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THE TRANSFERENCE NUMBERS OF SOLUTIONS OF MIXED CHLORIDES. DISCUSSION OF PAPERS BY SCHNEIDER AND BRALEY AND BY BRALEY AND HALL

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Schneider and Braley[1] have presented in THIS JOURNAL a paper on "The Transference Numbers of Sodium and Potassium in Mixed Chloride Solutions," in which they come to the conclusion that in a mixture of these salts there are ionic complexes of the type $K_x(NaCl_2)_y$. As evidence they present a large amount of data on the transference numbers of sodium and potassium ions in solutions of the mixed chlorides. It is clear that, if complexes of the type suggested are present, the transference numbers should vary in a different manner than would be expected if the solutions contain only simple ions. Further, they point out that proof of the presence of such complex ions in solution would be conclusive evidence against the possibility of complete dissociation of the solutions of strong electrolytes. Such proof would be, it may be added, equally effective evidence against the original ideas of Arrhenius. On account of the importance of the matter, it seems desirable to investigate the results of these authors carefully to see whether their conclusions are a necessary consequence of their experimental work.

In the first place, let us obtain an expression for the transference number of potassium ion in a mixture of sodium and potassium chlorides of total concentration C, in which x is the ratio of the number of moles of potassium chloride in the solute to this total concentration. It will be assumed that the two salts are equally ionized, that no complexes are present, and that the mobility of each ion is constant at any given total salt concentration.[2] If Λ_K, Λ_{Na} and Λ_{Cl} are, respectively the ion conductances at the concentration C of the ions represented by the subscripts, the transference number of the potassium ion in a mixture is given by the expression,

$$T_K = \frac{x\,C\,\Lambda_K}{C\,(x\,\Lambda_K + (1-x)\,\Lambda_{Na} + \Lambda_{Cl})} \tag{1}$$

The numerator contains the conductivity contributed to the solution by the potassium ion, and the denominator the conduction by all the ions in the solution. At any total concentration C the amount of chloride ion does not change with variations in the ratio x. The expression re-

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[1] Schneider and Braley, THIS JOURNAL, **45,** 1121 (1923).

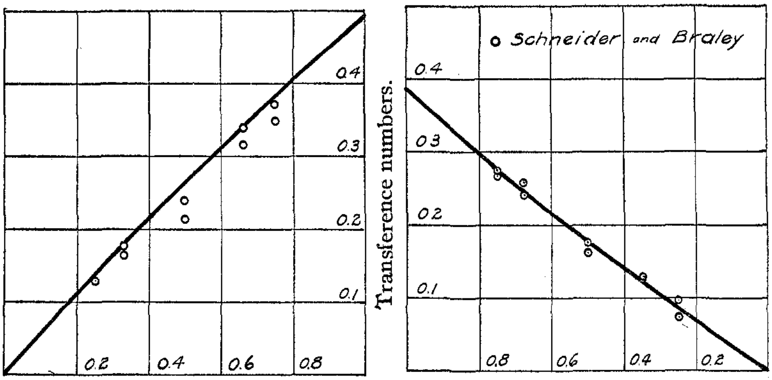
[2] Evidence in favor of this latter assumption for solutions of the pure salts is given in a paper by the writer [MacInnes, *ibid.*, **43,** 1217 (1921)].

duces to zero for $x = 0$ and to $T_K = \Lambda_K/\Lambda_{KCl}$ for $x = 1$. The similar expression for T_{Na} need not be given.[3]

If N_K and N_{Na} are the transference numbers of the potassium and sodium ions in the solutions of the pure salts, and as, for these solutions, $(1 - N_K)\Lambda_{KCl} = (1 - N_{Na})\Lambda_{NaCl}$, the following expression may be readily obtained from Equation 1,

$$T_K = \frac{N_K\,(1 - N_{Na})}{(N_K - N_{Na}) + (1 - N_K)/x} \tag{2}$$

Thus the transference number T_K in the mixture containing the proportion x of potassium chloride may be found from a knowledge of the transference numbers of the two salts only. The assumptions involved in Equation 2 are, of course, the same as those for Equation 1.



Ratio—moles of KCl: total concn. Ratio—moles of NaCl: total concn.

Fig. 1.—0.1 *M*.

In Figs. 1, 2 and 3 Schneider and Braley's results are compared with the predictions of this simple theory, for the total concentrations 0.1, 0.2 and 0.4 *N*, respectively. In these diagrams the observed transference numbers for both potassium and sodium are plotted against values of x varying from zero to 1 for each ion,[4] and for comparison the solid lines give

