calculated by use of the formula $\gamma = \Lambda T_I/\Lambda_{0I}(\eta/\eta_0)$ are given, and in Column VIII, for the sake of comparison, values calculated by use of the relation $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)$. The difference in the two sets of values is about 3%.

Since no transference numbers have been determined at concentrations lower than 0.002 normal, corresponding values of the degree of dissociation are not shown in Column VII. In fact no measurements of the transference number of hydriodic acid have been made at concentrations less than 0.05 normal. However, since neither the transference number of hydrochloric[1] nor that of nitric acid[2] shows any marked change of value in the range 0.05 to 0.002 normal, it is probable that that of hydriodic acid also does not. Consequently the ionization values are shown at concentrations as low as 0.002 normal. The formula presented in the introduction, if applied to the figures shown in Table III using the transference number 0.174, would indicate only 97% dissociation at infinite dilution. As has been pointed out, either the transference number is different at these low concentrations, or what seems much more reasonable, the conductance measurements are at fault.

5. Summary.

1. The transference number of the cation of hydriodic acid at 25° is 0.826 ± 0.001 between the concentrations 0.2 and 0.06 normal.

2. The conductances of hydriodic acid solutions have been measured and the degree of dissociation calculated for the concentration range 0.2 to 0.002 normal.

3. Adsorption of hydriodic acid by silver iodide is shown to be a source of error in transference experiments made with a silver iodide cathode.

We desire to express our indebtedness to E. W. Washburn for his kind criticism of this work.

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THE PURITY OF FUSED LITHIUM PERCHLORATE, AND ITS BEARING UPON THE ATOMIC WEIGHT OF SILVER.[3]

BY THEODORE W. RICHARDS AND MARSHALL W. COX.

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In a comprehensive research upon the atomic weights of lithium and silver, H. H. Willard and one of the present authors[4] devised and perfected an entirely new method for determining the latter of the two atomic weights. This method involved the treatment of pure anhydrous lithium

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[1] Noyes and Sammet, THIS JOURNAL, 24, 944 (1902); 25, 165 (1903).

[2] Noyes and Kato, *Ibid.*, 30, 318 (1908).

[3] A brief notice upon this topic was presented to the Eighth International Congress of Applied Chemistry in New York in September, 1912, and printed in the *Original Communications of this Congress*, 25, 157.

[4] Richards and Willard, *Publ. Carnegie Inst.*, No. 125.

chloride with excess of perchloric acid, and the drying of the lithium perchlorate thus formed for a long time in a state of fusion at a temperature of about 300°. From the weights of factor and product, together with the ratio of lithium chloride to silver (determined at the same time in another series of analyses made in the usual way), it is easy to calculate the atomic weight of silver with reference to that of oxygen in the following fashion. Assuming that four times the atomic weight of oxygen is 64.000:

$$\frac{Ag}{64.000} = \left(\frac{LiCl}{LiClO_4 - LiCl}\right)\frac{Ag}{LiCl}$$

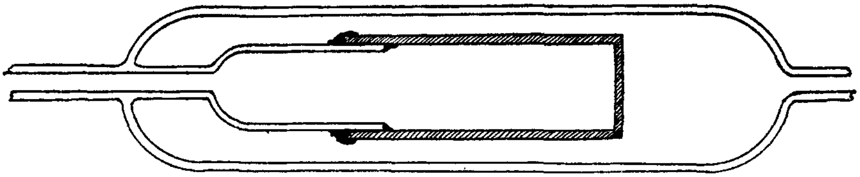
The value of the outcome depends as usual upon the purity of the three solid substances concerned. Silver is capable of being made nowadays in a state of great purity. Lithium chloride also can be prepared in a state very free from contamination, even with water, by methods elaborated at Harvard; but lithium perchlorate, which has been less studied, cannot be heated to a red heat without decomposition, and its freedom from volatile impurities is less certain. This fact was fully appreciated by the experimenters, and they promised to investigate further the question concerning the purity of the lithium perchlorate.

