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A REVISION OF THE ATOMIC WEIGHT OF POTASSIUM. THE
ANALYSIS OF POTASSIUM CHLORIDE¹

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Introduction

The atomic weight of potassium is a chemical constant of unusual interest and significance. Standing, as it does, in the middle of the series of five atomic weights of the most electro-positive metals—substances which exhibit in a highly marked degree both similarity and progressive change in properties—this number must be of unusual importance in the search for that undiscovered mathematical relationship which undoubtedly exists between these constants. Moreover, the atomic weight of potassium is essentially bound up with the atomic weights of oxygen, chlorine, and silver, this group forming a fundamental basis in the calculation of nearly all the other atomic weights; so that a change in the atomic weight of potassium has a widely ramified effect on the whole table of atomic weights. If any further evidence of this fact were needed, the recent paper of R. W. Gray² would furnish it.

The recent investigation upon the atomic weight of sodium by one of us in conjunction with R. C. Wells³ showed conclusively that Stas's work upon which rested earlier knowledge, was somewhat at fault in several respects. The most serious of these errors were, first, the existence of impurity in Stas's silver; secondly, the fact that in his work solid salt was dropped into the silver solution, causing occlusion of salt; and thirdly, inadequate knowledge concerning solutions of silver

¹ A somewhat less detailed statement of this work has appeared in *Ber.* **39**, 3611 (1906).

² R. W. Gray, *J. Chem. Soc.*, **89**, 1175 (1906).

³ Richards and Wells, *Carnegie Inst. of Washington*, Publication 28; *This Journal* **27**, 459 (1905); *Z. anorg. Chem.*, **47**, 56 (1905).

chloride. In view of these errors it seemed not impossible that a similar revision of potassium might likewise yield slightly lower results for potassium than had been found by this master of exact analysis. For this reason the present investigation was undertaken.

Before describing the present work a brief historical review of previous investigations may not be out of place. The determinations may be divided into two groups—the first group including all of those determinations in which the molecular weight of a potassium halide was found by decomposition of a chlorate, bromate, or iodate, and the second group, those in which data for determination of the relation of potassium to chlorine, bromine, or iodine were obtained. The second group alone is concerned with the present work.

The early work of Berzelius, Pelouze, and Marignac need scarcely be considered here.¹ It dealt for the most part with the precipitation of silver chloride from a solution of potassium chloride and gave very widely discrepant results. Even the later work of Marignac on chloride, bromide, and iodide of silver was of doubtful value, especially the last; and accordingly until the present research was undertaken, the atomic weight of potassium rested chiefly on the analyses of potassium chloride made by Stas, by Richards and Archibald, and by Archibald alone, and upon the analysis of potassium bromide made by Stas.

As in the case of sodium, Stas² made several series of determinations of the amount of silver needed to precipitate a known amount of potassium chloride. One of these series was made in 1865, a later one in 1881, and yet another shortly before his death. The earliest series, although in some respects more careful and thorough than the later ones, was greatly at fault, because in it he overlooked the solubility of silver chloride. Accordingly of this work only the later need be considered. The mean of seventeen analyses indicated that 100 parts of silver were equivalent to 69.122 parts of potassium chloride, corresponding to an atomic weight for potassium of 39.130, if silver is taken as 107.93 and chlorine as 35.473. Later, Richards and Archibald³ found as a side issue of a research upon the atomic weight of cesium that 100 parts of silver correspond to 69.115 parts of potassium chloride, and also that 100 parts of silver chloride correspond to 52.022 parts of potassium chloride; and still more recently, Archibald⁴ found results not very different. With the values given above for silver and chlorine these results indicate a

¹ For a brief discussion of this work Clark's *Recalculation of the Atomic Weights* (1897) p. 41, may be consulted.

² Stas. *Mém. Acad. Roy. Belg.*, 43 (1880); also *Oeuvres Posthumes* edited by W. Spring. See Clarke's *Recalculation* (1897), p. 42.

³ Richards and Archibald (1903), *Pr. Am. Acad.*, 38, 443 (1903). *Z. anorg. Chem.*, 34, 353, (1903.)

⁴ Archibald, *Trans. Roy. Soc. Can.* [2], 10, 111, 47 (1904).

value for potassium of 39.123 and 39.128, respectively, in the case of Richards and Archibald, and 39.122 and 39.135, respectively, in Archibald's research.

In the case of the bromide Stas found in an unusually varying series of experiments that 100 parts of silver needed 110.346 parts of potassium bromide for complete precipitation, a result not very far from that of the less precise early work of Marignac. If Baxter's value for bromine is accepted (79.953),¹ this corresponds to an atomic weight for potassium of 39.143, noticeably higher than the results from the chloride. At that time the discrepancy did not appear, because the atomic weight of chlorine was not properly evaluated, Stas believing that his work on the chloride also indicated an atomic weight above 39.14.

