

3. A solvated cupric formate of the formula $2\text{Cu}(\text{CHO}_2)_2 \cdot 3\text{HCHO}_2$ has been isolated and analyzed.

4. The results here obtained have been compared with those previously reported for the corresponding ternary system in acetic acid. Attention has been called to the similarity between these two cases, and certain relationships with analogous aqueous systems have been pointed out.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

THE TRANSFERENCE NUMBERS OF POTASSIUM CHLORIDE. NEW DETERMINATIONS BY THE HITTORF METHOD AND A COMPARISON WITH RESULTS OBTAINED BY THE MOVING BOUNDARY METHOD

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We have obtained, in this Laboratory, by the moving boundary method a large amount of data, for the most part still unpublished, on the transference numbers of electrolytes. Many of these data differ so widely from the published values for transference numbers obtained by the Hittorf method that the question arose seriously in our minds as to whether the two methods (the Hittorf and moving boundary) obtain measures of the same property of the solutions of electrolytes. With potassium chloride, for instance, the measurements in dilute solutions by Jahn and associates² of the cation transference number by the Hittorf method gave values on the average 1% above the determinations by the moving boundary method. On the other hand, Dewey,³ working at 0.2 *N*, obtained *lower* values for this constant by the Hittorf method than those obtained by MacInnes and Brighton⁴ and Smith and MacInnes⁵ using the moving boundary procedure. We have, however, found it possible to interpret the conductance and transference data, as a whole, for a group of simple electrolytes provided the newer moving boundary results are used. This is far from being true with reference to most of the Hittorf data now published. These new data and their interpretation will be the subject of a series of papers from this Laboratory. It was evidently very important to find out whether the disagreement of the results of the two methods for obtaining transference numbers is due to

¹ Department of Chemistry, Northwestern University, Evanston, Illinois.

² Jahn and Bogdan, *Z. physik. Chem.*, **37**, 673 (1901); Jahn and Hertz, *ibid.*, **58**, 641 (1907). The "best values" of the "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. VI, p. 310, are largely based on this work.

³ Jane Dewey, *THIS JOURNAL*, **47**, 1927 (1925).

⁴ MacInnes and Brighton, *ibid.*, **47**, 994 (1925).

⁵ Smith and MacInnes, *ibid.*, **47**, 1009 (1925).

experimental error or to a fundamental difference in the quantities measured. Hittorf and moving boundary measurements on solutions of potassium chloride were accordingly carried out, using all possible efforts to attain accuracy in the results. This paper will deal with the experimental details of the Hittorf measurements and their comparison with results obtained by the moving boundary method. The details concerning the latter will appear in another paper from this Laboratory.

The Hittorf Apparatus

The apparatus, shown in Fig. 1, used for the Hittorf measurements was similar to that developed by Washburn⁶ but differed from it in several details. It was made of

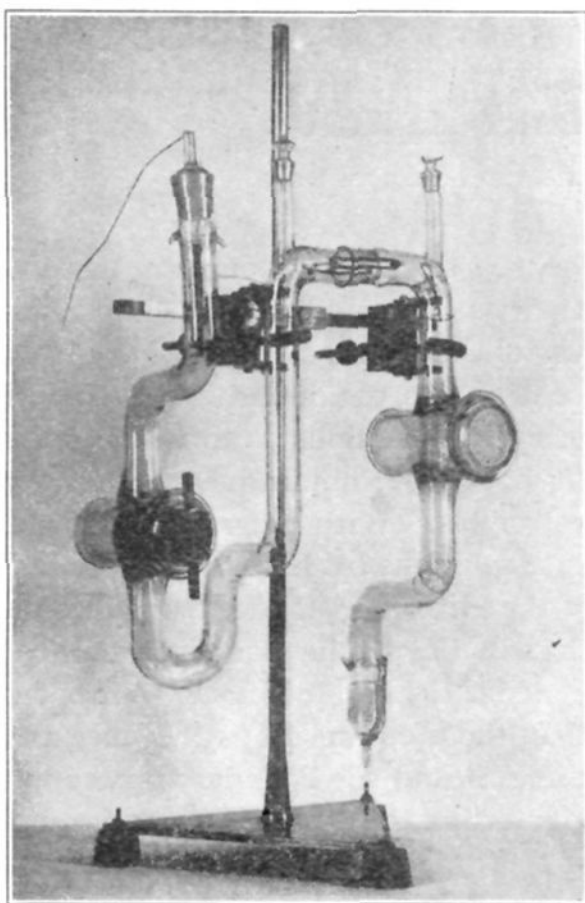


Fig. 1.