Obviously, any water retained by this salt would decrease the apparent atomic weight of silver, by increasing the denominator of the fraction within the parenthesis. On the other hand, any trace of decomposition suffered by the salt would have the opposite effect. The resulting contamination of the perchlorate by chloride or chlorate is easy to detect; but the retention of minute traces of water is much more difficult to discover. The present investigation, which has been greatly prolonged because of the subtle nature of the problem, has primarily to do with the question as to the anhydrous condition of the lithium perchlorate, and we take pleasure in stating that the question, if not wholly settled, has now at least been carried much further than before. The evidence now available points towards the improbability of the retention of weighable amounts of water by lithium perchlorate at 300°. It is true that this result was not wholly unexpected, for the salt came to satisfactory constancy in weight, even at 280°, and a rise of 30° had no effect upon this weight. Moreover, one of us, in collaboration with G. S. Forbes, showed, some time since, that silver nitrate, a salt nearly as soluble as lithium perchlorate, retained practically no water at all at a much lower temperature, namely, 200°. Nevertheless, the outcome is satisfactory, and leads one to believe that the method under discussion for determining the atomic weight of silver is one of the very best.

At first sight the problem involved in determining the trace of water possibly held by the salt might appear to be a simple one. It is merely necessary to decompose pure lithium perchlorate (which has been fused and dried to constant weight at 300°) and to determine the weight of water which may be evolved among the products of decomposition. But in decomposing a salt by heat under these conditions a portion of the solid is carried along with the stream of gas in a state of subdivision so fine as to evade capture in any ordinary train of purifying towers. If the complication of this train is greatly increased, the chance of losing a trace of water altogether on the one hand or fortuitously collecting water from some other source is a serious one.

Two methods of attack were considered. At first it was thought that oxygen and water, and any trace of chlorine evolved, might be condensed together by means of liquid air. The powder would then be held in the condensed liquid, and would doubtless be left behind when the oxygen was allowed to evaporate.[1] The problem of driving the water off from the remaining small amount of solid and collecting it in phosphorous pentoxide would obviously be easy.

After several trials, however, this method was abandoned in favor of another, yet simpler. The gas evolved by decomposing the perchlorate, carrying with it exceedingly fine powder and traces of chlorine, was passed first through a warm coil of closely packed finely divided silver wire to remove the chlorine, and then through a porous porcelain dry-filter or "dust-trap" to remove the powder. The water in the gas thus purified could be easily determined in the usual way.



Dust-trap.

The shaded portion indicates the porous cylinder; the black spots show where silver chloride was used as cement.

The coil of silver wire is an old device for the purpose of removing undesired chlorine. Its efficiency was shown by the fact that the portion of the silver nearest to the decomposing salt was tarnished, whereas the greater part of the coil kept its original lustre through many experiments.

The "dust-trap" also is not an entirely new idea. It was used by one of us in collaboration with Köthner and Tiede, in an investigation upon the atomic weight of nitrogen in 1907.[2] For the present purpose it was necessary to construct a filter which would certainly neither retain a trace of the water, nor evolve any into the stream of air passing through it. Moreover, the pores of the filter must be so fine as to allow no appreciable weight of

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[1] This method was proposed by one of us in 1907, and was used with success in a somewhat analogous case by Stähler and F. Meyer, *Z. anorg. Chem.*, 71, 378.

[2] *Z. anorg. Chem.*, 61, 320 (1909); THIS JOURNAL, 31, 6 (1909). Others also have doubtless employed it.

the fine dust from the decomposing salt to pass through them. After a number of experiments we found that a fine-grained unglazed "Pukal" porcelain cup, of the sort used in the coulometer or voltameter in 1899,[1] and since so strongly recommended for the purpose by E. B. Rosa, answers admirably. As a cement to connect this porcelain to the rest of the apparatus, fused silver chloride was found to be the most convenient substance. Each question involved was of course carefully tested. In the first place, a cup (previously cleaned by washing thoroughly with nitric acid and soaking for several days in many portions of distilled water until all acid was removed), was dried in an electric oven, cooled in a desiccator and weighed. The cup was now moistened with water, and again dried at 300°, cooled and weighed. This was done three times, with the result that during the whole period the cup remained constant in weight within two-hundredths of a milligram, the limit of the sensibility of the excellent balance used.

