neglected, since the mobilities of Mg^{++} and Cu^{++} are almost identical; in fact, the omission of $MgSO_4$ from the chain altered the total E. M. F. by only 0.0001 V. The potential $MgSO_4$ 0.05 M, KCl 0.1 M has been measured directly by Faragher[1] and found to be +0.0016 V. The potential KCl 0.01 M, KCl 1.0 M is calculated to be +0.0004 V. We have therefore exclusive of liquid potentials Cu, $CuSO_4$ 0.005 M || N. E.; **E** = 0.0168 V. Assuming that the concentration of Cu^{++} is 0.00315 M in $CuSO_4$ 0.005 M, and that the activity is proportional to the concentration, we calculate for the normal potential of copper against the normal electrode

$$\text{Cu, Cu}^{++} \parallel \text{N. E.; } \mathbf{E}^\circ = -0.0571 \text{ V.}$$

Now we have

$$H_2, H^+ \parallel \text{N. E.; } \mathbf{E}^\circ = +0.2776 \text{ V.}^2$$

and subtracting gives

$$\text{Cu, Cu}^{++} \parallel H^+, H_2; \mathbf{E}^\circ = -0.3347 \text{ V.}$$

which is the value obtained in this way for the normal potential of copper. This differs from the more accurate value obtained above by more than one centivolt. The large discrepancy is doubtless partly due to the assumption that the concentration and activity of Cu^{++} in $CuSO_4$ 0.005 M can be calculated directly from the conductivity, but is probably chiefly to be ascribed to the uncertainty in the liquid potentials, especially that between $CuSO_4$ 0.005 M and 0.05 M.

BERKELEY, CAL.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS, PUBLICATION NO. 17.]

THE TRANSFERENCE NUMBER, CONDUCTANCE, AND IONIZATION OF HYDRIODIC ACID AT 25°.

BY E. K. STRACHAN AND VEE GIH CHU.

Received March 23, 1914.

CONTENTS.

1. Purpose of the Investigation.

When the degree of dissociation of an electrolyte is calculated from the conductivity ratio in the usual manner, the assumption is made that the relative mobilities of the ions and hence also the transference numbers for the electrolyte are independent of the concentration. This assumption is approximately true for most dilute salt solutions, but in some in-

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[1] This work is about to be published.

[2] Based upon measurements of Sebastian about to be published.

stances, notably in the case of lithium chloride,[1] the condition is apparently not fulfilled. In the case of strong acids, also, the transference number in the concentration range 0.005 to 0.1 normal, as obtained by direct measurement, is not in agreement with the ordinarily accepted value for the conductance of the hydrogen ion at infinite dilution.[2]

In such cases the degree of ionization may be calculated from the values of the *individual ion conductances*, as explained in a previous paper.[3] The expression, there derived, for the degree of ionization, γ, of hydriodic acid is

$$\gamma = \frac{\Lambda T_I}{\Lambda_{0\,I}} \left(\frac{\eta}{\eta_0}\right) \tag{1}$$

in which Λ is the equivalent conductance of the hydriodic acid solution, (η/η_0) is its relative viscosity, T_I is the transference number of the iodide ion constituent in the solution and $\Lambda_{0\,I}$ is the equivalent conductance of the iodide ion at infinite dilution.

At the time of the investigation referred to, the above data were not available in the case of hydriodic acid solutions. Consequently the conductances of several such solutions were determined and these values, together with some preliminary values of the transference number, were made the basis of the calculations in the previous paper. Since then other more careful and complete conductance determinations have been made and the transference measurements completed. It is the purpose of the present paper to present the results of these determinations and the values of γ to which they lead.

2. The Transference Experiments.

The transference number was determined by the Hittorf method, using a silver anode and a silver iodide cathode. At the end of each experiment three middle portions as well as both electrode portions were analyzed in order to make sure that no mixing had occurred.