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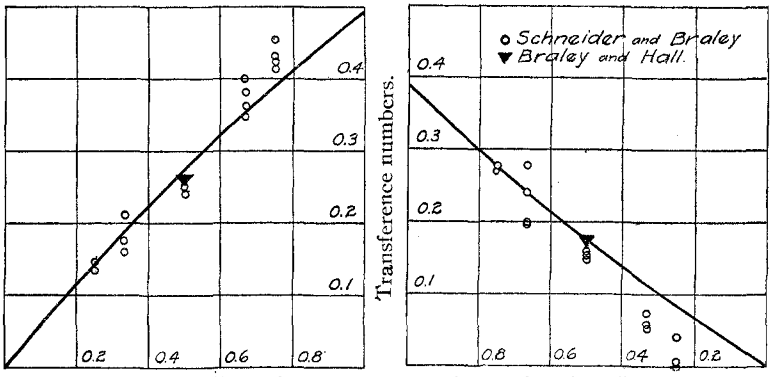
[3] It seems worth mentioning that the assumption that the transference numbers vary in the manner given in Equation 1, when combined with thermodynamic expressions, gives Lewis and Sargent's formula $E_{L_1} = RT/Fln\ \Lambda/\Lambda'$, which represents accurately a large proportion of the values for the liquid junctions of two equally concentrated salt solutions with a common ion. In a boundary such as is given in a flowing junction, there are mixtures that vary in composition from $x = 0$ to $x = 1$. See MacInnes and Yeh, THIS JOURNAL, **43**, 2563 (1921).

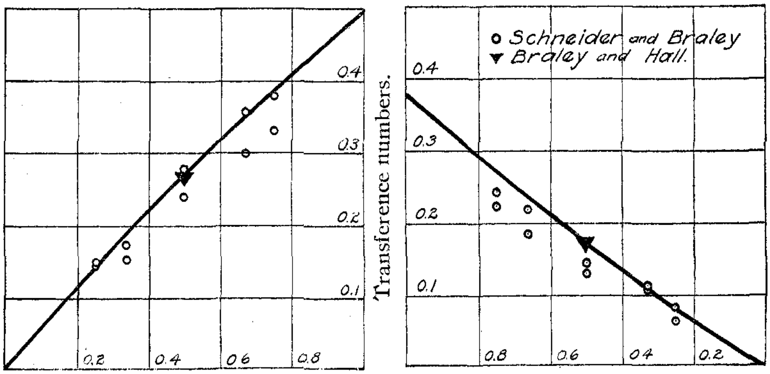
[4] For the transference numbers of the cation of potassium and sodium chlorides at 0.1 *N* the values 0.492 and 0.387, respectively, were used. These numbers have been recently obtained in this Laboratory [Smith and MacInnes, THIS JOURNAL, **47**, 1009 (1925)]. For these constants at 0.2 *N* see the following article. For 0.4 *N*, I have interpolated, on a logarithmic scale, with these values and those of Washburn [*ibid.*, **31**, 322 (1909)] and have obtained the values 0.484 and 0.373.

the transference numbers according to the assumptions given above. Considering the difficult nature of the experimental work the agreement is remarkably good, especially for the transference numbers of the sodium ion. For 0.2 and 0.4 N the agreement with the theory and of check determinations with one another is not so good. *The deviations of the observed values from the theoretical curve are, however, in no case greater than the variations of these values among themselves.* This is also true of the results at 0.8 and 1.6 N which are not reproduced in the figures.



Ratio—moles of KCl:total concn. Ratio—moles of NaCl:total concn.

Fig. 2.—0.2 M.



Ratio—moles of KCl:total concn. Ratio—moles of NaCl:total concn.

Fig. 3.—0.4 M.

The only series in which a systematic deviation of the results observed may possibly be greater than the experimental error, indicated in the results themselves, is at a total concentration of 0.2 N (Fig. 2) with a small proportion of sodium chloride. Here, the measured amount of transference of sodium ion, according to these authors' results, drops nearly to zero. This could be accounted for by the motion of the positively charged sodium ion being nearly balanced by the movement of a negatively charged complex such as $(NaCl)_xCl_y$. Since the transference of sodium chloride was determined by the difference between the weights of the dried chlorides and the directly determined amount of potassium chloride, any error which would give too much of the latter would result in too little sodium chloride. It will be noted that the values of the transference numbers for potassium are high in this region. In another set of experiments, at this same concentration, greater variations between the various determinations are found than constitute the whole difference between the first mentioned results and the curve representing the theory. It does not appear, therefore, that the experiments at 0.2 *N* are of sufficient accuracy to give evidence as to whether complexes are or are not present in the solutions. It is, indeed, difficult to see how it is possible for the measurements to show this abnormal behavior at 0.2 *N* when there is substantial agreement at adjoining concentrations, that is, at 0.1 and 0.4 *N*; particularly, as is shown below, there is no evidence of anything unusual reflected in the conductance measurements. However, since Schneider and Braley have made more experiments at 0.2 *N* than at the other concentrations, and since the subject is of great importance, furnishing as it does a crucial test of the possibility of holding to any theory postulating simple ions, it has been considered desirable to repeat the work of these authors. The results of the latter investigation are given in an article by Jane Dewey,[5] immediately following this.

Some results of similar measurements, of a higher order of accuracy, judging from the agreement of check determinations, have been published by Braley and Hall[6] and the results of these measurements are indicated in the plots by small triangles. These points fall on, or very near to, the curves which represent the assumption of simple ions. Braley and Hall also consider that their results prove the presence of complexes. Their proof, however, rests upon deviations of the measured transference numbers from their theory, which is based upon the tacit assumption that the mobilities of the ions do not vary with the concentration. This would require that the transference numbers remain constant from infinite dilution to the concentration in question, whereas all of these numbers show marked variation with the concentration.