In view of the fact that these results differ among one another to an extent beyond a reasonable limit of experimental error, it seemed advisable to investigate once more the atomic weight of potassium in order to detect the cause of the discrepancy. This appeared to be especially desirable on account of the recent gain in knowledge concerning the peculiarities of silver chloride in solution. Accordingly, the present research was begun, and simultaneously another concerning potassium bromide. A description of the latter investigation follows immediately after this one.

An investigation upon atomic weights naturally resolves itself into several different portions—first, the preparation of the pure material; second, the method of drying and weighing this material; third, the details of the analysis and the calculation of the results. These will be considered in order in the following pages.

Preparation of the Material.

Potassium Chloride.—Several methods of preparing potassium chloride were tried, the most efficacious being adopted. The problem, of course, was to effect the elimination of other metals and other acids, especially those of the same groups. Both ends are most quickly and completely attained by incorporating into the process of preparation successive crystallization of different salts, in order to eliminate by the crystallization of one salt an isomorphous substance which might have been retained during the crystallization of another salt. The commonest salts of potassium were therefore studied in relation to their fitness for the elimination of impurities in this way.

In the first place, on account of the good results which Richards and Wells had attained in preparing pure sodium chloride from recrystallized sodium sulphate by precipitation with gaseous hydrochloric acid, sulphate of potassium also was early considered. This method was, however, soon abandoned, because the relative solubilities of potassium sulphate and

¹ Baxter, This Journal, 28, 1322 (1906).

chloride are far less favorable for the purpose than those of the sodium salts. The method of Archibald, who converted sulphate into chloride through precipitation with barium chloride, is complicated and involves the double work of preparing pure barium chloride as well as pure potassium sulphate. Moreover, it is not easy to eliminate the last trace of barium sulphate from the resulting salt. This also was rejected.

Next potassium chlorate was studied—a salt which had already been used by Stas for the preparation of pure potassium material. Both in crystalline form and in solubility this salt is very suitable for the separation of sodium from potassium material. Sodium chlorate crystallizes in regular crystals which are six times as soluble in hot water and sixteen times as soluble in cold water as the monoclinic crystals of potassium chlorate. On the other hand, the data concerning the crystalline form and solubility of the chlorates of rubidium and cesium are not sufficient to enable one to make any certain prediction with regard to their behavior, and therefore experiments were made in order to discover whether or not these salts could easily be separated from potassium chlorate by recrystallization. The four salts of sodium, potassium, rubidium, and cesium were mixed together and qualitatively separated by fractional crystallization. The sodium was effectively separated from the crystals; but after three careful crystallizations the cesium line, although stronger in the mother liquor than at first, was still not absent from the crystals. Indeed, neither rubidium nor cesium lines had considerably diminished therein. Accordingly, this method was also abandoned.

Potassium nitrate showed itself to be much more satisfactory in its behavior. Its usefulness did not seem at first so certain as to be a foregone conclusion, especially as Stas had not succeeded in preparing a particularly pure material from this salt. Probably this failure was due to the circumstance that he carried out the crystallization in glass vessels, which of course continually introduced sodium and silica. The rather inadequate data concerning the four nitrates may be well put together as follows:

	Solubility in 100 parts of water.				Crystalline form.
	Cold.		Warmer.		
	Temperature.	Parts	Temperature.	Parts.	
CsNO_3	0	12	60	Very many	Tetragonal.
RbNO_3	0	20	10	43	Needles.
KNO_3	14	25	114	337	Rhombohedral and rhombic.
NaNO_3	15	84	114	200	Rhombohedral.

Because this series of results is not entirely conclusive, although promising, a series of crystallizations was carried out here also. This series showed that an admixture of the three other nitrates with a large excess of potassium nitrate was nearly all eliminated by as few as two

crystallizations. The separation of the sodium was especially marked in the spectroscopic tests. This method, therefore, appeared very well suited for the preparation of pure potassium material, which might easily be converted into chloride after the other metals had been eliminated

Pure potassium nitrate of commerce, obtained from Germany, was dissolved in a little water, freed from solid substances by filtration, and crystallized twice in Jena glass flasks. The salt was each time freed from the mother liquor in a porcelain centrifuge.¹ The resulting material was four times subsequently recrystallized in platinum vessels, and whirled in a platinum centrifuge. The pure crystals were now divided into two parts; one part was dried in a vacuum desiccator, while the other part was subjected to yet six more crystallizations and whirlings in platinum vessels.