Pyrex glass. A sufficient idea of the dimensions of the apparatus can be obtained from the data that the bore of the tubing used was 2 cm. and the full length of the tubing was 135 cm. The right angled turns of the tubes as shown were included for the purpose of breaking up convection currents due to heating, and were probably effective for the purpose because as soon as they were inserted in the apparatus the results showed a decided improvement. Convection currents were also minimized by the use of small current densities. A source of unequal heating along the tube which can cause convection is the bore of the large stopcocks. Though these were made the same size as the rest of the tube, adequate circulation of the thermostat water around them is not readily obtained. More adequate stirring around the portion of the solution in the bore of the stopcock was obtained by the design of stopcock shown in Fig. 1, and diagrammatically in section in Fig. 2. The usual key or handle for turning the stopcock has been cut away, leaving a hollow shell through which the thermostat water can flow freely. When it is necessary

to turn the stopcock a metal key is inserted as is shown on the left-hand side of Fig. 1 and by dotted lines in Fig. 2. As an additional precaution against mixing, the thermostat (a 30 × 30 × 40 cm. glass battery jar) was mounted on the vibration-free support, which has been described in a previous paper.⁷ The use of this support was also accompanied by an improvement in the results. The thermostat was stirred by a mechanism mounted independently of the vibration-free support. The stirring rate was regulated to produce no perceptible vibration of the thermostat.

⁶ E. W. Washburn, *THIS JOURNAL*, 31, 322 (1909).

⁷ MacInnes, Cowperthwaite and Huang, *ibid.*, 49, 1710 (1927).

Preparation of Electrodes and Apparatus.—The anode was made from No. 23 B and S gage silver wire coiled into concentric helices to a diameter such that it would fit readily into the apparatus. It was carefully washed by standing it for several hours in distilled water. It was then dried in an oven, after which it was sealed into the glass stopper of the apparatus with de Khotinsky cement. If the silver appeared dark it was heated in a flame, or in an electric furnace to 400°, until the oxide or sulfide was decomposed. If this was not done there was a tendency for the solution in contact with the electrode to become alkaline. Since, during an experiment, the wire becomes coated with silver chloride, it was reduced electrochemically before the next determination. Twenty-five grams of the wire was necessary for the more concentrated solutions, and proportionately smaller amounts for the dilute solutions.

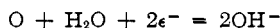
The cathode was also made of No. 23 silver wire coated electrolytically with silver chloride. It was cleaned thoroughly, usually by standing in distilled water overnight. It is very important that a thorough cleaning be carried out as the solution surrounding the electrode in the apparatus may readily become contaminated from occluded electrolyte. The cathode was dried for about an hour at 140°, after which it was sealed into the apparatus with cement.

Between each run the Hittorf apparatus was cleaned by allowing chromic acid to stand in it for some time. After rinsing with distilled water the apparatus was dried by playing a Bunsen flame over the surface while a current of dry air was passed through it. When dried the stoppers carrying the electrodes (previously greased and weighed) were inserted.

The stopcocks, after being partly warmed, were greased with a commercial preparation.

Preparation of Solutions.—The solutions were prepared by weighing out the requisite amounts of potassium chloride and water to yield solutions of the desired normalities in equivalents per liter at 25°. The computation was made using the density data on potassium chloride solutions given in the "Critical Tables." An excellent grade of conductivity water was used in making up solutions. The potassium chloride was a c. p. grade which was further purified by precipitation with hydrogen chloride gas, followed by crystallization from conductivity water and proved to be free from sodium by spectroscopic test.

A difficulty encountered early in this research was that the cathode portion tended to become alkaline even though there was no trace of gas evolution at the electrodes. An investigation disclosed the fact that this alkalinity was due to dissolved oxygen which, presumably, entered into the reaction:



By saturating the solution with purified nitrogen there was no further tendency for the solution to become alkaline. All the work recorded in this paper was carried out using oxygen-free solutions. The procedure for filling the transference apparatus with such solutions was as follows. The solution was placed in a special Erlenmeyer flask of a

