

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 paper¹ 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 Washburn³ 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

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).

heavily silver plated, and covered with an adherent coating of silver chloride by alternate chloridizing and reducing electrolytically. The anode was a spindle consisting of 3 meters of 1.2mm. silver wire formed in the manner described by Washburn. No chloride separated from either electrode, or entered into colloidal solution, and it was not found necessary to filter the electrode portions after the passage of the current. During a determination about 20 milliamperes was passed through the apparatus for 16 hours, using a potential of 16 v.

Instead of analyzing the middle portions chemically, measurements of their conductivity were made and the conductivities found were compared with that of the original solution. The maximum change observed was less than 0.1%, and was usually nearly zero. The electrode portions were always tested for alkalinity and if any was found the run was discarded.

Two silver coulometers of the Richards type with the anodes surrounded by alundum crucibles were used, one being connected in series at each terminal of the transference apparatus.

The transference measurements were made in a thermostat at $25^{\circ} \pm 0.1^{\circ}$.

The Conductivity Measurements

Conductivity measurements were used, in a manner to be described below, to analyze the solutions resulting from the transference determinations on salt mixtures, as well as for testing the constancy of the middle portions. An "extended wire" bridge with a total resistance of 233 ohms., of which one-tenth was due to the slide wire, was used, in connection with a Curtis resistance box, and a tuning-fork oscillator as a source of current. The capacity of the cell was balanced by the use of a large variable condenser. The conductance cell was of the pipet type, with electrodes 1 cm. in diameter and 8 cm. apart. As a thermostat for the conductance measurements a Dewar tube containing cracked ice in distilled water was used. With this apparatus a precision of 0.005% could be readily obtained.

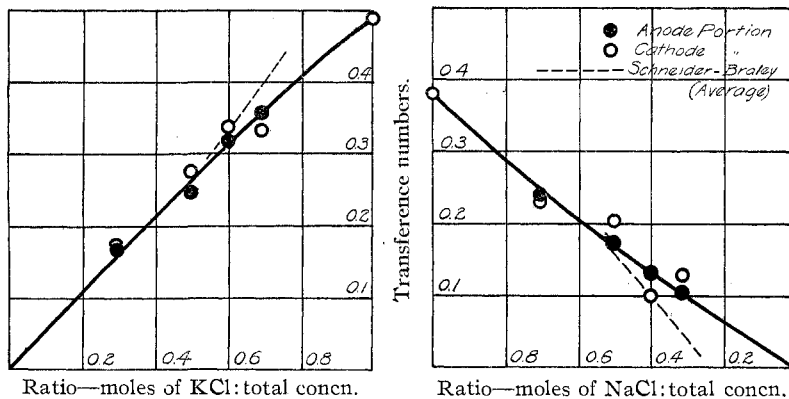
Preparation of Materials

Potassium chloride from a well-known German firm was recrystallized and fused before using. c. p. Sodium chloride of American manufacture was recrystallized twice by precipitation with hydrogen chloride and then fused. The water was redistilled from alkaline permanganate solution in a tin-lined still and stored in resistance-glass bottles.

Experimental Results

The Transference Numbers of the Pure Salts.—Since the transference numbers of the pure salts enter into the computation of the transference numbers of the mixtures (see Equation 2 of the preceding paper), measurements of the values of these constants for potassium and sodium chlorides at 0.2 *N* were first made. A large amount of effort was expended in this part of the research, since the results obtained for the transference number of the potassium ion in potassium chloride solution were consistently lower than those obtained by the moving-boundary method, with which

measurements were simultaneously being made in this Laboratory.⁴ The results are also considerably lower than those found by German investigators and summarized in a paper by Noyes and Falk.⁵ The average result for the transference number of the potassium ion in 0.2 *N* potassium chloride as determined in this research is 0.486, and that by the



Ratio—moles of KCl:total concn. Ratio—moles of NaCl:total concn.
Fig. 1.—The transference numbers of mixtures of potassium and sodium chlorides, at 0.2 *N*.

moving-boundary method 0.490. Many attempts were made to find the reason for this difference, all without success, the Hittorf method always yielding the same result in spite of changes in the design and nature of the electrodes, etc. The results are summarized in Table I, which is self-