The apparatus employed is shown in the accompanying diagram (Fig. 1). In order to prevent mixing from convection currents due to local heating, the constricted portions of the apparatus were, with one exception, placed at the top so that the heated portions could not rise and cause stirring. The exception occurs in the stopcock at the bottom of the anode section, *A*. This was made small on account of the difficulty in constructing one with a bore as large as that of the rest of the apparatus. Convection currents at this point, however, could cause stirring only within the anode portion and so would result in no harm. The apparatus was made in three sections, which were connected by rubber tubing at the points

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[1] Cf. Washburn, *Proc. Amer. Electrochem. Soc.*, **21**, 134 (1912).

[2] See Noyes and Falk, THIS JOURNAL, **33**, 1460 (1911).

[3] Washburn and Strachan, THIS JOURNAL, **35**, 690 (1913). See, further, Washburn, *Loc. cit.*

d and *e*. The anode portion extended from the anode, *A*, to the stopcock, and the cathode portion from the cathode, *C*, to the dotted line *c*. The remainder of the apparatus was designed to contain the three middle portions which are called the anode middle, the middle, and the cathode middle, and are designated, respectively, by the letters M_a, M, and M_c.

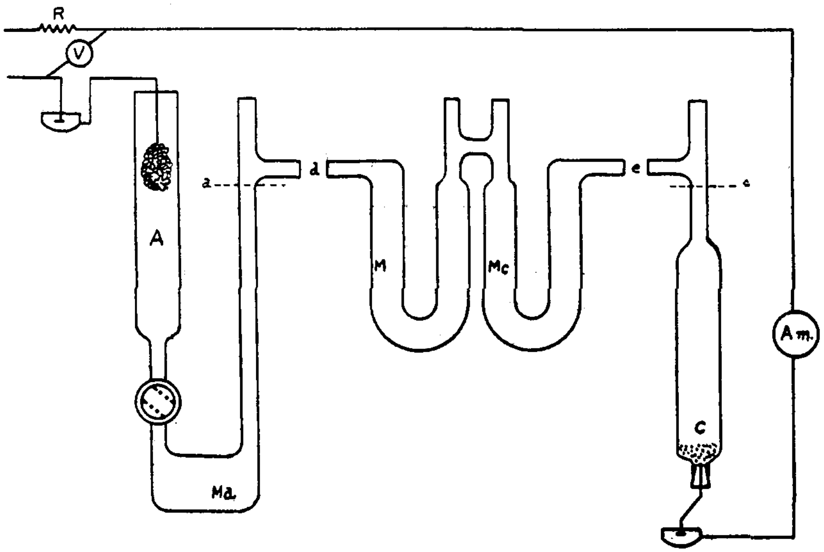

Fig. 1.

The three sections of the apparatus were of such sizes that the portions of the solution withdrawn for analysis amounted to about 250 cc. each, thus making it possible to secure an accuracy of about 0.01% in the analyses of the more dilute solutions.

The anode consisted of a silver spiral made of several hundred turns of fine wire in order to obtain a large electrode surface. Before using, it was cleaned by dipping in warm nitric acid until it was violently attacked, and then washing several times with water. After being dried, it was suspended in the top of the anode section of the apparatus and connected as shown in the figure. The cathode consisted of a few turns of silver wire which had been cleaned in warm nitric acid and coated with a thin layer of silver iodide by electrolysis. The wire so prepared, after it had been placed in the transference apparatus, was covered with an excess of freshly precipitated silver iodide as indicated in the figure.

The silver coulometers used in this investigation were of the ordinary filter paper type, the cathode consisting of a platinum dish and the anode of a silver button wrapped in filter paper. One coulometer was connected to the anode, and the other to the cathode as shown in Fig. 1, in order to detect any loss of the current that might occur during the experiment.

Preparation of Materials. Water.—All water used was conductivity water obtained from a special still.

