tinctly electropositive and electronegative constituents are not present the compound is not an electrolyte.

Summary

1. Many substances dissolved in liquid hydrogen sulfide give solutions that conduct the electric current.
2. Solutions of the halides of the phosphorus family show increased conductivity with increase of atomic weight in the family with the exception of bismuth which forms an insoluble compound with liquid hydrogen sulfide.
3. The conductance of derivatives of acetic acid follows the rule that the greater the negativity and positivity of the groups joining the compound, the better the conductance.
4. Ammonium chloride is practically insoluble in liquid hydrogen sulfide, but the introduction of alkyl groups in the place of the hydrogen causes it to become soluble and also conducting in proportion to the number of alkyl groups introduced.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 166]

THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. III. A NOVEL FORM OF APPARATUS

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The purpose of this paper is to describe an apparatus for determining transference numbers by the method of moving boundaries, in which the solutions which join at the boundaries are initially brought together by a new method. The history and theory of the determination are sufficiently described in the first paper of this series.[1] The original apparatus of Denison and Steele[2] as modified by MacInnes and Smith[1] has been found to give results of high accuracy, but it requires delicate manipulation at certain stages in the determination of a transference number. The apparatus to be described requires no special skill to operate, and for that reason the authors hope that it will prove to be useful in elementary laboratories in physical chemistry. A determination with this apparatus is more easily carried out and is far more accurate than the Hittorf method as included in most laboratory courses. The moving-boundary method is, also, very much more effective than the Hittorf method as a demon-

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[1] MacInnes and Smith, THIS JOURNAL, **45**, 2246 (1923).

[2] Denison and Steele, *Phil. Trans.* **205A**, 449 (1906). *Z. physik. Chem.*, **57**, 110 (1906–7).

stration of the phenomena of transference and of the relative velocities of ions.

In a determination by the moving-boundary method it is necessary to bring the indicator solutions into contact with the salt solution whose transference numbers are desired in such a way as to form sharp boundaries. For a description of the way this is accomplished with the older forms of the apparatus the reader is referred to the papers mentioned above. It has occurred to us that the solutions could be brought into sharp contact by means of the mechanism outlined in Fig. 1. The electrode vessel A is fitted into the disk B, and the graduated tube D into a corresponding disk C, the disks B and C both having plane surfaces. The electrode vessel A is filled with the indicator solution and is closed with a stopper which carries the electrode. A drop of the solution, *a*, hangs from the open end of the electrode tube. (The filling can be accomplished by holding a finger over the opening until the stopper is in place, and a tighter seating of the stopper then forms the pendant drop.) The graduated tube D is filled with a slight excess of solution so that a drop *b* protrudes. Now if the disk B is slid over the disk C the excess amounts of both solutions will be sheared away and a sharp boundary will result when the tubes are in place over each other. If the solutions are properly selected and a current of electricity is caused to flow, the boundary will travel down the graduated tube D.

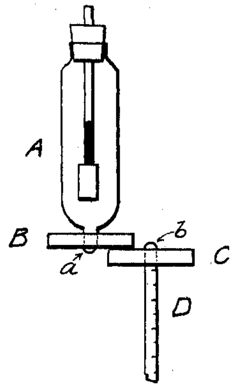

Fig. 1.

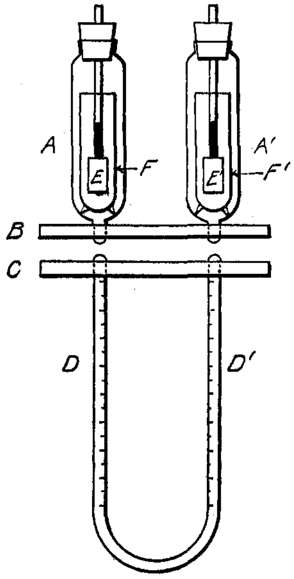

Fig. 2.