In order to test the fineness and evenness of grain of the cup, and to be sure that it was properly cemented to its glass support, it was wholly submerged in water after it had been cemented into place, and air was forced through it under pressure. If small bubbles formed rather slowly over the whole surface of the porcelain, sufficient evidence was obtained that air really passed through the many small passages in the walls, but if a rush of bubbles appeared from one or two points, the cup was obviously imperfect and was discarded. A similar test might be applied with advantage to cups used for the coulometer. No great trouble was experienced in finding cups which would pass this test; the main difficulty usually appeared where the porcelain was cemented to the glass. Very pure silver chloride, free from any infusible impurities or dust, was required to serve as a cement if a perfect joint was to be made.

Obviously it was necessary to collect in a perfectly unaltered condition all the gas emerging from the "dust-trap." Accordingly the porcelain cup was surrounded with a slightly larger glass tube. This wide tube was sealed by an inside joint to the narrow tube bearing the cup, and the open end of the surrounding jacket was drawn down to a small tube which could be connected with the quantitative drying apparatus. The completed dust-trap is shown in Fig. 1; it would allow air to pass under moderate pressure at the rate of two or three ordinary bubbles per second, and maintained its efficiency through a long series of experiments.

The air-filter thus constituted was found to be so efficient in its operation and so free from any disturbing effect that another one of the same type was used in purifying the air used for drying the perchlorate before its decomposition. The fact has long been known that minute particles of

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[1] Richards and Heimrod, *Proc. Am. Acad.*, **35**, 123 (1899); *Z. physik. Chem.*, **32**, 339 (1900).

dust not visible to the naked eye may be carried in a current of gas through many feet of tubing, or even, in bubbles, through deep layers of liquid. Clearly, then, it is important whenever a substance is to be dried in a considerable current of air, that this dust should be eliminated; for it might easily contaminate to some extent the pure substance to be treated. As will be shown, the outcome in the present case justified these considerations in a striking way, and indicated that in any such case a "dust-trap" of this sort should be employed if the highest accuracy is sought. This outcome in its bearing upon accurate work in general is one of the most interesting of the points enforced by the present research.

The point is most clearly demonstrated by a comparison of the experience of different experimenters upon lithium perchlorate. Potilitzin[1] found that the decomposition of lithium perchlorate into chlorate and chloride proceeded very rapidly at 268°. Richards and Willard were able on the other hand to subject the salt to continued treatment at 300° with a barely perceptible trace of decomposition. Their salt and the air with which it was in contact were both doubtless much purer than Potilitzin's; evidently impurities incite catalytic decomposition. At 350° the two Americans found that the salt decomposed so violently as to throw visible particles of dust through several feet of tubing; but in the present research lithium perchlorate dried and fused in a current of carefully filtered air, (otherwise precisely similar to that used in the research of 1910) could be heated for three or four hours at 400° with very slight decomposition and with no visible projection of material nor exit of gas. Only at 430° or a higher temperature did decomposition proceed with rapidity or completeness. Moreover, it was possible so to regulate the temperature between 410° and 430° that the decomposition was slow and the current of outgoing gas flowed quite steadily at the rate of from two to three bubbles per second. This previously unobserved stability of lithium perchlorate was doubtless due to the very high degree of purity of the material, probably never before attained; and the chief cause of this purity seems to have been the exclusion of impalpable and invisible dust from the current of many liters of air which passed over the salt during its synthesis, crystallization and long-continued drying in a fused condition. The exact mechanism of this catalytic effect cannot be studied quantitatively until the nature of this trace of dust is discovered; possibly the finely powdered steel, which is said to exist in the air of all cities, is responsible. Enough has been said to show that the air-filter served an important office, and to suggest that in other investigations also, where great purity is sought, its help should be employed.

