

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

## THE CONDUCTANCE AND TRANSFERENCE NUMBER OF THE CHLORIDE ION IN MIXTURES OF SODIUM AND POTASSIUM CHLORIDES

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RECEIVED MARCH 22, 1929

PUBLISHED SEPTEMBER 5, 1929

The transference numbers of the ion constituents in mixtures of sodium and potassium chlorides have been investigated by various workers, including Braley and Hall,<sup>1</sup> Schneider and Braley,<sup>2</sup> and Dewey.<sup>3</sup> In the first two papers mentioned the authors presented what they thought was evidence that there are ionic complexes in these mixtures. These conclusions were called in question by MacInnes<sup>4</sup> and Bjerrum,<sup>5</sup> who could find evidence, in the experimental work, for simple ions only. This conclusion was later accepted by Braley and Rippie<sup>6</sup> on repeating some of the experimental results of Schneider and Braley.

The question of ionic complexes has been raised again by McBain and Van Rysselberge.<sup>7</sup> They have concluded from transference number measurements made on 0.05 *N* salts containing divalent ions, to which rather large amounts of salts had been added, that complex ions occur in such mixtures.

Since the moving boundary method appears to be capable of greater precision than the Hittorf method, at least as usually carried out, it seemed desirable to test the applicability of the method in the case of mixtures. Furthermore, it seemed possible that, since McBain and Van Rysselberge's work, if confirmed, indicates large amounts of complexes in the solutions they worked with, precise measurements might show at least a small amount in mixtures of potassium and sodium chlorides.

It is not, however, possible, with the moving boundary method, to determine the separate transference numbers of the two positive ion constituents in these mixtures. The determinations were therefore carried out on the chloride ion constituent, which is common to both salts. The measurements described below are on the transference numbers and conductances of mixtures of potassium and sodium chlorides at a total (volume) concentration of 0.1 *N*, at 25°.

### Theoretical

If we let  $x$  represent the proportion of potassium chloride in the mixture

<sup>1</sup> Braley and Hall, *THIS JOURNAL*, **42**, 1770 (1920).

<sup>2</sup> Schneider and Braley, *ibid.*, **45**, 1121 (1923).

<sup>3</sup> Dewey, *ibid.*, **47**, 1927 (1925).

<sup>4</sup> MacInnes, *ibid.*, **47**, 1922 (1925).

<sup>5</sup> Bjerrum, *Kgl. Danske Videnskab. Selskab., Math. fys. Medd.* [vi] **9**, 3 (1925).

<sup>6</sup> Braley and Rippie, *THIS JOURNAL*, **49**, 1493 (1927).

<sup>7</sup> McBain and Van Rysselberge, *ibid.*, **50**, 3009 (1928).

of potassium and sodium chlorides, the transference number  $T_{Cl}$  of the chloride ion will be

$$T_{Cl} = \frac{\Lambda_{Cl}}{x\Lambda_K + (1-x)\Lambda_{Na} + \Lambda_{Cl}} \quad (1)$$

This formula assumes that we are dealing with solutions containing only simple ions. If the equivalent conductances  $\Lambda_{Cl}$ ,  $\Lambda_K$ ,  $\Lambda_{Na}$  of the ion constituents are independent of the values of  $x$ , or, in other words, if the mobilities of the ions are the same in the various mixtures as they are in the solutions of the pure salts at the same total salt concentration, the equivalent conductance of the mixtures should vary linearly with values of  $x$ . This, we will see below, is nearly but not exactly true. Since it follows from these assumptions, and has been found experimentally, that for these solutions  $N\Lambda_{KCl} = N'\Lambda_{NaCl} = \Lambda_{Cl}$ , in which  $N$  and  $N'$  are the transference numbers of the chloride ion for 0.1  $N$  solutions of pure potassium and sodium chlorides, Equation 1 can be put in the form

$$T_{Cl} = \frac{N\Lambda_{Cl}}{x(1-N)\Lambda_{KCl} + (1-x)(1-N')\Lambda_{KCl} N/N' + N\Lambda_{KCl}} \quad (2)$$

which can readily be rearranged to

$$T_{Cl} = \frac{N'}{x\left(\frac{N'}{N} - 1\right) + 1} \quad (3)$$

which gives the transference numbers of the chloride ion in the mixtures in terms of the transference numbers of the pure salts. Any large deviation from values of transference numbers in mixtures computed from Equation 3 would tend to indicate the presence of complexes in the solutions.

