to the exponent *n* is smaller at higher concentrations; thus it is 1.20 for these two salts for the concentration interval 0.01 to 0.1 normal.

2. The ionization of different salts of the same valence type is roughly the same at the same concentration. Thus that of the tetra-sodium salt has been shown to be substantially identical with that of potassium ferrocyanide, the other uni-quadrivalent salt that has been accurately investigated.

3. The un-ionized fraction of salts at a given formal (molal) concentration is roughly proportional to the product of the valences of their ions; thus at 0.05 formal the un-ionized fraction is $4 \times 13 = 52$ per cent. for the tetra-sodium salt, and $5 \times 12 = 60$ per cent. for the penta-sodium salt, while the average values previously obtained are $13^1/_2$ for uni-univalent, 2×14 for uni-bivalent, and 3×13 for uni-trivalent salts.

4. Increase of temperature causes only a slight decrease in the ionization of salts. Thus with these two salts the change between 0° and 25° is scarcely appreciable, and that between 25° and 50° amounts at 0.05 formal to 1.5 to 2 per cent. of the ionization value.

In addition, it is shown that at 25 and 50° the molal conductance of the quinquivalent ion $(C_{11}HO_{10})^{V}$ is 1.5 times that of the quadrivalent ion $C_{11}H_2O_{10}{}^{IV}$, while if these ions encountered the same frictional resistance the larger charge on the former ion would cause its molal conductance to be $5^2/4^2$ or 1.56 times that of the latter ion.

The conductance of benzenepentacarboxylic acid itself was also studied at 25° at the concentrations 0.0006 to 0.02 formal. The results show that it is a moderately strong acid with respect to both its first and second hydrogens.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 70.]

THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY. II. ELECTRICAL TRANSFERENCE NUMBERS.

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CONTENTS.—Introduction. 6. Theoretical Considerations. 7. Review of Previous Investigations upon Transference Numbers. 8. Values of the Transference Numbers. 9. Comparison of Transference Numbers Derived by the Three Different Methods. 10. Change of the Transference Number with the Concentration and Temperature.

Introduction.

In a previous article[1] was presented the first part of a systematic critical study of the existing data relating to the properties of aqueous salt solutions, interpreted with reference to the Ionic Theory. This article de-

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[1] THIS JOURNAL, 32, 1011–1030 (1910).

scribes a continuation of that study. The work has been carried on with the aid of a grant from the Carnegie Institution of Washington, to which we desire to express our indebtedness.

6. Theoretical Considerations.

In the development of the Ionic Theory, as is well known, the mechanism of the conduction of electricity has played a most important part. The three factors upon which, in accordance with that theory, the rate at which electricity is transported through an electrolyte must depend are the number and nature of the ions present in it, the rates at which they move, and the electric charge carried by them.

There are three kinds of phenomena which are closely related to these factors. Of these phenomena may be first mentioned that which is quantitatively described by Faraday's Law, which in its general form may be stated as follows: The passage of electricity through an electrolyte is attended at each electrode by a chemical change involving a number of chemical equivalents strictly proportional to the quantity of electricity passed through and dependent on that alone. Faraday's Law, interpreted as a law of conduction, evidently signifies that motion of electricity in an electrolyte, takes place only in conjunction with motion of the ion-constituents,[1] and that equivalent quantities of different ion-constituents transport equal quantities of electricity.

The quantity of electricity producing a chemical change involving one equivalent is called one *faraday*, and is commonly represented by (F). Its value in the ordinary electrical units, taking the atomic weights of oxygen and silver as 16.00 and 107.88, according to the latest investigations[1] is 96,470 coulombs.[2] This quantity obviously represents the electrical charge on one equivalent weight of any ion.

A second electrical phenomenon that is of special importance in relation to the Ionic Theory is the conductance of solutions. This will be considered in the third paper of this series.

The third important phenomenon is that known as electrical transference, and to the consideration of this the present paper will be de-

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[1] The term *ion-constituent* will be used in this series of articles to denote the positive or negative ion-forming constituent of the salt, without reference to the extent to which it may actually exist in the dissociated state. The term *ion* will be used to denote the electrically charged substances which have resulted from the dissociation of the salts and actually exist as such in the solution. The term *ion-molecules* will be used, when necessary, to denote the electrically charged particles, of which, according to the molecular theory, the ionic substances are composed; but when no confusion arises these ion-molecules may be called simply *ions*. Ion-constituents will be represented simply by the names and chemical formulas representing their composition (*e. g.*, sulfate, SO_4), ions by attaching to the name with a hyphen the word ion, and to the formula + or — signs representing the nature and magnitude of the electric charge (*e. g.*, sulfate-ion, $SO_4^{=}$).

[2] Smith, Mather, and Lowry, *Phil. Trans.*, 207, 579 (1908).

voted. In these two papers, however, only the data relating to solutions of single salts will be discussed, mixtures being considered in later articles.

The phenomenon of transference is briefly described by the following statement: The passage of electricity through an electrolyte is attended by a partial transfer of the positive ion-constituents of the electrolyte from the neighborhood of the anode to that of the cathode, and of the negative ion-constituents from the neighborhood of the cathode to that of the anode; and the total number of equivalents of all the ion-constituents so transferred in both directions is equal to the number of faradays of electricity passed through.

The ordinary method of determining transference, which may be called the gravimetric method, consists in subjecting the quantities of the constituents found to be present after the electrolysis in a portion of the solution extending from the electrode to a distance from it beyond which no change in content has taken place, from the quantities of the same constituents known to be associated before the electrolysis with the weight of solvent present in that portion.

The ratio of the number of equivalents of any ion-constituent transferred to the cathode to the arithmetical sum of the total number of equivalents of all the ion-constituents transferred to and from the cathode is called the *transference number* (T) for that constituent. Thus if an electrolyte contains the basic or positive ion-constituents B', B'',...and the acidic or negative ion-constituents A', A'',...and the equivalents of these transferred to the cathode are $N_{B'}$, $N_{B''}$,..$N_{A'}$, $N_{A''}$,.. the transference number $T_{B'}$ of the constituent B', is:

$$T_{B'} = N_{B'}/(N_{B'} + N_{B''}..—N_{A'} — N_{A''}..) = N_{B'}/(\Sigma N_B — \Sigma N_A). \quad (10)$$

It is evident that the transference number of any ion-constituent is equal to the equivalents of it transferred when one faraday of electricity is passed through the electrolyte (since in that case $\Sigma N_B — \Sigma N_A = 1$).