It now became a question how this nitrate could best be converted into chloride. The method recommended by Stas of heating the salt with pure ammonium chloride involves not only the preparation of this latter salt in a pure state, but also great danger of contamination from the vessel, whether of platinum or porcelain. Platinum is especially attacked because of the action of the oxychlorides of nitrogen and of chlorine. The more favorable method appeared to be to convert the nitrate into chloride by repeated evaporation with hydrochloric acid in quartz dishes. This method was found to have two objections. In the first place, dishes large enough for the raw material were not to be had. Moreover, the tendency of the branching crystals to grow over the edge of the dish caused serious loss of material and danger of impurity. Neither could potassium nitrate be heated to a high temperature with ammonium chloride, or in a stream of hydrochloric acid in quartz dishes; for there is always danger that the reaction $4\text{KNO}_3 + 2\text{SiO}_2 = 2\text{K}_2\text{SiO}_3 + 4\text{NO}_2 + \text{O}_2$ would occur.²

Because Stas had never been able to obtain a salt free from silica when working in glass vessels, we desired to avoid completely the use of glass. Therefore, only one way remained, namely, to convert the potassium nitrate into chloride by precipitation with hydrochloric acid in a platinum dish. The resulting aqua regia must naturally attack the platinum, but we preferred this impurity to that of silica, and found, moreover, that the amount of platinum dissolved is very small. In the presence of large masses of potassium salts, aqua regia, especially in the cold, dissolves platinum but little. For example, in one experiment in which about half a kilogram of potassium nitrate was treated with hydrochloric acid gas, only three-tenths of a gram of platinum was converted into the form of potassium chloroplatinate. In subsequent crystallizations the amount was

¹ Richards, *This Journal*, **27**, 105 (1905).

² Richards and Archibald, *loc. cit.*

very much less, because the great mass of the nitric acid was eliminated by the first crystallization. After the third recrystallization, the diphenylamine reaction failed to reveal the presence of any retained nitrate.

The precipitation was carried out in the following manner: The often recrystallized, very pure potassium nitrate was dissolved in the least possible quantity of cold water, contained in a platinum dish, packed in ice. Slowly, in order to prevent warming, hydrochloric acid gas was run into this solution. The gas was supplied by warming a pure concentrated solution, and was passed into the nitrate solution through an inverted platinum funnel. The potassium chloride, which appeared somewhat yellow from its slight platinum impurity, was whirled in the platinum centrifuge, and dissolved in purest water. Potassium chlorplatinate is practically insoluble in a concentrated solution of the chloride, as the law of concentration effect and the theory of ionization predicts; hence the impurity was easily separated upon a small, pure filter. The clear, colorless solution was again saturated with hydrochloric acid, and the same round of operations repeated. Upon a third repetition of this process, the nitric acid was eliminated and the salt, as a rule, was wholly colorless in consequence. On no occasion, even with large amounts of materials, did perceptible color remain after five treatments. No specimen was subjected to less than seven such recrystallizations, while some was passed yet five times more through the precipitation and centrifugal drying. Assuming that each time about three-quarters of the ordinarily adhering mother liquor was removed by the centrifugal separation, these crystals must have been as free from heteromorphous substances as if they had been recrystallized many thousand times in the ordinary fashion. It will be shown that all the samples gave the same results upon analysis, hence further purification according to this method was needless. The salt was found to be wholly free from sodium by a sensitive spectroscopic test. It was in every case freed from acid by a single recrystallization from the purest water, and by fusion in the manner to be described later.

Seven different samples were prepared after this fashion from varying raw material. These are given in the list below.

(*a*) The pure potassium material ("C. P." of German preparation) was recrystallized as nitrate six times, and precipitated as chloride seven times. This salt after the final recrystallization from pure water was dried in a platinum dish at 120° in an electric oven. The salt was snow-white, and was as clear as water when fused, as indeed, were all the other samples.

(*b*) This sample was similar to *a*, but obtained by the evaporation of the final aqueous mother liquor decanted from *a*. The mother liquor from *b* was rejected.

(*c*) Five extra precipitations with hydrochloric gas (or twelve in all)

yielded this salt, which was prepared for analysis in the same way as *a*.

(*d*) This salt bore the same relation to *c* that *b* bore to *a*, being essentially identical with *c*.

(*e*) For this sample and the next one the nitrate was recrystallized twelve times, and the chloride precipitated seven times.

(*f*) From the final mother liquor of *e*, *f* was prepared, as *b* followed after *a*.

(*z*) This sample was exactly like *a*, except that the raw material came from an entirely different source.

Silver Nitrate.—The nitrate of silver used for precipitating chlorine in the analysis was crystallized three times from pure dilute nitric acid solution and each time centrifugally freed from mother liquor. Before each analysis the aqueous solution of the salt was tested in the nephelometer¹ for a possible trace of silver chloride, and no material was ever used which showed to this exceedingly sensitive test the least trace of impurity. For preservation in a pure state it was kept in a tight desiccator over potash.

