver sulphate were found to displace 0.9532 gram of this toluene and therefore occupied 1.113 cc. (the mean of two determinations). Hence the density of silver sulphate is 5.45, as supposed. This involves an additive correction of 0.0000775 gram to each apparent gram of the salt, a value which is decreased 0.0000011 by an increase of a centimeter of atmospheric pressure, or decreased 0.00000026 by an increase of a degree of temperature. The correction to the weight was applied accordingly.

The Conversion of Silver Sulphate Into Chloride

The next step in the process was the conversion of the carefully weighed fused sulphate into chloride by heating it in a current of dry hydrochloric acid gas. This reaction has been observed by Hensgen[1].

The hydrochloric acid generator used for the previous work was constructed entirely out of glass. Pure ammonium chloride or concentrated hydrochloric acid was placed in the flask (I) shown in figure 2, and concentrated sulphuric acid was dropped upon it slowly. The gas was dried by passing through the tower (J) containing beads moistened with concentrated sulphuric acid[2]. The gas then passed through the stopcock (K)

[1]Hensgen, Rec. trav. chim. **2**, 124 (1883). "Lesulfate d'argent absorba 2 mol. HCl à la température ordinaire, avec un dégagement de chaleur notable, et se changea complètement en chlorure. En chauffant, même jusqu'a 300°, la réaction inverse (observée par M. H. avec le sulfate de cuivre) n'eut point lieu, mais l'acide sulphurique fut chassé complètement par un courant d'air. Parmi les sels susdits, le sulfate d'argent est celui qui d' après les données thermiques, doit se changer en chlorure avec le plus grand dégagement de chaleur." (See p. 83).

[2] In one of the preliminary experiments the hydrochloric acid was not dried. The sulphuric acid first formed absorbed considerable water, thus becoming diluted and nearly filling the tube with liquid sulphuric acid in which a large part of the silver sulphate dissolved. After heating for some time, the whole mass was solidified. This gave a non-porous mixture of silver sulphate and chloride. The hydrochloric acid had no appreciable further action until the mixture was fused, and then the action became very vigorous. The sulphuric acid which was formed boiled, and caused spattering and therefore danger of mechanical loss.

to the delivery tube (N). The ground-glass stopper at the top of the tower (J) acted as a safety-valve when the stopcock (K) was closed. Pure dry air might also be delivered at N by means of the stopcock (L), in order to sweep out the excess of acid at the conclusion of the reaction.

The quartz tube containing the silver sulphate was supported by means of hooks of hard glass in front of the delivery tube (N), as before, without making a tight joint.

In seven of the final experiments a condenser tube of quartz (O) was placed over the exit end of the tube (M) in order to condense the sulphuric acid and retain any silver which might escape. As will be shown, only very small traces of silver were found in the distillate. The condensation of sulphuric acid in the narrow tubes on the end was prevented by keeping them hot by means of a small fixed fish-tail burner.

A slow current of hydrochloric acid was generated and the tube warmed gently. The reaction took place readily and quietly, the only difficulty being that the silver chloride formed was inclined to creep over the walls of the vessel. This was probably due to the liberated sulphuric acid having dissolved undecomposed silver sulphate; the acid sulphate was then transported by surface tension and converted into chloride in another place. In two of the experiments one of the narrow end tubes was completely blocked up in this manner, making a successful completion of the experiment impossible; but in other cases the difficulty was avoided by starting with the silver sulphate in a band in the middle of the tube.

The sulphuric acid must be evaporated at a temperature below its boiling-point in order to avoid loss by the projection of small particles. The tube was heated by a flame held in the hand, the heating being regulated by watching the escaping fumes of acid and also the color of the silver chloride in the tube. It is well known that as the temperature increases, silver chloride acquires a deeper and deeper yellow color; and after acquiring the necessary experience, this change of color proved very helpful in regulating the temperature.

After from 2.5 to 4 hours no more fumes of sulphuric acid could be seen issuing from the tube. The silver chloride was then fused very slowly and quietly and kept in the fused state for 20 minutes in a current of hydrochloric acid. The tube was gently agitated in order to expose a fresh surface, at intervals of about 1 minute, by grasping the exit end with platinum forceps. The agitation can be performed without danger of loss because of the high surface tension of fused silver chloride. This material when liquefied does not adhere to quartz, and therefore is not drawn into the end tubes by capillarity. At the expiration of 20 minutes the current of acid gas was stopped by means of the stopcock (K), and a current of pure dry air was passed through the tube through L, the silver chloride being still maintained in the liquid state for at least 5 min-

utes with occasional agitation. The tube was rotated while subsequently cooling in a manner similar to that employed with the sulphate.