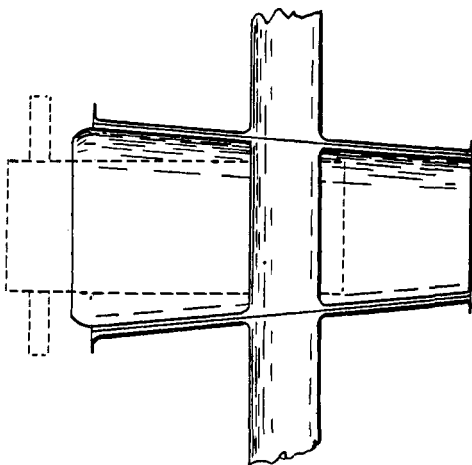


Fig. 2.

design already described.⁸ A stream of purified nitrogen was first passed through a saturator containing the same solution as that in the special flask which followed it. The gas bubbled through the solution in that flask and then passed to the transference apparatus, which was furnished with an exit trap to prevent entrance of air. After running the gas for about one hour, which was sufficient to sweep out the oxygen from the solution and apparatus, a half turn of the head of the special flask caused the gas pressure to force the solution into the transference apparatus.

The Coulometers.—Two Richards type porous-cup coulometers were used, one at the anode end and another at the cathode end of the apparatus. Agreement of the weights of these two coulometers is evidence that no current has leaked away in the thermostat. The electrolyte was 10% silver nitrate solution, and No. 8 silver wire was used as anode. Platinum dishes of 75-cc. capacity were used for the more concentrated solutions, and platinum crucibles were used as cathodes for the more dilute solutions. The coulometers were covered with glass bell jars to protect them from dust particles.

The Electrolysis and Analysis

After the Hittorf apparatus was filled as described above, it was placed in the thermostat for at least one-half hour before the current was turned on, after which the electrolysis could be allowed to proceed overnight without attention. The current was supplied from small storage cells yielding about 15 volts. For the 0.02 *N* solution a current of 0.002 ampere was used. This was increased progressively for measurements with higher concentrations until a current of 0.045 ampere for the 3 *N* solutions was reached.

Following the electrolysis the solution in the apparatus was separated, according to Washburn's scheme, into anode, anode middle, middle, cathode middle and cathode portions. The anode and cathode portions were separated merely by turning the stopcocks. The other samples were drawn from the volume between the two stopcocks. The three middle portions were removed by suction directly into weight burets through clean dry glass tubing. The solutions in the two electrode portions were not removed into weight burets until the two portions into which the apparatus may be separated had been cleaned on the outside, weighed and the solution thoroughly shaken after opening the stopcocks. Portions of the resulting solutions were then transferred into weight burets. Each half of the apparatus, with its electrode, was dried and weighed, and the weight of the solution in each electrode portion could then be computed.

The analyses were carried out using the differential potentiometric method described by MacInnes and Dole.⁸ Since the details of the method as applied to the determination of chlorides are given in that paper they will not be repeated here. However, a precision of about 0.003% is obtained in the analyses. With practice the determinations can be carried out quite rapidly, as many as six being possible in one day. The method has the great advantage of requiring no filtering or transfer of solutions, and

⁸ MacInnes and Dole, *THIS JOURNAL*, 51, 1119 (1929).

thus corrections for turbidity, etc., necessary with other precision methods for chlorides, are avoided.

Since the most concentrated solutions became turbid on dilution, it was evident that in such cases silver chloride from the electrodes was dissolving in the electrolyte. By allowing the diluted solution to stand, the colloidal material collected and could be filtered off and weighed and an appropriate correction made to the weight of the electrode portions.

The Results

A series of determinations at 0.1 *N* was made the results of which will not be tabulated, as they did not reach the accuracy of the later work. However, they demonstrated the desirability of the vibration-free support, the bends in the tubing of the Hittorf apparatus, and the air-free solutions, as well as minor experimental improvements. The data concerning the experimental results which attained the desired accuracy are given in Table I. This table is self-explanatory. Two figures for a weight or analysis refer to duplicate determinations. These agreements and the agreements of the analyses of the three middle portions give evidence of the accuracy of the work and of the, very essential, lack of mixing of the electrode and middle portions.

