[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 49.]

THE THEORY OF THE DETERMINATION OF TRANSFERENCE NUMBERS BY THE METHOD OF MOVING BOUNDARIES.

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Received May 2, 1910.

In spite of the very important rôle that the transference numbers of electrolytes have played in chemical theory, since Hittorf developed sixty years ago the method of determining these quantities by analysis of the electrode solutions, few really accurate transference numbers have been obtained. This is doubtless due to the very great patience and experimental skill demanded by the Hittorf method. The much simpler method of moving boundaries which was first conceived by Lodge has been so far developed, especially by the recent experiments of Denison and Steele,[1] that it yields results showing a degree of reproducibility rarely attained by the analytical method. It is therefore desirable to subject this method to a careful scrutiny in order to see the precise relation between the transference numbers obtained by its means and those determined by the classical method of Hittorf.

On account of certain discrepancies between the values obtained by the two methods it has frequently been surmised that these differences might be due to the existence of complex ions and that a comparison of the results of the two methods might therefore give some information as to the nature of the ions present in solution. The fallacy of this view has recently been clearly demonstrated by Lash Miller,[2] who emphasizes the fact that the direct method gives transference numbers that, when properly interpreted, are from every point of view identical with those obtained by the analytical determination of the amount of substance transferred from one electrode to the other during electrolysis.

There are, however, two distinct analytical methods of determining transference numbers. In the first, which gives the ordinary or Hittorf transference number, the ratio of the amount of salt to a given amount of water at each electrode is determined before and after electrolysis. This obviously shows the actual transference of the salt only in case the water itself is not transported by the current. The second method, which gives the so-called "true transference number," was first devised by Nernst,[3] and depends upon the use of some reference substance in solution which does not wander with the current, and with respect to which rather than to the water the salt content at each electrode is de-

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[1] Denison and Steele, *Z. physik. Chem.*, 57, 110 (1906). Denison, *Trans. Faraday Soc.*, 5, 165 (1909).

[2] *Z. physik. Chem.*, 69, 436 (1909).

[3] *Göttingen Nachricht*, 56, 86 (1900).

termined. The practicability of this method has recently been demonstrated by the experiments of Buchböck[1] on hydrochloric acid and especially by the very accurate investigation of the alkali chlorides by Washburn.[2]

If in any case there is a difference between the true and the Hittorf transference numbers, it is not at once obvious which, if either, of these values may be exactly calculated from the experiments on moving boundaries. For normal sodium and potassium chlorides the true and Hittorf numbers are accurately known and these salts have been investigated by Denison and Steele with the moving boundary method. The transference numbers of the anion obtained by the three methods are given in the following table:

	Hittorf.[3]	True.[3]	D. and S.
KCl (normal)	0.515	0.505	0.508
NaCl (normal)	0.631	0.613	0.614

The close agreement between the true transference numbers and those obtained by Denison and Steele was observed by Washburn, and led him to conclude that the method of moving boundaries gives immediately the true transference numbers. This view moreover has been accepted by Denison in a recent paper.[4]

We shall see, however, that the agreement is entirely accidental, and is due to the neglect of a correction which must always be made when the method of moving boundaries is employed, and which, although never entirely ignored by previous writers, has hitherto been neglected in practice. In order to show the nature and magnitude of this correction let us consider the accompanying figure, which represents (diagrammatically) the conditions of Denison and Steele's experiments. The apparatus consists essentially of two electrode chambers, a straight tube AB, and two small tubes E and F into which the liquid rises to a certain height. Assume that the transference number of normal sodium chloride solution is sought A column of this solution is introduced into the center tube, and bounded by two solutions in one of which (LiCl) the cation has a smaller mobility than the sodium ion, and in the other of which ($NaC_2H_3O_2$) the anion has a smaller mobility than the chloride ion. Under these circumstances a current sent through the cell, in the direction shown by the arrows, sharpens the boundaries A and B and causes them to move in opposite directions, say to A′ and B′. Denison and Steele would now

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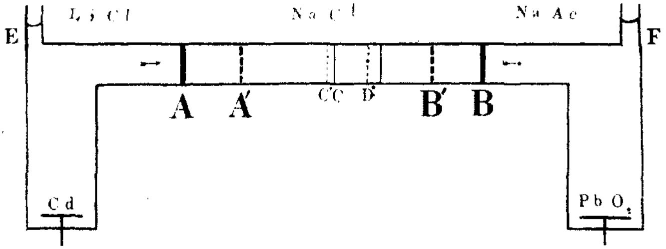
[1] *Z. physik. Chem.*, **55**, 563 (1906).