### Experimental

**The Moving Boundary Measurements.**—The technique of the moving boundary measurements followed that described in previous papers.<sup>8</sup> The only substantial addition to the procedure is an automatic device for initially forming the boundary. Since, as may be recalled, the rate of motion of the boundary was found to be influenced by vibration, the apparatus was placed in a thermostat which was mounted on a modified Julius suspension. The weakness of this arrangement was, however, that the initial turning of the plate-glass disks over each other in forming the boundary could not be carried out while the vibration-free support was effective. It was necessary to extend the springs so that the thermostat rested on a table, after which the disks could be turned by hand. Vibrations could thus disturb the boundary at its moment of formation, and there was a possibility of further disturbance on releasing the springs. Although recent work has shown that the result of slight mixing or diffusion is overcome, in time, by the potential gradients acting around the boundary,<sup>9</sup> an occasional run showed

<sup>8</sup> (a) MacInnes and Smith, *THIS JOURNAL*, **45**, 2246 (1923); (b) Smith and MacInnes, *ibid.*, **46**, 1398 (1924); (c) MacInnes and Brighton, *ibid.*, **47**, 994 (1925); (d) Smith and MacInnes, *ibid.*, **47**, 1009 (1925); (e) MacInnes, Cowperthwaite and Blanchard, *ibid.*, **48**, 1909 (1926); (f) MacInnes, Cowperthwaite and Huang, *ibid.*, **49**, 1710 (1927).

<sup>9</sup> MacInnes and Cowperthwaite, *Proc. Nat. Acad. Sci.*, **15**, 18 (1929).

variations which indicated more mixing than could be rectified in this manner. It was, therefore, decided to make the boundary formation take place without disturbing the vibration support. The arrangement adopted is shown in Fig. 1. In order to form the boundary the electrode tube A must swing around the pivot P until the lower opening of A is directly over the measuring tube D. This is accomplished by means of the spring S which is mounted on the upright of the support. By means of a sprocket, E, and chain the motion of this spring is transmitted to the upper disk B carrying the electrode vessel A. The chain carries a projection which fits into a hole in the disk. The procedure for forming a boundary is as follows. After filling the measuring tube and electrode vessel as described in previous papers, the disks are placed approximately as shown in the figure. The spring S is then given a number of turns by means of the milled head and is locked with the pin Q. The chain is next adjusted over the sprocket and disk and the pin Q is raised. This causes the disk B to swing through a small angle so that the edge of the sector I is resting against the projection of the rod R through the guide K. The whole apparatus is then placed in the thermostat on the vibration-free support and electrical connection is made to the electrodes and to the terminals of the solenoid M. Now if the circuit is closed through this solenoid the rod R is raised and the disk turns until the projection H encounters the edge of the guide K and the electrode vessel A is directly over the tube D. The projection H is arranged eccentrically around the screw fastening it to the brass sector I in order that the final position of the disk B can be adjusted exactly. Due to the viscosity of the lubricant between the two glass disks the turning takes place smoothly with no jerk at the end. The

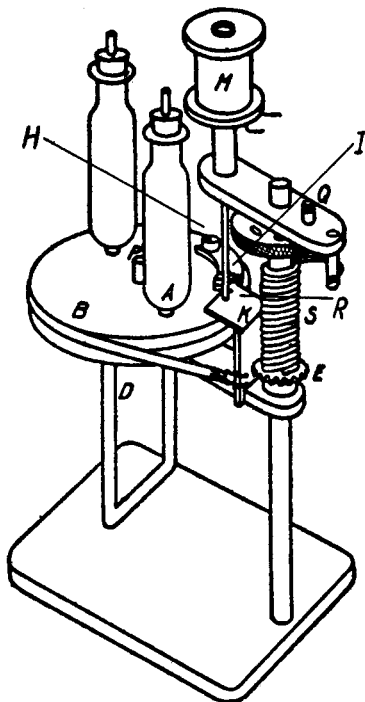


Fig. 1.

procedure as described causes a sharp boundary to form between the solution under investigation in the measuring tube D and the "indicator" solution in the electrode vessel A.