Now if two such boundaries are formed, one in which the cation of the solution under observation is followed by an indicator solution with a positive ion of lower mobility, and a corresponding boundary in which the anion is followed by an indicator solution containing a slower negative ion, the ratio of the volume swept through by either ion to the volume passed through by both ions is, with certain restrictions, the transference number. An apparatus by means of which two boundaries can be formed simultaneously is shown in Fig. 2. The electrode vessel A contains an indicator solution, of lithium chloride, for instance, and an electrode, E, which has been made of silver in all of our experiments. The vessel A′ contains the indicator solution for the negative ion and a silver-silver chloride electrode E′. The glass cups, F and F′, are put in the positions shown to keep the concentration changes around the electrodes from affecting the boundaries. The concentrated chloride solution forming around E′ during the electrolysis would otherwise sink into the graduated tube D′. The cups are provided with projections to lift them from the electrode vessels and to allow for the passage of current. The adjacent surfaces of disks B and C are lubricated with vaseline.

In addition to the determination of the transference number from the ratio of the volumes swept through, values of these constants can also be calculated from the data obtained from the movement of each boundary separately, by means of the formula[3]

$$T = \frac{FV}{\phi i t} \tag{1}$$

in which V is the volume swept through by the boundary during the experiment, F is the faraday, ϕ is the volume containing one gram equivalent of the salt, t is the time in seconds and i is the current (which must be kept constant) in amperes.

In a series of experiments in which the excess liquid in the drops was sheared off on the outer edges of the disks B and C, as shown in Fig. 1, it was found that although the ratio of the movement of one boundary to the sum of the movements of both usually gave the correct transference number, computation with Equation 1 gave values that were too low. It appeared, therefore, that all of the current was not passing through the graduated tube D-D′, some of it probably escaping through the wet streak, left in the lubricant when the boundary was formed, to the water of the thermostat in which the instrument was immersed. It was also possible that the lubricant itself was slightly conducting which would also shunt a portion of the current between the electrodes. The fact that the correct transference number may be obtained in spite of this leak would at first sight make it appear that the leak is a matter of no importance. However, as our previous work has demonstrated, it is necessary, if a boundary is to move at the theoretical rate, for the concentrations of the measured and indicator solutions to be adjusted fairly closely according to the equation,

$$C/T = C'/T' \tag{2}$$

in which C and C' are the concentrations of the leading and indicator solutions and T and T' are the corresponding transference numbers. If this is not done the correct transference number can only be obtained by compensation. The correct ratio of C and C' had, furthermore, been established in our determinations by previous work.

The difficulties due to electrical leak are entirely overcome and a considerable increase in the ease of manipulation gained when the disks B and

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[3] Smith and MacInnes, THIS JOURNAL, **46,** 1398 (1924).

C of the design shown in Fig. 3 are used. One of the disks is provided with a brass projection P and the other with a hole into which it fits; otherwise they are identical. A channel J forms an air insulation from the water of the thermostat when the two lubricated disks are in contact. In operation the vessels are filled as shown in Fig. 2. The disks, generously lubricated, are then placed at right angles to each other so that the pendant drops from the electrode vessels are over the depressions K and K′ (Fig. 3) on the lower disk, and the drops from the graduated tube D (Fig. 2) projecting into the corresponding spaces in the upper disk B. The apparatus is then placed in the thermostat, the level of the water coming nearly to the stoppers of the electrode vessels. Any expansions or contractions at this point due to changes of temperature will result only in slight changes in the size of the drops. The upper disk is next turned with the projection P (Fig. 3) as a center and the excess of liquid and lubricant is sheared off at the edges *a* and *a′* and at the corresponding points on the upper disk. Marks on the outer circumferences of the two disks indicate when the tubes from the electrode vessels are directly over the ends of the graduated tube. It will be noted that at this point the contacts of the two solutions are on a small plateau and are completely surrounded by air insulation so that there is no possibility of leak to the thermostat water or through the lubricant.

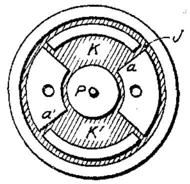

Fig. 3.

TABLE I

TRANSFERENCE NUMBERS OF 0.1 N POTASSIUM CHLORIDE SOLUTIONS AT 25°

From ratio	From movement of single boundaries; Equation 1		
T_K	T_K	T_{Cl}	Sum
0.492	0.492	0.508	1.000
.492	.491	.507	0.998
.4925	.492	.508	1.000
.492	.492	.508	1.000
.4915	.491	.507	0.998
.492	.491	.507	.998
.492	.4915	.5075	.999
.492	.492	.508	1.000
.492	.492	.5075	0.9995
.4915	.492	.508	1.000
.492	.492	.507	0.999