It will be noted that the determination of transference by the gravimetric method is substantially equivalent to determining the relative quantities of the various ion-constituents which pass in either direction through a cross-section of the solution whose position is defined by the statement that the quantity of solvent between it and the electrode remains unchanged during the passage of the current. It is evident, therefore, that the quantity (N) of any ion-constituent transferred is equal to the product of (1) the area a of the cross-section, (2) the time t, (3) the velocity U with which the constituent moves through the imaginary cross-section, and (4) its equivalent concentration; that is, $N = a\,t\,U\,C$.[1]

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[1] It is to be noted that N and U have negative values for negative ion-constituents under the convention here adopted, according to which transference and velocity, if taking place towards the cathode, are considered positive; if taking place away from the cathode, negative. The transference number T_A of a negative ion-constituent is therefore negative; and the relation $\Sigma T_B — \Sigma T_A = 1$ holds true.

The transference number of an ion-constituent B' is therefore:

$$T_{B'} = U_{B'}C_{B'}/(U_{B'}C_{B'} + U_{B''}C_{B''}\ldots - U_{A'}C_{A'} - U_{A''}C_{A''}\ldots) = U_{B'}C_{B'}/(\Sigma U_BC_B - \Sigma U_AC_A). \quad (11)$$

In the case of a solution of a single salt, where there are only two ion-constituents (B and A) and where these have, necessarily, the same equivalent concentration, equation (11) assumes the simple form,

$$T_B = U_B/(U_B - U_A). \quad (12)$$

That is, the transference number of either ion-constituent is the ratio of its velocity to the arithmetical sum of the velocities of the two constituents.

This principle forms the basis of the moving-boundary method of determining transference numbers experimentally developed by Steele and Denison.[1] In this method the relative velocities, under the same conditions, of the two ion-constituents of a salt are obtained by measuring the distances traversed by the two boundaries of a solution of it placed between solutions of approximate concentration of two other salts, one of which has the same anion but a slower moving cation, and the other of which has the same cation but a slower moving anion, these conditions being essential to the maintenance of sharp boundaries. Thus the transference relations in a potassium chloride solution could be studied by placing it in a tube between solutions of sodium chloride and potassium acetate, passing a current in the direction from the sodium chloride to the potassium acetate, and measuring the distances traversed by the boundary between the sodium and potassium chloride and by that between the potassium chloride and acetate.

Since in carrying out this method the distances have always been measured with reference to a point outside of the solution, they must be corrected, as has been shown in detail by Lewis,[2] for any mass displacement of the liquid that may arise from volume changes attending the chemical processes taking place at the electrodes. If the apparatus is closed at the cathode side, the relation between the corrected and observed transference numbers is: $T^{\text{corr}} = T^{\text{obs}} + C\Delta v_c$, where C represents the equivalent concentration of the solution and Δv_c the volume-increase due to the changes taking place at the cathode when one faraday of electricity is passed. If it is closed at the anode side, the relation is $T^{\text{corr}} = T^{\text{obs}} - C\Delta v_A$, where Δv_A represents the volume-increase due to the changes taking place at the anode when one faraday is passed. (Unfortunately, in the experiments thus far published, the apparatus was

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[1] Steele, *Z. physik. Chem.*, 40, 689 (1902). Denison, *Ibid.*, 44, 575 (1903). Denison and Steele, *Ibid.*, 57, 110 (1907). Denison, *Trans. Faraday Soc.*, 5, 165 (1909).

[2] THIS JOURNAL, 32, 863 (1910).

left open at both sides, so that the correction to be applied is uncertain.[1]) It will be noticed that the correction is proportional to the concentration. At 0.1 normal it would hardly ever exceed a few tenths of a per cent., but at higher concentrations it is likely to be so large as to make the uncorrected results of little significance.

The transference numbers obtained by the moving-boundary method, when corrected for the mass displacement of the liquid, and those obtained by the gravimetric method are in principle identical quantities, as has been shown by Miller[2] and by Lewis.[3] Both methods give values that correspond to the relative quantities of the ion-constituent transferred measured with reference to an imaginary cross-section of the solution so placed that the same quantity of solvent is present on either side of it before and after electrolysis. They correspond, therefore, also to the relative velocities of the ion-constituents through the solvent (regarded as stationary).

Since the solvent may be itself transferred, owing to the ions of the salt being combined with it (*i. e.*, being solvated), the transference results obtained by either of these methods can be fully interpreted only up to moderate concentrations, up to which the solvation does not materially influence the results. At higher concentrations, however, there may be added to the solution some substance which presumably does not migrate with the current, and the transferred quantities not only of the ion-constituents but also of the solvent may be determined with reference to this substance. Experiments were first made in this way by Nernst, Gerrard, and Oppermann[4] by the gravimetric method; but only a few accurate results have been thus far published, namely, those obtained by Buchböck[5] with hydrochloric acid and by Washburn[6] with the alkali-element halides.

It is important, with reference to the theoretical significance of the results, to formulate the relation between the ordinary transference number T (referred to the solvent assumed stationary) and the "true" transference number T^{Tr} (referred to a non-migrating substance). This relation can readily be shown[7] to be

$$T^{Tr} = T + \Delta N_0.N/N_0, \tag{13}$$

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[1] As suggested by Lewis, the best that can be done under these circumstances is to correct by means of the equation: $T^{\text{corr}} = T^{\text{obs}} + {}^1/_2(C\Delta v_c - \Delta v_A)$.

[2] *Z. physik. Chem.*, 69, 437 (1909).

[3] *Loc. cit.*

[4] *Nachrichten Göttinger Gesellsch. Wissensch.*, 56, 86 (1900).

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

[6] THIS JOURNAL, 31, 349 (1909).

[7] Thus if the quantity of water ΔN_0 mols has come into the cathode portion through transference, the original content of that portion in any ion-constituent is obviously less than that ordinarily calculated, by the number of equivalents of the

where ΔN_0 represents the number of mols of solvent transferred to the cathode per faraday and N the equivalents of salt in the solution associated with N_0 mols of the solvent.

The correction that must be added to the ordinary transference number to give the true transference number when N equivalents of the ion-constituent are associated with 1000 grams of water ($N_0 = 55.5$) is evidently $0.018\ N.\Delta N_0$. Thus for each mol of water transferred to the cathode per faraday it is 0.018 in a solution approximately normal, and 0.0018 in one approximatley 0.1 normal. The fractional correction is the ratio of this quantity to the transference number.