[2] *Technology Quart.*, 21, 288 (1908); THIS JOURNAL, **31**, 322 (1909); *Z. physik. Chem.*, **66**, 513 (1909).

[3] These values for the normal solutions have been obtained by interpolating between the values obtained by Washburn for 1.25 *N* solutions and the accepted values at infinite dilution.

[4] *Trans. Faraday Soc.*, 5, 165 (1909).

consider AA′ proportional to the mobility of sodium, and BB′ to that of chlorine, whence $\frac{AA'}{AA' + B'B}$ and $\frac{B'B}{AA' + B'B}$ are the transference numbers of cation and anion respectively.



The positions and motions of the boundaries are referred to marks on the glass tube or read by a telescope which is stationary with respect to the apparatus, and it is therefore obvious that any flow of the solution bodily through the tube would vitiate the results. Thus if during the experiment liquid were poured into the tube F and allowed to flow out at E, the boundary B would move more and the boundary A less than before, and entirely different transference numbers would be obtained. A like effect would be produced if the tube F were closed, and hydrogen gas evolved at the cathode. Here also there would be a considerable flow of solution through the middle portion of the apparatus. This is of course an extreme case and it is not difficult to find electrodes which permit no evolution of gas. Nevertheless there will always be a certain volume change at each electrode, and therefore to each of Denison and Steele's transference numbers a correction must be applied which depends both upon the salt investigated and upon the kind of electrode used.[1]

In order to illustrate the mode of calculation of this correction and to obtain an idea of its order of magnitude, let us determine the volume changes at each electrode in a typical experiment of Denison and Steele's, in which a normal solution of sodium chloride is electrolyzed with a cadmium anode and a cathode composed of a paste of lead and lead peroxide. Assume now that the tube E in the apparatus is closed and the tube F is open, and that one faraday of electricity passes, whereby the sodium boundary moves from the point A (on the glass tube) to the point A′ and the chloride boundary from B to B′. The solution between A′ and B′ will remain unchanged. Now let C be the original position

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[1] The transference numbers obtained from moving boundaries without this correction are analogous to those obtained by the Hittorf method when the amounts of salt transported are referred, not to given weight of water, but, incorrectly, to the contents of a given volume of the apparatus.

of what we may call an *average* water particle, and CC′ the change in position of this particle due to flow of liquid caused by a volume change at the cadmium electrode; or, if this idea of the average water particle seems too indefinite, let C and C′ be two points such that there is the same amount of water to the left of C′ after the experiment as there was to the left of C at the beginning. It will now be obvious from our definition that if we measure the positions of A and B from the point C and the positions A′ and B′ from the point C′ we shall be referring the transference of salt to a given quantity of water[1] and thus obtain exactly the Hittorf transference numbers, which are, for the cation, $N_C = \frac{AA' + C'C}{AA' + B'B}$ and for the anion, $N_A = \frac{B'B - C'C}{AA' = B'B}$.

To calculate the distance C′C, when one faraday passes, we must find the volume change occurring during electrolysis to the left of our "average water particle." In this calculation we may use a principle which, although not absolutely correct, is sufficiently so for our present purpose. This principle states that the volume of an aqueous solution differs from the volume of pure water which it contains, by a quantity that is proportional to the number of equivalents of the solute present. The proportionality constant is called the apparent equivalent volume of the solute. Thus in the present case the distribution of lithium chloride is changed by the electrolysis, since its concentration between A and A′ will in general be different from that immediately to the left of A.[2] But the total amount of lithium chloride in the portion to the left of C will be unchanged and the volume therefore due to lithium chloride will remain unchanged. The only changes that will affect the volume considered are (1) the disappearance of one equivalent of metallic cadmium, which occupied 6.5 cc.;[3] (2) the formation of one equivalent of cadmium chloride in solution where it has the apparent volume of 12.0 cc.; and (3) the loss of N_C equivalent of sodium chloride, N_C being the Hittorf transference number, for the cation, of sodium chloride. We have given above the value of N_C for normal sodium chloride as about 0.37. The apparent equivalent volume of this salt is 18.0 cc. The total increase of volume, which is the volume between C and C′, is then $12.0 - 6.5 - (0.37 \times 18.0) = -1.2$ cc.

If now the tube E is open and F closed, the flow through the tube is determined by the volume changes in the right-hand portion of the apparatus. Here one equivalent each of lead peroxide (6.7 cc.) and of

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[1] See also Lash Miller, *Loc. cit.*

[2] See Kohlrausch, *Ann. d. Physik*, **62**, 237 (1897).