The condensed sulphuric acid evolved by the reaction and the condenser tube were tested for silver by means of the nephelometer[1]. The acid was transferred to a small flask and the tube was rinsed with ammonia, which was added to the acid. The excess of ammonia was then neutralized with nitric acid, and hydrochloric acid was added to precipitate any trace of silver present as an opalescent cloud of silver chloride. This opalescence was compared in the nephelometer with a standard which had been made in a manner very similar to the unknown solution[2]. A measured volume of a standard silver solution was taken; to it were added approximately the same amounts of sulphuric acid, ammonia, and nitric and hydrochloric acids as were present in the unknown solution; and it was made up to the same volume (about 30 cc.).

The greatest amount of silver chloride thus found in any experiment was 0.00009 gram and the average amount 0.00004 gram. The trace found in this way was of course added to the weight of the silver chloride. In three of the experiments (Nos. 4, 5, and 7) this determination was not made, but the average amount is added in these cases. The probable reason for the escape of this trace of silver will be discussed later.

The question as to whether or not this reaction is complete is, of course, of fundamental importance. There are four pieces of evidence bearing on this point.

In the first place, the silver chloride was fused for twenty minutes in a current of almost pure hydrochloric acid. Since the temperature was far above the boiling-point of sulphuric acid, this product of the reaction was driven off as fast as formed. Therefore according to the law of concentration effect it is to be expected that through the agency of the continually renewed hydrochloric acid all the silver sulphate would be decomposed and all the sulphuric acid would be driven off This would be hastened by the fact that fresh surfaces were continually exposed through agitation.

Again, in this case the law of concentration effect is assisted by the relative affinity, indicated approximately by the large amount of heat evolved by the reaction. It can be calculated from Thomsen's data that the reaction gives out 40,400 grams calories[3], or 170 kilojoules. Rarely, if ever, is

[1] Richards and Wells, Am. Ch. J., **31**, 235 (1904).
[2] Richards, Am. Ch. J., **35**, 510 (1906).
[3] Thomsen, Thermochemische Untersuchungen: $2Ag+Cl_2=2AgCl+58760$. (Vol. 3, p. 381.) $Ag_2SO_4=2Ag+O_2+SO_2—96200$. (Vol. 3, p. 382.) $SO_2+O_2+H_2=H_2SO_4+121840$. (Vol. 2, p. 255.) $2HCl=H_2+Cl_2—44000$. (Vol. 2, p. 114.) Therefore, Ag_2SO_4+2HCl (gaseous) $=2AgCl+H_2SO_4$ (Liquid) $+40,400$. A different set of equations gave 40,200. The result of course only applies to 18°. In this connection it is worth while to note that $Ag_2SO_4+Cl_2=2AgCl+SO_2+O_2—37440$ cal.: which indicates that chlorine would not be as suitable for our purpose as hydrochloric acid. This expectation is confirmed by the experience of Krutwig, Ber. **14**, 306 (1881): "Die Einwirkung ist hier (chlorine on silver sulphate) keine direkte; nur bei sehr hoher Temperatur, nachdem das Salz geschmolzen ist und sich zersetz, giebt es schweflige Saüre, Chlorsilber und Sauerstoff ab."

the difference between total-energy and free-energy changes in a reaction of this kind as great as this, hence it is safe to infer that there is a considerable preponderance of driving tendency in the desired direction, arising from the mutual affinities concerned.

Thirdly, constancy of the weight on continued treatment indicated the completion of the reaction. In seven of the experiments the silver chloride was fused a second time in hydrochloric acid for 15 minutes with occasional agitation, followed by 5 minutes in air. The following table gives the changes in weight found in this way:

THE EFFECT OF CONTINUED TREATMENT WITH HYDROCHLORIC ACID.

No of experiment.	AgCl, first weighing	AgCl, second weighing.	Difference.
6	4.67812	4.67809	— 0.00003
7	4.93119	4.93118	—0.00001
11	4.67373	4.67375	+ 0.00002
13	4.74491	4.74489	—0.00002
14	4.77995	4.77990	—0.00005
15	4.94088	4.94088	— 0.00000
Average			—0.000015

The constancy in weight was thus entirely satisfactory, the average loss being only 0.0003 per cent. of the weight of the chloride.

This experiment, however, does not absolutely preclude the possibility that a small but constant amount of sulphate may remain. In order to test this question 4.90 grams of silver chloride which had never been contaminated with sulphate was fused in the tube, and then 0.00479 gram of pure silver sulphate was added and thoroughly mixed with the chloride by fusion. On cooling the appearance was very different from the pure chloride, the mass being translucent or almost opaque, instead of transparent. It was then fused in a current of hydrochloric acid for twenty minutes after the sulphuric acid could no longer be seen escaping from the tube, as before. On the assumption that the sulphate was converted completely into chloride the loss in weight would have been 0.00039 gram, while the actual loss in weight was 0.00044 gram. The reaction was evidently complete, and a fourth argument was added to the other reasons for believing that the process should yield satisfactory results.