The success of this apparatus is best indicated by Table I, which gives the result of a series of measurements on the transference numbers of a 0.1 N solution of potassium chloride, at 25°. The indicator solution for the potassium ion was 0.065 N lithium chloride solution, and for the chloride ion 0.070 N potassium acetate solution. These are adjusted values established by previous investigations. The first column gives the transference number of the potassium ion from the ratios of the velocities of that ion to the velocities of both ions. The second and third columns contain values of the transference numbers computed from Equation 1. The fourth column contains the sum $T_K + T_{Cl}$ which, it will be seen, is either 1.000 or differs from that value at most by 0.2%. The agreement of the simple ratio with the values computed from Equation 1 is important since the latter values include measurements of the current, time and concentration, whereas the ratio is independent of all these factors.

In these experiments the current, about 7 ma., was kept constant by hand regulation. The current was measured by means of a potentiometer which measured the potential drop across a known resistance. The source of current was a battery of storage cells yielding about 300 volts. Of this current, 50 volts was shunted across an adjustable rheostat, the sliding contact of which was connected to the transference apparatus. Since the movement of the boundaries resulted in an increase of the resistance, movement of this sliding contact furnished the increments of potential required to keep the current constant, indication of which was obtained by observing the galvanometer in the potentiometer circuit. It is probable that the principal error in the determinations was this hand regulation of the current.[4]

A series of determinations was also made on 0.2 N potassium chloride solutions. Here the "adjustment" concentrations had not been determined beforehand by independent measurements. Determinations were therefore carried out in which the indicator solutions (lithium chloride and potassium acetate, as in the work described above) were varied through ranges of concentration. The results, which are given in Table II, show

TABLE II

TRANSFERENCE NUMBERS OF 0.2 N POTASSIUM CHLORIDE SOLUTION AT 25°

From ratio T_K	From movement of separate boundaries				
	Concn. LiCl	T_K	Concn. KAc	T_{Cl}	Sum $T_K + T_{Cl}$
0.4915	0.120	0.490	0.130	0.507	0.997
.486	.123	.490	.142	.518	1.008
.491	.125	.490	.135	.508	0.998
.490	.125	.489	.137	.509	.998
.490	.125	.490	.138	.509	.999
.490	.125	.489	.139	.509	.998
.490	.125	**.490**	.140	**.510**	**1.000**
.490	.125	.491	.141	.510	1.001
.489	.125	.491	.142	.513	1.004
.489	.127	.492	.145	.514	1.006
.471	.130	.493	.150	.553	1.046

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[4] The difficulties encountered when an attempt was made to obtain the time-current product with a coulometer are discussed in the second paper of this series [Smith and MacInnes, THIS JOURNAL, **46,** 1398 (1924)].

that the "transference numbers," both from the ratio and from the movements of the separate boundaries, change with the concentrations of the indicator solutions. However, there is a range of concentrations of these solutions in which the value obtained from the ratio (*0.490*, for the positive ion) is equal to the value for the same ion computed from Equation 1, and also, the numbers found from the movements of the positive and negative ion add up to unity. These values are given in italics in the table. Since in these experiments the indicator concentrations were, in general, increased and decreased together, the ratio gives the correct value of the transference number throughout a wider range of concentration than do the separate boundaries. This is due to the fact that the increase or decrease of rate of movement when the indicator concentration is changed is in the same direction for both boundaries, tending to keep the ratio constant, whereas the values of the transference numbers obtained from the movement of the separate boundaries are found to vary in the same range. For careful work it does not appear to be safe to rely on the ratio alone to give the correct transference number, since, unless the indicator solutions are known to have the right concentrations, it may give results that are considerably in error. If, however, as in the case given above, the ratio and the movements of the two boundaries lead to the same value of the transference number, the worker can feel confident that the correct value has been obtained.

Summary

A convenient apparatus for the measurement of transference numbers by the method of moving boundaries is described.

The transference numbers obtained from the ratio $T_K = V_K/(V_K + V_{Cl})$, in which V_K and V_{Cl} are the volumes swept through by the boundaries in which the potassium and chloride ions, respectively, are leading, have been shown to agree, for 0.1 N and 0.2 N potassium chloride at 25°, with values computed from the rates of movement of the separate boundaries. Transference numbers determined by the latter method involve measurements of current and time whereas values obtained from the ratio are independent of these measurements.

CAMBRIDGE, MASSACHUSETTS