In adjusting the other atomic weights the determinations by Richards[1] and his colleagues have generally been given preference. They are certainly entitled to the highest weight, but probably not to exclusive consideration. The work of Guye and his associates at Geneva, and the recent direct measurements of the chlorine-hydrogen ratio are also of very great importance. It is to work of this order that we must look for ultimate precision. Important investigations upon atomic weights are now being carried on in several laboratories, and our knowledge of these constants will doubtless become much more exact within the near future.

(Signed) F. W. CLARKE,
W. OSTWALD,
T. E. THORPE,
G. URBAIN.

FURTHER INVESTIGATION OF THE ATOMIC WEIGHTS OF NITROGEN AND SILVER.

BY THEODORE WILLIAM RICHARDS, PAUL KÖTHNER AND ERICH TIEDE.

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The Analysis of Ammonium Chloride.

The subject of atomic weights has acquired new interest recently, because of the striking demonstration by Landolt that the law of the conservation of weight holds true to a great degree of precision in common chemical reactions.[2] The fact that the sum of the reacting weights remains perfectly constant, within the limit of error of the most exact experimentation, strengthens the conviction that each of these reacting weights possesses fundamental significance. Evidently no error is committed in calculating one atomic weight by subtracting another from the molecular weight of a substance containing two elements, and the whole structure of the table of atomic weights is seen to rest on a satisfactory basis.

These assurances are timely in view of the extraordinary discoveries concerning radioactivity in recent years. Not a few radical thinkers have supposed that these discoveries lessen the importance of exact atomic weight determinations, because of the doubt cast on the permanence of the supposed atom, but Landolt's admirable work assures us that under ordinary circumstances the chemical combining proportions are wonderfully permanent, and therefore as full of meaning as they have ever been supposed to be. The new discoveries concerning radioactivity extend the bounds of knowledge, but in no wise lessen the significance of that which went before.

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[1] An excellent summary of the Harvard work is given by Richards in *J. Chim. Phys.*, 6, 92.

[2] Landolt, *Sitzungsber. kgl. preuss. Akad.*, 15, 16, 354 (1908).

Nitrogen and silver are two of the elements whose atomic weights are at present especially in the focus of attention. Each element is important in many ways because of its frequent occurrence, and each is particularly important in the present connection because of the extent to which the value of its atomic weight is involved with the values of other atomic weights. Therefore the value of these two should be settled precisely as soon as possible.

During the past one hundred years as many as ninety different investigations, carried out by more than thirty chemists, have been concerned with the atomic weight of nitrogen, and many of these have also had to do with the atomic weight of silver. Most of this work is unsatisfactory in the light of modern knowledge. The compounds of nitrogen and oxygen on the one hand, and silver and oxygen on the other, are not stable enough to be subjected to exact analysis suitable for this purpose, therefore by the chemist both elements have to be evaluated with the help of other compounds, involving other elements. This introduces difficulties, upon which many have stumbled.

The physical method of determining molecular weight through gas densities avoids this complication, but on the other hand introduces troubles of its own, the chief of which is the difficulty of extrapolating to the ideal condition. It is true that in the case of nitrogen, as Lord Rayleigh has pointed out, the method is especially applicable—but it must of course be supported by chemical evidence to be wholly satisfactory.

Two methods of determining the atomic weight of nitrogen in the chemical fashion have been used by most chemists, namely, the analyses of nitrates, and the analyses of ammonium salts. In each of these sets of compounds nitrogen exists in combination with two other elements, but in the case of the nitrates one of these other elements is the standard of the atomic weights itself, namely, oxygen, and in the case of the ammonium salts the two other elements both have many other accurately determined quantitative relations. The study of silver nitrate was undertaken by Stas and more recently by Richards and Forbes in the chemical laboratory of Harvard College. These results were not very different, and the latter pointed strongly to a value for the atomic weight of nitrogen equal to 14.008, if silver is taken as 107.88; but if silver is taken as 107.93, with Stas, nitrogen will be almost 14.04. It seemed highly desirable therefore to obtain an entirely different set of evidence upon this point through the study of the ammonium halides in their relation to silver—a study which likewise led Stas to a higher value—and the present paper treats the first of a series of investigations upon this subject, concerning the analysis of ammonium chloride.

