4. While the k of Ramsay and Shields is a constant for non-associated liquids, $\gamma(M/d)^{2/3}$ becoming zero at 6° below the critical temperature, k for *associated* liquids is found to be a linear function of the temperature, which attains a maximum value at 6° below the critical temperature, and consequently would become zero at 6° above the *negative* critical temperature, if such a point could be attained.

5. A third class of liquids, based upon their k values, is formed by acetone and propionic acid, which show a constant, but compared to 2.12, abnormally low value of k.

6. The above formulas are applied, for the calculation of critical temperature, with exceedingly good results, to the values of $\gamma(M/d)^{2/3}$ as found by Ramsay and Shields for methyl alcohol, water, ethyl alcohol, and acetic acid.

LABORATORY OF PHYSICAL CHEMISTRY,
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THE HYDRATION OF IONS DETERMINED BY TRANSFERENCE EXPERIMENTS IN THE PRESENCE OF A NON-ELECTROLYTE.

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I. Introduction.

Since 1900, evidence has been gradually accumulating which points strongly to the existence of hydrated ions in aqueous solutions of electrolytes. Practically all of this evidence, however, has been of a nature which in law would be classed as "circumstantial." It is probably for this reason that the importance of the part played by "solvation" in the process of electrolytic dissociation is only now beginning to receive general recognition among the advocates of the Ionic Theory. Indeed, with but few exceptions, the standard text-books on physical and electrochemistry, in use to-day, treat the ion simply as an atom or atom group possessing an electric charge and having an independent existence within the solution. If hydration is spoken of at all in this connection, it is usually referred to very briefly as a possible explanation of certain peculiarities in the mobilities of some of the ions.

The present investigation was undertaken for the purpose of studying hydration by a method which would not only yield direct and definite results with respect to the existence of hydrated ions, but which would also yield quantitative data concerning the relative degree of hydration of the different ions. The principle at the basis of the method employed is very simple. If the ions are hydrated, not only the electrolyte but also some of the water should be transferred from one electrode to the other during electrolysis. This transfer of water would make itself apparent if the solution contained a small amount of some non-electrolyte, which would not migrate with the current and which would be increased in concentration at one electrode and decreased at the other, as a result of the water transference. This method was proposed by Nernst in 1900; but up to the time of the commencement of the present investigation, all attempts to apply it had failed to yield conclusive results. The present investigation was begun in the latter part of 1904, and was directed toward the determination of the relative degrees of hydration of the ions of the alkali elements in solutions of their chlorides. In the early part of the research, a solution of sodium chloride, containing sucrose as the non-electrolyte, was investigated. The results of this portion of the investigation, in which it was definitely shown that water is transferred from anode to cathode during the electrolysis of this solution, were presented at the May (1905) meeting of the Harvard-Technology Physico-Chemical Club and later in the same year at a meeting of the North Eastern Section of the American Chemical Society.

In order to obtain quantitative results, however, it became necessary to find a more suitable non-electrolyte than sucrose, and to devise a more perfect transference apparatus than had previously been used. The investigation was finally successful and yielded quantitative data on the degrees of hydration of the ions of the chlorides of sodium, potassium, and lithium, as described in the following pages. During the progress of this research, corresponding data for solutions of hydrochloric acid have been given us by the investigation of Buchböck, so that we are able to compare quantitatively the degrees of hydration of the ions of four different electrolytes. In addition it is pointed out that certain of our present views regarding transference numbers must be modified.[1]

II. Review of Previous Investigations.

The first attempt to apply this principle was made by Nernst and his students.[2] In their experiments solutions of sulphuric, hydrochloric, hydrobromic, and nitric acids, containing boric acid as the reference substance, were electrolyzed between platinum electrodes. The electrode at which the concentration of the electrolyte increased was con-

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[1] In the Hittorf method of determining transference numbers, the assumption is made that the solvent is absolutely stationary during the passage of the current; that is, that no transfer of solvent takes place from one electrode to the other. If such a transfer of solvent takes place, the calculation of the transference number by the ordinary method is not justified and will not give the *true transference number*, T. Only in dilute solutions, where the amount of solvent transferred becomes negligible in comparison with the total solvent present, will the ordinary or Hittorf transference number, T_H approach the true one, T.

[2] Nernst, Gerrard, and Oppermann, *Nachr. Gesells. Wissensch., Göttingen*, **56**, 86 (1900).

tained in a pipette placed in a beaker filled with the solution. The strong acid was determined by titration with 0.05 normal baryta solution, using methyl orange; and the boric acid, after the addition of mannite, was titrated similarly, using phenolphthalein. The errors involved in the analytical methods, amounting to from 0.2 to 0.3 per cent., render it impossible to draw any definite conclusion from their results, except that if water is transported at all under these conditions the amount is not very large.

Two years later Lobry de Bruyn[1] took up the problem. In his experiments a solution of silver nitrate containing methyl alcohol as the reference substance was electrolyzed between silver electrodes in the "ordinary transference apparatus." The content in silver nitrate was determined by titration, and that in methyl alcohol by the distillation method. The author concludes that, "On peut facilement calculer que si l' ion Ag (ou l'ion NO_3) devait transporter, par exemple, une molecule du dissolvant, on trouverait pour une quantité de 4 grammes Ag à l' anode ou à la cathode respectivement une augmentation et une diminution, en eau de 0.6 à 0.7 gramme, ou en alcool méthylique de ± 1.2 grammes. L'analyse aurait montré qu'il en était ainsi, même si par diffusion les quantités avaient diminuées...; il est donc à propos d'admettre que les ions... n'emportent pas le dissolvant avec eux, mais se meuvent seuls et libres." An examination of the experimental data does not justify this conclusion. Owing to the change in the boiling point of the solution with varying content of silver nitrate, the above mentioned change in composition might easily have escaped detection by the distillation method of analysis. Furthermore, the use of methyl alcohol as a reference substance, especially in the high concentrations used by de Bruyn (24 to 64 per cent.), is open to grave objections, as will be explaned below.

These two investigations constituted the only attempts which had been made to apply the method up to the time of the commencement of the present investigation. During the progress of this investigation two other contributions to the problem have appeared. Morgan and Kanolt[2] attacked the problem, using solutions of silver nitrate in mixtures of alcohol and water. The analytical method for estimation of the alcohol content of the solutions before and after the electrolysis was considerably improved over the one used by de Bruyn, and every precaution was taken to prevent evaporation of the alcohol. As the experiments were intended to be qualitative only, the form of the apparatus was not adapted to quantitative experiments, since no middle portion was taken; and the electrolysis was prolonged, so that mixing of the electrode portions undoubtedly took place to some extent. The

[1] Lobry de Bruyn, *Rec. trav. chim.*, **22**, 430 (1903).
[2] Morgan and Kanolt, *J. Am. Chem. Soc.*, 28, 572 (1906).

authors reasoned that "the best conditions for the detection of the combination of the water with the ions are found in a solution containing much less water than alcohol;" consequently they used solutions containing 53 per cent. and 66 per cent., respectively, of alcohol. Such a procedure is open, however, to serious objections. There is reason to believe[1] that in alcoholic solutions combination between this solvent and the ions also takes place, and if such is the case, the use of high concentrations of alcohol simply serves to complicate the problem. In fact, it is essential that the concentration of the reference substance shall be as small as possible, so that if there is any tendency on its part to combine with the electrolyte, this effect shall be reduced to a minimum. Morgan and Kanolt were able to detect a change in the ratio of water to alcohol only in the 66 per cent. alcohol solution. In this case the change, while small, was probably outside the errors of experiment, and indicated that water was carried by the silver-ion or alcohol by the nitrate ion, two possibilities of equal *a priori* probability between which it is impossible to distinguish.

The results of the three investigations just described were therefore inconclusive. To Gustav Buchböck[2] we owe the first successful application of the principle of this method. Working with solutions of hydrochloric acid and using mannite and resorcinol at small concentrations as the reference substances, he was able to prove that water is transported from the anode to the cathode during the electrolysis of these solutions. A satisfactory measurement of the amount transported was also obtained, the results at the two electrodes checking very well with each other. The results obtained with the two reference substances are also nearly identical within the experimental error. The two halves of his transference apparatus were connected by a ground glass joint and by means of two stopcocks the solution could be separated into three parts at the completion of the electrolysis. The cathode was a small platinum wire sealed into the apparatus, and the anode a torus made of the finest silver gauze. Each electrode was enclosed between the wall of the apparatus and a short insert tube. A diaphragm of silk gauze over the bottom of the insert tube on the cathode side served to restrict the stirring caused by the evolution of hydrogen at this electrode.

The concentration of the hydrochloric acid was determined with an accuracy of a few hundredths of one per cent. by titration with an alkali solution free from carbonate in a weight burette, using phenolphthalein as the indicator. To determine the mannite, the solution, after neutralization with pure silver carbonate and removal of the excess of silver with hydrogen sulphide, was evaporated to dryness in a platinum dish

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[1] See Carrara, *Ahrens' Sammlung*, **12**, 413 (1908).

[2] Buchböck, *Z. physik. Chem.*, **55**, 563 (1906).

and the mannite weighed directly. An accuracy of 0.05 to 0.10 per cent. was attained. In the experiments with resorcinol as the reference substance the content was determined by extracting the solution ten times with ether, evaporating the ethereal solution in a specially constructed apparatus, drying the residue in a current of hydrogen, and weighing it directly. The accuracy was probably not better than 0.1 per cent.

In order to show that the reference substance did not of itself migrate when subjected to a potential gradient a regular transference experiment was made with a pure mannite solution in which 110 volts were applied to the electrodes for ten and a half hours. The silver coulometer showed a deposit of 0.004 gram of silver, and the analyses did not indicate any tendency on the part of the mannite to migrate with the current. The experimental data of Buchböck will be given and discussed later in connection with the results of the present investigation.

III. The Properties of the Reference Substance.

The plan of the present investigation was to find a suitable material to use as a reference substance, and then to measure the true transference numbers of the chlorides of the alkali metals and the quantity of water simultaneously transferred. Since the success or failure of this method depends almost entirely upon the properties of the reference substance, this phase of the problem will first be discussed.

A satisfactory reference substance must possess all of the following properties:

1. It must be a non-electrolyte and must remain stationary with respect to the water when a current of electricity is passed through a solution containing it. This excludes all substances of a colloidal nature.
2. It must be a stable substance and must not react with or be acted upon by the electrodes, the solvent, the electrolyte, or any substance formed during the electrolysis.
3. Since the object of the investigation is to obtain information in regard to the state of hydration of the ions in *aqueous* solution, it is obvious that the reference substance must be present at such a small concentration that it shall not appreciably change the character of the solvent.
4. Since, moreover, the changes in the ratio of water to reference substance at the electrodes will be small, the reference substance must be capable of very accurate estimation.