Silver.—The metallic silver used in the research was made from silver nitrate which had been six times recrystallized. The metal was precipitated as a fine powder by ammonium formate,² melted on pure lime, and further purified by electrolysis.³ The beautiful crystals thus prepared were fused in a stream of pure electrolytic hydrogen and finally in a vacuum of 0.1 mm. The metal was supported on a boat of the purest lime, prepared from calcium carbonate precipitated from the nitrate for this purpose. The boat was provided with several compartments, each of which held enough silver for one analysis, in order to avoid the possible introduction of impurity into the metal by subsequent cutting. It was inclosed in a stout porcelain tube, provided with Hempel water-cooled stoppers, and was heated electrically in a Heraeus tube-furnace.⁴ The vacuum was maintained by a motor-driven Geryk oil air-pump. Except for these minor improvements, the preparation was essentially similar to the best methods employed by Richards and Wells in their often-cited work, to which the reader is referred for further details.

Nitric and Hydrochloric Acids.—Very carefully tested preparations of commerce were used as the raw materials in the preparation of these acids. They were redistilled with platinum condensers until they were fully pure enough for the purposes for which they were needed. The hydrochloric acid had been shown in the research on sodium to be free from bromine or iodine.

Water.—This substance, because it is used in larger quantities than

¹ Richards, Pr. Am. Acad., 30, 385 (1894); Z. anorg. Chem., 8, 269 (1895).

² Richards and Wells, This Journal, 27, 475 (1905).

³ J. L. Hoskyns Abrahall, J. Chem. Soc. (1892), 660; also Richards, Pr. Am. Acad., 28, 22, (1893).

⁴ Heraeus, Z. Elektrochem., 8, 201 (1902).

any other, must be especially pure. All the water used, either for preparation or analysis, was twice distilled, once with alkaline permanganate and once alone. For the best work a platinum condenser was used. All that was needed for analysis was tested in the nephelometer immediately before use.

The Drying and Weighing of the Potassium Chloride.

The final preparation of the salt for analysis is given a special chapter to itself, because the proper execution of this feature is of very great importance, not less than the purification of the material. It is clearly useless to separate 0.001 per cent. of a metallic impurity if 0.01 per cent. of water is allowed to remain in the salt.

Obviously, superficial drying can not remove the imprisoned moisture in the crystals, hence they must be fused.¹ Except in a few preliminary experiments, where a common platinum crucible was used, this fusion was conducted in a platinum boat or open bottle contained in a porcelain tube through which a current of nitrogen was passing. The experience in a number of similar cases, that the simultaneous presence of oxygen and traces of hydrochloric acid inclosed in the crystals is likely to cause perceptible corrosion of the platinum boat, was confirmed in this case; hence an inert gas was needed. The nitrogen was prepared by the well-known method of Wanklyn, by passing air charged with ammonia over red-hot copper. The excess of ammonia was carefully eliminated by washing the gas with much dilute acid. Because fused sodium chloride was found to be essentially free from dissolved nitrogen, we did not think it necessary to fuse this very similar potassium salt in a vacuum.

Potassium chloride, although not so hygroscopic as some other salts, used in similar researches, is nevertheless far too hygroscopic to weigh safely when directly exposed to the air of the balance room. Its tendency to attract water was seen in perceptible crackling when the tube containing fused salt was opened in the moist atmosphere of the beaker to be used for the solution of the salt.

At first the bottling apparatus so often used in the Chemical Laboratory of Harvard College was employed to protect the fused chloride from moisture during the determination of its weight, the chloride being contained in a platinum boat protected by a glass-stoppered weighing bottle. Because, however, the weighing room was not wholly constant in temperature or in moisture, time and trouble were needed to obtain exact weighings, even although the apparatus was always weighed by substitution against a similar empty boat and bottle. The use of quartz weighing bottles proved to be no advantage, indeed, if anything, a disadvantage. In either case, if time enough were taken, satisfactory weighings could be made; but

¹ Richards, *Z. physik. Chem.*, 46, 189 (1903).

as time was especially precious, another device was used which wholly overcame the trouble.

This effective and satisfactory device consisted in the use of small weighing bottles of platinum, shaped like the long Lawrence Smith crucible, which were closed by small platinum capsules, fitting into the bottles like ground stoppers. One of these bottles, containing the potassium chloride, was supported by a loop of platinum wire in an inclined porcelain tube, and above it in the tube was placed its platinum stopper. Glass stoppers fitted into each end of the porcelain tube, which was encircled by a suitable furnace. After the potassium chloride had been dried for a long time at a high temperature, just barely fused in nitrogen, and cooled in a current of pure dry air, the stopper was shaken into place and the platinum bottle quickly removed and placed in a desiccator. This arrangement is essentially similar to the bottling arrangement of Richards and Parker, except for the additional advantages that glass is wholly eliminated and that the enclosed air-volume in the tube is much smaller. Probably the burnished platinum joint is not as tight as the ground-glass joint; but it is amply tight enough to prevent any appreciable diffusion of moisture during the very brief exposure of the tube. This was evident from the constancy of the weighings, which were made by substitution against a similar empty platinum bottle kept in the same desiccator. The weighings were very quickly performed and were trustworthy. Before being used, the platinum bottles were repeatedly ignited with pure sublimed ammonium chloride in order to remove iron; they remained satisfactorily constant in weight during subsequent experiments, the one used for the fusion losing only 0.3 mg. in fourteen experiments, or on the average 0.02 mg. in a single experiment. In one experiment, where oxygen was present during the fusion, as much as 0.3 mg. was taken from the boat, the platinum being plainly visible on solution. This was of course not used for analysis.