The history of the analysis of this compound is quickly told. Stas found as an outcome of a number of experiments that 49.597 grams of ammonium chloride required 100.0000 grams of silver for precipitation. These analyses, careful as they were, are open to doubt from two causes, one of which has been pointed out by Alexander Scott in an interesting paper upon this subject.[1] Scott calls attention to the fact that Stas was never able to prepare ammonium salts wholly free from color—an evidence that he had never succeeded wholly in eliminating the carbon compounds always present in chemical substances. Scott himself, by means of more drastic treatment, probably succeeded better in this respect.

Unfortunately, both Stas's extensive work and Scott's two analyses of ammonium chloride were evidently inadequate as regards taking account of the solubility of silver chloride, so that these determinations throw but little light upon the question. This deficiency, which occurs in most other early work, is the second cause of doubt concerning Stas's work with chloride.

It is clear, therefore, that the whole subject needs a thorough investigation and revision in the light of modern knowledge concerning both the purity of materials and precision in analysis.

Preparation of Material.—The most important new problem conce ning the analysis of the ammonium chloride is the preparation of the material to be used in the analyses, for of course the purity and constant composition of this salt must be beyond suspicion. The inpurities most commonly to be found in ammonium salts include various compounds of carbon, and these are usually the most difficult to eliminate. Non-volatile substances, such as salts of the alkali metals, are of no great consequence. They may easily be eliminated by converting the ammonium salt into ammonia gas and collecting the gas in pure acid.

Stas sought to eliminate the amines by two oxidizing processes, one, the treatment of ammonium chloride by nitric acid and the other, the treatment of ammonium sulphate at high temperature with concentrated sulphuric and nitric acids. Scott used the latter of these methods. These methods undoubtedly decompose most of the amines, but no one has proved that all are eliminated in either of these ways. In view of this doubt it was deemed advisable to use quite another method for the purpose, and nothing seemed more suitable than an application of one of the devices of Kjeldahl for eliminating carbon from ammonium compounds. To every 100 grams of ammonium sulphate and 75 grams of concentrated sulphuric acid, contained in a beaker of Jena glass and heated to the point where the sulphuric acid began to volatilize, were added in very small portions a few grams of finely powdered potassium permanganate. The solution was then heated for many hours to a high

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[1] A. Scott, *J. Chem. Soc.*, 70, 147 (1901).

temperature until the evolution of carbonic acid and oxygen had ceased and the solution had become wholly colorless—an evidence that the oxidation had reached its limit. After cooling, the cakes of acid ammonium sulphate were dissolved in pure water and the ammonia was set free by means of freshly prepared milk of lime. The lime for this purpose was made by the ignition of pure calcium carbonate in an electric oven for many hours, and could have introduced no impurity. The simplest method of collecting the gas was found to be the placing of a quartz or platinum dish, containing the purest hydrochloric acid, over the mixture of ammonium sulphate and milk of lime in a vacuum desiccator or ground glass bell jar. The ammonia quickly transfers itself from the mixture to the acid, and without trouble or danger from spattering the preparation is easily made. This simple method proved itself very much more satisfactory than the attempt to distil the ammonia with steam either from an outside source or by heating the semi-solid mixture of calcium sulphate and ammonium hydroxides. The salt prepared in this way is always beautifully white in appearance. The sample prepared in platinum showed no trace of contamination but, even supposing a small amount of platinum had been dissolved,[1] it would have been eliminated by the subsequent sublimation described later. This sample of ammonium chloride is given the designation *A* in the following pages.

No single method of preparation is adequate for a case of this sort, as has often been pointed out. Some entirely different method must be adopted for preparing another sample, in order to be certain that constant impurity has not found its way into the first in spite of all precautions. Stas, realizing this, prepared ammonia also by reducing potassium nitrate. He thought that in this way he must obtain a salt free from organic compounds. In the first place he made the nitrite out of saltpeter and lead, and then reduced it by means of zinc and potash. It is by no means certain that these materials were all free from carbon, and if they were not, the doubt concerning the existence of amines synthesized during the process of reduction still remains. Although thus Stas's execution of his idea was not without reproach, the idea was a good one, and we sought to carry it out in another way, using substances really free from carbon, and bringing into play new physico-chemical knowledge. Vortmann[2] made at the beginning of the last decade an observation that under proper experimental conditions it is possible to reduce nitric acid quantitatively to ammonia by means of the gal-

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[1] Dr. F. W. Hinrichsen found difficulty from this source, but it is possible that the air was less fully exhausted from his apparatus. In the absence of air the platinum is not attacked. *Z. anorg. Chem.*, **58**, 59 (1908).