It is also to be noted that the solvent transferred to the cathode is the arithmetical difference between that carried to it by the positive ion-constituents and away from it by the negative ion-constituents. Thus, if in a solution of a single salt each equivalent of the positive constituent B carry n_W^B mols of water or other solvent and each equivalent of the negative constituent A carry n_W^A mols, and if the transference number of the former be T_B, then the solvent transferred per faraday would be

$$\Delta N_0 = n_W^B T_B + n_W^A T_A.^1 \qquad (14)$$

Attention may also be called to the fact that, if the ion-constituents of a salt are solvated, it is the true transference number, not the ordinary one, that must be substituted in equation (12) if U_B and U_A are to signify the velocities of the solvated ion-constituents through the (uncombined) solvent.

Next may be considered the factors which from a molecular standpoint must determin the velocity and transference of any ion-constituent, first in the case where it dissociates only into a single ion. Since at any moment only that fraction γ of the ion-constituent migrates which is in the state of (free) ion, the relation between the velocity (U_B or U_A) of the ion-constituent B or A and that (U_{B^+} or U_{A^-}) of the ion B^+ or A^- follows is:

$$U_B = \gamma_B U_{B^+}; \text{ or } U_A = \gamma_A U_{A^-}. \qquad (15)$$

In the case of a single salt consisting only of two such constituents, which must necessarily be equally dissociated ($\gamma_B = \gamma_A$), the degree of ionization will evidently not influence the transference number.

Any cause which affects differently the velocities of the two ions must, however, exert such an influence. Now the velocity of any (free) ion

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ion-constituent associated in the solution with that quantity of water (that is, by $\Delta N_0 . N/N_0$). The number of equivalents of the constituent transferred to the cathode is therefore greater by the same amount.

[1] For example, assuming arbitrarily that the ions of sodium sulfate have the composition $(Na.2H_2O)^+$ and $(SO_4.8H_2O)^=$, equation (14) becomes (since $T_B = 0.39$ and $T_A = -0.61$) $\Delta N_0 = (2 \times 0.39) - (4 \times 0.61) = -1.66$ mols water per faraday. If the sodium ion be anhydrous, ΔN_0 would equal -2.44.

must be equal to the ratio of the electric force driving it to the frictional resistance which it encounters when the velocity is unity.[1] The electric force under a given potential-gradient is proportional to the charge upon the ion and, therefore, to its valence. The frictional resistance may be expected to vary in the same direction in which the viscosity of the solution varies, the two variations being in general roughly proportional, but probably not exactly so, nor identically related in the case of different ions.[2] If the different ions are differently affected by changes in the medium, their relative velocities, and hence the transference number will evidently change with the concentration and temperature, though much less rapidly than the velocities of the separate ions. Since the viscosity of 0.1 normal solutions differs from that of water scarcely ever by more than 4 per cent., and usually by a much less amount, it is not to be expected that up to this concentration any considerable change in the transference number will take place from this cause; but it may well do so at considerably higher concentrations.

In the case in which there are two or more ions, $D'^{\pm}$ and $D''^{\pm}$ corresponding to an ion-constituent D (as would be true, for example, of either constituent of potassium sulfate if it be assumed that the salt is dissociated not only into K^+ and $SO_4^=$ ions, but also into KSO_4^- ions), the quantity of the constituent transferred is evidently equal to the algebraic sum of the two quantities of it that would be separately transferred as a result of the motions of the two ions containing it.[3] If the concentration of the constituent is C_D, the fraction of it existing as ion $D'^{\pm}$ is $\gamma_{D'}$, and that existing as ion $D''^{\pm}$ is $\gamma_{D''}$, and the velocities of these two are $U_{D'\pm}$ and $U_{D''\pm}$, then evidently the quantity of it passing through a cross-section of area a in the time t is $a\,t\,(\gamma_{D'}U_{D'\pm} + \gamma_{D''}U_{D''\pm})C_D$, and the resultant velocity U_D of the ion-constituent D is:

$$U_D = \gamma_{D'}U_{D'\pm} + \gamma_{D''}U_{D''\pm}. \tag{16}$$

By substituting this value in equation (12) the following expression is obtained for a single salt whose two ion-constituents B and A are each transferred in the form of two or more ions:

$$\frac{T_B}{T_A} = \frac{\gamma_{B'}U_{B'\pm} + \gamma_{B''}U_{B''\pm} + \ldots}{\gamma_{A'}U_{A'\pm} + \gamma_{A''}U_{A''\pm} + \ldots} \tag{17}$$

Since the fractions $\gamma_{B'}$, $\gamma_{A'}$ . . of the ion-constituents dissociated into their various ions may change with the concentration, even while this is small,

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[1] See Nernst, *Theoret. Chemie*, 4th edition, p. 13 (1903).

[2] For a fuller discussion of this relation, see the third paper of this series.

[3] That the presence of intermediate or complex ions has, as here postulated, no other effect on the concrete phenomena of transference than that of being one of the factors which determins the quantity of each ion-constituent transferred and its velocity through the solution has been shown by Lash Miller (*Z. physik. Chem.*, 69, 437 (1909).

it is obvious that the transference number may do so likewise whenever intermediate or complex ions are present.

The application of this expression to the case in which a salt of the types B_2A or BA_2 (such as K_2SO_4 or $BaCl_2$) forms, in addition to the simple ions B^+ and A^-, an intermediate ion BA^- or BA^+ (such as KSO_4^- or $ClBa^+$) is of special importance. In this case expression (17) becomes

$$\frac{T_B}{T_A} = \frac{\gamma_B U_{B^+} + \gamma_{BA}^{B} U_{BA^\pm}}{\gamma_A U_{A^-} + \gamma_{BA}^{A} U_{BA^\pm}}, \qquad (18)$$

where γ_{BA}^{B} and γ_{BA}^{A} represent the fractions of the constituent A and of the constituent B, respectively, which exist in the form of the intermediate ion. Representing by γ_1 the fraction of the salt that is dissociated into BA^+ and BA^- or into A^- and BA^+, and by γ_2 the fraction of the salt that is dissociated into B^+ and A^-, the preceding equations may be written in the following forms:[1]

$$\frac{T_B}{T_A} = \frac{\left(\frac{\gamma_2}{\gamma_1} + \frac{1}{2}\right) U_{B^+} + \frac{1}{2} U_{BA^-}}{\frac{\gamma_2}{\gamma_1} U_{A^=} + U_{BA^-}} \text{ for a salt } B_2A. \qquad (19)$$

$$\frac{T_B}{T_A} = \frac{\frac{\gamma_2}{\gamma_1} U_{B^{++}} + U_{BA^+}}{\left(\frac{\gamma_2}{\gamma_1} + \frac{1}{2}\right) U_{A^+} + \frac{1}{2} U_{BA^+}} \text{ for a salt } BA_2. \qquad (20)$$