TABLE I

DATA CONCERNING DETERMINATIONS OF TRANSFERENCE NUMBERS OF POTASSIUM CHLORIDE AT 25°

Concentration.....	0.02 <i>N</i>	0.05 <i>N</i>	0.1 <i>N</i>	0.5 <i>N</i>	0.5 <i>N</i>	1.0 <i>N</i>	1.0 <i>N</i>	3.0 <i>N</i>	3.0 <i>N</i>
Amperes.....	0.002	0.0035	0.006	0.026	0.018	0.03	0.03	0.036	0.044
Volts.....	15	15	15	15	10	8	8	6	5
Time of electrolysis, hours.....	23	22	23	20.5	26	19.5	20.5	20.5	16.5
Wt. Ag in coulometers.....	0.16024	0.3217	0.6136	2.1132	1.9769	1.9184	2.4837	2.8758	2.7760
	.16043	.3215	.6135	2.1128	1.9767	1.9180	2.4833	2.8756	2.7756
Wt. anode portion..	117.79	116.18	117.51	119.69	119.48	124.00	121.41	130.29	131.10
Wt. cathode portion	120.99	120.34	120.17	122.93	125.66	135.30
% KCl in anode portion.....	0.10336	0.27963	0.56662	3.0778	3.1151	6.6655	6.5099	19.1821	19.207
	.10342	.27950	.56665	3.0780	3.1151	6.6660	6.5100	19.1814	19.203
% KCl in anode middle portion...	.14932	.37299	.74219	3.6520	3.6531	7.1502	7.1478	19.775	19.777
% KCl in middle portion.....	.14948	.37297	3.6537	3.6537	7.1474	7.1474	19.776
% KCl in cathode middle portion...	.14939	.37302	.74217	3.6543	7.1495	7.1485	19.777	19.775
% KCl in cathode portion.....	.19410	.46274	.91350	4.1788	7.7673	20.329
	.19398	.46294	.91369	4.1784	7.7668	20.327
KCl transferred anode.....	.05428	.1090	.20768	0.71470	0.6680	0.6457	0.8343	0.9655	0.9331
KCl transferred cathode.....	.05408	.1086	.20763669883809309
Trans. No. T_K (anode).....	.4902	.4904	.4898	.4895	.4890	.4871	.4861	.4859	.4864
Trans. No. T_K (cathode).....	.4884	.4884	.4897490348824853
Mean value T_K4893	.4894	.4898	.4895	.4896	.4871	.4871	.4859	.4858

Discussion of the Results

The average values of the cation transference numbers at each concentration are given in Table II, and, for comparison, the values by the moving boundary method obtained in this Laboratory by Dr. L. G. Longworth, to whom we are indebted for permission to quote his results before their formal publication. It will be seen that, at the concentration at which measurements were made by both methods, there is quite extraordinary agreement

TABLE II
CATION TRANSFERENCE NUMBERS, T_K , OF POTASSIUM CHLORIDE DETERMINED BY THE HITTORF AND MOVING BOUNDARY METHODS

Concn., N ...	0.01	0.02	0.05	0.10	0.20	0.50	1.0	3.0
T_K , Hittorf...4893	.4894	.48984896	0.4875	0.4857
T_K , M. B.	0.4898	.4896	.4900	.4899	.4891

Comparisons could not be made at higher concentrations because it is not yet possible to get accurate data by the moving boundary method at concentrations above about 0.2 N . That method is, however, accurate at concentrations so low that the chemical analyses necessary in the Hittorf method become difficult. It is interesting and most gratifying, that the two methods based on phenomena, superficially at least, so dissimilar should yield results that are in such excellent agreement.

As has been said in the introductory paragraph of this paper, these results differ quite widely from the measurements of previous workers in this field. That these early determinations led to values that differed considerably among themselves, and varied widely from later measurements is shown in Fig. 3.⁹ Here the determinations, made between 18 and 30°, of the cation transference number of potassium chloride are given as ordinates against the cube root of the corresponding concentrations, the latter function being used only to obtain a convenient plot. Comparisons may be made of data in this temperature range because, within the experimental error, there is no apparent temperature coefficient of the transference number.¹⁰ Washburn's solutions contained 0.1 mol of raffinose in addition to 1.24 mols of potassium chloride. The earlier moving boundary results will be considered in another paper.

It is not possible to assign, with certainty, reasons for the deviations of the earlier work from what we believe to be the correct values, particularly as there are many chances for obtaining inaccurate results with the Hittorf

⁹ Where determinations by the German workers yielded checks to 0.001 the points have been shifted slightly along the ordinates so as not to overlap. They can still, however, be read from the plot to the accuracy given.