TABLE I

THE TRANSFERENCE NUMBER OF POTASSIUM ION IN 0.2 WEIGHT NORMAL POTASSIUM CHLORIDE AT 25°

Wt. of silver deposited	Change in chloride content Millimoles		Transference number T_K	
	Anode portion	Cathode portion	Anode	Cathode
0.7648	3.438	3.424	0.4850	0.4830 (a)
1.4203	6.390	6.397	.4854	.4859 (a)
1.7529	7.926	7.915	.4878	.4871 (b)
1.0650	4.790	4.789	.4852	.4851 (c)
0.7393	3.5434835 (d)

(a) Silver plated platinum anode and cathode. (b) Silver wire anode. (c) Run in air. (d) Zinc anode. Av., omitting (d) 0.4856 ± 0.0005 .

THE TRANSFERENCE NUMBER OF SODIUM ION IN 0.2 WEIGHT NORMAL SODIUM CHLORIDE AT 25°

1.0504	3.671	3.686	0.3786	0.3771
0.9685	3.370	3.358	.3762	.3748
Av. 0.3767 ± 0.0006				

⁴ See Smith and MacInnes, *THIS JOURNAL*, **47**, 994 and MacInnes and Brighton, *ibid.*, **47**, 1009 (1925).

⁵ Noyes and Falk, *ibid.*, **33**, 1436 (1911).

explanatory. One determination was made in the air instead of in a thermostat to test for possible leaks, and another was made with a zinc anode to repeat the practice of the German experimenters. The results by the two latter procedures are, however, slightly lower than the others. The difference, about 0.8%, between the results of the Hittorf and the moving-boundary methods makes no difference in the conclusions of this paper, being of imperceptible magnitude on a plot of the scale of Fig. 1. The difference will, however, be investigated further.

The Transference Numbers of the Salt Mixtures

In the determinations of the transference numbers for the solutions of mixtures of sodium and potassium chlorides, the electrolyses were carried out as for the pure salts. The analysis of the resulting electrode portions was, however, more complicated. After these portions had been collected and weighed, check determinations were made of their conductances, after which the amount of chloride-ion constituent was found by precipitation and weighing as silver chloride. These latter data yielded the total number of moles of salt in the portion under consideration. With this information and with a knowledge of the manner in which the conductance of the solutions changes with the concentration and the proportion of each salt present, this proportion could be found with precision. The computation, however, required the use of a short series of approximations. The fact that the conductivity at any one total concentration varies, for this pair of salts, with the fraction x of potassium chloride in a manner very close to linear greatly facilitated the computations. The data for the conductances of the mixtures of the salts are given in Table II, in which it can be seen that the maximum deviation from linearity is about 0.3% at 0.2 *N* and 0.4% at 0.25 *N*. A single measurement was also made at 0.1 *N* with a fraction x of 0.5 and the deviation was found to be 0.00%. For any intermediate concentration this deviation from the law of mixtures can be interpolated with all the accuracy necessary. The changes of the conductances of the pure salts at 0° for the range of concentrations involved in this research are given in Table III.

The actual computation was carried out as follows. From the weight of the sample of electrode portion, corrected to vacuum, was subtracted the approximate weight of salt in the portion. The total salt concentration of the sample was then calculated from the weight of the water found in this way and from the weight of the silver chloride found in the analysis. The conductances of pure potassium chloride and of pure sodium chloride at this concentration were then interpolated exactly from the data contained in Table III. The fraction x of potassium-ion constituent in the sample was then calculated on the basis of a linear relation between this fraction and the conductance. This gave the necessary data to compute

a new, and very close to exact, value of the weight of salt in the sample and of the total salt concentration. The calculation of the fraction α was then repeated, taking account of the deviation of the conductance values from the linear relation at the given concentration. This process could, of course, be continued until repetitions yielded the same values. Then, having the total concentration and the proportion of each salt in the solution the calculation of the transference numbers was continued in the usual way.