[3] All data concerning equivalent volumes are taken or calculated from the tables of Landolt and Börnstein.

water (9.0 cc.), and N_A ($=0.63$) equivalents of sodium chloride with apparent equivalent volume 18.0 cc. have disappeared, one each of lead (4.6 cc.) and sodium hydroxide (-4.1 cc.) have been formed.[1] The total increase in volume is therefore $4.6 - 4.1 - 6.7 - 9.0 - (0.63 \times 18) = -26.6$ cc. In the previous case, where the tube E was closed, we found the volume change hardly greater than the probable error of the calculation, but in the present case, with F closed, the change of 26.6 cc. means a very considerable flow of solution through the tube from left to right.

As a matter of fact Denison and Steele left both E and F open. This complicates the matter, but if we assume that both tubes were of the same diameter, then, since the solutions in the two tubes have about the same density, the volume change will be distributed evenly, and the flow of solution will be the mean of the two values we have just calculated, 1.2 in one direction and 26.6 in the other. This is 12.7 cc. or in round numbers 13 cc. flow from left to right.

We have seen that the Hittorf transference numbers are to be calculated by the equations $N_C = \frac{AA' + C'C}{AA' + B'B}$, $N_A = \frac{B'B - C'C}{AA' + B'B}$ while the Denison and Steele transference numbers, which we may represent by N'_C and N'_A are $\frac{AA'}{AA' + B'B}$ and $\frac{B'B}{AA' + B'B}$. Hence $N_A = N'_A - \frac{C'C}{AA' + B'B}$. Now since the tube A B has a uniform bore the quantities AA′, B′B, C′C may represent volumes as well as distances. We will replace C′C then by v, which will denote the total flow of solution from cathode to anode when one faraday passes. It is obvious that $AA' + B'B$, the total distance moved by both boundaries during the passage of one faraday, is simply equal to the volume containing one equivalent of salt, which is the reciprocal of the equivalent concentration, c. The above equation therefore becomes,

$$N_A = N'_A - vc.$$

In the above case of normal sodium chloride, $c = 1$, $v = -0.013$ (in liters), N'_A was found to be 0.614, hence N_A, the Hittorf number obtained from Denison and Steele's value, is 0.627.

In the case of normal potassium chloride we may make a similar calculation. Here N_A is about 0.51 and the apparent equivalent volumes are 28.5 cc. for potassium chloride and 6.6 cc. for potassium hydroxide. Proceeding as before we find that the increase of volume is -8.3 cc.

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[1] Denison and Steele added a trace of acetic acid near the cathode and of alkali near the anode. These substances, if present at the electrodes, would make the reactions somewhat different from those given above. It seems, however, most probable that these substances were used up in the immediate neighborhood of the electrodes by the preliminary current which was always passed through before the readings were begun, and I have assumed this to be the case.

on the left side, and —18.3 cc. on the right. Assuming again that tubes E and F are both open and of the same size, the flow of liquid, v, through the apparatus amounts to —5.0 cc., that is, in the same direction as for sodium chloride. We must therefore add 0.005 to Denison and Steele's value to find the Hittorf transference number for the anion, and thus obtain 0.513 for the latter.

These two transference numbers, 0.627 for normal sodium chloride, and 0.513 for normal potassium chloride obtained by the moving boundary method are close to those found by the analytic method, namely 0.631 and 0.515.

The uncertainty as to the exact conditions of Denison and Steele's experiments makes it impossible to go further into these corrections; but we see at least that they are so large as to render it necessary in the future to carry out moving boundary experiments in such a way that the flow of liquid through the apparatus may be exactly determined. In general it would seem advisable that only one of the tubes, represented by E and F in our figure, be open at a time. The calculation of the correction would then be simplified. Moreover successive experiments with E open and with F open would give independent data, and thus furnish a mutual check. It would also be well to measure the total volume change in the apparatus after the passage of a given amount of current and compare with the calculated.

Denison and Steele found that their transference numbers were much nearer those obtained by the Hittorf method, when they passed from normal to tenth normal solutions. The reason for this is evident from our equation,

$$N_A = N'_A - vc.$$

Since the quantity v is nearly independent of the concentration, the difference between the Denison and Steele and the Hittorf numbers is only one-tenth as great in tenth normal as in normal solutions. Nevertheless the difference even in tenth normal solution may in some cases amount to 1 per cent. or more, and in most cases is larger than the apparent experimental error of the moving boundary method.