Since nearly all of the substances which fulfil the first of these conditions are organic compounds, and since such compounds do not fulfil the second condition in solutions of the alkali chlorides when they are electrolyzed between platinum electrodes, it became necessary, first of all, to devise electrodes which could be used in these solutions without the appearance of oxygen or hydrogen, or the formation of acid or alkali, during the electrolysis. To meet this requirement the transference apparatus and electrodes described in Section IV were devised.

IV. The Transference Apparatus and Electrodes.

The apparatus used in this investigation is of general applicability to the measurement of transference numbers, by the Hittorf method, in solutions of the halogen acids and their salts. As it embodies several improvements over previous forms, it seems desirable to describe its construction and use somewhat fully.

The conditions which must be fulfilled in order to attain the highest degree of accuracy in a transference measurement by the Hittorf method may all be summed up in the following statements:

1. The passage of electricity from electrode to solution or from solution to electrode must take place by one path only, that is, side reactions and partial secondary reactions must be excluded.
2. The amount of electrolyte transferred and the concentration changes resulting at the electrodes should both be as large as possible.
3. The amount of electricity passed through the solution must be accurately known.

The first condition depends upon the nature of the electrodes, while the second condition, once the electrodes are determined, is dependent chiefly upon the form of the apparatus used. We shall proceed to the consideration of each condition separately.

The Electrodes.—If a solution of an alkali chloride be electrolyzed between platinum electrodes, hydrogen and hydroxyl ions are formed at anode and cathode, respectively. These rapidly moving ions soon migrate away from the electrodes and mix with the electrolyte in the middle portion of the solution. To avoid the formation of hydrogen ion, Hittorf[1] used a cadmium anode, placing it at the bottom of his apparatus. The slowly moving cadmium ion which formed around this electrode effectually prevented any stirring. This use of a soluble anode (usually cadmium or zinc) to avoid the formation of hydrogen ion was followed also by Hopfgartner,[2] Bein,[3] and Jahn[4] in their investigations. According to Bein, the use of these soluble anodes is complicated by side reactions resulting in the formation of basic salts. This statement, however, is contradicted by Jahn, who could find no evidence of any such action.

To prevent the formation of alkali at the cathode, Hopfgartner and Jahn used a mercury electrode covered with a layer of a strong solution

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[1] Hittorf, *Pogg. Ann.*, 106 (1859).

[2] Hopfgartner, *Z. physik. Chem.*, **25**, 115 (1898).

[3] Bein, *Ibid.*, **27**, 1 (1898).

[4] Jahn, *Ibid.*, **37**, 675 (1901).

of the salt of some metal which amalgamated readily with mercury, usually zinc or copper. These devices effectually prevent the formation of the rapidly moving hydrogen and hydroxyl ions and the evolution of gas at the electrode. (This latter effect is to be avoided, owing to its tendency to produce stirring and to carry away mechanically a portion of the solution in the form of a fine spray.) They have the disadvantage, however, of introducing foreign ions into the solution, thus preventing a large transport of electrolyte and complicating the analyses. A. A. Noyes,[1] in his investigation of the transference numbers of the alkaline-earth metals, modified the method by making both electrodes of platinum and by adding during the electrolysis, at the anode and cathode, respectively, measured quantities of alkali and of acid, so as to keep the solution at a uniform concentration and to prevent the formation and migration away from the electrodes of hydrogen or hydroxyl ion. By this means he was able to obviate the above mentioned difficulties and to obtain a much larger transport of electrolyte than had any of the previous investigators.

Obviously the ideal electrodes to use in a transference measurement would be composed of the metal whose salt was under investigation. The process then would consist simply in the formation of the metal ion at the anode and its discharge at the cathode, accompanied by the transference of T^a equivalents of the salt from one electrode to the other. While in the case of the alkali halides we cannot use the reversible metal electrodes, we can attain the same result by using reversible electrodes composed of the corresponding insoluble halide salt of some other metal, such as silver. Thus, if one equivalent of electricity be passed through a sodium chloride solution between silver chloride electrodes, or more strictly speaking between a silver anode and silver chloride cathode, the process which takes place consists essentially in the formation of chloride ion at the cathode and its discharge at the anode where insoluble silver chloride is formed. At the same time T^c equivalents of electrolyte are transferred from anode to cathode, T^c being the transference number of the cation. By means of this simple arrangement it is possible to carry on the electrolysis without the formation of any acid or alkali, or the evolution of any gas, or the introduction of any foreign substance into the solution. In the present investigation only silver chloride electrodes have been used, but a few qualitative experiments with silver iodide and bromide electrodes indicate that when prepared in an analogous manner they also will give good results.

Preparation of the Silver Anode.—The use of a silver anode[2] for trans-

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[1] Noyes, THIS JOURNAL, **23**, 148 (1901).

[2] In McBain's compilation (see note 1, p. 336 of this paper) incorrectly given as platinum anode.

ference work with solutions of chlorides was introduced by Noyes and Sammet[1] in their transference measurements on hydrochloric acid. If a solution of a chloride be electrolyzed, using a silver rod as the anode, the following series of phenomena takes place. The bottom of the rod is first attacked and a coating of dark gray silver chloride is formed, which extends slowly upward until the rod is entirely covered. The layer gradually increases in thickness, and the potential between electrode and solution rises until oxygen begins to be evolved and the solution becomes acid in the vicinity of the electrode. At the same time the layer of chloride near the bottom of the rod begins to turn white, and finally, as the electrolyte in the vicinity of the electrode becomes exhausted, a white cloud of colloidal silver chloride is given off from the electrode and migrates downward with the current.

If the current density is increased, gaseous chlorine is also evolved at the electrode. Noyes and Sammet found that with a current density of not more than 4.5 milliamperes per square centimeter no chlorine was evolved, but the formation and migration of the cloud of silver chloride from the electrode was always obtained, as was also the liberation of oxygen and the formation of an equivalent amount of acid in the solution. In the analysis of their anode portion they were therefore obliged to dissolve the silver chloride from the anode by means of ammonia, and determine it along with the total chloride in the anode portion. This formation of acid can, however, be entirely prevented by using an electrode with a sufficiently large surface and taking precautions to prevent the exhaustion of the electrolyte in its immediate vicinity. At the same time a closely adherent layer of dark gray silver chloride is obtained, and the formation of the white colloid in the solution is entirely prevented. Two types of anodes were used in the present investigation. Type A, made from silver wire, is best adapted for use with dilute solutions, say from 0.2 molal down. For more concentrated solutions, a much larger surface of electrode must be available, and type B was devised to meet this requirement.

Preparation of Type A Anode.—This anode is made of No. 21 B. & S. gauge, pure silver wire (diameter 0.7 mm.), which is wound into a loose spindle about 3 cm. long and 2.2 cm. in diameter. In order to secure the necessary distance between the successive layers of the coil, each layer is separated from the preceding one by a few sheets of guncotton, which is burned out after the coil is completed. The guncotton is prepared by the nitration of an ashless filter paper in a mixture of three parts of concentrated sulphuric and one part of fuming nitric acid for

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[1] Noyes and Sammet, THIS JOURNAL, 24, 947 (1902).

forty-eight hours, followed by a thorough washing. When properly prepared, these guncotton layers burn out readily, leaving an electrode with a large surface easily permeable by the solution in all its parts. After burning out the guncotton, the electrode is plunged into warm dilute nitric acid until it is attacked violently, washed with boiling distilled water and then with alcohol, the excess of which is finally removed by ignition. This treatment removes the grease and dirt and imparts a matte surface to the wire, in which condition it is more readily attacked by the chlorine.

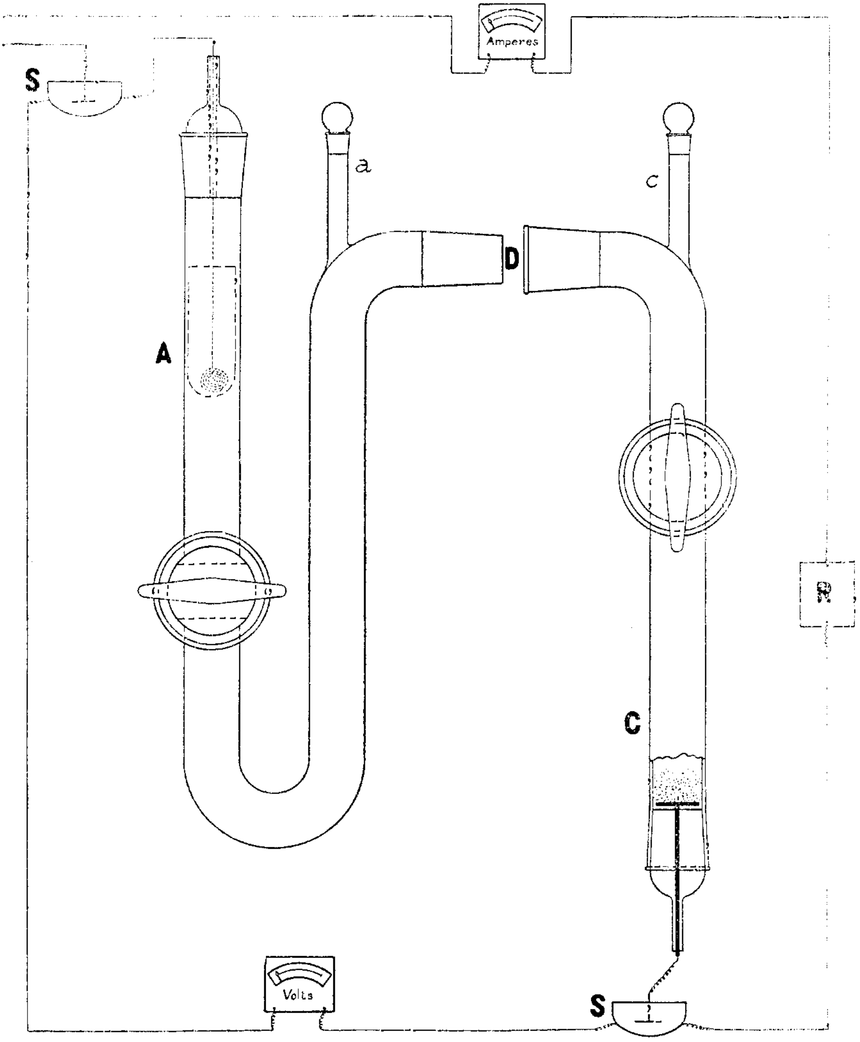

Fig. 1.—Diagram of apparatus and connections.