It is evident from these expressions that the transference number will, in general, vary with the ratio (γ_2/γ_1) of the fractions of the salt that are dissociated in the two ways. It can be shown, however, by differentiating these equations with respect to γ_2/γ_1 and placing the derivatives equal to zero, that the transference number will be independent of the character and extent of the ionization in the case that the following definit relation between the values of U_{B^+}, U_{A^-}, and U_{BA^-} holds true:

$$\frac{1}{U_{BA^-}} = \frac{2}{U_{A^=}} - \frac{1}{U_{B^+}} \text{ for } B_2A; \text{ or } \frac{1}{U_{BA^+}} = \frac{2}{U_{B^{++}}} - \frac{1}{U_{A^-}} \text{ for } BA_2. \qquad (21)$$

The separate terms in these expressions are evidently proportional to the frictional resistances which the ions encounter in their motion through the solution;[2] hence, it may be concluded that, in case the frictional resistance of the intermediate ion BA^- or BA^+ is the arithmetical sum

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[1] These forms are obtained in the case of a salt B_2A by putting $\gamma_B = (\gamma_2 + \frac{1}{2}\gamma_1)$, $\gamma_{BA}^{B} = \frac{1}{2}\gamma_1$, $\gamma_A = \gamma_2$, and $\gamma_{BA}^{A} = \gamma_1$; and in the case of a salt BA_2 by putting $\gamma_B = \gamma_2$, $\gamma_{BA}^{B} = \gamma_1$, $\gamma_A = (\gamma_2 + \frac{1}{2}\gamma_1)$, and $\gamma_{BA}^{A} = \frac{1}{2}\gamma$; and by dividing both numerator and denominator by γ_1.

[2] This is true since the velocity is proportional to the ratio between the electric force driving the ion (which force is twice as great for a doubly as for a singly charged ion) and the frictional resistance which it encounters.

of the frictional resistances of the simple ions B^+ and A^-, then the transference number will be independent of the proportion of intermediate ion that may be present.[1]

It is impossible to determin experimentally in any case whether the frictional resistance of the intermediate ion is really additive, since no method of obtaining the conductance or velocity of such ions in the case of salts has yet been developed. It may be pointed out, however, that such additivity implies, from the kinetic standpoint, the existence of a definit, unique relation between the dimensions of the single ions and that of the intermediate ion—a relation which, in view of the uncertainties as to the degree of proximity of the constituents in the intermediate ion and as to their relative hydration after union has taken place, can not be even approximately predicted. If, therefore, the transference number of any tri-ionic salt is found to be constant through a considerable range of concentration, this makes it somewhat probable, though it does not prove, that the intermediate ion is not present in considerable proportion in the solution. If such constancy of the transference number is found to be a common characteristic of tri-ionic salts, it shows that transference phenomena afford no evidence of the existence of intermediate ions.

Another special case in which a constituent may give rise to two or more different ions is that in which its ions may combine with different quantities of water. The relative proportions of the differently hydrated ions will, however, vary only when the solution becomes fairly concentrated. This matter will be more fully discussed in the third paper of this Series.

Reference must finally be made to a third, somewhat indirect method which enables transference numbers and ionic velocities to be determined at zero concentration. This method is of especial importance since it is difficult to make accurate transference determinations at very small concentrations, since it affords a valuable check on the transference numbers directly obtained at greater concentrations, and since it enables new ones to be calculated. The method consists in determining first the equivalent conductances of the ions of some uni-univalent salt for which a reliable transference number at small concentrations has been measured, this being done by multiplying this transference number by the equivalent conductance of the salt at zero concentration. Then the conductances of other ions are derived by subtracting the known value for one of these ions from the equivalent conductance at zero concentration of other salts containing it. Since the equivalent conductance Λ_{B^+} or Λ_{A^-} is directly proportional to the velocity U_{B^+} or $-U_{A^-}$

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[1] This conclusion has already been reached by Lewis, THIS JOURNAL, **32**, 1569 (1910).

under unit potential gradient, the transference numbers T_B and T_A are evidently given by the expressions:

$$T_B = \frac{\Lambda_{B+}}{\Lambda_{B+} + \Lambda_{A-}}; \text{ and } - T_{A-} = \frac{\Lambda_{A-}}{\Lambda_{B+} + \Lambda_{A-}} \qquad (22)$$

The relation of equivalent conductance to ionic velocity and the possible errors involved in deriving by extrapolation the equivalent conductance of salts at zero concentration will be discussed more fully in the third paper. The values of the equivalent conductance of the salts and of the separate ions obtained from them as just described will also be there presented. The transference values calculated by means of equation (22) will, however, be included in this article, so that they may be compared with the results of direct determinations.

7. Review of Previous Investigations upon Transference Numbers.

In the following pages the attempt will first be made to bring together in tabular form all the fairly reliable transference values previously obtained for single salts in aqueous solution up to normal concentration, and to derive from these data the values which it seems best to adopt in the light of the now existing knowledge.[1] This section will be devoted to a consideration of the criteria of reliability in transference measurements and to a brief review of previously published investigations, especially with reference to the accuracy apparently secured and the relative weight that can appropriately be assigned to the results.

In determining the reliability of a transference determination by the gravimetric method the following factors are to be considered: 1. Whether the cathode and anode portions were both analyzed for one or both of the constituents, and how concordant the changes in content found in the two portions are. 2. The ratio of the change in content to the total content of the electrode portions, since, other things being equal, the accuracy increases as this ratio increases. 3. Whether one or more middle portions were analyzed, and the magnitnde of the change in content. 4. The character of the electrodes used, considered with reference to the possible formation of migrating substances and to the introduction of complications in the analysis of the electrode portions. 5. The character of the transference apparatus employed, especially with reference to the likelihood of convection during the electrolysis and during the subsequent removal of the portions, and with reference to the employment of membranes. 6. The probable accuracy of the analytical method employed. In addition, the usual criteria of a pre-

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[1] A complete bibliography of articles relating to transference and a summary of all the transference data published up to the end of 1905 has been already published by McBain (*Proc. Washington Acad. Science*, 9, 1–78 (1907)). The present summary covers work published up to the end of 1910.

cision discussion, such as the number of duplicate measurements made and the concordance of the results are also to be considered.

There are few physical or chemical measurements which yield results that afford so conclusive a test of their own accuracy as do complete transference measurements, by determining in both of the electrode portions the change in content of one, or still better, of both, of the constituents, and by making sure by the analysis of at least two middle portions that the change has not extended into them in consequence of convection or migration of products of the electrolysis. Comparatively few determinations, however, have been made in this complete way.

No results have been included in this article in which membranes were used in the transference apparatus, for Bein[1] and Hittorf[2] have shown that they frequently give rise to a selective transmission of the ions. Nor will any of the other results published prior to 1888 be included, as the errors involved in the early work were large for other reasons.