Hydriodic Acid.—Iodine was distilled from potassium iodide solution, and then reduced by yellow phosphorus and water. The resulting crude product was distilled twice in an atmosphere of hydrogen, and yielded a perfectly colorless distillate which boiled at 127°. Solutions of various concentrations were prepared by diluting this acid with the requisite amount of air-free distilled water, the exact concentration being determined by precipitating the iodine as silver iodide. In some of the earlier experiments the crude acid was distilled in contact with the air. The distillate in those cases was colored dark brown by the free iodine. When this had been removed by shaking the solution with benzene, the same transference number was obtained as when the originally iodine-free acid was used. These earlier experiments are, therefore, included with the later. During the transference experiments some free iodine appeared in the solution, owing to the reaction $4HI + O_2 = 2H_2O + 2I_2$, but this was shown by analysis never to exceed a few hundredths of a per cent.

The *silver nitrate* used both for the analyses and in the coulometers was Kahlbaum's C. P. salt. A 20% solution was used in the coulometers. It was usually freshly prepared, and never used more than twice. A 0.03 normal solution was used in the analyses.

Experimental Procedure.—The apparatus was thoroughly cleaned and dried, and the three glass parts placed in the supports and joined at *d* and *e*. The electrodes were inserted and the cathode covered with about 3 g. of freshly precipitated silver iodide which had been washed repeatedly with the solution to be used in the experiment. Then the cathode side was filled with the solution, care being taken not to stir up the silver iodide on the electrode. To accomplish this the solution was poured very slowly through a dropping funnel with a long stem, at the lower end of which was an upward hook with a small opening. While the hydriodic acid was being added the funnel was gradually raised so that the liquid would be delivered just at the surface of the solution already in the apparatus. After this the other sections of the apparatus were also filled with the solution. Air bubbles were removed by means of a clean dry rod. The anode spiral was fixed so as to occupy a position about three centimeters above the stopcock. This left considerable solution above the electrode, which stirred slowly during the run and prevented the exhaustion of the electrolyte in the immediate vicinity of the electrode. To prevent any leakage of the solution or current, all joints of the apparatus were covered with liberal amounts of melted beeswax, and the lead wire from the cathode was conducted out of the bath through a rubber tube. The whole apparatus was then placed in the thermostat to such a depth that the water of the bath and the solution in the apparatus were at the same level so as to eliminate hydrostatic pressure. The electrical connections were then made as shown in the diagram.

After the solution had come to the temperature of the thermostat, which was maintained at 25°, the circuit was closed, and the rheostat, *R*, adjusted to give the proper current strength. The strength of the current and the duration of the experiment varied with the concentration of the solution. In most cases the current was about 30 milliamperes, and the time about eight hours.

As soon as the experiment was completed, the circuit was broken and the stopcock closed. Then by introducing a clean, dry pipet into the apparatus through the small tubes at the top, samples of the three middle portions were obtained. These were transferred to tared Erlenmeyer flasks and weighed. After the removal of these portions the anode and cathode lead wires were disconnected, the apparatus taken out of the thermostat and dried on the outside. It was then disconnected at *d* and *e* and the anode and cathode sections were stopped with paraffined rubber stoppers. Next, the glass stopcock in the anode section was opened and the anode portion mixed thoroughly by shaking. The contents of the cathode section were mixed in a similar manner. The two parts of the apparatus containing the electrode portions were then cleaned and dried on the outside and weighed to the nearest milligram. As much of the clear solution from the anode as possible was then transferred to a tared Erlenmeyer flask, weighed and analyzed. The anode section, together with the silver spiral, was washed, dried with alcohol, and weighed. This weight, subtracted from the weight of the anode section filled with the solution, gave the weight of the anode portion. The bulk of the cathode portion was filtered through a tared Gooch crucible into a clean, dry filter flask. The filtrate was immediately transferred to a tared Erlenmeyer flask and weighed, and served as the sample for analysis. The residue from the cathode, which consisted of gray metallic silver and silver iodide, was left in the Gooch crucible, and was washed, dried and weighed. The empty cathode section was also cleaned, dried and weighed. In order to obtain the weight of the total cathode portion the weight of the cathode section plus the weight of the silver and iodide in the Gooch crucible was subtracted from the weight of the cathode section before it was emptied.