[2] *Ber.*, **23**, 2798 (1890).

vanic current, provided only that copper is present in the solution and forms the material of the electrodes. In those days the advantage to be obtained by stirring the solution during electrolysis was not fully realized, but very recently Ingham[1] has shown that this process, like all other electrolytic processes, is much hastened in this way. The subject has also been investigated in an empirical fashion by Patten.[2] The experience of this last investigator was not available to us at the time of our work, having not yet been published; accordingly, as the process promised well for the present purpose, Dr. F. W. Hinrichsen[3] kindly tested the process with the idea of finding out its efficiency and the best conditions for obtaining high purity of product and maximum yield. This work has already been described in another place. It is enough to say that he found it convenient to use a cathode of copper netting in a cylinder about 10 centimeters in diameter and 10 centimeters high and an anode of platinum foil, with a current of not over 3 amperes, if the solution was tranquil. It was found advantageous to use a large platinum dish coated inside with copper for the cathode when working with a rotating anode. Equal weights of copper sulphate and redistilled nitric acid were mixed with about ten times their combined weight of water, and, as the nitric acid was exhausted by reduction and the copper by deposition, more was added. In order to stir the solution he used also the device of Frary[4] by which the solution was whirled by means of the electromagnetic effect of a surrounding solenoid. Considerable current is needed in order to cause such agitation in the liquid, but the method has the advantage for the present purpose of excluding the danger of dust which comes from any sort of mechanical stirring run by an outside motor. Obviously the pure nitric acid for this purpose, having been twice distilled, was prepared with great care and diluted with the purest water. The copper sulphate used was also purified by several recrystallizations. The solution was heated in order to avoid the formation of hydroxylamine,[5] for Tafel has shown that under these circumstances the electrolyte contains less of this substance. Even if some had been formed, however, it would have inevitably been decomposed in the later operations. From the ammonium sulphate made in this way pure ammonium chloride was made in the manner already described. This sample was called *B*.

For a few analyses a cruder preparation was used, made according to Stas's first method by repeated treatment of ammonium chloride

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[1] THIS JOURNAL, **26**, 1251 (1904).

[2] *J. Am. Electrochem. Soc.*, **12**, 325 (1907).

[3] Hinrichsen, *Z. anorg. Chem.*, **58**, 59 (1908).

[4] Frary, *Z. Elektrochem.*, **13**, 308 (1907).

[5] Tafel, *Z. anorg. Chem.*, **31**, 289 (1902). Patten (*loc. cit.*) apparently never worked above 30°, and accordingly was not able to verify this statement.

with nitric acid, at a boiling temperature, and five recrystallizations. For freeing the crystals from mother liquor the new centrifugal apparatus of Richards and Staehler was employed. A fourth preparation, prepared by a student at Harvard by the same process was also used for two analyses. These two similar preparations, possibly less pure than the others because of the method used in their preparation, were called *C* and *D*.

The ammonium chloride thus prepared was—at least, as regards samples A and B—very pure with the exception of the presence of an excess of hydrochloric acid and water. Most of the preparations showed a feebly acid reaction after evaporation to dryness. They were each recrystallized several times out of water containing a little ammonia prepared by the same process. These crystallizations were effected in quartz or platinum dishes, and the heating was conducted by electricity in order to avoid contamination from illuminating gas. Needless to say, dust was excluded as carefully as possible. The mother liquor was separated as usual by means of the platinum centrifuge of great power. The preparation thus obtained was snow-white and possessed a slight smell of ammonia. It was dried in a vacuum desiccator and kept over potash in quartz or platinum dishes. The final preparation of this material for analysis was by sublimation. Each sample was sublimed twice immediately before analysis, collecting it the second time in the vessel in which it was to be weighed. This operation will be discussed in a subsequent chapter.

All the other substances, water, hydrochloric, nitric and sulphuric acids, silver, calcium carbonate, etc., were prepared by essentially the methods which have been used for a number of years in Harvard University and are described in detail in the various papers from that institution, especially in Publication 69 of the Carnegie Institution of Washington. There is no need of reviewing these well-known methods. It goes without saying that great care was taken to avoid the use of utensils whose solubility could contaminate the products or influence the reactions. Whenever possible quartz dishes were used with acid liquids, and platinum ones with alkalies; and where glass was unavoidable the best Jena glass was employed. Electric heating was used almost universally in order to avoid objectionable products of combustion. For vacuum work the convenient, almost automatic mercury pump of Ubbelohde-Stock was used with profit, and apparatus was constructed without rubber connections, being fused together wherever it was possible. For the necessary glass joints a paraffin lubricant of vanishingly small vapor tension was kindly given us by Professor Brauner, of Prague. Many bell jars served to protect the substances from dust and objectionable gases. The laboratory was a room in the 1st Chemical Institution of

Berlin especially dedicated to the purpose through the kindness of Geheimrat Emil Fischer, and this room was kept as free as possible from soluble gases of all kinds. The quantitative work was carried out in an especial room used by the experimenter alone, and another special room served for the balance. The dark room used for the preparations was not interfered with by any other investigation during the time while this was in progress.