The investigations from which the results given in the next section of this article were taken may be briefly described as follows:

1. Löb and Nernst, *Z. physik. Chem.*, **2**, 948–958 (1888).

30 experiments on 10 silver salts at 0° and at 22–29° between 0.01 and 0.1 normal. Silver electrodes. Middle portion in a few of the experiments, but in these no change in content was found. Anode and cathode portions both analyzed. Analytical data not communicated except in a single experiment. Total amount of solution 40–60 cc., but percentage change in content very large. Weight assigned 1–2.

2. Bein, *Z. physik. Chem.*, **27**, 1–54 (1898).

154 experiments on most of the salts given in Table I at temperatures between 0° and 97°, mostly between 0.005 and 1.0 normal. Different forms of apparatus used, depending on concentration and temperature. Cathode, platinum; anode, cadmium or platinum (copper or silver in special cases). Total salt content unchanged. Middle portion in some experiments. Percentage change in content variable (10–20 per cent. in some experiments but amount of solution small). Weight assigned $^1/_2$–2, in general in accordance with the relative weights given by the author.

3. Hopfgartner, *Z. physik. Chem.*, **25**, 115–143 (1898).

65 experiments on sodium chloride, barium chloride, hydrochloric acid, copper sulfate, and magnesium sulfate at 6–26° between 0.1 and 1 normal. Cathode, mercury covered with concentrated zinc chloride solution; anode, copper for copper sulfate and magnesium sulfate, cadmium in other cases. One middle portion. Anode solution alone analyzed. Percentage change large. Weight assigned 2.

4. Mather, *Am. Chem. J.*, **26**, 473–491 (1901).

15 experiments on silver nitrate and silver acetate between 0° and 49.4° at 0.025 and 0.1 normal. No middle portion. Electrode solutions separated by a stopcock presumably of smaller cross section than remainder of apparatus. Silver electrodes. Both electrode solutions analyzed. Concentrations referred to definit volume of solution. Percentage change in content large. Weight assigned $^1/_2$.

5. Jahn and associates, *Z. physik. Chem.*, **37**, 673–712 (1901); **58**, 641–658 (1907).

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[1] *Z. physik. Chem.*, 28, 439 (1899).

[2] *Ibid.*, 39, 613 (1902).

Experimental work by students. Very large number of experiments on uni- and bivalent metal halides and sulfates, hydrochloric acid, nitric acid, and sulfuric acid, at 0°, 18° and 30° between 0.005 and 1 normal. One middle portion and anode solution only analyzed. Anode, zinc, cadmium or silver; cathode, mercury covered with a concentrated copper nitrate solution. Analytical work extremely accurate (details in first paper only). Percentage change in content large. Weight assigned 2.

6. Noyes, THIS JOURNAL, **23**, 37–57 (1901).

20 experiments on potassium sulfate, barium chloride, and barium nitrate at 0.04 and 0.2 normal at 25°. Three middle and both electrode portions analyzed in case of barium nitrate, two middle portions and the cathode portion in case of the other salts. Platinum electrodes. Neutrality maintained by addition of requisit base or acid. Percentage change in content large. Weight assigned 6 in case of barium nitrate, 3 in other cases.

7. Noyes and Sammet, THIS JOURNAL, **24**, 944–968 (1902); **25**, 165–168 (1903).

42 experiments on hydrochloric acid at 10°, 20°, and 30° at 0.00556, 0.0167, and 0.051 normal. Both electrode portions and three middle portions analyzed. Silver anode; platinum cathode. Percentage change in content large. Weight assigned 6.

8. Steele and Denison, *J. Chem. Soc.*, **81**, 456–469 (1902).

21 experiments on potassium chloride, and on calcium sulfate, nitrate, and chloride at 18° between 0.0025 and 0.0053 normal. One middle portion. Cathode portion only analyzed. Platinum electrodes. Neutrality maintained by addition of base and acid. Large volume of solution. Solution flowing through the two sides of apparatus. Percentage change in content large. Weight assigned 2.

9. Tower, THIS JOURNAL, **26**, 1039–1065 (1904).

85 experiments on sulfuric acid at 8°, 20°, and 32° between 0.02 and 1 normal. Both electrode solutions and three middle portions analyzed. Cadmium anode; platinum cathode. Percentage change in content large. Weight assigned 4.

10. Jones and Bassett, *Am. Chem. J.*, **32**, 429–438 (1904); Jones and Rouiller, *Ibid.*, **36**, 462–466 (1906).

16 experiments on silver nitrate at 25° and 0°, at 0.1 and 0.02 normal. Silver electrodes. No middle portion. Both electrode portions analyzed. Separated by stopcock with bore 0.8 cm. diameter, remainder of apparatus 2 cm. diameter. Referred to constant volume. Percentage change in content large. Weight assigned $^1/_2$.

11. Noyes and Kato, THIS JOURNAL, **30**, 318–334 (1908).

10 experiments on 0.0021 normal hydrochloric acid at 20° and 37 on nitric acid at 20° at 0.0022, 0.0067, 0.018, and 0.058 normal. Both electrode portions and three middle portions analyzed. Platinum electrodes. Percentage change in content large. Weight assigned 6 (at concentrations above 0.006 N).

12. Whetham and Paine, *Proc. Roy. Soc.*, **81A**, 58–80 (1908).

4 experiments on sulfuric acid at 18° between 0.01 and 0.1 normal (also some with much more dilute solutions). Platinum electrodes. No middle portion. Concentration of electrode portions determined by conductance. Percentage change in content small. Weight assigned $^1/_2$.

13. Drucker and Krsnjavi, *Z. physik. Chem.*, **62**, 731–742 (1908).

7 experiments on 0.0358 normal hydrochloric acid at 18° and 31°. Both electrode portions and three or five middle portions analyzed. Cathode, palladium; anode, palladium saturated with hydrogen. Percentage change in content large. Results from the two electrode portions not very concordant. Weight assigned 3.

14. Denham, *Z. physik. Chem.*, **65**, 641–656 (1909).

4 experiments on cobalt bromide and cupric bromide at 25° between 0.17 and 0.92

normal (also at higher concentrations). Cathode solution analyzed. No middle portion. Copper or cobalt anode; platinum cathode. Percentage change in content small. Weight assigned $^1/_2$.

15. Washburn, THIS JOURNAL, 31, 322–355 (1909).

3 experiments on sodium chloride, potassium chloride, and lithium chloride at 25° at 1.2–1.3 normal. Both electrode portions and three middle portions analyzed (for sodium chloride anode portion only). Reversible silver — silver chloride electrodes. Primarily a study of the relative hydration of the ions. Solutions contained also 0.1 mol raffinose per 1000 grams of water. Percentage change in content large. Weight assigned 3 for sodium chloride, 6 for the other two salts.