All weighings, whether of this salt or of silver or silver chloride, were made by substitution in the manner already described in other papers.¹ The balance was a short-armed instrument made by Troemner of the type adopted in other similar investigations; it was used only for this work and that to be described afterward. The weights were of platinized brass, carefully standardized according to the usual Harvard method.²

All weighings were reduced to the vacuum standard. Thus from every apparent gram of silver, 0.00003 gram was subtracted, and to every apparent gram of silver chloride, 0.000071 was added, if the temperature

¹ For example see Richards and Rogers, *Z. anorg. Chem.* 10, 19 (1895); also, Richards and Wells, *This Journal*, 27, 465 (1905).

² Richards, *This Journal*, 22, 144 (1900). These weights had an average density of 8.3.

was 20° and the pressure normal. Assuming the density of potassium chloride to be 1.995, the similar correction for this salt was ± 0.000456 . Changes in temperature and pressure occasionally caused slight but usually inessential changes in these corrections.¹

The wholly colorless, transparent, fused salt was dissolved in the purest water in a covered beaker of Jena glass under a tightly fitting bell-jar. The solution was always perfectly clear, except in the rejected case already cited and one other similar one. After this solution had been very thoroughly washed away and used for analysis, the platinum weighing bottle was heated for a short time in another crucible, and weighed in preparation for another analysis. The constancy of these weighings has already been discussed.

The details of preparation having been described, the analytical methods themselves must be indicated. The problem was, as in the case of sodium, to determine the amount of chlorine present, the weight of potassium being found by difference. Both of the previously used methods for finding the amount of chlorine were used, and the details are so much like those discussed by Richards and Wells² that much may be assumed as understood. For a full understanding of the present work, that upon sodium should be read in connection with it.

The two methods for the determination of chlorine, namely, the weighing of the precipitated silver chloride on the one hand, and the discovery of the necessary amount of silver on the other, are discussed below in order.

The Precipitation and Weighing of Silver Chloride.

For purpose of analysis, the solution of potassium chloride was carefully and completely transferred to a large Jena glass Erlenmeyer flask with a finely ground glass stopper, and diluted to the volume of a liter or more. To this in the dark room under the red light was added exactly the calculated weight of silver nitrate, never more concentrated than one fiftieth normal; and the mixture was shaken for a short time in order to aggregate the great mass of the precipitate. Because of the absence of an excess of silver nitrate, the danger of the occlusion of this salt was slight. On the following day the supernatant liquid was usually quite clear, and to it was now added the excess of perhaps 0.05 gram of silver nitrate needed for complete precipitation. This method of treatment was found to be more satisfactory than the immediate addition of all the silver nitrate at once, as in this case long and tiresome shaking and washing of the precipitate was needed to eliminate wholly the occluded silver nitrate. Thus one of the chief difficulties met by previous experimenters was almost entirely overcome. It was shown in the

¹ Richards and Wells, *This Journal*, 27, 465 (1905).

² *loc. cit.*

paper on sodium that the simplest test for the presence of silver nitrate is the appearance of the silver chloride after fusion, even a small trace of nitrate causing a perceptible grey-violet cloudiness. In all cases when the above precaution was used the fused mass was perfectly clear and transparent. This is, however, an anticipation of the latter part of the process; the collection, abluition and dessication of the precipitate should first be described.

In preliminary experiments, the Gooch perforated platinum crucible with asbestos mat was used with all the precautions previously adopted in this laboratory. In this way it is certain that good results may be obtained; but the necessary second filtration of the filtrate in order to collect the traces of disintegrated asbestos is a tiresome process. On this account preliminary experiments were made with Gooch crucibles provided with a smooth and burnished mat of platinum sponge, as prepared by Heraeus.¹ Such crucibles are named by him after Neubauer, but might more properly be called Gooch-Munroe crucibles. In these preliminary tests it was found that such crucibles as a matter of fact answer very well for the purpose in hand if certain special precautions are taken. It is not permissible to ignite them at a high temperature, unless the precipitate also is to be ignited at a high temperature. A crucible brought to constant weight at 150° was found to lose 0.15 mg. on ignition, probably because of loss of previously absorbed water. Moreover, when a dilute solution of silver nitrate, potassium nitrate, and nitric acid, such as remains after an analysis, was passed through the filter, and this was five times washed with water, and dried at 150°, yet 0.15 more was gained, probably due to adsorbed salts. Very thorough washing after this brought the crucible back to its original weight, after drying at 150.°

These experiments showed that the washing of the platinum sponge must be very thorough, and that a definite temperature must always be used for drying. Other experiments showed that constant weight could always be obtained, if these conditions were fulfilled.