All the solutions were analyzed by precipitating the iodide as silver iodide by a 0.03 normal silver nitrate solution. Before precipitation, the hydriodic acid solution was decolorized with a few drops of sodium sulfite and then diluted to 0.03 normal. Baxter[1] has shown that at this concentration of hydriodic acid and silver nitrate there is little danger of occlusion taking place during the precipitation.

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[1] *Proc. Am. Acad. Arts and Sci.*, 41, 78 (1905).

Calculation of Results.—The calculation of the transference numbers given in Table I was made in the following manner. The mass of water in the electrode portion was obtained by subtracting from the weight of the portion the weight of hydriodic acid contained in it. The mass of the water was then multiplied by the ratio of hydriodic acid to water in the original solution, and thus the mass of hydriodic acid in that amount of water before electrolysis was obtained. To determine the mass of hydriodic acid transferred, the mass of hydriodic acid present in the electrode portion before electrolysis was subtracted from that present after electrolysis in the case of the cathode portion, and *vice versa* in the case of the anode portion. The transference number of the cation was obtained by dividing the number of equivalents of hydriodic acid transferred by the number of equivalents of electricity passed through the solution.

The results of the transference-number measurements are given in Table I, the number at the top of each column being the number of the experiment. Concentrations are expressed in equivalents per 1000 g. of solution.

TABLE I.—TRANSFERENCE NUMBER OF HYDRIODIC ACID AT 25°. DATA AND RESULTS.

	1.	2.	3.	4.
Concentration	0.2	0.16	0.09	0.06
Wt. Ag in coulometer A	1.3272	1.0084	0.6891	0.7239
Wt. Ag in coulometer C	1.3269	1.0076	0.6886	0.7239
Wt. electrode portion A	197.313	203.471	192.58	202.811
Wt. electrode portion C	237.704	239.261	236.663	236.376
% HI in portion M_c	......	2.1064	1.1897	0.70501
% HI in portion M	2.6527	2.1060	1.1889	0.70452
% HI in portion M_a	2.6528	2.1070	1.1888	0.70392
% HI in portion A	2.0112	1.6317	0.84169	0.36619
% HI in portion C	3.1818	2.5085	1.4686	1.0233
Equivalents of electricity	0.012301	0.009344	0.0063859	0.006710
Grams HI transferred (A)	1.2987	0.9859	0.6762	0.7076
Grams HI transferred (C)	1.2915	0.9839	0.6700	0.7035
Transference no. of cation (A)	0.825	0.825	0.828	0.825
Transference no. of cation (C)	0.821	0.823	0.820	0.819

The values of the transference number contained in Table I are summarized in Table II.

TABLE II.—TRANSFERENCE NUMBER OF HYDRIODIC ACID AT 25°.

	Transference number as calculated from	
Concentration.	Anode portion.	Cathode portion.
0.20	0.825	0.821
0.16	0.825	0.823
0.09	0.828	0.820
0.06	0.825	0.819
Mean	0.826	0.821
A. D.	0.001	0.001