16. Riesenfeld and Reinhold, *Z. physik. Chem.*, 68, 440–458 (1909).

9 experiments on hydrochloric acid at 18–23° between 0.1 and 1.0 normal. Both electrode and two middle solutions analyzed. Nickel anode; platinum cathode. Percentage change in content large. Weight assigned 4.

17. Falk, THIS JOURNAL, 32, 1555–1571 (1910).

12 experiments on 0.03 and 0.1 normal thallous sulfate and lead nitrate at 25°. Both electrode portions and three middle portions analyzed. Thallium or lead anode; platinum cathode. Percentage change in content large. Weight assigned 4.

Comparatively few investigations have been described in which the moving-boundary method was employed. The results obtained by Lodge,[1] Whetham,[2] and Masson[3] are not accurate, because either gelatin was used or the composition of the solution was not definit, or for other reasons. In the earlier work of Steele,[4] gelatin was used to separate the electrode compartments from the tube in which the actual measurements of the speed of the boundary were made. This introduced considerable error owing to cataphoresis, as Abegg and Gaus[5] showed. Denison[6] studied, experimentally, the effect of the presence and absence of gelatin and of cataphoresis. He also measured a few transference values, but as these apply entirely to concentrations of 0.5 normal or greater, and as gelatin was used to separate the electrode compartments, they will not be used in this paper. The more recent work of Denison and Steele[7] and of Denison[8] was carried on without the use of gelatin or of any membrane; but no correction was made for changes in the volume resulting from the reactions taking place at the electrodes.[9] For this reason only the results will be used that were obtained at concentrations not greater than 0.1 normal, up to which the volume correction is not important.

8. Values of the Transference Numbers.

Table IV contains the values of the cation-transference numbers ($\times 10^3$)

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[1] *British Assoc. Rep.*, 389 (1886).

[2] *Phil. Trans.*, 184A, 337 (1893); 186A, 507 (1895).

[3] *Z. physik. Chem.*, 29, 501 (1899).

[4] *Phil. Trans.*, 198A, 105; *Z. physik. Chem.*, 40, 689 (1902).

[5] *Z. physik. Chem.*, 40, 737 (1902).

[6] *Ibid.*, 44, 575 (1903).

[7] *Phil. Trans.*, 205A, 449; *Z. physik. Chem.*, 57, 110 (1906).

[8] *Trans. Faraday Soc.*, 5, 164 (1909).

[9] Cf. Lewis, THIS JOURNAL, 32, 862 (1910).

TABLE IV.—VALUES OF THE CATION-TRANSFERENCE NUMBER × 10^3 OBTAINED BY THE GRAVIMETRIC METHOD.

Substance.	Temp.	Observer.	Wt.	0.002 to 0.008	0.008 to 0.015	0.015 to 0.025	0.025 to 0.040	0.04 to 0.06	0.06 to 0.08	0.08 to 0.15	0.15 to 0.25	0.25 to 0.40	0.40 to 0.60	0.60 to 0.80	0.8 to 1.0
NaCl	0	Jahn, Schulz	2	388	388	387	387	...	386	385	...	...	...	...	...
	7.5	Bein	1	...	...	...	...	...	...	...	...	383	...	...	...
	10.5	Bein	1	382	394	...	...	...	386	...	...	...	...	...	...
	16	Hopfgartner	2	...	...	...	...	...	...	383	378	...	377	365	365
	18	Jahn, Schulz, Bogdan	2	...	396	397	395	...	395	395	...	...	...	...	...
	19	Bein	1	...	...	...	...	392	...	...	...	...	...	...	...
	25	Washburn	3	...	...	...	...	...	...	...	...	...	...	...	366*
	30	Jahn, Schulz	2	405	405	404	403	...	404	403	...	...	...	...	...
	51	Bein	1	...	418	...	...	...	...	...	...	...	...	...	...
	76	Bein	1	...	...	...	...	...	414	430	...	...	...	...	...
	96	Bein	1	...	453	...	...	441	...	...	...	443	...	...	...
KCl	0	Jahn, Hertz	2	495	494	493	491	491	...	491	491	...	...	...	...
	10	Bein	2	...	495	...	...	...	...	495	...	...	...	...	...
	18	Steele, Denison	2	495	...	...	...	...	...	...	...	...	...	...	...
	18	Jahn, Bogdan, Hertz	2	...	498	498	495	493	...	495	494	...	...	...	...
	25	Washburn	6	...	...	...	...	...	...	...	...	...	...	...	482*
	30	Jahn, Hertz	2	498	499	499	499	497	...	498	496	...	...	...	...
	76	Bein	½	...	...	...	...	...	...	490	482	...	...	...	...
LiCl	10	Bein	½	...	...	...	...	...	...	339	...	...	...	...	...
	18	Jahn, Goldhaber	2	...	330	330	330	...	316	312	...	300	...	...	...
	18	Bein	½	...	...	...	...	...	333	...	...	...	...	...	...
	20.5	Bein	2	...	376	...	...	...	...	...	...	...	...	...	...
	24	Bein	2	...	...	...	...	324	...	...	...	...	...	...	...
	25	Washburn	6	...	...	...	...	...	...	...	...	...	...	...	276*
	97	Bein	1	...	379	...	...	390	...	...	...	...	...	...	...
NH_4Cl	0	Jahn, Schulz, Hertz	2	...	490	489	487	...	...	...	...	...	...	...	...
	18	Jahn, Schulz, Hertz	2	...	493	491	490	...	...	...	...	...	...	...	...
	20	Bein	2	...	...	...	...	493	...	...	...	...	...	...	...
	30	Jahn, Schulz, Hertz	2	...	496	495	494	...	...	...	...	...	...	...	...
NaBr	18	Jahn, Bogdan, Oppenheimer	2	394	395	396	393	...	...	...	...	...	...	...	...

* Concentration = 1.25 normal.