It will be recalled that the narrow end tubes were kept very hot by small stationary burners in order to prevent the condensation of sulphuric acid. At the close of several of the experiments a very slight sublimate was observed on the portion of the narrow tubes which was kept somewhat cooler by the protection of the supporting hooks. This sublimate, although never large in amount, appeared largest in experiments 6 and 10. There was a smaller amount in experiments 7, 11, and 14, but none worthy of consideration in experiments 4, 5, 12, 13, and 15. In experiments 10 and 14 a slight amount of the sublimate was visible in the condenser also, near the end of the tube.

Although the most rational explanation of this trace of sublimate, which was usually too slight to be weighable, was probably to be found in the assumption that it was silver chloride and therefore entirely without sinister meaning except as suggesting the risk of the loss of other traces, the matter was studied further. Careful tests for arsenic[1] and copper were made with negative results, and the hydrochloric acid was demonstrated to contain no trace of anything which could be deposited in a red-hot quartz tube. On the other hand, the sublimate was soluble in ammonia and behaved in every way like silver chloride, so that its nature was considered as nearly proved as was possible with such a minute amount of material. Having settled the nature of the sublimate, its source and significance must be traced. Evidently it could not have come from the main body of the silver sulphate, because it appeared at the very beginning of the experiment, as soon as the current of hydrochloric acid was started and the end tubes heated, before the heat was applied to the main body of the silver sulphate. Moreover, the mass of the silver chloride was never heated to a temperature high enough to volatilize weighable amounts of this substance, as was shown by the constancy of weight on continued heating in a current of gas[2].

In view of these considerations, it seemed probable that a few invisible crystals of silver sulphate had been left in the end tubes by the feather used in cleaning it, or carried into the end tube by the current of sulphur trioxide before fusion. As soon as the hydrochloric acid was admitted and the end tubes heated, these small invisible crystals of silver sulphate must have been at once converted into chloride and sublimed to the cooler portion of the tube—for the end tubes were usually raised to a red heat. This explanation is consistent with the frequent absence of any significant sublimate, especially in the case of experiment 15. In this experiment the tube had been dusted and treated with particular care, in order to test the point.

Because the sublimate was weighed in the tube which had previously contained the sulphate, its presence could not affect the accuracy of the results even if it had been weighable. Nevertheless the suggestion that another portion might have been carried out of the tube was worth considering. Doubts on this point were set at rest by the analysis of the contents of the condenser tube which received the volatile products of the reaction. The average amount of silver found in this tube was less than 0.001 per cent. of that taken in each experiment, and the small appropriate correction was easily applied.

Although it was not probable that silver chloride which had been fused in air for five minutes still retained any dissolved hydrochloric acid, this

[1] This test was kindly made by Mr. O. F. Black.
[2] See the preceding description; also Richards and Wells, loc. cit., p. 60; Baxter, Pr. Am. Acad., 41, 83 (1905).

point also was tested. In experiment 13, the silver chloride after the first heating in hydrochloric acid and fusion in air for five minutes as usual, weighed 4.74491 grams. After the second fusion in hydrochloric acid, and finally in air, the weight was 4.74489 grams. After another fusion for twenty minutes in a current of pure air, the weight was 4.74493 grams. These slight changes in weight can only be ascribed to errors in the weighing; the outcome shows that the silver chloride after the usual treatment did not retain any dissolved hydrochloric acid. Richard and Wells have already shown that it does not dissolve weighable amounts of air[1].

In still another case the outside of the tube was washed with water to make sure that nothing had deposited on it during the long exposure to the flame and acid. The loss in weight was only 0.02 mg., which again is not greater than the possible error in weighing.

The Final Results

Having shown the feasibility of the plan of operations and gained practice by three preliminary experiments, a final series was undertaken, whose outcome is detailed below.

Sample A of silver sulphate was used in experiments 4 and 5 and sample B in the remainder. In experiments 5 and 6 the hydrochloric acid was generated from ammonium chloride, and in the other experiments from concentrated hydrochloric acid. The corrected weight of silver chloride was obtained by adding the trace found in the condenser to the average weight after fusion in hydrochloric acid. In experiments 4, 5, and 7 the correction for the silver chloride in the condenser was not determined directly, but the mean of the other determinations (0.00004 gram) was added.

In experiments 8 and 9 the narrow exit tube became completely blocked by the creeping of the silver chloride. This made it necessary to fuse the solid while there was still present considerable silver sulphate; and therefore the sulphuric acid boiled and material was lost by being projected out of the tube. The first of these was rejected, and the second not finished. All the other determinations are recorded in full in the table. The weighings have, of course, been corrected to the vacuum standard.