The lithium perchlorate employed in the present work was prepared

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[1] See Abegg, "Handbuch der anorganische Chemie," quoting from Potilitzin, *J. Russ. Phys. Chem. Soc.*, **20**, I, 541 (1888).

from very pure materials made several years ago by H. H. Willard and remaining from the research on atomic weights already mentioned. We are greatly indebted to him for this service. Lithium chloride free from any other base or acid was treated by slight excess of the purest aqueous redistilled perchloric acid in a flask of fused quartz as described in the earlier research.[1] The evaporation of the water and excess of acid into a current of dry or moist air at gradually rising temperature was also conducted as before. In this way samples of salt fused and dried at 300° were prepared in a condition duplicating closely the portion weighed by the previous investigators. The only difference already mentioned lay in the greater care taken to free the air-current from dust and other impurities. To this end, the air, drawn directly from out-of-doors by a water pump, was forced by the same pump over nearly fifty centimeters of hot copper oxide, through two towers containing potassium hydroxide solution containing a little manganate, through other towers containing a little potassium permanganate, over fused potassium hydroxide, through another shorter tube of red hot copper oxide, again over a large quantity of fused potassium hydroxide, over fifty centimeters of the best obtainable phosphoric pentoxide, that had previously been resublimed in an electrically heated apparatus, and finally through a dust-trap which was placed just before the flask in which the lithium perchlorate was synthesized. The object of the tube of hot copper oxide was to eliminate the trace of hydrogen or hydrocarbon which may exist in the air of cities; the objects of the other tubes are sufficiently evident without explanation. The air filter or dust-trap was placed at the end of the train so that any dust which might have been carried away from any part of the train itself might be eliminated.

No rubber connections were used in this system; it was all fused together except when the juxtaposition of hard and soft glass necessitated ground joints.

Before attempting to measure any moisture that might be retained by the lithium perchlorate, it was necessary to prove that no weighable quantity of water passed through this elaborate drying train. The test was effected by means of a weighed U tube of phosphoric pentoxide as usual. Of course great care was bestowed on the preparation and handling of this tube, since faulty technique here would vitiate the whole work. The tube possessed two tightly fitting glass stopcocks; it had been scrupulously cleaned and was filled with very pure resublimed phosphoric pentoxide. After the work had once begun, this tube was never touched with the hands, but was handled by means of chemically clean cloths or by platinum-tipped forceps. The least possible lubricant of paraffin and fused rubber was used on the stopcocks, and a vanishingly thin layer of

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[1] Richards and Willard, *Publ. Carnegie Inst.*, No. 125, pp. 39, 40 (1910).

the same lined the rubber connectors by which the tube was connected with the train. After a test, only the side-arms of the tube were wiped with several thicknesses of a dry chemically clean cloth. Before each weighing, the U tube was allowed to remain over night under a bell-jar containing a small dish of sulfuric acid. An exactly similar tube, to be used as a counterpoise, containing glass pearls, was kept under a separate similar bell-jar. Before weighing, the tubes were allowed to adjust themselves to the conditions obtaining in the balance case, the air pressure and in both the tube and its counterpoise was made equal to that in the room by very brief opening. An excellent balance, previously used in many atomic weight determinations, was employed, and a tube containing radium bromide was kept in the case, to eliminate electric charges. Weighing took place by the method of substitution, the two tubes being placed on the balance alternately until perfect equilibrium was obtained. Under such conditions, successive weighings of the tube never but once differed from each other by more than 0.00002 g., and the single exception was 0.00003 g. This means that it was possible to weigh the minute quantity of water contained in two or three cubic centimeters of ordinary atmospheric air.