TABLE IV.—VALUES OF THE CATION-TRANSFERENCE NUMBER $\times 10^3$ OBTAINED BY THE GRAVIMETRIC METHOD (*Continued.*)

Substance.	Temp.	Observer.	Wt.	0.002 to 0.008	0.008 to 0.015	0.015 to 0.025	0.025 to 0.040	0.04 to 0.06	0.06 to 0.08	0.08 to 0.15	0.15 to 0.25	0.25 to 0.40	0.40 to 0.60	0.60 to 0.80	0.8 to 1.0
NaBr	22	Bein	1	...	...	...	...	375	...	...	...	...	...	...	...
KBr	18	Jahn, Hertz, Bogdan	2	...	495	496	495	...	...	...	...	...	...	...	...
$AgNO_3$	0	Jones, Bassett, Rouiller	½	...	...	445	...	...	...	437	...	...	...	...	...
	0	Löb, Nernst	2	...	...	462	...	...	...	...	...	...	...	...	...
	0	Mather	½	...	...	462	...	...	...	459	...	...	...	...	...
	18	Jahn, Berliner	2	474	469	472	472	...	...	...	...	...	...	...	...
	20	Löb, Nernst	2	...	...	...	...	...	...	472	...	...	...	...	...
	25	Jones, Bassett, Rouiller	½	...	...	460	...	...	...	472	...	...	...	...	...
	26	Löb, Nernst	2	...	478	478	...	476	...	...	...	...	...	...	...
	29.1	Mather	½	...	...	...	...	...	...	468	...	...	...	...	...
	30	Jahn, Berliner	2	482	481	482	482	...	475	480	485	...	481	...	...
	46.5	Mather	½	...	...	475	...	...	...	472	...	...	...	...	...
	74	Bein	½	...	...	...	...	483	...	...	...	...	...	...	...
$AgC_2H_3O_2$	0	Mather	½	...	...	627	...	...	...	...	...	...	...	...	...
	24	Bein	1	...	...	...	...	587	...	...	...	...	...	...	...
	24.5	Löb, Nernst	2	...	624	...	...	...	...	...	...	...	...	...	...
	28.3	Mather	½	...	...	618	...	...	...	...	...	...	...	...	...
	46.5	Mather	½	...	...	611	...	...	...	...	...	...	...	...	...
	96	Bein	½	...	...	...	562	...	...	...	...	...	...	...	...
HCl	0	Jahn, Joachim, Wolff	2	847	847	845	840	...	839	833	...	...	...	...	...
	9.5	Bein	1	832	834	...	...	...	...	...	...	...	...	...	...
	10	Noyes, Sammet	6	...	...	841	...	...	...	...	...	...	...	...	...
	14	Bein	2	...	...	...	...	...	...	830	...	...	...	...	...
	18	Jahn, Joachim, Wolff	2	833	833	833	835	...	...	...	...	...	...	...	...
	18	Drucker, Krsnjavi	3	...	...	...	833	...	...	...	...	...	...	...	...
	18	Bein	1	...	...	...	...	834	...	...	...	...	...	...	...
	18	Hopfgartner	2	...	...	...	...	...	...	833	836	...	833	843	841
	18	Riesenfeld, Reinhold	4	...	...	...	...	...	...	839	...	...	844	...	845
	20	Noyes, Sammet	6	833[1]	...	833	...	834	...	...	...	...	...	...	...

[1] At 0.00556 normal.

HCl	20	Noyes, Kato	2	829[1]	...	...	...	...	...	...	...	...	...	...	...
	30	Jahn, Joachim, Wolff	2	817	817	818	819	...	820	814	...	...	...	...	...
	30	Noyes, Sammet	6	...	...	823	...	...	...	...	...	...	...	...	...
	31	Drucker, Krsnjavi	3	...	...	...	821	...	...	...	...	...	...	...	...
	50	Bein	2	...	801	...	...	...	...	...	...	...	...	...	...
	76.5	Bein	1	...	...	...	...	...	781	781	...	...	...	...	...
	96.5	Bein	2	...	748	...	...	...	...	...	...	...	...	...	...
HNO_3	18	Jahn, Bukschnewski	2	829	830	830	829	...	830	832	830	...	...	...	...
	20	Noyes, Kato	6	839[2]	...	840	...	844	...	...	...	...	...	...	...
	25	Bein	½	...	...	...	...	828	...	...	...	...	...	...	...
$BaCl_2$	0	Jahn, Wolff	2	438	438	434	427	...	...	...	...	...	...	...	...
	11	Bein	2	...	441	...	...	...	...	429	417	416	...	...	...
	16	Hopfgartner	2	...	...	...	...	...	...	421	408	...	389	383	...
	18	Jahn, Bukschnewski	2	447	447	452	457	...	...	...	...	...	...	...	...
	25	Noyes	3	...	...	...	442	...	...	...	415	...	...	...	...
	30	Jahn, Wolff	2	445	445	443	443	...	...	...	...	...	...	...	...
	50	Bein	1	...	475	...	...	...	...	...	...	...	...	...	...
	76	Bein	½	...	...	...	...	...	...	447	...	...	...	...	...
	97	Bein	½	...	485	...	...	...	...	...	446	...	...	...	...
$CaCl_2$	18	Steele, Denison	2	438	...	...	...	...	...	...	...	...	...	...	...
	21	Bein	1	...	447	...	...	...	...	...	395	390	...	...	...
	24.5	Bein	2	...	...	...	...	418	...	405	...	...	...	...	...
	49	Bein	1	...	445	...	...	...	...	...	...	...	...	...	...
	96	Bein	1	...	470	...	...	...	...	426	451	...	...	...	...
$SrCl_2$	20.5	Bein	1	...	440	...	...	425	...	...	...	...	...	...	...
$CdCl_2$	8	Bein	1	...	...	...	...	...	...	...	...	433	...	...	...
	17	Bein	½	...	...	...	...	...	...	433	...	...	...	...	...
	18	Jahn, *et al.*[3]	2	430	431	429	431	429	432	430	...	...	...	...	...
	20	Bein	1	...	443	...	...	...	...	...	...	...	...	...	...

[1] At 0.0021 normal.

[2] 837 at 0.0022 normal, and 840 at 0.0067 normal.

[3] Jahn, Goldhaber, and Bukschnewski.

Table IV.—Values of the Cation-Transference Number × 10^3 Obtained by the Gravimetric Method (*Continued*).