Preparation of Type B Anode.—A silver wire of suitable length is wound into a flat spiral, the ends being brought up vertically through the centre of the spiral and twisted together to form the lead wire. The spiral is placed in the bottom of a filter paper tube, as shown in the diagram (Fig. 1). The tubes used for this purpose are the familiar Soxhlet extraction cartridges, which can be purchased in several sizes. The size to be used depends upon the dimensions of the apparatus and the amount of electricity to be sent through it. Those used in the present investigation were 6 cm. long and 1.9 cm. in diameter.

After the wire is in place, the cartridge is filled with "electrolytic crystals" of pure silver, which are packed tightly around the lead wire. These crystals are prepared by the electrolysis of a silver nitrate solution with a silver anode and platinum cathode. The clusters of crystals so obtained are broken up somewhat and are then washed with hot water and finally with methyl alcohol, which is removed by ignition. The result is a mass of bright crystals of pure silver, which when packed in the cartridge as described give a silver electrode of maximum surface in the minimum volume. When the electrode is prepared, the filter paper cartridge is punctured with numerous needle holes to insure ready penetration of the solution throughout the mass of silver. This form of electrode has been found to be eminently satisfactory. All of the silver surface is available as electrode, the crystals being changed to silver chloride without losing their form or porosity. Moreover, the electrode is easily broken up and mixed with the anode portion when the electrolysis is completed. An electrode of the above dimensions will carry a current of 0.1 ampere for sixteen hours without the formation of the slightest trace of acid or of colloidal silver chloride in the solution.

Preparation of the Silver Chloride Cathode.—This electrode consists essentially of a silver disk covered with the necessary amount of granular silver chloride. The disk is of such a diameter as to just slip into the apparatus tube. A silver rod welded into its center passes out through the stopper of the apparatus, where it is joined to the lead wire, as shown in the diagram. The disk is first cleaned by plunging it into warm nitric acid and is then suspended in a molal sodium chloride solution in a U-tube. Using it as an anode, a current of 0.025 ampere is passed through the solution until gas is evolved freely at the anode. The electrode is then removed, washed thoroughly with hot water and dried. The rod is then drawn through the opening in the stopper of the apparatus and cemented firmly in place, after which the stopper is inserted in the apparatus and a suspension of silver chloride is poured in until a column of the desired thickness is formed upon the electrode.

The silver chloride for this purpose is prepared by precipitating a hot solution of silver nitrate with an excess of an alkali chloride solution and washing thoroughly with boiling water. The precipitate is then washed by decantation with some of the solution under investigation, until the liquid in contact with it has the same composition as the solution. This mixture is then poured upon the cathode by means of a thistle tube reaching nearly to the bottom of the cathode half of the apparatus. After the silver chloride has settled, the supernatant liquid is pipetted off, and after filling the apparatus the electrode is ready for use. During the passage of the current the silver chloride is reduced to gray metallic silver. It is only necessary to keep the current density low enough so that the rate of solution of the silver chloride is sufficiently rapid to supply the necessary amount of silver ion to carry the current from solution to electrode. An electrode 2.3 cm. in diameter will carry 0.5 ampere without the evolution of hydrogen or the formation of the slightest trace of alkali. It has been found that the physical condition of the silver chloride plays an important part in this action. If it is prepared by precipitation in the cold, it fails to act as a depolarizer. Boiling the precipitate seems to affect its physical condition so as to render it more soluble or more easily reduced. It should, of course, be protected from the action of white light.

The Apparatus.—It is very desirable that the apparatus for transference experiments be as simple in form as is consistent with its main requirement, which is to secure the maximum transport of electrolyte and the maximum concentration change at the electrodes. The chief disturbing element is the mixing of the solution around the electrode with the rest of the solution. This may be caused by diffusion, by convection due to heat developed by the current, or by currents set up when the different portions of the solution are separated from one another at the end of the experiment.

The form of apparatus[1] finally adopted is designed to reduce these effects to a minimum. It is a modified form of the apparatus used by A. A. Noyes in his investigation of the transference numbers of the alkaline-earth metals.[2] It is shown in Fig 1. The anode tube, *A*, is a U-tube having the top of its shorter arm bent at right angles and fitted by means of a ground glass joint, *D*, into the corresponding por-

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[1] The apparatus designed for this investigation was constructed by Mr. Otto Presler, of Leipzig, under the direction of Dr. W. Böttger, who was a research associate in this laboratory at the time this investigation was begun (1904–05), and who kindly offered to superintend the construction of the apparatus for me upon his return to Leipzig the following year. The construction of the apparatus offered considerable difficulty at first, owing chiefly to the size of the stopcocks, and I gladly take this opportunity to express my indebtedness to Dr. Böttger, to whose kindness and friendly interest is largely due the final construction of a satisfactory apparatus.

[2] A. A. Noyes, THIS JOURNAL, 24, 946 (1902).

tion of the cathode tube *C*. The short tubes *a* and *c* are provided with glass stoppers and serve to admit the stem of a pipette for the removal of the solution The top of the anode tube *A* is fitted with a ground glass stopper carrying a small tube sealed through its centre for admission of the lead wire to the anode. The bottom of the cathode tube *C* is provided with a similar stopper. As soon as the cathode disk has been prepared as directed above, its lead wire is sealed into the small tube with Khotinsky cement and the stopper is then sealed in place with the same cement.

The two large stopcocks serve to cut off the two electrode portions when the electrolysis is finished. The *whole* apparatus is of uniform bore (2.3 cm. diameter) throughout, including the cross tubes of the stopcocks. This is essential in order to prevent local heating and consequent stirring during the passage of the current. The apparatus is kept in a water thermostat at constant temperature during the passage of the current. The keys of the two stopcocks are hollow, the rear face of each being cut off so that the water of the thermostat can circulate about the cross tube.

Procedure of a Transference Experiment. Setting Up the Apparatus.—The apparatus is cleaned thoroughly with warm chromic acid solution, and after washing with water and drying with pure alcohol the two tubes are placed in their supports. Each stopcock is lightly greased with vaseline, the surface immediately opposite the cross tube being, however, left free from vaseline, so that on closing the cock the lubricant will not come in contact with the solution in the apparatus. After the insertion and alignment of the stopcocks, a thin layer of melted paraffin is applied by means of a camel's-hair brush to the joint between the key and the sheath, both front and rear. This paraffin seal entirely prevents all connection between the solution in the apparatus and the water of the thermostat, and at the same time allows the cock to be turned easily.

After the insertion of the electrodes the two halves of the apparatus are joined at the ground glass joint, which is also lubricated with vaseline[1] and protected with the paraffin seal in the same manner as the stopcocks. The lead wires from the electrodes are protected from the water of the thermostat by rubber tubes which are brought out through rubber bushings in the side of the thermostat and the wires connected to binding posts. As a further precaution a piece of rubber band tubing is drawn over the bottom of the cathode tube as far as the stopper, and is then brought up above the surface of the water.

After filling the apparatus with the solution, the anode is moved up

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[1] The vaseline used for lubrication should be freed from all soluble matter by repeated extraction with boiling water.

and down a few times to remove air bubbles, and is then fixed so as to occupy a position about three centimeters above the stopcock. This arrangement leaves considerable solution above the electrode, which stirs slowly during the run and prevents the exhaustion of the electrolyte in the immediate vicinity of the electrode. The three glass stoppers at the top of the apparatus are sealed with the paraffin seal, and the whole apparatus is adjusted so that the water in the thermostat and the solution in the tube are at the same level.

The connections are made as shown in the diagram. Two silver coulometers, S, one connected to the anode and the other to the cathode, serve to detect any leakage during the passage of the current. After the solution has come to the temperature of the thermostat, the circuit is closed and the rheostat, R, adjusted to the proper current strength. The voltmeter which is connected in shunt just outside the coulometers serves to indicate the progress of the electrolysis. During the first hour or two the potential across the apparatus gradually falls to a value which remains constant until near the end of the run, when it begins to rise gradually. This increase begins when the whole surface of the anode is covered with the chloride layer. When the potential has risen one volt, the circuit should be broken or oxygen will be evolved at the anode.

Removal of the Solution.—As soon as the circuit is broken the two stopcocks are closed, and by introducing a pipette into the apparatus through the small tube on the cathode side the solution is drawn out of the horizontal portion of the tube and down to the cathode stopcock. This portion, which will be called the cathode middle portion (M_c), is transferred to a 150 cc. glass-stoppered, tared, Erlenmeyer flask. In a similar manner two other portions are removed; the middle portion (M), which extends down to the bend in the anode tube, and the anode middle portion (M_a), which comprises the rest of the solution around to the anode stopcock.[1]

After the removal of these portions the apparatus is taken from the thermostat, dried on the outside, the rubber tubes removed, and the cathode lead wire disconnected. The two halves of the apparatus are disconnected at the ground glass joint and paraffined rubber stoppers are inserted in each. After first opening the stopcock, the contents of the cathode tube are mixed thoroughly, and then after sealing all joints with paraffin it is set aside to allow the silver and silver chloride to settle

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[1] In most cases the concentration changes in these middle portions are so small that no correction need be applied for them. It is very essential, however, that more than one middle portion be obtained and analyzed in accurate transference work. If only a single middle portion be taken, it may be found on analysis to be practically unchanged, even though mixing has taken place with *both* electrode portions, since these two effects would tend to counterbalance each other. With three middle portions, however, all uncertainty on this point is removed

out. The anode stopcock is opened and the anode lowered until it can be caught between the stopcock and the wall of the tube. In this manner it can be broken up and mixed with the solution. After thorough mixing this half of the apparatus is also sealed with paraffin and set aside to allow the silver chloride and filter paper shreds to settle.

Each half of the apparatus is cleaned and dried on the outside and weighed to the nearest centigram. The bulk of the clear solution is removed with a pipette and transferred to a small, glass-stoppered Erlenmeyer flask. The residue from the electrode is washed out into a beaker, and after drying the empty apparatus with alcohol and ether it is weighed. The electrode residue of silver and silver chloride is collected on a filter, washed with alcohol and ether, dried and weighed. The necessary data for calculating the total weight of the electrode portions are thus obtained.

Modification of the Apparatus for Use with Dilute Solution.—The procedure as described above is applicable only to comparatively concentrated solutions, say from 0.2 molal up. For more dilute solutions the apparatus is modified slightly in order to effect the necessary concentration changes at the electrodes and to provide a larger amount of solution for analysis. This is effected at the anode by increasing the length of the anode tube above the stopcock without, however, altering the position of the electrode, which in this case is type A. The increased amount of electrolyte above the anode stirs during the run, thus supplying the necessary amount of chloride for carrying the current to this electrode and allowing a corresponding greater transport to be obtained. It is better to obtain this increase in electrolyte by increasing the depth of solution above the electrode rather than by using an apparatus of larger cross section, since as the diameter of the tube increases it becomes increasingly difficult to maintain a constant temperature throughout the tube and avoid the convection currents due to heating. At the cathode the increased volume is secured by an expansion of the tube for a short distance above the electrode. The same apparatus can be employed for both concentrated and dilute solutions by having the two additional tubes ground to fit the same socket as the stoppers, so that they can be inserted when desired.