After the long drying train had been swept out with pure air for a number of days, the tube of pentoxide was attached directly to the end of the drying train, in the position usually occupied by the quartz flask of lithium perchlorate, and air was passed through the whole for sixteen hours. During this time the tube gained but 0.00017 g. in weight. Without allowing the current of air to cease flowing, the empty quartz evaporating flask was placed in position and swept out for eight hours, and the pentoxide tube was attached to the side arm of this flask, while air continued to pass through for sixteen hours more. During this test, the tube showed a gain in weight of but 0.00020 g.—essentially the same amount as before. This quantity appeared to be a constant; two attempts to eliminate even this last trace of water by a condensing coil, submerged in liquid air, were unsuccessful.

The final control experiments were now obtained by placing the tube of silver wire and the second dust-trap in position beyond the quartz flask and passing air through the empty apparatus while the weighed tube of pentoxide was adjusted in its place beyond the dust-trap. Many experiments were made in this way, but in no case could a perfect control experiment be obtained. It is probable that moisture gains access during the fitting up of the apparatus, and the amount seemed to be not very different in protracted experiments from what it was during very brief ones. The gain in weight of the pentoxide tube varied from 0.0002 to somewhat over 0.0003 g. Two final control experiments made, one just at the beginning, of the series in which lithium perchlorate was decomposed, and one in the middle of that series, were conducted precisely under the conditions maintained in that series, except that in the control experiments no lithium perchlorate was present. In the first of the blank tests the tube of pentoxide gained 0.00028 g. during five hours; in the second, 0.00034 g., the average being 0.00031 g. Although it would have been more satisfactory to find the source of the water, this was not essential for our purpose, since constancy was all that was needed. As time pressed, and it was necessary to hasten the experiments, the decomposition of lithium perchlorate in this complicated apparatus was now undertaken. Five experiments were made; in three of these only a small amount of the salt was decomposed, although it was kept above 385° for over two hours; whereas in the other two experiments more than half of the lithium perchlorate was decomposed. In the first group the procedure was as follows: Very pure lithium perchlorate, prepared in the quartz flask by the evaporation of lithium chloride with a slight excess of perchloride acid, was heated in a current of dry air for at least five hours at a temperature of 280–300°. This gave samples of the salt in the same condition as the final weighed product of the previous investigators. At this stage the new pieces of apparatus, *i. e.*, the tube of silver wire and the dust-trap, were placed in position; and these were swept out over night by the same air that was passing over the lithium perchlorate, which was kept at 200° throughout that time. In the morning, while the current of air continued without interruption, the tube of silver wire was warmed until the hard glass barely showed a sodium flame, and the dust-trap was heated at 150°. At noon, the tube of phosphoric pentoxide, just previously weighed, was securely wired into position, and a protecting tube of pentoxide was added, so as to prevent any moisture from diffusing backwards into the weighed tube. The temperature of the perchlorate was then raised, during an hour, to the maximum used, and was held within 5° of that point during two hours. Finally the material was gradually cooled to 300°, at which point the pentoxide tube was removed to be weighed the next day. After further cooling, the lithium perchlorate was removed for weighing, so that the extent of its decomposition might be calculated. During the whole experiment, the air pressure in the apparatus was in the outward direction as shown by a mercury manometer sealed into the apparatus at a point just before the air entered the flask of perchlorate. Hence there was very slight opportunity for moist air to penetrate inwards. A new sample of lithium perchlorate was prepared for each experiment, amounting to from 10–15 g. The maximum temperature was 385° in the first experiment, 400° in the second, 400° in the third. The percentage of decomposition, assuming that all of the decomposed material was converted into chloride, varied from 0.033 % in the first to 1.25 % in the third experiment. The weight of water caught was in each case slightly less than that found in the control experiments, namely, 0.00020, 0.00027 and 0.00029 g. Hence no perceptible amount of water was evolved by raising the temperature of the fused perchlorate from 300° to 400°.