No. of experiment	Weight of colorless Ag_2SO_4 in vacuum.	Weight of total AgCl in vacuum.	Parts of AgCl obtained from 100,000 parts of Ag_2SO_4.
4	5.21962	4.79859	91.934
5	5.27924	4.85350	91.932
6	5.08853	4.67810	91.934
7	5.36581	4.93118	91.934
10	5.16313	4.74668	91.934
11	5.08385	4.67374	91.933
12	5.13372	4.71946	91.931
13	5.16148	4.74490	91.929
14	5.19919	4.77992	91.936
15	5.37436	4.94088	91.934
Average			91.933

[1]Richards and Wells, loc. cit., p. 60.

Thus 100.000 parts of colorless silver sulphate were found to yield 91.933 parts of silver chloride, with a vanishingly small "probable error." If the weights of the darkened samples are used in the calculation the result becomes 91.934, a value which certainly represents the maximum. To have reduced the chief uncertainty to within such narrow limits was to have solved the problem as far as it need be solved at present. The interpretation of the result alone remains.

In comparing this result with that of Stas on silver sulphate, it may be noted that Stas found in silver sulphate 69.203 per cent. of silver. Because Richards and Wells found in silver chloride $\frac{100.000}{132.867} 100 = 75.2632$ per cent., it is clear that our results indicate $0.91933 \times 75.2632 = 69.192$ per cent. of silver in silver sulphate, or 0.011 less than Stas's, one is forced to the conclusion that Stas's silver sulphate was not completely reduced by hydrogen, and that his silver obtained in this way was no purer than the silver used in his other work. The only test of complete reduction used at the time was the solution of the residual metal in nitric acid; but this test could not reveal undecomposed sulphate and might not reveal traces of sulphide.

The Atomic Weight of Sulphur

The interpretation of the new results is very similar to that already discussed in the preceding paper on nitrogen and silver. In this case, as in that, there are two uncertain ratios; and one of these ratios, namely, that of silver to oxygen, occurs in each. In the present case, the other uncertain ratio is that of sulphur to oxygen, while in the former case the other uncertain ratio was that of nitrogen to oxygen.

In order to obtain a complete solution of the numerical relations in either of these cases, it is therefore obviously necessary to obtain another series of results, bringing in such a ratio as that of silver to sulphur, or oxygen to sulphur, or chlorine to oxygen. Such an additional ratio is not known at present with modern accuracy. Because of the fact that silver and oxygen are concerned in each of the cases, a single new result, properly chosen, will solve both problems at once; but of course many new results with different compounds, confirming one another, are greatly to be desired. As has been said in the foregoing paper, some of these are already in the process of determination at Harvard College, and it is intended to pursue the matter further at the University of Berlin as well.

For the present it is necessary to state the interpretation of the results in a conditional manner, assuming various possible ratios between oxygen and silver, and stating the corresponding values for sulphur. In the future, when the assumed relationship is replaced by knowledge of the facts, intelligent choice can be made between the alternatives.

If oxygen is taken as 16.000, the following table gives the atomic

weights of sulphur corresponding to the several atomic weights of silver.

ATOMIC WEIGHT OF SULPHUR.
If Ag=107.930 and Cl=35.473, S=32.113
If Ag=107.890 and Cl=35.460, S=32.078
If Ag=107.880 and Cl=35.457, S=32.069

The lowest value in this case, as well as in the case of nitrogen, is the one supported by the recent work on the densities of gases. The unanimous verdict of these very different results is interesting, and possibly significant.

In conclusion, it is a pleasure to acknowledge the generous assistance of the Carnegie Institution of Washington, without which the present work could not have been performed.

Summary

The most important results of the research may be briefly summed up as follows:

(1) A method for the preparation of pure silver sulphate was devised.

(2) The specific gravity of silver sulphate (previously fused) was found to be 5.45.

(3) Indication was obtained that Stas was unable wholly to reduce silver sulphate in hydrogen.

(4) Silver sulphate was found to be occluded by silver chloride from solutions containing an excess of sulphuric acid.

(5) It was proved that silver sulphate can be completely converted into silver chloride by heating in a current of hydrochloric acid gas.

(6) 100.000 parts of silver sulphate were thus found to yield 91.933 parts of silver chloride.

(7) The atomic weight of sulphur as calculated from this ratio, if oxygen is taken as 16.000, with several assumed values for silver is:

Ag=107.93   S 32.113
Ag=107.89   S 32.078
Ag=107.88   S 32.069

THE CONSTITUTION OF AMMONIUM AMALGAM.

By George McPhail Smith.

The substance known as ammonium amalgam was first obtained by Seebeck[1], immediately following Davy's announcement of the discovery of potassium and sodium. Seebeck prepared the amalgam by the electrolysis of moistened ammonium carbonate, with a mercury cathode. About the same time, Berzelius and Pontin obtained a like result with a

[1] Ann. 66, 191 (1808).