As an additional precaution against stirring, the use of diaphragms will be found advantageous for the more dilute solutions. These diaphragms, which are made of a medium-mesh silk bolting-cloth, are conveniently inserted in the cross tubes of the stopcocks. The cloth is drawn over a thin vulcanite ring, which is then pressed into the cross tube of the stopcock, which it just fits. Hittorf[1] has shown that dia-

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[1] Hittorf, *Z. physik. Chem.*, **39**, 617 (1902).

phragms of this character do not produce cataphoresis. No diaphragms of any kind were used in the present investigation, however.[1]

V. The Coulometers.

The silver coulometers used in this investigation were of the ordinary type, the cathode consisting of a platinum dish and the anode of a silver disk covered with a close filter paper. Guthe[2] has recently shown that the results obtained with this type do not differ by more than 0.05 per cent. from those obtained with the more accurate Richards type, a degree of accuracy which is amply sufficient for transference work.

VI. Testing the Reference Substance.

In choosing the reference substance no substance was considered unless its concentration in a 0.1 to 0.3 molal solution could be determined to 0.01 per cent. Three substances were found which fulfilled this condition, sucrose, raffinose, and arsenious acid. The final test of the availability of a compound for use as a reference substance is its ability to remain entirely unchanged in the solution during an electrolysis with a current of 0.1 ampere for a period of at least fifteen hours. This final test is applied by making what is called a "straight tube run." This run differs in no way from the regular transference runs, except that it is made in a straight tube, with the silver anode at the top and the silver chloride cathode at the bottom. At the end of the run, instead of separating the solution into several portions, it is thoroughly mixed without opening the apparatus, and after the silver chloride has settled a portion of the solution is removed with a pipette and analyzed for the reference substance. The substance is considered to be satisfactory if its concentration is the same (to 0.01 per cent.) at the end of this test as it was in the original solution. When the three substances mentioned above were subjected to this test only one of them, raffinose, was found to fulfil this condition rigorously. The results obtained with the other two are, therefore, only approximate. They will, however, be described, since they furnish checks on the order of magnitude and direction of transport of the water.

VII. Purification of Material.

Sucrose.—The sucrose employed was a special unblued product, obtained directly from the refinery. It was further purified by three precipitations from water solution by the addition of pure alcohol. After washing with pure alcohol and ether, the crystals were dried at 95° and kept over calcium chloride. It had a specific rotatory power in 9.43 per cent. solution of $[\alpha]_D^{25°} = 66.410° \pm 0.0038$, and the specific conductance of the solution was less than 3.10^{-6} reciprocal ohms.

Raffinose.—This material was obtained from Kahlbaum, and was further puri-

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[1] An excellent and exhaustive compilation and criticism of all transference work up to the end of 1905 will be found in a paper by J. W. McBain. [*Proc. Wash. Acad. Sci.*, **9**, 1 (1907).] [Univ. Toronto Pub. No. 67.]

[2] Guthe, *Bull. Bureau Stand's*, **1**, 28 (1904).

fied by several recrystallizations from hot, pure methyl alcohol. The viscous mass which resulted from these crystallizations was dissolved in water and thrown out by diluting with pure ethyl alcohol. The beautifully crystalline product thus obtained was washed with alcohol and ether and dried at 50°.

Sodium Chloride.—This salt was prepared from Kahlbaum's product by precipitation with hydrochloric acid gas. After washing and drying, the salt was fused in platinum to insure the removal of the last traces of hydrochloric acid.

Potassium Chloride.—Kahlbaum's product was recrystallized four times from conductivity water and the crystals fused in platinum. The salt gave a pure potassium flame.

Lithium Chloride.—Pure lithium carbonate was prepared from the commercial article by eight precipitations of the nitrate solution with pure ammonium carbonate, according to the method of Stas.[1] The resulting product was heated to 600° in an electric oven to remove ammonium salts. A solution of hydrochloric acid was prepared by expelling the gas from pure hydrochloric acid solution (sp. gr. 1.20) with sulphuric acid and receiving it in conductivity water. This solution was saturated with the lithium carbonate, and after filtering, the filtrate was acidified with an excess of hydrochloric acid and evaporated to dryness. The lithium chloride thus obtained was dissolved to form a 1.3 molal solution. In order to make sure that the solution was exactly neutral it was tested with phenolphthalein, rosolic acid, and congo red, according to the method of Salm;[2] and the hydrogen-ion concentration was found to lie between the values 10^{-6} and 10^{-8}. The solution was consequently neutral, and it was used in preparing the solution for the lithium chloride experiments.

Arsenic Trioxide.—Kahlbaum's preparation was once resublimed and then twice recrystallized from hot water.

VIII. Preparation of Solutions.

All the water used in preparing the solutions was conductivity water from the special still in this laboratory.[3] The raffinose and sugar solutions were prepared on the same day that the transference experiment was made, and were filtered through hardened filters to insure the absolute clarity which is necessary for accurate polariscopic work. Just previous to filling the apparatus with the solution all dissolved oxygen was removed by boiling for five minutes at 30° under reduced pressure. All solutions were cooled to 2° above the dew-point whenever the transference of the solution from one vessel to another involved a possibility of a change in concentration due to evaporation.

In preparing the arsenious acid solutions, arsenic trioxide was dissolved in hot conductivity water and, after dilution to the proper concentration, the sodium chloride was added, and the whole solution was rotated for twenty-four hours at 25° in contact with a mixture of silver chloride and silver[4] to insure equilibrium. Dissolved oxygen was removed by evacuation, and the solution was ready for use.

IX. Analytical Methods.

Sucrose and Raffinose.—The concentrations of these two substances were determined by the optical method. This method, which is capable of a high degree of accuracy, has the further advantage that the whole of the electrode portion can also

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[1] Stas, *Ouvres*, I, 689.

[2] Salm, *Z. physik. Chem.*, **57**, 500 (1907).

[3] See Noyes and Coolidge, *Proc. Am. Acad.*, **39**, 190 (1903); Carnegie Inst. Pub., No. **63**, 39 (1907).

[4] Such a mixture as is obtained from the cathode after a transference experiment.

be used for the determination of the electrolyte, since the estimation of the carbohydrate does not affect the solution in any way when precautions are taken to prevent evaporation.

The polariscope used was a Schmidt and Haensch half-shade instrument of the Lippich type, the scale reading directly to tenths of a degree and the vernier directly to thousandths. The light was furnished by igniting sticks of fused sodium carbonate in an oxyhydrogen flame, and was further purified by filtration through a Landolt-Lippich ray filter. The instrument was kept in a dark room of even temperature, and was connected with a thermostat maintained at 25°, from which water was caused to circulate around the jacket of the 60-cm. polarizing tube. The average deviation of a set of six readings on this instrument amounted to only 0.003° for a total rotation of 30°, thus permitting an accuracy of 0.01 per cent. in the reading. The same 60-cm. tube was used throughout this investigation. It was jacketed with a nickel-plated water jacket, and was provided with a thermometer in the side tube.

For the determination of the specific gravity of the solutions, pycnometers of the Ostwald-Sprengel type, having a capacity of 20 cc. and provided with ground glass caps, were used. (All specific gravities are, at 25°, referred to water at 4°.) Air-free conductivity water was used in obtaining the water value of the pycnometer. A second pycnometer of the same type was used as a counterpoise, and all weights were reduced to vacuo. The error in the specific gravity determination never amounted to 0.01 per cent.

Effect of Salts on the Specific Rotatory Power.—Sodium chloride is known to reduce the specific rotatory power of cane sugar solutions, the lowering depending upon the initial concentration of the sugar and being proportional to the amount of salt added.[1] It became necessary, therefore, to make a careful determination of this effect, so that corresponding corrections could be applied without introducing too large an error. The result of these determinations is shown in Fig. 2, curve *A*. In this figure values of $[\alpha]_D^{25°}$ are plotted as abscissae (on lower line) and values of P_s/P_r as ordinates, P_s representing the per cent. of salt (in this case NaCl) and P_r the per cent. of sugar in the solution, the ratio of sugar to water, P_r/P_w, being kept constant and in this case equal to 9.60. As is evident from this figure, the graph obtained is a perfectly straight line; its position, however, varies according to the ratio of sugar to water in the solution.

The effects of KCl, NaCl, and LiCl upon the specific rotatory power of raffinose were also investigated. A solution of raffinose, containing 0.1 formula-weight ($C_{18}H_{32}O_{16}$) per 1,000 grams of water, was employed. The results are given in the following table:

Salt.	Molal conc. of salt.	$[\alpha]_D^{25°}$.
....	0.0	123.00°
KCl....................................	1.3	123.08°
NaCl....................................	1.71	123.12°
LiCl....................................	1.30	123.24°

It is to be noted that the presence of the salts produces an increase in the specific rotatory power instead of a decrease, as in the case of sucrose. The effect of LiCl was determined at three different concentrations and found to be linear. In none of the solutions, however, was it found necessary to apply any correction to the specific rotatory power of the raffinose due to the changes in the salt concentration at the electrodes, the correction being entirely negligible. Raffinose seems to possess the

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[1] See Muntz, *Z. Ver. Zuckerind*, **26**, 376 (1876), and Farnstelner, *Ibid.*, 41, 168 (1891).

properties of an ideal reference substance, being very stable in the apparatus and having a high specific rotatory power, which is not appreciably affected by changes in temperature or by changes in the concentration of the raffinose itself or of salts in the solution. The curves, showing the effects of these salts upon the specific rotatory power of raffinose, are also given in Fig. 2. Curve *B* is for KCl, *C* for NaCl, and *D* for LiCl. Values of $[\alpha]_D^{25°}$ are plotted as abscissae (upper line) and values of P_s/P_r as ordinates.