All these favorable conditions contributed greatly to the sucesss of the undertaking. Without advantages of this sort much time and experimental energy may be wasted, because one's efforts are rendered vain by the inevitable introduction of impurities from the atmosphere. Not only in this way, but also by providing plentiful apparatus of rare and expensive kinds, Professor Fischer did much to further the work, and we take great pleasure in recording our grateful thanks. To Dr. A. Staehler we are also greatly indebted for his kindness in attending to the arrangement of the laboratory, and for help in many details.

The Final Preparation and Weighing of Ammonium Chloride.—The ammonium chloride, as prepared by the methods described in the preceding section, was exceedingly pure, except from the presence of water and the doubt as to whether the substance had attained exact neutrality. These two doubts, however, would be enough to vitiate the whole work, provided that they were not removed—for the presence of water is just as serious, weight for weight, as the presence of any other substance; and it would be indeed foolish to spend much thought on eliminating traces of sodium, for example, while leaving much larger weights of water in the final material. Again an excess of ammonia or hydrochloric acid would have an equally pernicious effect upon the results. The presence of either would obviously be very much worse than the presence of equal amounts of sodium chloride.

Taking this into account, it was obviously necessary to dry thoroughly the ammonium chloride and sublime it in such a way as to insure, as definitely as possible, the proper proportion of acid and volatile alkali. Ammonium chloride is an especially convenient substance to use as the basis of an atomic weight determination, because it is so easily sublimed. In this way it may be purified, and moreover, an admirable test is furnished by sublimation, enabling one to determine whether or not non-volatile impurities are eliminated. Unfortunately, however, as is well known, the substance ordinarily sublimes by transition into a dissociated state, and the experimenter can never be certain that during the sublimation in another gas a portion of the lighter gas, ammonia, has not escaped, because of its more rapid diffusion. Sublimation brings with it a further difficulty common to most cases of the kind, namely, dangerous interaction between hot gases and the vessels in which the operation must be conducted. Hence, although sublimation furnishes an admirable means of leaving behind non-volatile impurities, it must be used with caution, especially in this particular case.

Turning first to the latter cause of danger, we found by preliminary experiments that for this purpose both hard glass and platinum are unsuitable—each being attacked sufficiently to endanger the purity of the product. On the other hand, repeated experiments proved that fused quartz is entirely resistant to ammonium chloride, ammonia, and hydrochloric acid at the temperatures needed in the present work, and accordingly it alone was used wherever ammonium chloride came in contact with the containing vessel.[1]

The best method of avoiding the former cause of uncertainty and inexactness seemed to be the following: Every sample of ammonium chloride was sublimed twice, once in a current of ammonia gas in order to prevent the possibility of the existence of free acid, and again, in a Sprengel vacuum in order to insure the elimination of the extra ammonia.

The three quartz tubes used for the double sublimation were shaped in such a way that the first yielded its product into the second, and the second yielded its product into the third, which in turn could be used directly for the weighing of the preparation.

The difference in treatment involved different apparatus in the two cases. For sublimation in a current of ammonia the apparatus shown in Fig. 1 was employed. In *a* was placed a concentrated solution of calcium chloride saturated with the purest ammonia gas. By heating this solution a continuous stream of fairly dry ammonia gas may be obtained. This was further dried by means of purest lime in towers t^1 and t^2. Cotton wool in the upper stopper of the second tower served to hold back powdered lime which might have been swept along, and at *p* was a glass tube containing a porous porcelain diaphragm filter—according to Stock.[2] The complete absence of dust was found to be necessary in order to prevent contamination of the product. Hence these special precautions were taken, and moreover the complete elimination of rubber connections was effected by fusing or grinding the tubes together.

The substance to be sublimed was placed in a small tube, *d* (shown also on a larger scale on the right-hand side of the figure), and upon this tube was placed the somewhat larger glass tube *b* which was heated by means of a suitable magnesia tube wound with resistance wire. The excess of ammonia which flowed through the apparatus during the sub-

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[1] We take this opportunity for thanking the firm of Heraeus in Hanau for their kindness in furnishing some of the quartz apparatus with great promptness at one crisis in the experimentation.