It is well known that silver chloride sometimes clings to a platinum surface, and always shrinks much on drying. On this account the somewhat delicate upper surface of the sponge was protected by a closely fitting disk or diaphragm of platinum punched with many fine holes. This diaphragm, merely laid upon the top of the sponge at the base of the crucible, was easily loosened with the precipitate, and formed an effectual protection for the sponge. After this was done, no

¹ *Z. angew. Chem.* 14, 923 (1901). A number of experimenters have recommended and used a mat of platinum sponge in a Gooch crucible, but Munroe was probably the first. *J. anal. Chem.* 2, 241 (1888), also *Chem. News* 58, 101 (1888). The burnished form made by Heraeus is probably due first to Neubauer.

platinum was ever lost from the upper surface; and none was ever carried away mechanically from below in the wash-water.

In spite of the presence of the disk, small particles of silver chloride always clung here and there to the sponge. As a possible means of removing these when preparing for a new analysis, potassium cyanide was tested. It was found, however, that not only was this salt adsorbed by the sponge, but that in the presence of air platinum was dissolved even to the extent of a milligram—a fact not new, but none the less pertinent. Thiosulphate was not tried, because sulphate was an impurity little wished. Finally, while ammonia for a short time was inefficient, this liquid, when concentrated and applied for twelve hours or more, dissolved every trace of the silver salt without harming the crucible.

The technique of the Gooch-Munroe crucible having thus been mastered, this utensil was used with satisfaction as a means of collecting and weighing the precipitate in hand. The latter was first washed often by decantation, as is recounted below, and finally on the filtering crucible, which was dried to constant weight by a temperature gradually rising to 150° . After careful weighing, the main mass was separated from the clinging platinum disk, and was carefully fused in porcelain, as has often been described. The accurately determined loss on fusion, amounting sometimes to a milligram, was calculated from the part to the whole, and applied as a correction to the total weight of the precipitate.

This weight, even as thus corrected, did not, however, exactly represent the total in weight of the chlorine, as some of the silver chloride was dissolved by the wash-water. The ablation had been conducted in three stages, just as in the often-cited investigation of sodium. The first stage included the mother liquor and first five wash-waters, containing intentionally as much silver nitrate as the mother liquor, and added to remove the greater part of the potassium nitrate. This first quantity of liquid was entirely free from chlorine in every accepted analysis, as was shown by careful testing in the nephelometer, and so was at once cast aside.

The second stage of washing was conducted with very dilute nitric acid, and yielded 0.5 or 0.6 liter of a very dilute solution of mixed nitric acid and silver chloride and nitrate. The traces of chloride which it contained were carefully estimated in the nephelometer after addition of excess of silver nitrate.

The third stage of the washing, also conducted with pure water acidified with nitric acid to prevent colloidal irregularities, yielded a liter or more of liquid containing much silver chloride. The analysis of this liquid constituted a very important part of the work, and gave much trouble.

In order to be as certain as possible of the weight of chlorine it contained, this liquid was tested in five cases according to two very different methods. The first of these consisted in evaporation of the solution under diminished pressure and actual weighing of the precipitate, and the second consisted in a new modification of the nephelometer test. Although the latter evidently gave the more satisfactory results, the former is worthy of brief discussion, because its outcome certainly represents the maximum value.

In order to carry out these two parallel quantitative tests, the collected wash-water was divided into two parts; and the larger part, about 90 per cent. of the whole, was evaporated to dryness under low pressure at 40° to 50° in a specially made Jena glass 2-liter flask with a glass stopper. In the course of this evaporation, the silver chloride began to separate out when the volume had been reduced to about 0.2 liter, if 2 mg. of the salt were present—a fact agreeing well with the recent observations concerning this solubility.¹ The dried residue was dissolved in a very little ammonia freshly distilled in platinum, and washed into a small precipitating flask, where it was reprecipitated with excess of silver nitrate and nitric acid. This trace of precipitate was collected and weighed on a fresh Gooch-Munroe crucible in the same way as the larger mass. The results are given below in comparison with those obtained from the same solutions by the nephelometer.

An important modification was introduced into the nephelometric determination. One of us has repeatedly pointed out that in order to obtain satisfactory results with this instrument the solution to be tested and that used as the standard of comparison must be treated in exactly the same way.² Hence the use of a ground-glass plate³ as a standard of comparison is a very questionable proceeding. It appears that the precipitation of silver chloride from solutions of this salt differ perceptibly in mechanism from the precipitation of the same substance from other chloride solutions, even when silver nitrate in great excess is used in each case⁴. Accordingly, in order to secure a perfectly satisfactory comparison, both precipitates must be dissolved in ammonia and reprecipitated. The precipitate then appears in each case in precisely the same condition, and yields trustworthy results.