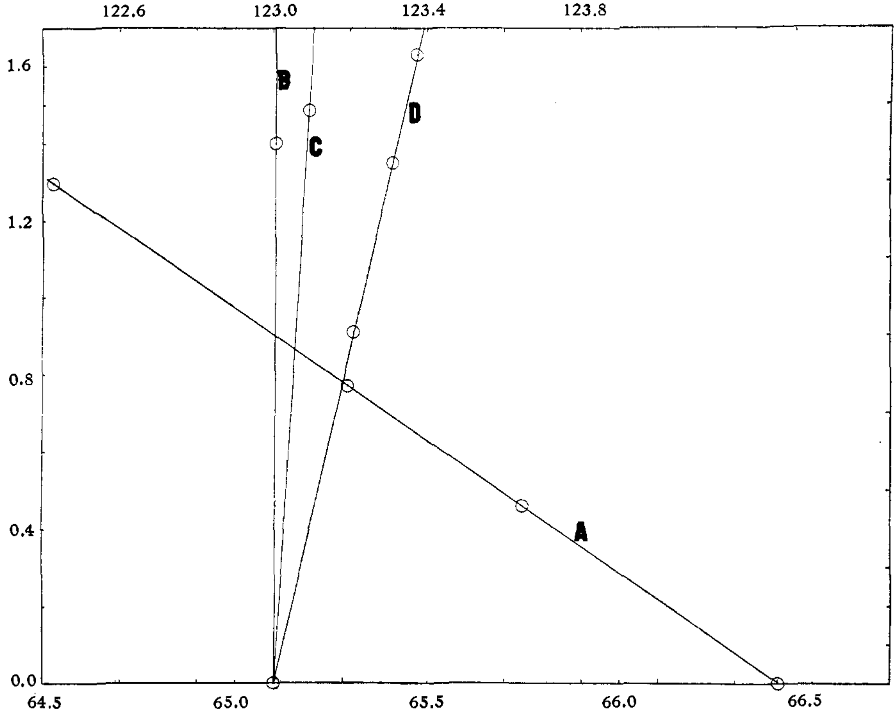

Fig. 2.

Arsenious Acid.—This substance was estimated by titration with standard iodine solution, using disodium phosphate as the neutralizing agent. The details of this method, when an accuracy of 0.002 per cent. is required, have been described by the author in a previous paper.[1]

The Electrolyte.—The chloride in the solution was determined by precipitating it from a weighed amount of the solution by means of an excess of a pure silver nitrate solution, and collecting and weighing the precipitate on a platinum Gooch crucible. The procedure was substantially that followed by Richards and Wells[2] in their "Revision of the Atomic Weights of Sodium and Chlorine." An accuracy of 0.01 per cent. was attained. The weights used in this investigation were carefully calibrated, and all weighings have been reduced to vacuo.

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[1] Washburn, This Journal, 30, 31 (1908).

[2] Richards and Wells, *Carnegie Inst. Pub.*, No. 28; This Journal, 27, 459.

X. Notation.

$\alpha^{25°}$,	angular rotation of the plane of polarization by the solution at 25°.
$d^{25°}_{4°}$,	specific gravity of the solution at 25° referred to water at 4°.
P_r,	per cent. of the reference substance in the solution.
P_s,	per cent. of the electrolyte in the solution.
Ag^c,	grams of silver deposited in the coulometers.
m^e,	total mass in grams of the electrode portion.
Δm_w, Δn_w,	increase in grams (resp. mols) of water in the electrode portion.
Δm_s, Δn_s,	increase in grams (resp. mols) of electrolyte in the electrode portion.
$\mathcal{N}$,	equivalents of electricity passed through the solution.
T^c, T^a,	true transference number of the cation (resp. anion).
T^c_{H}, T^a_{H},	ordinary or Hittorf transference number of the cation (resp. anion).
Δn^{F}_w,	number of mols of water transferred from anode to cathode per faraday of electricity.
A,	anode portion.
M_{A}, M, M_c,	anode-middle, resp. middle, resp. cathode-middle portion.
C,	cathode portion.

The most rational quantity to use in comparing the results at the two electrodes is the ratio of water transferred to salt transferred, *i. e.*, $\Delta n_w / \Delta n_s$ since this quantity depends only upon the analyses and is independent of the total weight of the electrode portion. This quantity will accordingly be inserted in the tables.

The final results of each experiment are most conveniently expressed by an equation which will be written in the two forms, A and B.

$$T^c\, N^c_w - T^a\, N^a_w = \Delta n^{\mathrm{F}}_w. \tag{A}$$

$$N^c_w = \Delta n^{\mathrm{F}}_w / T^c + T^a / T^c\, N^a_w. \tag{B}$$

In these equations N^c_w and N^a_w are the number of mols of water combined with one equivalent of cation and of anion, respectively. The product of each of these quantities by the corresponding transference number is evidently the total amount of water carried by each ion when one equivalent of electricity passes through the solution, and the difference between these quantities represents the number of mols of water transferred from anode to cathode per Faraday equivalent. Form B expresses the number of mols of water combined with the cation as an explicit function of the number combined with the anion. In this equation the constant, $\Delta n^{\mathrm{F}}_w / T^c$, is evidently identical with the quantity, $\Delta n_w / \Delta n_s$. In using these general equations in the following sections, the superscripts, c and a, will be replaced by the symbol of the element in question in each case.

XI. Data and Results with Sodium Chloride.

Reference Substance—Raffinose.

Composition of solution:

Sodium chloride,	1.21 formula-weights of NaCl per 1,000 grams of water.
Raffinose,	0.1 formula-weight of $C_{18}H_{32}O_{16}$ per 1,000 grams of water.
Applied e. m. f.,	19 volts.
Current,	0.075 ampere.
Duration of run,	12 hours.

TABLE I.

	A.	M_A.	M.	M_c.	C.
$\alpha^{25°}$	34.99°	34.32°	34.33°	34.31°	33.80°
$d^{25°}/_{4°}$	1.0495	....	1.0608	....	1.0705
P_r	4.584	....	4.449	....	4.341
P_c	4.731	....	6.344	6.343	7.702
Ag^c	6.788	....	....	....	6.787
m^c	78.13	....	....	....	.....
Δm_w	—0.96	....	.....	....	.....
Δn_w	—0.53	....	.....	....	.....
Δm_s	—1.41	....	.....	....	.....
Δn_s	—0.0241	....	.....	....	.....
$\mathcal{N}$	—0.0629	....	.....	....	.....
$T^c = \Delta n_s/\mathcal{N}$	0.383	....	.....	....	.....
T^a	0.617	....	.....	....	.....
T^c_H	0.366	....	.....	....	.....
T^a_H	0.634	....	.....	....	.....
$\Delta n_w/\Delta n_s$	2.2	....	.....	....	2.0
Δn^F_w	0.84	....	.....	....	0.78

The data and results are shown in Table I. Owing to an uncertainty in the total weight of the cathode portion in this experiment, the transference number could not be obtained from this portion. The ratio of water to salt transferred $\Delta n_w/\Delta n_s$, however, checks with the value obtained from the anode portion.

Reference Substance—Sucrose.—Several experiments were made with sodium chloride solutions, using sucrose as the reference substance. In every case an increase in the concentration of the sugar at the anode and a corresponding decrease at the cathode were observed. Owing, however, to the uncertain stability of the sugar under the action of the electrode processes, the results were not very accurate from the quantitative standpoint. The best of these runs, with a 0.3-molal sugar solution, gave a value of the ratio $\Delta n_w/\Delta n_s = 2$ at the anode and $\Delta n_w/\Delta n_s = 4$ at the cathode.

The low value of the conductivity of à pure sugar solution indicates the absence of any tendency on the part of the sugar to migrate under the influence of a potential gradient. However, in order to make sure that the presence of the sodium chloride is necessary in order to produce a concentration change at the electrodes when the electromotive force is applied for several hours to a sugar solution, the following experiment was made. A 10 per cent. sugar solution, containing 0.008 per cent. of sodium chloride, was placed in the regular transference apparatus, and a potential of 231 volts applied at the electrodes for the same length of time as in the regular transference runs. At the end of this time the solution in the neighborhood of each electrode was polarized, and the result was found to be identical with that given by the middle portion and by the original solution. It is thus evident that no concentration change takes place at the electrodes in the absence of the electrolyte, even with an electromotive force twelve times as great as in the regular runs.

Reference Substance—Arsenious Acid.—Arsenious acid did not prove to be a satisfactory reference substance, owing to its uncertain stability during the passage of the current. One run, however, was obtained in which the arsenious acid had apparently undergone no oxidation at the electrodes, since the total amount present in the two electrode portions was equal to the amount present in the same weight of original solution. An increase of concentration was observed at the anode and a corresponding decrease at the cathode. The results are shown in the following table:

Composition of the solution:
Sodium chloride, 1.25 formula weights of NaCl per 1,000 grams of water.
Arsenious acid, 0.20 formula-weight of H_3AsO_3 per 1,000 grams of water.

TABLE II.

	Anode.	Cathode.
Ag^c	4.245	4.246
Δm_w	−0.35	0.36
Δn_w	−0.019	0.020
Δn_s	−0.0147	0.0149
$\mathcal{N}$	0.0393	0.0393
$T^c = \Delta n_s/\mathcal{N}$	0.374	0.379
$\Delta n_w/\Delta n_s$	1.3	1.3

Numerous attempts were made to repeat the results with arsenious acid, but without success, as check results at the two electrodes could not be obtained. A "straight tube run" showed a loss of arsenious acid, apparently due to oxidation. In view of this fact, the quantitative agreement of the results at the two electrodes, as shown in the above table, is to be regarded as more or less accidental, and the results are, therefore, chiefly of value as showing a concentration change in the same direction and of the same order of magnitude as in the case of sugar and raffinose.

Summary of the Results with Sodium Chloride.—Three solutions of sodium chloride (1.2 molal), containing, respectively, as reference substances, raffinose, sucrose, and arsenious acid, each at low concentration, were electrolyzed between reversible electrodes. In each case an increase in the concentration of the reference substance was observed at the anode and a corresponding decrease at the cathode. If the assumption be made that the change in concentration is due to the transfer of water from anode to cathode during the electrolysis, the three experiments agree in showing that the ratio of mols of water transported to mols of salt transported, $\Delta n_w/\Delta n_s$, lies between the values 1 and 4. The value obtained with raffinose is to be regarded as the most reliable value. The final values adopted for NaCl are given by the following equations:

$$0.383\, N_w^{Na^+} - 0.617\, N_w^{Cl^-} = 0.76 \pm 0.08,$$

or

$$N_w^{Na^+} = (2.0 \pm 0.2) + 1.61\, N_w^{Cl^-}.$$

XII. Data and Results with Potassium Chloride.

Reference Substance—Raffinose.

Composition of solution:

Potassium chloride,	1.24 formula weights of KCl per 1,000 grams of water.
Raffinose,	0.1 formula-weight of $C_{18}H_{32}O_{16}$ per 1,000 grams of water.
Applied e.m.f.,	19 volts.
Current,	0.096 ampere.
Duration of run,	14 hours.

	$C_{18}H_{32}O_{16}$. Grams.	KCl. Grams.
Total amount of solute in anode and cathode portions at completion of the run	8.32	15.27
Total amount of solute in same weight of original solution	8.33	15.27

The results are shown in Table III.

Table III.