TABLE II

EQUIVALENT CONDUCTANCES OF MIXTURES OF SODIUM AND POTASSIUM CHLORIDES AT 0°
TOTAL CONCENTRATION 0.2000 WEIGHT NORMAL

α	Δ observed	Δ calculated	Δ
0.00	54.639
.25	58.265	58.294	-0.029
.50	61.908	61.949	-.041
.75	65.572	65.603	-.031
1.00	69.258
TOTAL CONCENTRATION 0.2500 WEIGHT NORMAL			
0.00	53.725
.25	57.282	57.323	-0.041
.50	60.858	60.921	-.063
.75	64.480	64.520	-.040
1.00	68.118

TABLE III

SPECIFIC CONDUCTANCES OF POTASSIUM AND SODIUM CHLORIDES AT 0°

		Concn., moles per 1000 g. of water					
		0.15	0.16	0.17	0.18	0.19	
Sp. conductance, KCl		.010481	.011144	.011803	.012460	.013115	
	NaCl	.0083685	.0088860	.0094037	.009911	.010422	
		Concn., moles per 1000 g. of water					
		0.20	0.21	0.22	0.23	0.24	0.25
Sp. conductance, KCl		.013852	.014419	.015078	.015731	.016380	.017030
	NaCl	.010928	.011430	.011933	.012435	.012937	.013431

TABLE IV

TRANSFERENCE NUMBERS OF 0.2 WEIGHT NORMAL MIXTURES OF POTASSIUM AND SODIUM CHLORIDE AT 25°

Portion	Mole ratio KCl	Silver deposited G.	Size of portion G. of water	Transference numbers	
				T_K	T_{Na}
Anode	0.2960	1.0122	107.56	0.174	0.239
Cathode	.2960	82.80	.178	.229
Anode	.4988	1.2037	97.18	.275	.172
Cathode	.4988	83.75	.247	.203
Anode	.6002	1.1702	103.19	.316	.131
Cathode	.6002	84.01	.339	.097
Anode	.6936	1.0013	108.14	.357	.105
Cathode	.6936	81.77	.332	.127

The results of the experiments on the transference numbers of the ions in the solutions of the mixtures of the two salts are given in Table IV,

which is self-explanatory, and are plotted in Fig. 1. In the figure it can be seen that the results from the anode portions are accurately represented by the theoretical line. The results from the cathode portions were subject to a greater error from some unknown cause, but the points are scattered uniformly about the theoretical curve. Some measurements were also made with a still smaller proportion of sodium chloride than those shown in the table, but were not successful. They at least, however, showed movement of sodium-ion constituent in a region of concentrations in which the results of Schneider and Braley would lead one to expect no such movement. It is hoped to continue this research with somewhat changed experimental arrangements, although these experiments, together with the considerations outlined in the preceding article, appear to be ample to decide the matter under discussion.

Conclusion

The results of Schneider and Braley on the transference numbers of sodium- and potassium-ion constituents in a mixture of the chlorides at a total concentration of 0.2 *N* have been repeated, with a modified experimental technique. Their experiments indicated that with a low proportion of sodium chloride the transference number of the sodium-ion constituent drops nearly to zero, a result which has not been confirmed by the experiments described in this paper. Since the new results follow closely the prediction based on the assumption of simple ions, and no ionic complexes, the conclusion of Schneider and Braley that such complexes are present in these solutions is also not confirmed.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY OF THE UNITED STATES DEPARTMENT OF AGRICULTURE]

THE MECHANISM OF THE FIXATION OF NITROGEN AS SODIUM CYANIDE

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The fixation of nitrogen by a heated mixture of sodium carbonate and carbon, with finely divided iron as a catalyst, is usually represented by the equation, $\text{Na}_2\text{CO}_3 + \text{N}_2 + 4\text{C} = 2\text{NaCN} + 3\text{CO}$. The investigation of this system would be greatly simplified if we could study separately the intermediate reactions leading to the final result expressed by the above equation. This paper describes a series of experiments which, it is believed, establishes the nature of these intermediate reactions.

Those who have speculated on the mechanism of this reaction have generally agreed that metallic sodium is first formed, but varying hypotheses have been advanced regarding the formation of cyanide from the