[2] Stock, *Ber.*, **40**, 4956 (1907).

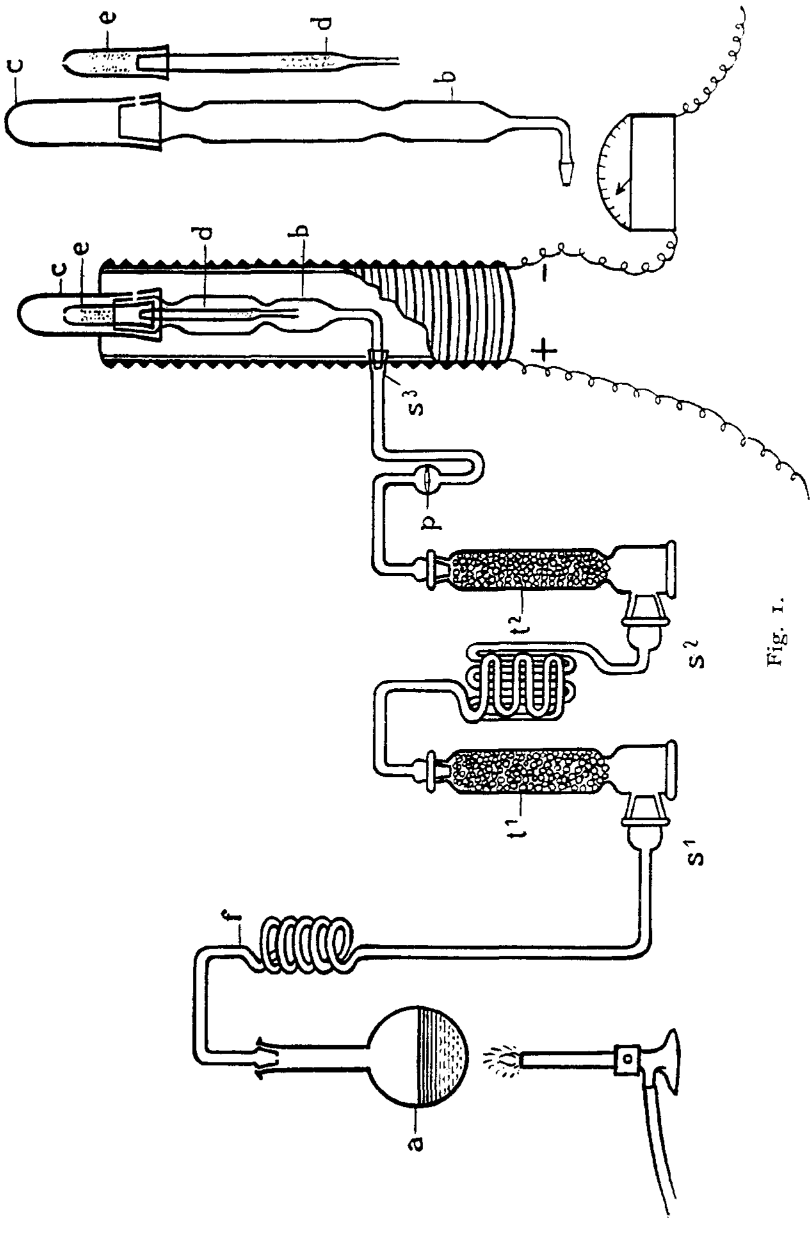

Fig. 1.

limation escaped from the small hole at the top of *e*. It was easily possible to regulate the sublimation so that most of the solid material deposited within the quartz tube *e*, for the condensation occurs in the zone just beyond the hotter part of the tube, as the preliminary experiments had demonstrated.

The final purification by sublimation in a vacuum took place immediately after this by fitting into the tube (*e*), after it had been removed from the apparatus just described, a third quartz tube, named *z* in Fig. 2. This was of a projectile-like shape, open at both ends, and small enough to fit into the weighing bottle, which formed its final resting place.

The arrangement of the apparatus for the second sublimation is shown in Fig. 2, its form having been devised by degrees with the help of many unsuccessful attempts. The tubes containing the ammonium chloride, *e* and *z*, were placed in a larger tube, *y*, made of the hardest Jena glass. This larger tube was closed above with a ground glass cup, provided with a glass stop-cock for connecting with a mercury air pump. After the complete exhaustion of the tubes, the sublimation was conducted with the help of the electric heater. A lead tube with running water cooled the sublimate, so that a sufficient amount of it was deposited on the inner wall of *z*. Prepared in this way ammonium chloride deposits itself in beautiful diamond-like crystals, which become clouded only upon cooling, and are then pure white. No residue was left in the tube *e*. All the material used in the analyses was sublimed twice in this way.