	A.	M_A.	M.	M_C.	C.
$\alpha^{25°}$	35.262°	34.827°	34.824°	34.825°	34.213°
$d^{25°}/4°$	1.0578	1.0681	1.0681	.....	1.0807
P_r	4.516	.....	4.418	.....	4.290
P_s	6.510	8.105	8.108	8.108	10.030
Ag^c	5.3685	.....	.....	.....	5.3681
m^e	103.21	.....	.....	.....	85.280
Δm_w	—0.47	.....	.....	.....	0.61
Δn_w	—0.026	.....	.....	.....	0.034
Δm_s	—1.836	.....	......	.....	1.839
Δn_s	—0.02460	.....	a.....	.....	0.02465
$\mathcal{N}$	0.04974	.....	.....	.....	0.04974
$T^c = \Delta n_s/\mathcal{N}$	0.495	.....	.....	.....	0.495
T^a	0.505	.....	.....	.....	0.505
T^c_H	0.483	.....	.....	.....	0.481
T^a_H	0.517	.....	.....	.....	0.519
$\Delta n_w/\Delta n_s$	1.1	.....	.....	.....	1.4
Δn_w^F	0.52	.....	.....	.....	0.68

Summary of Results with Potassium Chloride.—The direction of the concentration change is the same as with sodium chloride, but the amount of water transported is less. An especially noteworthy result is the value, 0.495, of the true transference number for the cation. *This is identical with the value interpolated for 25° from Jahn's*[1] *results for KCl at infinite dilution, showing that the transference number for KCl is independent of the concentration up to 1.2 molal at least.* The value of the ordinary transference number at this concentration is 0.482, which illustrates the error introduced in transference work if hydration is neglected. The final values adopted for KCl are shown in the following equations:[2]

$$0.495\, N_w^{K^+} - 0.505\, N_w^{Cl^-} = 0.60 \pm 0.08, \qquad \text{(A)}$$

or

$$N_w^{K^+} = (1.3 \pm 0.2) + 1.02\, N_w^{Cl^-}. \qquad \text{(B)}$$

XIII. Data and Results with Lithium Chloride.

Reference Substance—Raffinose.

Composition of solution:

Lithium chloride, 1.28 formula weights of LiCl per 1,000 grams of water.
Raffinose, 0.104 formula weight of $C_{18}H_{32}O_{16}$ per 1,000 grams of water.
Applied e. m. f., 19 volts.
Current, 0.096 ampere.
Duration of run, 13 hours.

	$C_{18}H_{32}O_{16}$. Grams.	LiCl. Grams.
Total amount of solute in anode and cathode portions at the completion of the run	8.78	9.17
Total amount of solute in same weight of original solution	8.79	9.18

The results are shown in Table IV.

TABLE IV.

	A.	M_A.	M.	M_C.	C.
$\alpha^{25°}$	37.045°	36.540°	36.558°	36.557°	35.819°
$d^{25°}/_{4°}$	1.0427	1.0454	1.0452	.....	1.0484
P_r	4.806	.....	4.730	.....	4.619
P_s	4.440	4.938	4.939	4.943	5.565
Ag^c	5.0116	.....	.....	.....	5.0112
m^e	104.4	.....	.....	.....	81.47
Δm_w	—1.1	.....	.....	.....	1.3
Δn_w	—0.62	.....	.....	.....	0.070
Δm_s	—0.604	.....	.....	.....	0.594
Δn_s	—0.0142	.....	.....	.....	0.0140
$\mathcal{N}$	0.04643	.....	.....	.....	0.04643
$T^c = \Delta n_s/\mathcal{N}$	0.306	.....	.....	.....	0.301
T^a	0.694	.....	.....	.....	0.699
T_H^c	0.278	.....	.....	.....	0.273
T_H^a	0.722	.....	.....	.....	0.727
$\Delta n_w/\Delta n_s$	4.3	.....	.....	.....	5.1
Δn_w^F	1.4	.....	.....	.....	1.6

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[1] Jahn, *Z. physik. Chem.*, **58**, 645 (1907).

[2] In addition to the run with KCl and raffinose, a run with KCl and sucrose was

Summary of the Results with Lithium Chloride.—The concentration change is in the same direction as in the case of NaCl and KCl, but the amount of water transported is larger than with either of the other salts. The final values adopted for LiCl are shown by the following equations:

$$0.302\, N_w^{Li^+} - 0.698\, N_w^{Cl^-} = (1.5 \pm 0.1), \qquad \text{(A)}$$

or

$$N_w^{Li^+} = (4.7 \pm 0.4) + 2.29\, N_w^{Cl^-}. \qquad \text{(B)}$$

XIV. Results with Hydrogen Chloride.

TABLE V.

Reference Substance—Mannite.

Conc. reference substance.	Conc. HCl.	T^c.			$\Delta n_w/\Delta n_s$.		
		Anode.	Cathode.	Mean.	Anode.	Cathode.	Mean.
0.135	1.0	0.844	0.844	0.844	0.30	0.28	0.29 ± 0.01
0.297	1.0	0.845	0.845	0.845	0.21	0.28	0.25 ± 0.03
0.141	1.47	0.836	0.840	0.838	0.33	0.34	0.33 ± 0.01
0.353	1.47	0.844	0.844	0.844	0.25	0.24	0.24 ± 0.02
0.353	1.47	0.843	0.844	0.844	0.22	0.26	
0.717	1.47	0.845	0.847	0.846	0.21	0.23	0.22 ± 0.01
Reference Substance—Resorcinol.							
0.214	1.1	0.840	0.842	0.841	0.29	0.39	0.34 ± 0.05
0.408	1.1	0.843	0.842	0.842	0.38	0.34	0.36 ± 0.02
1.07	1.1	0.845	0.844	0.845	0.46	0.39	0.42
1.98	1.1	0.845	0.844	0.844	0.49	0.41	0.45
0.328	3.07	0.839	0.840	0.840	0.40	0.41	0.41
0.636	3.07	0.837	0.838	0.837	0.43	0.39	0.41
1.31	3.07	0.839	0.838	0.839	0.47	0.47	0.47

The results obtained by Buchböck have been recalculated so as to show the values of $\Delta n_w / \Delta n_s$ and of T^c obtained at each electrode.[1] These values are shown in Table V, concentrations being expressed in formula weights per 1,000 grams of water. The excellent agreement of the results at the two electrodes attests the high degree of accuracy which this in-

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also made, and an increase in the sucrose concentration at the anode and a corresponding decrease at the cathode were observed. The analyses were not completed, however, as quantitative results could not have been obtained without a careful investigation of the change in specific rotatory power of the sucrose, with varying concentrations of potassium chloride, and such an investigation did not seem worth while in view of the uncertain stability of the sugar during the electrolysis.

[1] Buchböck apparently did not make use of the total number of equivalents of electricity passed through the solution, as shown by his coulometer. The values of T given by him are, therefore, the means of the two values which can be obtained from each electrode separately. He gives, also, only the change in the number of *grams* of water at each electrode, a quantity which is dependent upon the total weight of the electrode portion and which is more liable to be affected by any error arising from admixture with the middle portion than is the value of $\Delta nw/\Delta n_S$. I have accordingly computed values of T^c and of $\Delta n_w/\Delta n_s$ for each electrode from his original data.

vestigator was able to attain in his analyses. In fact, only two criticisms of the experimental part of the work can be made: (1) the failure to maintain a constant temperature by use of a thermostat, and (2) the analysis of only one middle portion. In regard to the first of these, the author does not record the temperature at which his experiments were carried out, but simply makes the statement: "Ein grosser Teil der Unsicherheiten . . . mag übrigens darauf zurückzuführen sein, dass die Temperatur bei diesen Versuchen nicht berücksichtigt wurde, . . . so kann zwischen einzeln, Differenz von etwa 10° bestanden haben, was auf die Resultäte nicht einflusslos geblieben sein durfte." The necessity for analyzing more than one middle portion in transference work has already been discussed. (See note 1, page 334.)

An examination of the results obtained with mannite leads to the conclusion that the value of $\Delta n_w/\Delta n_s$ is independent (within the experimental error) of the concentration of the mannite up to 0.4 molal, and of the concentration of the hydrochloric acid up to 1.5 molal. The same conclusion holds for the results obtained with resorcinol, but the value seems to be somewhat higher. This may be due, as the author suggests, to a combination of some of the resorcinol with the ions, and the more or less progressive change with the concentration of the resorcinol at the higher concentrations would seem to support this view. In view, however, of the uncertainty with respect to the temperature and of the fact that the results obtained with resorcinol are probably not so accurate as those obtained with mannite, it seems best to adopt the value $\Delta n_w/\Delta n_s = 0.28 \pm 0.04$ as the most probable one. The most probable values of the transference numbers are, similarly, $T^c = 0.844$, $T^a = 0.156$.[1]

The final values adopted for HCl are given by the following equations:

$$0.844 N_w^{H^+} - 0.156 N_w^{Cl^-} = 0.24 \pm 0.04,$$

or

$$N_w^{H^+} = (0.28 \pm 0.04) + 0.185\, N_w^{Cl^-}.$$

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[1] Buchböck treats his result in a somewhat different manner. Using the means, he extrapolates his hydration values to zero concentration, both of the hydrochloric acid and of the reference substance. Although, as the table indicates, there seems to be a somewhat regular change in the mean hydration values, $\Delta n_w^F/T^a$, with the concentration, an extrapolation to infinite dilution seems not to be exactly warranted, in view of the variations in the values obtained at the two electrodes. It seems better to adopt a mean value from the data for the more dilute solutions and to conclude that, in moderate concentrations of HCl (up to, say, 1.5 molal) and with the concentration of the reference substance so small that it does not appreciably change the activity of the water (say up to 0.3 molal), the results obtained both for transference number and for relative hydration are independent of the concentration of both electrolyte and reference substance within the experimental errors.

XV. Discussion of the Results.

The *facts* which have been thus far established may be stated thus: *The electrolysis of a solution of potassium, sodium, or lithium chloride, or of hydrochloric acid, containing a non-electrolyte at low concentration, is attended by an increase in the concentration of the non-electrolyte at the anode and a corresponding decrease at the cathode, but no change in concentration takes place in the absence of the electrolyte.* These results are open to but two possible interpretations: (1) the reference substance is carried by the electrolyte from cathode to anode, or (2) water is carried by the electrolyte from anode to cathode during the passage of the current.