**The Results of the Moving Boundary Experiments.**—As already stated the transference numbers measured in this series of determinations were those of the chloride ion in potassium chloride-sodium chloride mixtures. As "indicator" solutions mixtures of potassium and sodium acetates were used, having in each case the same ratios of the positive ion constituents. Surrounding the silver-silver chloride electrode in the (closed) cathode chamber was a strong solution of potassium acetate. The results of the transference number measurements are given in Table I. It will be seen that for each proportion of potassium chloride the transference number obtained is independent of the indicator concentration, within the range studied, showing that adjustment was obtained in each case. This observation is supported by an earlier series of determinations which

were made in order to test the possibility of measurements of the type here described. In this earlier series the range of indicator concentrations was still wider than that given in Table I. It should, further, be emphasized that each transference number in the table is the average of six figures rarely if ever differing more than 0.1% from the average. Each of these figures is the result of a measurement in which the boundary has moved eight or more centimeters.

TABLE I

TRANSFERENCE NUMBERS OF CHLORIDE ION IN 0.1 *N* POTASSIUM CHLORIDE-SODIUM CHLORIDE MIXTURES AT 25°

Transference number	Indicator concn.	Transference number	Indicator concn.	Transference number	Indicator concn.
0.25 Potassium Chloride		0.50 Potassium Chloride		0.75 Potassium Chloride	
0.5839	0.068	0.5560	0.064	0.5311	0.068
.5838	.068	.5557	.066	.5313	.070
.5828	.068	.5566	.066	.5314	.072
.5832	.068	.5560	.068		
.5831	.070				

The figures in Table I have been corrected for the volume change at the electrode as described by Lewis.<sup>10</sup> This correction is  $-0.0009$  and  $-0.0002$  to the observed transference numbers of pure 0.1 *N* sodium and potassium chloride solutions. The values for the mixtures have been interpolated from these figures.

**The Conductance Measurements.**—Conductance measurements were made on the solutions whose transference numbers had been determined, as well as on the 0.1 *N* solutions of the pure salts. Since it is intended to describe the bridge used in these measurements in some detail in a later article, only the more essential facts concerning the results will be given here. The Washburn pipet cell used was calibrated with "dema" solution prepared as described by Parker and Parker.<sup>11</sup> The resistance box used was calibrated against a box which had been standardized by the Carey Foster method against B. of S. standard resistances. During the measurements the cell was placed in an oil thermostat, a description of which will also be deferred. This maintained a constant temperature within 0.002°, as shown by a platinum-resistance thermometer.

The results of the measurements are given in the appropriate column in Table II. We feel that all variables that may affect the accuracy of these measurements have been controlled at least within 0.02%. Our  $\Lambda$  values for the pure salts (106.69 for NaCl and 128.86 for KCl) are not far from the values (106.71 and 128.82, respectively) given in Noyes and Falk's<sup>12</sup> compilation, which are based on Bray and Hunt's, and Melcher's

<sup>10</sup> Lewis, *THIS JOURNAL*, **32**, 862 (1910).

<sup>11</sup> Parker and Parker, *ibid.*, **46**, 312 (1924).

<sup>12</sup> Noyes and Falk, *ibid.*, **34**, 454 (1912).

work. The latter figures have been corrected for a change of  $-0.14\%$  in the constants used in calibrating the cells since Parker and Parker<sup>11</sup> have shown that Kohlrausch's value for the conductance of the  $0.1 N$  calibrating potassium chloride solution used by these authors is in error by that amount. For the mixtures the only earlier conductance work with which comparison can be made is that of Stearn,<sup>13</sup> which is not of sufficient accuracy for our purpose.