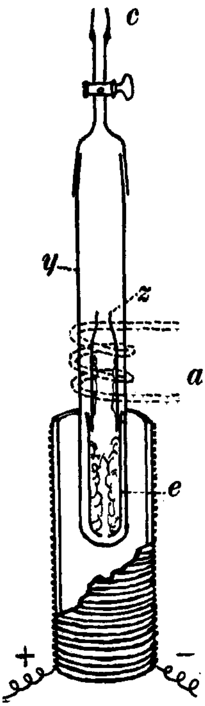

Fig. 2.

Stas has shown that ammonium chloride gains more weight when it is weighed in a vacuum than would be expected from its weight in air and its specific gravity. He found that one gram of ammonium chloride under ordinary atmospheric conditions weighs +0.00080 more in a vacuum than in air.[1] The present experience entirely supports this value, and it is worth while now to describe the apparatus by which the conclusion was tested. This apparatus was a modification of the familiar bottling apparatus which has served for so many researches in Harvard University. In the present case the apparatus was modified for use in a vacuum, and the details are sketched in Fig. 3. The projectile-shaped boat or receptacle *z*, filled with ammonium chloride in the manner just described, was placed in a hard glass tube, *x*. This in

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[1] Stas, *Untersuchungen* (Aronstein's translation), p. 56 (1867).

turn was ground into a tube similar to the familiar bottling apparatus except that its side excrescence was elongated so as to contain a small glass hammer as well as the cap-stopper of the weighing tube *r*. After the air had been wholly removed, the apparatus was disconnected from the pump and tilted. Thus the ammonium chloride with its container, *z*, was allowed to glide into the weighing bottle *r*, and the cap, already carefully provided inside with a thin film of lubricant, was allowed to fall into place. The weighing bottle was finally securely closed by means of gentle blows of the small glass hammer *h*. It was customary to heat the ammonium chloride almost to sublimation before disconnecting the pump. When the weighing bottle was effectually sealed, dry air was admitted to the apparatus, and the weighing bottle removed to the desiccator and weighed at leisure. Afterwards dry air was admitted and the tube was weighed again later; when the ammonium chloride had been dissolved away, the weighing bottle and quartz container were exhausted in a similar way and once more weighed, both evacuated and filled with air, using the same closed counterpoise in each case. Thus the weight of ammonium chloride in vacuum was determined directly, and the vacuum correction could be easily calculated. After Stas's vacuum correction had been verified, time was saved for many of the analyses by simply weighing the ammonium chloride in air by means of the usual bottling apparatus without the additional heating and confining in a vacuum.

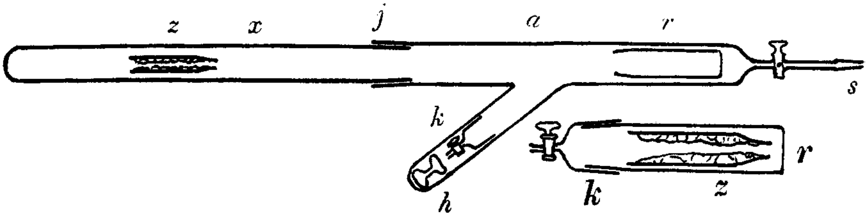

Fig. 3.

Analysis of the Ammonium Chloride.—In the present research the amount of chlorine present was determined by precipitating the halogen as silver chloride and weighing this substance. A further check upon the method, obtained by finding the silver necessary for precipitation, was not completed for lack of time, but this further step is now being taken in the Chemical Laboratory of Harvard College. The method of analysis is so similar to that used in the case of sodium and potassium chlorides[1] that few words need be spent upon the description. In the first place exactly the equivalent amount of silver was added to effect the precipitation, and then after much shaking and long standing, a slight

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[1] Publ. Carnegie Inst. of Washington, Nos. 28 and 69.

excess of about 0.05 gram per liter of silver nitrate was added. Filtration was effected by means of the Gooch-Munroe-Neubauer crucible with the help of the water pump. The first two washings were made with water containing a trace of silver nitrate, then three further washings with about 0.2 liter of pure water each were used, and then 3 to 5 washings with small volumes of water containing nitric acid. Afterwards the precipitate was conveyed with the greatest care by means of a jet of water driven by hydrostatic pressure into the crucible, and finally the flask was rinsed with ammonia and the solution tested in the nephelometer in order to be sure that every trace of silver chloride had been collected. The further drying and fusing of the silver chloride happened precisely in the usual way and the product was as pure and white in appearance as could have been desired. Concentrated ammonia was used to remove traces of silver chloride from the perforated crucible in order to prepare it for further work.