In the last two experiments the same procedure as before was followed, except that the perchlorate was heated to a higher temperature, which caused much more far-reaching decomposition. In the fourth experiment, the temperature of 450° was reached after one and one-half hours. At this point the evolution of oxygen was too violent and the experiment had to be stopped. Nevertheless, one would be inclined to think that if any water had existed in the salt it would have been expelled during these ninety minutes; but the tube of pentoxide showed a gain of only 0.00026 g. or less than that during the control experiments (0.00031).

A fifth experiment was more carefully regulated at between 410° and 430° during two hours, so that all the escaping gas passed through the weighed tube of pentoxide at a rate never exceeding three bubbles per second. The perchlorate (of which about three-quarters were decomposed) evolved bubbles and fine dust continuously, carpeting the whole apparatus as far as the dust trap with a thick film; but none could be seen beyond the porcelain cup in the trap. The pentoxide tube gained in weight by 0.00039 g., a trifle more than that shown by the two control experiments, (0.00031). It is possible that a trace of the powder, of almost molecular fineness, may have escaped the trap and caused this slight and unimportant difference.

In conclusion, the results show quite clearly that, within the limit of experimental error, no significant quantity of water can be expelled from lithium perchlorate which has been fused to constant weight, even when the temperature is raised to 430°, and most of the salt is decomposed. The first three experiments show an average gain in weight by the tube of pentoxide less than in the control experiments by 0.00006 g., while the two remaining experiments show an average gain greater than that of the average of the control experiments by but 0.00002 g. None of these differences is greater than the probable error of experiment, and even the largest is not large enough to have an important effect in the atomic weight of silver as found by the method of Richards and Willard. A tenth of a milligram of water in 15 g. of lithium perchlorate would lower the apparent atomic weight of silver calculated with the help of this salt by only about 0.001. Our results therefore seem to afford important evidence in confirmation of the value Ag = 107.871, found by those investigators.

A possible source of uncertainty in the interpretation remains to be considered. It is conceivable that a very small amount of water might be retained by lithium perchlorate without dislodgement up to the point of incipient decomposition, and beyond that point held in new combination as lithium hydroxide. Further consideration suggests arguments against this objection, however. We have found that the raising of the temperature by 130° (that is from 280° to 410°), a change amounting to about one-fifth of the original absolute temperature, causes no water to be evolved. One would expect that were water present in large enough quantity to be of importance, at least a fraction of it large enough to be detected, would have been volatilized before the salt suffered any decomposition at the higher temperature. Again, if any lithium hydroxide had been formed, might it not have attacked the flask, and thus have had its water set free, according to the equation $2LiOH + SiO_2 = Li_2SiO_3 + H_2O$? Usually the susceptibility of the containing vessels to attack is to be regretted, but here it would seem to be possibly more helpful than not.

Although the present paper cannot be considered as more than a preliminary attack upon the problem concerned, it serves to outline the difficulties and especially emphasizes them. With the added knowledge of lithium perchlorate now available, especially in regard to the greater stability of the salt when prepared in a dust-free condition, it will doubtless be possible to obtain an even more accurate evaluation of the ratio of oxygen to lithium chloride and hence of the atomic weight of silver than that found in 1910. It is hoped that this work may soon be undertaken in the Wolcott Gibbs Memorial Laboratory. We take pleasure in expressing our indebtedness to the Carnegie Institution of Washington for generous financial support.

Summary.

1. An effective air-filter or dust-trap for removing impalpable powder from a moderate current of air is described. The importance of its frequent use is emphasized.

2. Lithium perchlorate, prepared entirely in contact with air filtered through this contrivance, was found to be much less easily decomposed by heat than less carefully treated material.

3. The purest lithium perchlorate was found to decompose slowly at from 410° to 430° and rapidly at 450°.

4. It has been shown that no significant quantity of water can be driven out of fused lithium perchlorate by raising the temperature from 300° to 450°, even although most of the salt is decomposed at the higher temperature.

5. This outcome tends to confirm the use of lithium perchlorate as a basis for determining the ratio of oxygen to silver, and supports the value Ag = 107.871 found by Richards and Willard in 1910.

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