So far we have made no assumption concerning the hydration of the ions, and our conclusions are equally valid whether or not water is itself carried with the current. But suppose now that in that portion of the apparatus lying between A and B there is present in solution a small amount of a non-electrolyte which is known not to migrate with the current, and let this substance extend to the point D where its boundary is recognizable by optical methods, or otherwise. Assume that the ions of the electrolyte under investigation are hydrated and that more water is carried by the cation than by the anion. As a result water will be carried during electrolysis, through the non-electrolyte, towards the cathode, and while the point C, which we have defined above, moves to C′, the boundary D will move a greater distance to D′. A little consideration will show that the difference between the volumes C′C and D′D is a direct measure of the volume of water carried by the current, and furthermore that the *true* transference numbers of the electrolyte are given at once by the expressions, $\frac{AA' + D'D}{AA' + B'B}$ for the cation, and $\frac{B'B - D'D}{AA' + B'B}$ for the anion. In this case it is not even necessary to calculate the volume changes at the electrodes, for these are measured directly by the movements of the boundary D.

The only experimental difficulty in such an experiment as we have just proposed would be found in keeping the boundary D sufficiently sharp for accurate reading; for this boundary is not automatically sharpened by the electrolysis as in the case of the boundaries A and B. The difficulty seems, however, by no means insurmountable and this device should furnish a very simple method of investigating ionic hydration, and true transference numbers.[1]

We have seen that the analytical method of Hittorf is capable of yielding the true transference numbers when a stationary non-electrolyte is employed, as in the experiments of Buchböck and Washburn. Another familiar method of obtaining transference numbers consists in the determination of the electromotive force of cells with and without transference. I have shown in another place[2] that by the use of a stationary non-electrolyte it is possible to determine ionic hydrations and thus true transference numbers. These methods together with the one outlined above suggest that any method of determining the Hittorf transference numbers may with some modification be made to yield true transference numbers, but only by the employment of a non-electrolyte which does not migrate with the current.

Summary.

It is shown that the transference numbers of Denison and Steele are subject to a considerable correction on account of volume changes at the electrodes, the correction being larger, the more concentrated the solution. When this correction is applied the method of moving boundaries gives, theoretically and practically, the Hittorf transference numbers, and not the true transference numbers.

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[1] Evidently when the amount of water carried by the current has been determined by some other method the true transference number may be obtained directly from the Denison and Steele values. It is to be noted that either the true or the Hittorf number is obtained from Denison and Steele's by making a correction for the volume changes at the electrodes. In the first case the volume change includes the volume of the water carried, in the second case it does not.

[2] THIS JOURNAL, 30, 1355 (1908); *Z. Elektrochem.*, 14, 509 (1908).

A method is proposed for obtaining true transference numbers from moving boundary experiments through the aid of a non-electrolyte which does not migrate with the current.

BOSTON, MASS., April 16, 1910.

THE PHOSPHATES OF CALCIUM. IV.[1]

BY FRANK K. CAMERON AND JAMES M. BELL.

Received May 12, 1910.

Owing to the increasing importance of the phosphates of calcium in the fertilizer industry, a knowledge of their behavior in water and in solutions becomes increasingly important. Some years ago two papers[2] were published from this laboratory, in which it was shown that at 25° the solutions, resulting from the mixture of the phosphates of calcium with water, always contain a greater ratio of P_2O_5/CaO than does the original solid. Thus the effects observed are not merely solubility effects but there is also an hydrolysis. So, each of the phosphates of calcium may exist in equilibrium with a series of solutions, in which the ratios of P_2O_5/H_2O and CaO/H_2O vary between rather wide limits.

It was found that at 25° solid monocalcium phosphate could exist in equilibrium with solutions containing over 320 grams phosphoric anhydride per liter. Below this concentration the stable solid was dicalcium phosphate. In the former analyses of these solids, only the ratio P_2O_5/CaO was determined, no estimation having been made of the amount of water of crystallization. The solids analyzed were always contaminated with the adhering mother liquor. In the determination of the above ratio this contamination is not a very serious source of error, as the mother liquor was present in small quantity compared with the crystals, and as the mother liquor was always much poorer both in phosphoric anhydride and in calcium oxide than were the crystals. Further, any determination of the amount of water would have been subject to an enormous error, as the percentage of water in the crystals is small, and that in the adhering liquid was very large. Consequently, the composition of the solid phase was taken as $CaHPO_4.2H_2O$, the ordinary dihydrate of dicalcium phosphate.

That this assumption seemed to be confirmed was indicated in a paper published subsequently by Bassett.[3] In this paper it was announced that above 30° the solid dicalcium phosphate dihydrate changed into the anhydrous salt. At 30° there is an invariant point, the five phases being the two forms of dicalcium phosphate (anhydrous and dihydrate), monocalcium phosphate monohydrate, solution and vapor. Also it was

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[1] Published by permission of the Secretary of Agriculture.

[2] Cameron, Seidell and Bell, THIS JOURNAL, **27**, 1503, 1512 (1905).

[3] *Z. anorg. Chem.*, **53**, 34 (1907).