The former hypothesis involves the assumption of the formation of a complex between the reference substance and the chloride ion in each case. This assumption alone is not sufficient, however, since it requires that the result obtained shall depend only upon the concentration of the chloride ion, and shall be independent of the nature of the cation. The experiments with raffinose in solutions of potassium, sodium, and lithium chlorides show that this is not at all the case. In order that the first hypothesis shall explain the results, it is therefore necessary to assume, not only the formation of a complex with the chloride ion in each case, but also the formation, but to a less degree, of a complex with the cation, the amount of the latter complex varying with the nature of the cation and increasing in the series Li, Na, K. This involves, moreover, in the case of sodium chloride, the assumption of the same kind and degree of complex formation with the ions in the case of substances of such highly different character as raffinose and arsenious acid. Similarly, in the case of hydrochloric acid, the two very different substances, mannite and resorcinol, must unite practically in the same way with the ions of hydrochloric acid in order to explain the facts according to the first hypothesis. Moreover, Buchböck's experiments show that an increase of *300 per cent.* in the concentration of the non-electrolyte or of *50 per cent.* in the concentration of the hydrochloric acid is without appreciable influence upon the results, which obviously could not be the case if the ions were forming complexes with the non-electrolyte.

In order to explain by this hypothesis the concentration changes resulting when a solution of potassium chloride containing sucrose is electrolyzed, it is necessary to assume that more sucrose is combined with chloride ion than with potassium ion. This state of things might result in two ways, as shown by the following equilibria:

$$\begin{aligned} C_{12}H_{22}O_{11} + K^+ &= [K(C_{12}H_{22}O_{11})]^+ \\ C_{12}H_{22}O_{11} + Cl^- &= [Cl(C_{12}H_{22}O_{11})]^- \end{aligned} \qquad (1)$$

$$\begin{aligned} x(C_{12}H_{22}O_{11}) + K^+ &= [K(C_{12}H_{22}O_{11})_x]^+ \\ y(C_{12}H_{22}O_{11}) + Cl^- &= [Cl(C_{12}H_{22}O_{11})_y]^- \end{aligned} \qquad (2)$$

In the first case we must assume that more of the chloride-ion-sucrose complex is formed than of the potassium-ion-sucrose complex. In the second case we must assume that y is greater than x, and sufficiently greater to give always more sugar in combination with the chloride ion. In either case, application of the Mass-Action Law shows that increasing the concentration of the sugar will affect the two equilibria differently, the chloride-ion complex increasing at a more rapid rate than the potassium-ion complex. The mobilities of the two ions will, therefore, not change at the same rate, and the conductivity of a potassium chloride solution with varying concentrations of sucrose in the solution should be some other function than a linear one. The accompanying plot (Fig. 3), obtained by Masson and Martin,[1] shows no indication of any such combination of sucrose with the ions, the effect of the presence of the sucrose being simply to increase the viscosity of the medium and retard both ions. In this figure, in which the curve for hydrochloric acid is also given, values of the equivalent conductivity, λ, are plotted as abscissae and molal concentration of sucrose as ordinates.

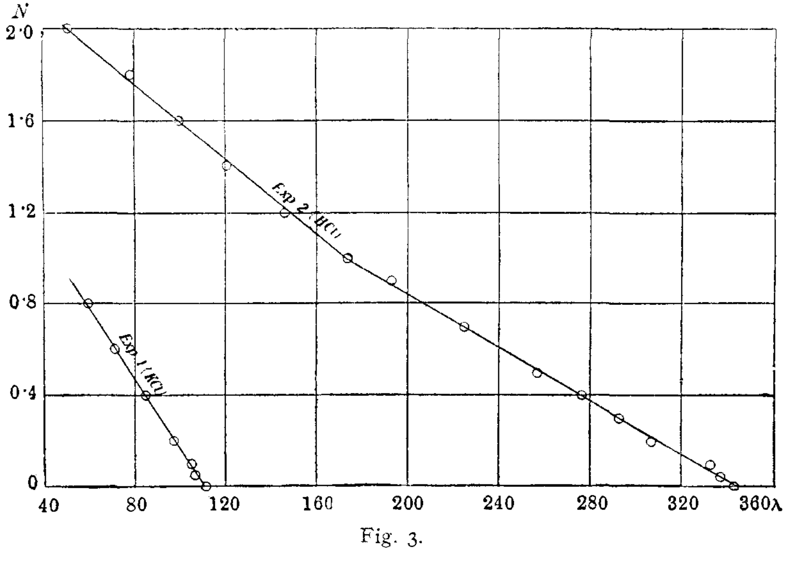

Fig. 3.

The first hypothesis may therefore be considered as eliminated so far as any considerable effect is concerned.[2] The results obtained must, therefore, be due to the migration of water with the current; and, since

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[1] Masson and Martin, *J. Chem. Soc.*, 79, 707 (1901).

[2] It is, of course, possible that the numerical values obtained are affected to some extent by a slight tendency on the part of the reference substance to combine with the ions. Such an effect, if present at all, is probably very small, however. This is readily understood, since the active mass of the reference substance is very small compared with that of the water (about 1 to 500).

the presence of the electrolyte is necessary to produce the result, we must assume some sort of a complex between the water and one or both ions in each solution. This assumption is entirely in accord with all the results, and moreover serves to explain a number of facts in connection with the Ionic Theory which would otherwise be difficult to understand.[1]

Let us now consider the results as interpreted quantitatively upon the basis that the reference substance does not migrate at all during the passage of the current. The results presented above for all the different electrolytes are collected in Table VI.

Table VI.[2]

Electrolyte. Conc. 1 to 1 5 M.	$\Delta n_w^F / T^C$.	Δn_w^F.	T^C.	T^C_∞.	T^C_H.
HCl	0.28 ± 0.04	0.24 ± 0.04	0.844	0.83	0.82
KCl	1.3 ± 0.2	0.60 ± 0.08	0.495	0.495	0.482
NaCl	2.0 ± 0.2	0.76 ± 0.08	0.383	0.396	0.366
LiCl	4.7 ± 0.4	1.5 ± 0.1	0.304	0.330	0.278

$$N_w^{H+} = 0.28 \pm 0.04 + 0.185\, N_w^{Cl-}. \tag{1}$$

$$N_w^{K+} = 1.3 \pm 0.2 + 1.02\, N_w^{Cl-}. \tag{2}$$

$$N_w^{Na+} = 2 \pm 0.2 + 1.61\, N_w^{Cl-}. \tag{3}$$

$$N_w^{Li+} = 4.7 \pm 0.4 + 2.29\, N_w^{Cl-}. \tag{4}$$

Absolute Hydration of the Ions.—From the above equations, which give a relation between the hydration of the separate ions of each salt, the absolute hydration could be calculated if the value were known for any one ion. In Table VII the number of mols. of water combined with one equivalent of each ion is given for different assumptions regarding the number combined with the chloride ion.

A glance at this table shows several interesting facts. The first row of figures evidently represents minimum values, since a negative hydration for the chloride ion would have no meaning. The last row represents impossible values, since it requires that in a solution containing 1.2 mols of LiCl per 1,000 grams of water, approximately 70 mols of water must be combined with the two ions. Since such a solution contains only 55.5 mols of water altogether, the assumption of 20 mols of water on the

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[1] For a full discussion of these facts in relation to the general problem of hydrates in solution, see Washburn, "Hydrates in Solution: Review of Recent Experimental and Theoretical Contributions to this Problem," *Jahrb. Rad. u. Elec.*, December, 1908; also *Technology Quarterly*, **21**, 360 (1908).

[2] In this table, as well as in previous instances, the values given are the *means* of the two results obtained from each electrode independently. The deviation of this mean from the two individual values is indicated in each instance. Since most of the errors peculiar to transference experiments have a tendency to make the changes at the electrodes smaller in magnitude, if anything, than they should be, the deviations indicated may be considered as a fairly reliable measure of the maximum error of the results.

TABLE VII.

MOLS. OF WATER COMBINED WITH ONE MOL. OF EACH ION.

Cl^-.	H^+.	K^+.	Na^+.	Li^+.
0	0.28	1.3	2.0	4.7
1	0.46	2.3	3.6	7.0
2	0.65	3.3	5.2	9.3
3	0.83	4.3	6.8	11.6
4	1.02	5.4	8.4	13.9
5	1.2	6.4	10.0	16.2
6	1.4	7.4	11.6	18.5
7	1.6	8.4	13.2	20.8
8	1.8	9.5	14.9	23.1
9	2.0	10.5	16.6	25.3
10	2.1	11.5	18.0	27.6
11	2.3	12.5	19.4	30.2
12	2.5	13.5	21.3	32.2
20	5.0	21.7	34.2	50.5
..	±0.04	±0.2	±0.2	±0.4

chloride ion is incorrect. Even the assumption of 12 mols of water combined with each mol of chloride ion leads to the necessity of assuming that 44 out of a total of 55 mols of water is in combination with the ions, to say nothing of the amount in combination with the undissociated electrolyte. We may, at any rate, safely conclude that this row gives us maximum values.[1] It is therefore clear that all the cations in question are hydrated, that all those of the alkali elements are more hydrated than the chloride ion, and that the hydration increases markedly between each two successive members of the series, hydrogen, potassium, sodium, lithium.

Relations between the Hydration and the Conductance of Ions.—The remarkable fact early attracted attention that in the case of elementary

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[1] In order to decide which set of values to adopt, it is necessary to know some other relation between the hydration of the ions for some one of the above substances. As explained by the author in another place (*Loc. cit.*, Jahrb. u. Elec.), if accurate data were available on the lowering of the vapor pressure at 25°, of say 0.5 molal solution of the above chlorides, a fair idea of the *total* amount of water in combination might possibly be obtained; and once this is known for any one salt, approximate values for the absolute hydration of all the above ions could be calculated. Vapor pressure data on several of the above chlorides would also make it possible to test the assumptions, since if these are correct the same values for the hydration of the ions should be obtained from the lowering of vapor pressure for each salt. It is to be hoped that such data will soon be available. It is, of course, possible to calculate the vapor pressure lowering at 25° from the data on the lowering of the freezing point if the heats of dilution are known. Data on the lowering of the freezing point and heat of dilution are available but are of doubtful accuracy, and it has not, therefore, seemed advisable to attempt the calculation of the total amount of combined water until accurate data are available. From the data at present available, we should conclude that the true values lie somewhere in the first six rows of Table VII.

ions of any one group of the periodic system, those of smaller atomic weight possess a lower equivalent conductance, and therefore a smaller migration velocity. As a plausible explanation of this fact, it has been suggested[1] that the ions of the lighter elements are more hydrated (and therefore really larger and heavier) than those of the heavier elements. This explanation has now for the first time, by the results of this research, received conclusive confirmation.

This investigation has shown further that the values which have heretofore been obtained for the transference numbers of many, if not all, electrolytes in concentrated solutions by the Hittorf method are to be regarded as erroneous, since their calculation involves the assumption that the solvent remains stationary during the electrolysis. A glance at Table VI shows the error produced in the transference number by neglecting hydration. In the case of potassium chloride, instead of decreasing from 0.495 at infinite dilution to 0.482 at 1.2 molal, as heretofore assumed, the transference number is found to remain unchanged over this range of concentration. This is in entire agreement with the fact that the mobilities of the potassium and chloride ions are very nearly the same, and consequently a change in the viscosity of the medium should affect the velocities of both ions about equally.