An examination of the table shows that the value of the transference number calculated from the cathode portion is in every case smaller than that calculated from the anode portion. This difference is greater than the experimental error and requires an explanation. It can not be attributed to the formation of the slow moving AgI_2^- ion at the cathode, for a simple calculation shows that this ion could move toward the anode but a few centimeters during the course of the experiment, and so could not remove any iodine from the cathode portion.[1] The source of the discrepancy in the values obtained from the two electrode portions undoubtedly lies in the adsorption of some of the acid by the silver iodide cathode. The concentration of acid in contact with the cathode may change during the course of the experiment from about 0.1 normal to 0.4 normal or higher. It is to be expected that the silver iodide will adsorb a greater amount of acid in contact with the stronger solution. Any acid so adsorbed would be removed when the silver iodide was separated from the cathode portion of the solution. Consequently the value of the transference number derived from the cathode portion would be too small. A brief experiment was made in order to test this hypothesis. A weighed amount of silver iodide was shaken with a weighed amount of hydriodic acid solution, the strength of which was accurately known. After having stood over night a portion of the acid was removed and analyzed. In this way it was found that, after correction was made for the water originally present in the silver iodide, 5 g. of the latter had removed 0.0190 g. of acid from a 0.1 normal solution, and 0.0256 g. from a 0.4 normal solution. This result is not in quantitative agreement with the results of the transference experiments, yet is sufficiently close to show the cause of the discrepancy, and to indicate this as the probable source of error in the above transference experiments. For this reason the value 0.826 obtained from the concentration change of the anode portion has been adopted as the transference number of the cation of hydriodic acid.[2] Within the concentration range studied it appears to be independent of the concentration.

3. The Relative Viscosities of Hydriodic Acid Solutions.

We are indebted to G. Y. Williams for measurements of the viscosity of the acid in the quartz viscosimeter devised in this laboratory.[3] Two solutions were examined, one of 0.1963 normal concentration, and

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[1] That some $HAgI_2$ is formed at the cathode is evidenced by the slight precipitate of silver iodide which occurred when the cathode portion was diluted preparatory to analysis. Such a precipitate occurred only when the stronger solutions of acid were used, and then, of course, was filtered out of the solution before proceeding with the analysis.

[2] An additional reason for accepting this value as the correct one is the fact that when it is substituted in the equation $\Lambda_H = \Lambda/Ta - \Lambda_{0I}(\eta_0/\eta)$ the value 364 is obtained for the equivalent conductance of the hydrogen ion, which agrees with the observations of Noyes and Sammet based on transference experiments with hydrochloric acid, *loc. cit.* For values of Λ and (η_0/η) see Table III.

[3] Washburn and Williams. THIS JOURNAL, **35**, 737 (1913).

the other 0.09839 normal, and their relative viscosities found to be 0.99542 and 0.99660, respectively. Values of the viscosity at other concentrations were obtained by linear interpolation.

4. Conductance and Ionization.

The conductance measurements were made by the Kohlrausch method, the pipet form of conductance cell in use in this laboratory,[1] and the extended bridge wire described by Washburn and Bell[2] being employed. All of the glass apparatus employed in handling the solutions was cleaned with warm chromic acid cleaning-mixture and steamed out for several hours before being used. The conductivity water was obtained from a special still and had a specific conductance of 0.6×10^{-6} mhos at 25°. Two stock solutions of hydriodic acid were prepared, one being about 0.2 normal and the other about 0.02 normal. Each was carefully analyzed by precipitating the iodide as silver iodide. The rest of the solutions were made by diluting weighed amounts of the stock solutions with weighed amounts of conductivity water.

Immediately after the preparation of each solution its conductivity was measured. The solutions remained almost if not quite colorless during the determination. After filling the conductance cell, it was placed in the thermostat at 25 ± 0.01°, and left there a short time. The conductance was then measured twice at intervals of fifteen minutes, in order to be sure that the solution had attained the temperature of the bath. The cell was then emptied and refilled with the solution and another measurement made. The various determinations of the conductance of the same solution agreed within less than 0.02%. The conductance cell was one that has been in use in this laboratory for a number of years, and has a cell constant of 0.6222. It was calibrated again by means of a 0.1 normal solution of potassium chloride just before being used in this investigation, and the constant found to be unchanged.