The present tests were carried out in the following manner: Two test tubes of precisely the same volume (0.025 liter) were provided. Into one of these was placed 0.015 liter of the wash-water, and into the other, serving as the standard of comparison, a like volume of water contain-

¹ See for example Böttger, *Z. physik. Chem.*, **56**, 93 (1906).

² *Am. Ch. J.* **31**, 242 (1904); **35**, 509 (1906).

³ Wells, *Am. Ch. J.*, **35**, 99 (1906).

⁴ Richards and Wells, *Carnegie Inst. Pub.*, **28**, (1905); *This Journal*, **27**, 485 (1905).

ing about as much carefully measured chlorine (in the form of potassium chloride) as was present in the first. Into each was now run 5 cc. of a three-hundredth normal solution of silver nitrate. The solutions were stirred with a platinum stirrer, previously cleansed with ammonia and the purest water. After five minutes the precipitates were well formed; they were then both dissolved with the help of a milliliter of freshly distilled ammonia, and reprecipitated with a slight excess of nitric acid, being filled to similar marks near the top of the tubes. The two cloudy solutions, thoroughly stirred, were allowed to stand and compared optically in the nephelometer in the usual way.

The following table compares the results obtained by the two methods. The varying solubility of the halide in the wash-water was mainly due to difference in temperature at the time of the ablation.

The Comparison of Weights of Silver Chloride found Nephelometrically and by Evaporation.

Experiment No.	Volume. Liters.	Weights of Silver Chloride.		Difference. Mg.
		By evaporation. Mg.	By nephelometer. Mg.	
10	1.45	3.96	3.12	-0.84
11	1.88	3.82	3.22	-0.60
12	1.18	2.59	1.97	-0.62
13	0.90	1.70	1.35	-0.35
14	1.00	1.74	1.45	-0.29

Thus the nephelometer always indicated less silver chloride than the gravimetric process. At first the nephelometer was suspected, but the steadily diminishing difference between the two series of results indicated that they were approaching the point where they would indicate the same values, as the nephelometric treatment was invariable, but on the other hand the evaporating flask might easily be attacked, it seemed probable that the decreasing difference exhibited by the figures was due to something added to the weight of the precipitate from the latter source. Apparently, as is reasonable, the flask was less and less attacked as it continued in use.

For this reason the gravimetric results were wholly rejected, and the nephelometric ones alone used in the calculation of the final results.

The Ratio of Potassium Chloride to Silver Chloride.

The final results of the series of analyses discussed above are recorded in the following table. A number of preliminary experiments are omitted from this table, since it is clear that no doubtful or imperfectly executed experiment should find a place in such a table of final data. The list is nearly consecutive, however, as but few experiments met with misfortune after the processes had been mastered. The original numbering of the experiments is retained; they were recorded in the notebook

in chronological order. All the silver chloride referred to in this table was clear and colorless, a fact which is one of the best proofs that it was free from silver nitrate or from organic dust.

Final Series of Determinations of the Ratio KCl : AgCl.

No. of Analysis.	Preparation of KCl.	Weight of Fused KCl in vacuum Grams.	Weight of Fused AgCl in vacuum Grams.	AgCl : KCl = 100,000 : X.	Atomic Weight K if Cl = 35.473.
13	a	4.36825	8.3986	52.012	39.114
14	a	5.56737	10.7038	52.013	39.115
15	a	6.41424	12.3323	52.012	39.114
20	b	3.27215	6.2913	52.011	39.112
31	b	4.83028	9.2870	52.011	39.112
Average.....				52.0118	39.1134

This result will be discussed after the next series has been presented. It has a probable error, calculated by the method of least squares, of only about 0.0004; accordingly further repetition was deemed unnecessary.

The Ratio of Potassium Chloride to Silver.

In this series of experiments, weights of the purest silver equivalent to entirely new portions of fused potassium chloride, as calculated from the preceding table, were dissolved in nitric acid, and the two equivalent solutions were mixed. Great care was used. The presence of an excess of silver or of chlorine was then determined with the nephelometer, exactly according to the details of manipulation adopted by Richards and Wells, whose accounts should be consulted for particulars. The table below contains the final results; the preliminary practice experiments are omitted for the same reason as before.

Final Series of Determinations of the Ratio Ag : KCl.