In the case of the other ions the change of the transference number with the concentration is much less than has heretofore been assumed. Thus in the case of sodium chloride it is from 0.396 to 0.383 instead of to 0.366; in the case of lithium chloride from 0.330 to 0.304 instead of to 0.278.

XVI. The Relation between the True Transference Number and the Hittorf Transference Number.

We have seen that the ordinary transference number (T_{H}) for concentrated solutions, as obtained by the Hittorf method, is erroneous in cases where the ions are hydrated, since it is calculated on the assumption that the water remains stationary during the passage of the current. A relation, however, exists between the quantity so calculated (T_{H}), the true transference number (T), and the number of mols of water (Δn_w^{F}) transferred per equivalent of electricity. The derivation of this relation will be readily understood from the following considerations. Let one equivalent of electricity be passed, for example, through a potassium chloride solution with a silver anode and silver chloride cathode. As a result, T^c equivalents of KCl and Δn_w^{F} equivalents of water are transferred from anode to cathode. As a result of the water transference, the ratio of salt to water at the cathode is not so great as it would be if no water were transferred. Consequently, if the whole concentration

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[1] Bredig, *Z. physik. Chem.*, **13**, 277, No. 2 (1894). Euler, *Wied. Ann.*, **63**, 273 (1897). Kohlrausch, *Proc. Roy. Soc.*, **71**, 338 (1901).

change be attributed to the transfer of salt alone, the number of mols of salt transferred by the current will appear smaller than it really is. It should be increased by the amount of salt originally associated with the water transferred. This amount is obviously the quantity $\Delta n_w^F n_s/n_w$, where n_s/n_w is the ratio of mols of salt to mols of water in the original solution. When this correction is made we obtain the relation

$$T^c - T_{II}^c = \Delta n_w^F n_s/n_w.$$

This is an important equation; for, since the Hittorf transference number (T_{II}) is usually known or can be determined experimentally, this equation offers a means of calculating either the true transference number (T) or the water transference (Δn_w^F), provided the other is known. By the method of the present investigation all three quantities are directly measured. Other methods are available, however, which give the value of either T or Δn_w^F alone.

Lewis[1] has recently described a method for obtaining the quantity Δn_w^F. The principle of this method consists in measuring the potential of a concentration cell, both solutions of which are saturated with the electrolyte, the latter being only sufficiently soluble to form a dilute solution. One of the solutions, however, contains in addition a certain amount of some non-electrolyte, so that the vapor pressure of the water is different on the two sides of the cell. If the non-electrolyte does not combine with the ions, the only change attending the operation of such a cell would be the transfer of water from one solution to the other. The potential of the cell would therefore be a direct measure of the work done in transferring the water; and the amount so transferred (Δn_w^F) could be calculated from the relation of this work to the known work involved in transferring one mol of water from a solution with one vapor pressure to a solution with another vapor pressure. This method is now being applied experimentally in this laboratory.

It has been shown by Mr. R. C. Tolman, who is now investigating it in this laboratory, that the centrifugal method of des Coudres[2] gives directly the true transference number. In this method a solution of the electrolyte is placed in the tube of a centrifugal apparatus and rotated at a high speed. As a result of the different forces acting on the two ions, an electromotive force is set up between the inner and outer ends of the tube and can be measured by the use of suitable electrodes. From the principles of thermodynamics an equation can be derived connecting this electromotive force with the speed of rotation, the distances of the inner and outer electrodes from the centre of rotation, the partial volume of the electrolyte and of the electrode material in the solution, and the

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[1] Lewis, *Z. Elektrochem.*, **14**, (1908). THIS JOURNAL, **30**, 1355 (1908).

[2] *Wied. Ann.*, **49**, 284 (1883). See also his gravitation method involving the same principles, *Ibid.*, **57**, 232 (1896).

true transference number. Since all the other quantities are capable of measurement, the true transference number, under these conditions, can be calculated. No sufficiently accurate data are yet available, however.

Another method for obtaining the true transference number is the method of moving boundaries. This method has recently been so perfected by Denison and Steele[1] as to equal in accuracy the Hittorf method. In dilute solution the true transference number and the ordinary one as obtained by the Hittorf method are identical, as is evident by referring to the equation connecting them (since the ratio n_s/n_w is then very small). Denison and Steele found, in fact, that all their results for dilute solutions agreed satisfactorily with those obtained by the Hittorf method. In concentrated solutions large deviations, however, were observed which these investigators were unable to explain. Thus, they remark: "Wir haben die Messungen öfters widerholt, aber immer mit demselben Resultat, und zwar 0.508 bis 0.510 für die Anionüberführungszahl von 1.0 norm. KCl und 0.613 bis 0.615 für 1.0 norm. NaCl. Die allgemein angenommenen Werte dieser Grössen sind etwa 0.514 für 1.0 norm. KCl und 0.63 für 1.0 norm. NaCl. Der Grund dieser Abweichung muss vorläufig dahingestellt bleiben; für unsern Zweck genügt es aber, dass schon in 0.1 norm. Lösungen der Unterschied zwischen unsern Zahlen und den durch die analytische Methode gelieferten nicht mehr besteht."

The explanation for this difference between the values obtained by Denison and Steele and the Hittorf values is now apparent: *The rate of motion of the ion-boundary through the solution is a direct measure of the true transference number*;[2] consequently, the results obtained by this method *should* differ from those obtained by the Hittorf method for concentrated solutions. It is therefore interesting to compare the results obtained by Denison and Steele with the values obtained in the present investigation. These are brought together in the following table (Table VIII). The values are those for the cation.

TABLE VIII.

Salt.	True transference numbers.		Hittorf transference numbers.
	Denison and Steele.	Washburn.	Washburn.
KCl	0.492[3]	0.495[4]	0.482[4]
NaCl	0.386[3]	0.383[4]	0.366[4]

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[1] Denison and Steele, *Z. physik Chem.*, **57**, 110 (1906).

[2] It is true that when the motion of the boundary is measured, as in the experiments of Denison and Steele, by means of a reference point *outside* of the solution, any displacement of the solution as a whole through volume changes accompanying the electrode processes would affect the apparent rate of motion of the boundary. The authors state, however, that in the case of their experiments, there was not an appreciable change of volume as a result of the electrode processes.

[3] For a molal solution at 18°.

[4] For a 1.25 molal solution at 25°.

When the difference in temperature and concentration is considered the agreement seems to be satisfactory.[1] Denison and Steele also obtained identical values for the transference number for molal and for 0.1 molal potassium chloride solutions, which agrees perfectly with the result of the present investigation.

By measuring true transference numbers by the method of moving boundaries and "ordinary" transference numbers by the Hittorf method, it is obvious that we are in possession of an excellent method for determining the relative degrees of hydration of the ions, a method which does not require the presence of any third constituent in the solution and which is free from all arbitrary assumptions. Future investigations in this direction seem to offer the most promising line of attack upon the problem of hydration in solutions of electrolytes.

XVII. Summary.

1. This investigation has shown that the electrolysis of a solution of potassium, sodium, or lithium chloride, containing a non-electrolyte at low concentration, is attended by an increase in the ratio of the quantity of non-electrolyte to that of the water at the anode and by a corresponding decrease at the cathode, but that no change takes place in this ratio in the absence of the salt.

2. It is shown that this change is to be attributed mainly, if not wholly, to a transfer of water from the anode to the cathode during the electrolysis.

3. By referring the changes in the content of water and of salt to the non-electrolyte as a reference substance, a relation between the degrees of hydration of the chloride ion, the lithium ion, sodium ion, and potassium ion has been derived. A similar relation involving the hydrogen ion had been previously obtained by Buchböck.

4. The results show that all these cations are hydrated; that the hydration increases markedly between each two members of the series H^+, K^+, Na^+, Li^+; and that the smallest values of the hydration consistent with the data are represented by the formulae: $[H(H_2O)_{0.3}]^+$, $[K(H_2O)_{1.3}]^+$, $[Na(H_2O)_{2.0}]^+$, and $[Li(H_2O)_{4.7}]^+$. The hydration of all these ions may, however, be considerably greater than these values.

The fact that the ions of the elements of a group of the periodic system increase in migration velocity with increasing atomic weight has heretofore been explained by assuming that the ions of the lighter elements are more highly hydrated. The correctness of this explanation has been demonstrated by the results of this research.

5. It is further shown that, owing to the transfer of water during

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[1] Denison and Steele found that the values they obtained for concentrated solutions varied somewhat with the nature of the "indicator salt," so that the method must be pursued further, experimentally, before a final decision can be arrived at regarding the correct values for concentrated solutions.

the electrolysis, the transference numbers hitherto obtained for the more concentrated solutions of these chlorides are erroneous, since the calculation involved the assumption that the water remained stationary. The true transference numbers, derived by reference to the non-electrolyte, are found to vary with the concentration much less than the apparent ones previously computed. In the case of potassium chloride, there is no variation whatever up to a concentration of 1.2 molal.

6. A mathematical relation between the true transference number and the ordinary one as obtained by the Hittorf method is derived. It is also pointed out that the method of moving boundaries gives the true transference number. The results of Denison and Steele obtained by this method are compared with the true transference numbers obtained in the present investigation and shown to agree. Attention is called to the fact that the combination of transference numbers obtained by the Hittorf method with those obtained by the method of moving boundaries furnishes a promising method for further investigating the hydration of ions.

It is with pleasure that the author takes advantage of this opportunity to acknowledge his indebtedness to the generous assistance of Professor Arthur A. Noyes, whose interest, coöperation, and encouragement throughout the progress of this, at times, discouraging investigation, have contributed largely to its successful completion. To the Carnegie Institution of Washington, whose generous financial assistance has rendered possible the continued prosecution of this research, grateful acknowledgments are also due.

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THE POTENTIAL OF THE FERRO-FERRICYANIDE ELECTRODE.

BY GILBERT N. LEWIS AND LEDYARD W. SARGENT.

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An electrode of platinum or other noble metal, in a solution containing potassium ferrocyanide and potassium ferricyanide, gives an extremely well defined potential.[1] In order to employ a method, which will be described in another paper, for determining accurately the potential between two liquids, it became necessary to study the properties of this ferro-ferricyanide electrode under varying conditions and especially in the presence of other salts. The results of the investigation not only acquaint us with a unique kind of oxidation and reduction electrode,

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[1] Fredenhagen, *Z. anorg. Chem.*, **29**, 396 (1902). Schoch, THIS JOURNAL, **26**, 1422 (1904).