The determination of the silver chloride dissolved by the wash waters, one of the most important parts of the whole proceeding, occurred in the usual way with a nephelometer, proceeding as has already been described by Richards and Staehler. The weighing was conducted entirely by methods of substitution as usual, and all the weights were corrected to the vacuum standard. In view of the fact that the details are essentially like the previous work of the kind, further particulars are unnecessary and the final table of results may be given at once. This table contains only those analyses which were believed to be free from error. Two

RATIO OF ARGENTIC TO AMMONIC CHLORIDE.

Final Results.[1]

Ag = 107.881; Cl = 35.4574; H = 1.0076.

No.	Sample.	NH_4Cl (in vac.) Grams.	AgCl (in vac.) Grams.	$AgCl : NH_4Cl = 100 : x$. $x =$	Atomic weight of nitrogen. Ag = 107.881; Cl = 35.4574; H = 1.0076. N =
3	C	2.02087	5.41469	37.3220	14.009
4	A[1]	2.23894	5.99903	37.3217	14.008
7	B	1.55284	4.16076	37.3211	14.008
9	A	1.36579	3.65959	37.3209	14.007
11	B	1.61939	4.33914	37.3205	14.007
12	D	1.93795	5.19219	37.3243	14.012
13	D	2.89057	7.74498	37.3219	14.009
14	B	1.31405	3.52082	37.3223	14.009
15	B	1.82091	4.87921	37.3198	14.006
			Average,	37.3217	**14.0085**
				Probable error,	±0.0004

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[1] The analyses tabulated in this list were all made in Berlin by E. Tiede, with the immediate collaboration of P. Köthner, after T. W. Richards had been obliged by his duties in Harvard University to return to America.

preliminary determinations, vitiated by inexperience, were rejected. Four other experiments also, Nos. 5, 6, 8 and 10, were likewise rejected, because of the small amount of material used, averaging less than a gram in these cases. One of these four, No. 6, was known to be in error for other reasons. The three of these which might possibly have been included, namely, Nos. 5, 8, and 10, would have made very little difference in the final result, but it was thought safer to exclude them, because the method is too complicated to yield satisfactory results with so small a quantity of substance.

Discussion of the Results.—From these figures it is clear that the atomic weight of nitrogen cannot be far from 14.008 if silver is taken as 107.88. The results agree with one another as well as could reasonably be expected. The maximum deviation from the mean is 4 in the third decimal place, and in no other case does the deviation exceed 2. The average deviation from the mean is only about 1 in the third decimal place, and the probable error calculated according to the theory of least squares is ±0.0004. This probable error of course gives no clue to any constant error which may possibly have escaped detection, but its small value shows at least that further repetition of the process by this method is not necessary.

It is interesting to compare the results from the four different samples of ammonium chloride. Sample A and A′ were made from ammonia prepared from ammonium sulphate oxidized by nitric acid and by sulphuric acid with permanganate. The preparation of the salt occurred in the case of A in quartz dishes, in A′ in platinum dishes. The results of these two are essentially identical, giving an average of 14.0075. Sample B was made from ammonia prepared by the electrolytic reduction of nitric acid, neutralized with pure hydrochloric acid in quartz vessels alone. The four analyses of this substance gave exactly the same result, on the average, 14.0075. Samples C and D, which were made, the one in Germany and the other in America, by the action of nitric acid on ammonium chloride gave a slightly higher value, the average of the three being 14.010. It is probable that the method of preparation in these cases was not so effectual as in the others; small quantities of carbon compounds may have still remained in the material. The number of analyses is, however, too small to make certain of this difference, which is at worst very slight; and accordingly the results may be averaged in with the others without causing serious error.