No. of Analysis.	Preparation of KCl.	Weight KCl in Vacuum Grams.	Weight Ag in Vacuum Grams.	Ratio Ag : KCl = 100,000 : X.	Atomic Weight of K if Cl = 35.473.
19	a	3.88074	5.61536	69.109	39.117
21	a	7.44388	10.77156	69.107	39.114
24	c	5.00681	7.24514	69.106	39.113
27	e	5.04833	7.30515	69.107	39.114
30	e	8.19225	11.85412	69.109	39.117
32	d	4.99795	7.23230	69.106	39.113
33	f	5.16262	7.47042	69.107	39.114
Average.....				69.1073	39.1145

In this case the "probable" error is even somewhat less than before, being under 0.0004.

Discussion of Final Results.

Thus two results have been obtained, giving for the atomic weight of potassium the value 39.113 by reference to silver chloride, and the value 39.114 by reference to pure metallic silver. The close agreement of

these results is an important evidence of their verity, and a striking confirmation of the new atomic weight of chlorine found by Richards and Wells. The atomic weight of chlorine is very simply calculated from the results of the two series above as follows: $\text{Cl} = (69.1073/52.0118 - 1.00000) 107.93 = 35.475$ —very near the most likely value 35.473.

Such difference as exists is probably due to the slight remaining trace of occlusion of foreign salts by the silver chloride. In the present case, this source of error was eliminated more successfully than ever before, hence the agreement between the two values of the atomic weight of potassium was closer than usual.

It may be noted that the difference between the new value and the old value of Stas is somewhat less than in the case of sodium. Stas's results with potassium chloride led him to the value 39.146, about 0.032 higher than the new result, while with sodium chloride the difference was 0.042. A large part of this difference in each case is due to Stas's error in the atomic weight of chlorine; corrected for this error, the differences become 0.016 and 0.026 respectively. The differences are to be referred to the same causes in this case as in the others—namely, to Stas's incomplete knowledge concerning solutions of silver chloride, to his practice of dropping solid salt into the precipitating solution, and to the presence in his preparations of traces of impurity taken from containing vessels. In the case of potassium, one or more of these errors must have been less than in the case of sodium.

The results of Richards and Archibald, although very few in number and not intended to figure in a discussion of this kind, were somewhat better—probably because solid salt was never used directly in precipitation. Assuming the present research to yield the true value, their errors in the two series were, respectively, 0.009 and 0.014. The result of Archibald alone for the ratio of silver to potassium chloride was about the same amount (0.008) different from the present value; but his result for the other ratio was less satisfactory, having an error of 0.021, even greater than Stas's. These differences are not surprising, because less was known at that time than at present concerning the behavior of silver chloride in solution.

Although the present paper presents strong evidence that the atomic weight of potassium is really as low as 39.114, more remains to be done. It would have been desirable to have used also some other wholly different method of preparing potassium chloride, and, moreover, to have evaporated large samples of the salt in nitrogen in order to discover a possible non-volatile residue. It is very doubtful if these additional experiments would have altered the present result, especially considering the precautions taken in the work and the result of the following research; but, nevertheless, it is planned to pursue these matters further.

Even when every conceivable precaution is taken, a single salt is not an adequate basis for the certain decision of an atomic weight. For this reason a parallel investigation on potassium bromide was simultaneously in progress at the Chemical Laboratory of Harvard College. The next communication, describing this other research, must be considered in connection with the work which has just been described. As will be seen, excellent confirmation of the present work is afforded by the work with the bromide.

Summary.

This investigation concerning the quantitative composition of potassium chloride resembled in many respects the recent investigation of Richards and Wells on sodium.

In several details, however, improvements were introduced which effected a considerable saving of time and a perceptible gain in accuracy.

The precautions necessary for the accurate use of the Gooch-Munroe perforated crucible were ascertained; its employment was found to be advantageous.

Platinum weighing bottles with conical ground-platinum stoppers were used instead of boats and glass tubes for weighing the potassium salt.

Occlusion of silver nitrate by the precipitated chloride was diminished by allowing the latter to stand for a long time in a solution containing neither excess of silver nor excess of soluble chloride, and by adding more silver nitrate only after the precipitate had assumed a fairly permanent condition of aggregation.

The nephelometric estimation of small amounts of suspended silver chloride was increased in accuracy by redissolving in ammonia both of the opalescent precipitates to be compared, and reprecipitating, in order to equalize the conditions.

As final results, the outcome of twelve experiments, 100.000 parts of silver were found to correspond to 52.0118 parts of potassium chloride, and 100.000 parts of silver chloride were found to correspond to 69.1073 of this salt.

The corresponding values for the atomic weight of potassium (if silver is assumed to be 107.930 and chlorine 35.473) are 39.1134 and 39.1145, in unusually close agreement.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE].

A REVISION OF THE ATOMIC WEIGHT OF POTASSIUM. THE ANALYSIS OF POTASSIUM BROMIDE

By THEODORE WILLIAM RICHARDS AND EDWARD MUELLER.

Received February 15, 1907.

Introduction

The foregoing quantitative study of potassium chloride by Arthur Staehler and one of the present authors affords strong evidence that