If the transference number varied with the composition of the solution in the complicated manner that Schenider and Braley consider that their results show, it would certainly be expected that some effect of these

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[5] Dewey, This Journal, 47, 1927 (1925).

[6] Braley and Hall, *ibid.*, 42, 1770 (1920). These authors include a few figures that do not check with those plotted but give the same ratio of the potassium-to-sodium transference numbers.

variations would be seen in the conductance measurements. Fig. 4 shows, however, that Stearn's[7] results for the conductance of mixtures of potassium and sodium chlorides yield smooth curves which are very nearly straight lines, when the conductances of the mixtures are plotted against values[8] of the ratio x. In a paper already referred to, I have presented evidence that the conductance of the chloride ion $(N_{\mathrm{Cl}}\Lambda_{\mathrm{MCl}})$ is the same when that ion is in solution with any of the alkali metals or hydrogen. This is true up to molal concentration if corrections are made for differences in viscosity. This observation is inconsistent with the presence of complexes in solutions of single salts unless they are of such a nature that they do not vary for such dissimilar substances as hydrochloric acid and cesium chloride, which seems hardly possible. The closely linear variation of the conductances of the mixtures, which was assumed in deriving Equations 1 and 2, appears to be good evidence that simple ions only are present in the mixtures.

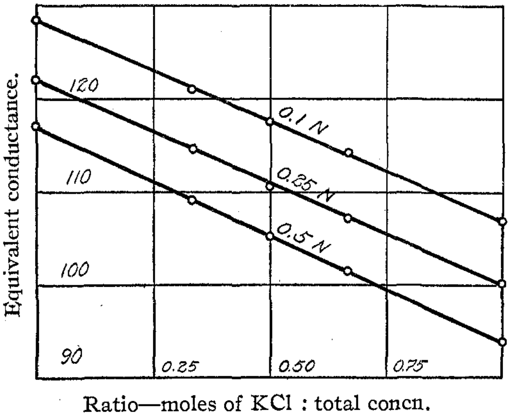

Fig. 4.—The conductances of potassium and sodium chloride solutions and their mixtures.

Conclusion and Summary

Braley and Hall, and later Schneider and Braley, have published results of transference measurements on solutions of mixtures of sodium and potassium chlorides, which they hold to prove that ionic complexes such as $K_x(NaCl_2)_y$ are present in these solutions. However, a reëxamination of these investigations leads to the conclusion that their data are in accord with the assumption that simple ions only are present in the solutions, within the experimental error, which for many of the results is quite large. The results of Schneider and Braley on mixtures at a total concentration of 0.2 N indicate, however, sufficient divergence from the theory

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[7] Stearn, This Journal, **44,** 670 (1922).

[8] Schneider and Braley's own conductance measurements lead to similar straight lines when plotted as shown. The curves they give for a plot similar to Fig. 4 are due to the use of a scarcely defensible scale of abscissas. Also they give no comparative values for the conductances of the pure salts. Compared with published values for these constants their data appear to be high. Measurements on these mixtures at 0° by Dewey (following paper) indicate a maximum deviation of 0.3% from linearity at 0.2 N and of 0.4% at 0.25 N.

to make a redetermination desirable, the results of which are given in the following article.[5]

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THE TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM CHLORIDES AND OF THEIR MIXTURES

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The paper[1] just preceding this contains a discussion of the experimental results and conclusions of Schneider and Braley[2a] and of Braley and Hall,[2b] relative to the question of the presence or absence of ionic complexes in aqueous solutions of potassium and sodium chlorides. It is shown in that paper that their results are in accord with the assumption of simple ions only, within their experimental error, with the possible exception of some of the measurements in which the sum of the concentrations of the two salts is 0.2 N, and the proportion of sodium chloride small. In that region, according to the measurements of the first mentioned authors, the transference number of the sodium ion drops nearly to zero. This could be accounted for by the presence of complex negative ions, containing sodium, which carry as much of this element when moving under the influence of the current as the positively charged ion moving in its normal direction. Their results, if verified, would make some such assumption necessary. On account of the importance of the subject, and since none of the more recent ideas on ionization are tenable if such complexes are present in solutions, it has seemed desirable to repeat the experiments at the concentration mentioned. In addition, the transference numbers of the pure salts have been found at the same concentration, since without them the results of measurements on mixtures cannot be interpreted. A change in the method of analysis of the mixtures resulting from the electrolysis was also made.

The Transference Measurements

The transference apparatus described by Washburn[3] was used except that no stopcock was placed on the cathode side. The cathode was made by winding a piece of platinum gauze, about 10 cm. long and 1 cm. wide, into a coil just small enough to slip into the apparatus. This coil was

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[1] MacInnes, THIS JOURNAL, **47,** 1922 (1925).

[2] (a) Schneider and Braley, *ibid.*, **45,** 1121 (1923). (b) Braley and Hall, *ibid.*, **42,** 1770 (1920).

[3] Washburn, *ibid.*, **31,** 322 (1909).