¹⁰ References to values plotted in Fig. 3 and not mentioned elsewhere in this paper are, Richter, *Z. physik. Chem.*, 80, 449 (1912), and Steele and Denison, *J. Chem. Soc.*, 81, 456 (1902).

method. Errors may arise from inaccurate analytical procedures, evaporation of the solvent, mixing of electrode and middle portions, electrical leaks, etc. An important source of error which would, since anion concentrations were determined, tend to give high cation transference numbers, particularly in the dilute solutions, is the fact that in the early work no correction was made for the conductance of the water used. It is difficult to estimate the magnitude of errors arising from this source. Ordinary distilled water would produce deviations of about 0.5% in the most dilute solutions. If the water stood for any time in soft glass containers, it could readily produce errors of several times this magnitude in

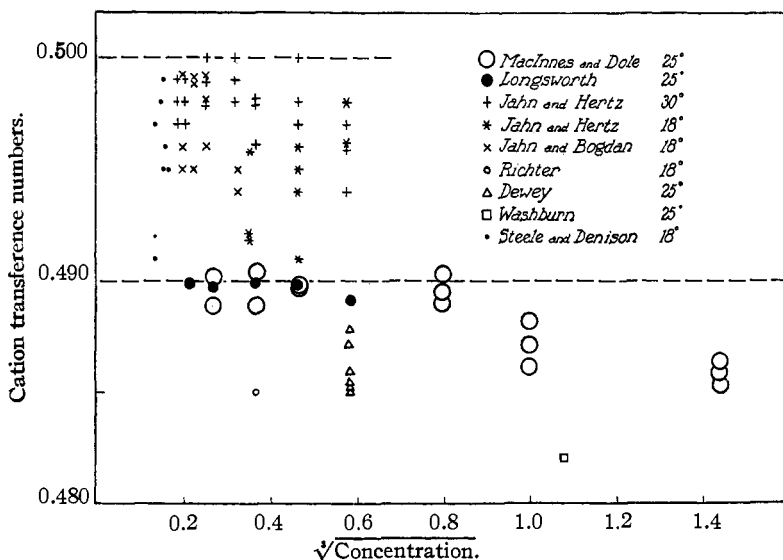


Fig. 3.

the direction observed in Jahn's work. In the work described in this paper the best conductivity water was used. It was stored and measurements were made in Pyrex apparatus. No solvent correction was necessary within the experimental error in our Hittorf work. Small corrections have been made, for this effect, to the moving boundary data at the lower concentrations.

It is certainly evident from the discussion of our work and that of the previous investigators that it is difficult to obtain accurate transference numbers by the Hittorf method. Much higher precision can be obtained by the moving boundary method, and with relative ease. The width of the dots representing the moving boundary results in Fig. 3, illustrates roughly, on the scale of ordinates, the limits of error of these results. The value at each concentration represents the mean of at least four determinations,

the deviation being 0.05% at most. Furthermore, fifteen figures which are averaged are obtained in each determination, the greatest variation being about 0.1%. Three complete determinations may be carried out in one day. A Hittorf determination which, if successful, gives one figure each for the anode and cathode portions, requires nearly a week.

On the other hand, the theory underlying the Hittorf measurements is simpler than that of the moving boundary method. Since the results of the latter method have been questioned recently,¹¹ the agreement of the results of these two accurate series of determinations is welcome.

The transference numbers of potassium chloride have been universally used in computing tables of limiting ion mobilities. The results given above indicate that the figures in those tables must be in error. A later paper from this Laboratory will deal with the determination of a new table of those constants based on recent conductance and transference data and on modern theories of solutions of strong electrolytes.

Summary

A series of measurements, by the Hittorf method, of the transference numbers of potassium chloride, at 25°, for the concentration range 0.02 to 3 normal is described. The cation transference numbers are decidedly lower than the generally accepted values for these constants, on which the tables of ionic mobilities are based. The new values are, however, in excellent agreement with a series of values for the same constants obtained by the moving boundary method, the details of the determinations of which will be published later.

Within the experimental error the transference numbers are constant between 0.01 and 0.1 *N* and the cation number decreases slowly above the latter concentration.

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¹¹ Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., 2d ed., 1931, p. 685; also Mukherjee, *Nature*, **122**, 608 (1928); *J. Indian Chem. Soc.*, **5**, 593 (1928). This author considers that there is a large space charge at a moving boundary which appreciably affects its motion. This, he thinks, is caused by the sudden change of the transference number of the common ion at the plane of the boundary. It can readily be shown (though it would lead us too far afield at this point) that this supposed effect is due to a neglect of the fact that the boundary *moves*, the apparent deficiency in the number of the common ions behind the boundary being accounted for by a change of concentration of the ion as the boundary passes a given point.