**Preparation of Solutions and Purification of Material.**—The solutions were prepared on a volume normal basis, *i. e.*, 0.1 mole of the fused salt, or mixture of salts in the desired proportions, in a liter of solution at  $25^\circ$ , in carefully calibrated pyrex volumetric flasks, using conductivity water. The best obtainable samples of potassium and sodium chloride were first crystallized from concentrated solution with hydrogen chloride gas, after which they were recrystallized several times from conductivity water.

### Discussion of Results

The results and conclusions of our measurements are outlined in Table II. In the second column, under the heading "transference numbers observed," are given the averages of the values from Table I, and also the transference numbers for the two pure salts from earlier moving boundary measurements. The next column contains the transference numbers of the mixtures as computed from Equation 3. In the fourth and fifth columns are given the conductivity data for the pure salts and the mixtures, and also the conductance values computed on the basis of a simple linear variation of these values with the proportion of potassium chloride in the mixture.

TABLE II  
TRANSFERENCE NUMBERS AND EQUIVALENT CONDUCTANCES OF  $0.1 N$  KCl-NaCl  
MIXTURES AT  $25^\circ$

KCl, %	Transference numbers, $T_{Cl}$		Equivalent conductance, $\Lambda$		Chloride-ion conductance $T_{Cl} \Lambda$
	Observed	Computed	Observed	Computed	
0	0.6137	...	106.69	....	65.48
25	.5834	0.5832	112.13	112.23	65.42
50	.5563	.5553	117.67	117.78	65.45
75	.5313	.5309	123.25	123.32	65.48
100	.5080	...	128.86	....	65.46

In the last column will be found the product of the observed transference numbers and the observed conductances. If simple ions only are present this is the equivalent conductance of the chloride-ion constituent in the mixtures and in the pure salts. As can be seen, this product is a constant well within the experimental error. It is an interesting fact that the observed transference numbers are all slightly larger than the computed

<sup>13</sup> Stearn, THIS JOURNAL, 44, 670 (1922).

values, whereas in the case of the equivalent conductances the reverse is true. This would follow if the chloride ion has the same mobility in the mixtures as in the solutions of the pure salts and one or both of the mobilities of the positive ions are slightly lowered in the solutions of the mixed salts. However, the effect, though definite, is all within 0.1%. There is, quite obviously, no evidence whatever of complex ions in these solutions.

### Summary

An addition to the moving boundary apparatus for determining transference numbers is described, with the aid of which the boundary can be formed without disturbing the apparatus while it is mounted on a vibration-free support.

Transference numbers of the chloride-ion constituent in tenth-normal mixtures of sodium and potassium chlorides have been determined. Accurate conductance measurements have been made on the same solutions.

Within the experimental error chloride-ion conductance is the same in the mixtures as in the solutions of the pure salts. There is no evidence of complex ion formation.

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## A LABORATORY OZONIZER

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RECEIVED MARCH 28, 1929

PUBLISHED SEPTEMBER 5, 1929

It is of general knowledge that ozone is by far the most suitable reagent for the oxidation of double linkages; there is also a general impression that this method requires special and expensive equipment as well as a trained operator. The purpose of this note is to show that the method is exceedingly simple and to give practical information concerning the installation and the cost of the equipment.

L. I. Smith<sup>1</sup> has described an ozonizer which is very satisfactory from the stand-point of the ozone yield. The present apparatus is a simplification of that described by Smith. The purposes of the alterations were to eliminate the use of mercury, which renders the apparatus heavy, expensive and liable to breakage, to modify slightly the shape of the ozone tubes in order to simplify the glass-blowing and to allow the use of sulfuric acid as an electrode, to eliminate the litharge joints, which always have a tendency to expand and break the glass tubes and to render the building of the unit a much shorter and less complicated task. All these features substantially decrease the cost.

<sup>1</sup> L. I. Smith, *THIS JOURNAL*, 47, 1844 (1925).