The results of the conductance measurements are shown in Table III. Column I contains the concentrations in equivalents per liter of the various solutions measured, and Column II their respective equivalent conductances expressed in reciprocal ohms. Column III contains the densities corresponding to the concentrations shown in Column I. The figures in Column V are the equivalent conductances at the round concentrations shown in Column IV. They were obtained from the figures in Columns I and II by graphical interpolation. The conductances of solutions above 0.01 normal were read off a curve obtained by plotting the equivalent conductance, Λ, against the concentration, C. In order to arrive at the conductances at round concentrations below 0.01 normal and the conductance at zero concentration, $1/\Lambda$ was plotted against

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[1] Washburn and MacInnes, This Journal, 33, 1686.

[2] Washburn and Bell, *Ibid.*, 35, 177.

$(C\Lambda)^n$ in the usual way, employing different values of n until one was found that made the curve nearest to a straight line. In this way 0.40 was obtained as the value of n. The equivalent conductance at zero concentration was found to be 426.2. The equivalent conductance of the iodide ion may be taken to be 76.5, which makes that of the hydrogen ion appear practically 350, a result obtained by a number of observers. The measured values of Λ for the concentrations 0.002 and 0.001 normal fall below the curve drawn through the points corresponding to the values shown in Column of V the table. Owing to the uncertainty which exists as to what water correction should be applied to the measured conductances of very dilute solutions, it is difficult to state whether the interpolated or the measured values are the most nearly correct. Other observers have noted the same phenomenon.[1] The water correction was applied by subtracting the specific conductance of the water from that of the solution.

TABLE III.[2]—CONDUCTANCE AND DISSOCIATION OF HYDRIODIC ACID AT 25°. 1913 ATOMIC WEIGHTS.

I. C.	II. Λ.	III. D_4^{25}	IV. C.	V. Λ.	VI. η/η_o.	VII. $\gamma = \Lambda Ta/\Lambda_o 1(\eta/\eta_o)$.	VIII. $\gamma = \Lambda/\Lambda_o(\eta/\eta_o)$.
0.2217	381.2	1.0181	0.200	383.0	0.9954	86.71	89.45
0.1124	391.8	1.0082	0.100	393.6	0.9966	89.21	92.04
0.05435	400.4	1.0025	0.050	401.2	0.9980	91.07	93.95
0.02507	406.6	0.9996	0.020	408.2	0.9992	92.77	95.70
0.01036	412.2	0.9980	0.010	412.4	1.0000	93.80	96.76
0.005144	415.5	0.9975	0.005	415.7	1.0000	94.55	97.54
0.002152	417.5	0.9972	0.002	418.7	1.0000	95.23	98.24
0.001009	418.6	0.9971	0.001	420.5	1.0000	...	98.66
....	...	0.9971	0.000	426.2	1.0000	...	100.00

In Column VII of the table, values of the degree of dissociation of the acid

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[1] Goodwin and Haskell, *Proc. Am. Acad.*, **40**, 514; Bray and Hunt, THIS JOURNAL, **33**, 786 (1911).

[2] The values of the degree of dissociation shown here differ from those used in calculating the equilibrium between arsenious acid and iodine (THIS JOURNAL, **35**, 690) by about 1%, the discrepancy being due to an error in calculating the concentrations of the solutions employed in the former investigation. The figures shown here indicate that the true value of the arsenious acid iodine equilibrium is 4% higher than that given (*loc. cit.*), that is, 5.76×10^{-2} in place of 5.54×10^{-2}, a difference, however, which is within the experimental error in determining this constant. Another more serious error occurs in Part III of the former investigation where the details of the calculation of the heat of the reaction are presented. Some of the thermochemical data employed in this calculation were not corrected for the work of the process. When these corrections are made a heat effect of 1540 calories is obtained and this heat effect indicates that the equilibrium constant *decreases* with rise in temperature, a result which is contrary (in sign) to the observations of Roebuck. This result is probably to be attributed to errors in some of the thermochemical data employed, and the question of the value of the heat of the reaction must be left open until the equilibrium has been studied at another temperature.

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.

Received March 6, 1914.

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.