The relation of these results to other atomic weights is very far-reaching and important. Clearly, they connect the atomic weight of nitrogen with that of hydrogen, silver, and chlorine, and therefore with the help of other well-known relations affect the atomic weight of each of these elements in relation to the other. The calculation is very simply carried out as follows:

Let

$$\frac{\text{AgCl}}{\text{Ag}} = a, \tag{1}$$

$$\frac{\text{NH}_4\text{Cl}}{\text{AgCl}} = b, \tag{2}$$

$$\frac{\text{AgNO}_3}{\text{Ag}} = c. \tag{3}$$

The three atomic weights supposed to be unknown may be designated as follows: Ag $= x$, Cl $= y$, N $= z$. From the work of Morley[1] hydrogen may be taken as 1.0076, if oxygen = 16. Substituting these values in equations (1), (2), and (3), we obtain the following:

$$x + y = ax, \tag{4}$$

$$z + y + 4.0304 = b\,(x + y), \tag{5}$$

$$x + z + 48.000 = cx. \tag{6}$$

Substituting in equation (5) the value of z as found from equation (6), we have:

$$(1 - c)\,x - bx + (1 - b)\,y = 43.9696,$$

but according to equation (4) $y = (a - 1)\,x$; hence

$$x = \frac{43.9696}{1 - c - b + (1 - b)(a - 1)}.$$

The values a, b, and c are all known. a (the quantity of silver chloride obtained from 1 gram of silver) was found by Richards and Wells[2] to be 1.32867; c (the quantity of silver nitrate obtained from the same quantity of silver) was found by Richards and Forbes[3] to be 1.57479. The present investigation gives the value of b as 0.373217, the average of the fifth column in the preceding table. Substituting these values in the equation (7), we obtain x, the atomic weight of silver, = **107.881**. Substituting this value in equation (4), we obtain y, the atomic weight of chlorine, = **35.4574**, and substituting these values in equation (5) or (6), we obtain z, the atomic weight of nitrogen, = **14.0085**. These three values for the atomic weights of silver, chlorine and nitrogen are entirely independent of any but the most recent work, and rest directly, through silver nitrate and water, upon the international standard of atomic weights, O = 16.000. It may be noted that if hydrogen is taken as 1.0078 with Noyes,[4] the values of the atomic weights are altered but slightly. Silver becomes 107.879, chlorine 35.456, nitrogen 14.008.

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[1] E. W. Morley, *Am. Chem. J.*, **17**, 267. *Z. physik. Chem.*, **17**, 87 (1895).

[2] Publ. Carnegie Inst., No. 28. THIS JOURNAL, **27**, 526.

[3] Publ. Carnegie Inst., No. 69. THIS JOURNAL, **29**, 826.

[4] W. A. Noyes, THIS JOURNAL, **30**, 4 (1908).

The present work thus completes a connected chain of data, and furnishes striking evidence in favor of the low values for silver and nitrogen which have recently found support in so many other different ways.

It is not without interest also to note that if one chooses the value for silver, 107.93, and for chlorine, 35.473, the present work makes nitrogen 14.017—a value inconsistent with the value 14.037 calculated from silver nitrate, if silver is assumed as 107.93. Thus the present results are incompatible with the work of Stas, both as regards silver and as regards nitrogen.

Summary.

In the present paper is described a series of analyses of ammonium chloride. These analyses were superior to any other that have ever been made in respect, first, to the purity of the material; second, to the choice of conditions for subliming the salt; and third, to the accuracy of the analyses. The ammonium salt was prepared in such a way as to render the presence of amines very unlikely; the sublimation was conducted first in a current of ammonia, and then the same substance was resublimed in a vacuum; the analysis was carried out with all the care used in the recent work in Harvard University, taking due account of the solubility of silver chloride. As a result, it was found that if oxygen is taken as 16.000 and hydrogen as 1.0076, the three following values result: Ag = 107.881, Cl = 35.457, and N = 14.008.

1st Chemical Institute of the University of Berlin, 1907 and 1908.

THE ATOMIC WEIGHT OF TELLURIUM.

By Victor Lenher.

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The atomic weight of tellurium has received an unusual amount of study ever since attention was directed to it by the statement of Mendeleef in his memorable paper before the Russian Chemical Society in 1869. In outlining the principles of the periodicity of the elements he observed that "The atomic weight of tellurium must be between 123 and 126 and cannot be 128."

Various lines of experimentation have been followed to test the validity of this assertion: (*a*) Critical studies have been on the elementary character of tellurium but nothing thus far has developed which would warrant a belief in its complexity from the character of the experimental evidence produced. (*b*) The spark spectrum of the element has been studied, especially by Köthner[1] who purified his material by various processes, and who used tellurium from various sources. His results show no differences in the spectrum. (*c*) Numerous atomic weight

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[1] *Ann.*, 319, 1.