Substance.	Temp.	Observer.	Wt.	0.002 to 0.008	0.008 to 0.015	0.015 to 0.025	0.025 to 0.040	0.04 to 0.06	0.06 to 0.08	0.08 to 0.15	0.15 to 0.25	0.25 to 0.40	0.40 to 0.60	0.60 to 0.80	0.8 to 1.0
$CdCl_2$	24.5	Bein	1	...	...	...	...	431	...	...	...	...	...	...	...
	96	Bein	1	...	...	...	...	525	...	...	...	...	...	...	...
$CdBr_2$	18	Jahn, *et al.*[1]	2	426	428	430	431	431	434	432	423	399	350	...	218
CdI_2	18	Jahn, *et al.*[2]	2	444	442	443	425	407	381[3]	...[3]	...[3]	...[3]	...[3]	...	...
Na_2SO_4	18	Jahn, Goldlust	2	...	392	391	387	...	379	...	...	...	...	...	...
K_2SO_4	18	Jahn, Goldlust	2	...	494	495	490	...	488	...	...	...	...	...	...
	25	Noyes	3	...	...	...	496	...	...	...	493	...	...	...	...
Tl_2SO_4	23	Bein	1	...	...	...	...	472	...	...	...	...	...	...	...
	25	Falk	4	...	...	...	479	...	...	476	...	...	...	...	...
H_2SO_4	8	Tower	4	...	...	832	...	836	...	836	...	...	...	...	...
	11	Bein	2	...	...	...	...	825	...	...	...	...	...	...	...
	18	Whetham, Paine	½	...	814	...	...	...	...	814	...	...	...	...	...
	18	Jahn, Hugbrechts	2	...[4]	...[4]	824	825	...	826	824	832	...	...	...	...
	20	Tower	4	...	...	819	...	821	...	824	819	...	813	...	812
	30	Jahn, Hugbrechts	2	...[5]	...[5]	814	812	...	805	...	...	...	...	...	...
	32	Tower	4	...	...	809	...	808	...	808	...	...	...	...	...
	96	Bein	1	...	...	...	...	696	...	...	...	...	...	...	...
$Ba(NO_3)_2$	25	Noyes	6	...	...	...	456	...	...	...	455	...	...	...	...
$Pb(NO_3)_2$	25	Falk	4	...	...	...	487	...	...	487	...	...	...	...	...
$MgSO_4$	12	Hopfgartner	2	...	...	...	...	...	...	...	...	...	...	...	25.
	18	Jahn, Hugbrechts	2	387	386	381	376	...	369	...	...	...	...	...	...
	24	Bein	1	...	...	...	...	459	...	...	...	...	...	...	...
	30	Jahn, Hugbrechts	2	...	388	387	384	...	376	...	...	...	...	...	...
$CdSO_4$	18	Jahn, Goldlust, Redlich	2	...	388	386	381	379	371	365	354	341	323	...	294
$CuSO_4$	0	Bein	1	...	385	...	...	...	...	389	...	...	...	...	...
	11	Hopfgartner	2	...	...	...	...	...	...	...	...	...	...	316	304
	15	Bein	1	...	367	...	...	...	...	...	368	...	...	...	...
	18	Jahn, Metelka	2	...	...	375	375	375	376	374	366	328	328	...	...
	50	Bein	1	...	...	...	...	...	...	393	...	...	...	...	...
	76	Bein	½	...	...	...	...	...	...	...	378	...	...	...	...

[1] John, Goldhaber, and Bukschnewski.

[2] Jahn, Redlich, and Bukschnewski.

[3] 343 at 0.08 normal, 281 at 0.12 normal, 223 at 0.16 normal, 75 at 0.25 normal, and —3 at 0.5 normal.

[4] 824 at 0.011 normal, 827 at 0.010 normal, 843 at 0.0093 normal, and 845 at 0.0078 normal.

[5] 816 at 0.012 normal, 830 at 0.0097 normal, 839 at 0.0093 normal, and 838 at 0.0081 normal.

Substance.	Temp.	Observer.	Wt.	0.002–0.008	0.008–0.015	0.015–0.025	0.025–0.040	0.04–0.06	0.06–0.08	0.08–0.15	0.15–0.25	0.8–1.0
RbCl	22	Bein	1	...	...	...	...	485	...	...	...	...
CsCl	20	"	1	...	...	...	...	492	...	...	...	...
TlCl	22	"	1	...	484	...	...	...	...	...	...	...
KI	25	"	1	...	...	...	...	495	...	...	...	...
NaOH	25	"	$^1/_2$	...	...	...	201	...	...	...	...	...
$NaNO_3$	19	"	1	...	...	...	...	371	...	...	...	...
$KMnO_4$	23	"	1	...	...	...	...	441	...	...	...	...
$AgClO_3$	25	Löb, Nernst	1	...	...	499	...	...	...	...	...	...
$AgClO_4$	25	"	1	...	...	486	...	...	...	...	...	...
$AgC_2H_5SO_4$	25	"	2	616	...	613	...	...	...	...	...	...
$AgSO_3C_{10}H_7$	25	"	1	...	...	614	...	...	...	...	...	...
	29	"	1	...	610	...	...	...	...	...	...	...
$AgSO_3C_6H_5$	25	"	1	...	...	653	...	...	...	...	...	...
$AgSO_3C_9H_{11}$[1]	0	"	1	...	...	727	...	...	...	...	...	...
	24	"	1	...	...	707	...	...	...	...	...	...
	29	"	1	...	...	705	...	...	...	...	...	...
$Ag_2S_2O_6$	0	"	1	...	...	396	...	...	...	...	...	...
	24.5	"	1	...	...	395	...	...	...	...	...	...
	29	"	1	...	...	396	...	...	...	...	...	...
Ag_2SiF_6	22	"	1	...	...	...	535	...	...	...	...	...
$MgCl_2$	21	Bein	1	...	...	...	...	385	...	...	...	...
$MnCl_2$	18	"	1	...	...	...	...	387	...	...	...	...
$CuCl_2$	23	"	1	...	...	...	...	405	...	...	...	...
$CoCl_2$	18	"	1	...	...	...	...	404	...	...	...	...
$CoBr_2$	25	Denham	1	...	...	...	...	...	...	...	409	413
$CuBr_2$	25	"	1	...	...	...	...	...	...	...	445	440
$Ca(OH)_2$	24.5	Bein	1	...	...	...	214	...	...	...	...	...
$Ca(NO_3)_2$	18	Steele, Denison	2	450	...	...	...	...	...	...	...	...
$CaSO_4$	18	"	2	441	...	...	...	...	...	...	...	...

obtained by the gravimetric method by various investigators. The headings of the first four columns are self-explanatory; those of the following columns show the content of solution expressed in equivalents of substance per liter of solution. For convenience in tabulation all the results obtained at any content falling within the small intervals indicated by the headings have been placed in the same column. The weights assigned are only estimates based upon the considerations presented in the last section, without reference to the agreement of the results with those of other investigators.

In order to determin the best values to adopt for the transference numbers, the method of procedure was as follows: In cases in which the transference number shows throughout a considerable concentration-interval a change not greater than corresponds to the probable experimental error, the weighted mean of all the values within such an interval

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[1] Silver pseudocumenesulfonate.

was taken. In cases in which there was an appreciable change with the concentration, the transference numbers were plotted against the logarithm of the concentration, and the curve was drawn best representative of the separate results, regard being paid to their relative weights. (When results exist at different temperatures removed from each other by only two or three degrees, they were first reduced to a common temperature.)

Table V contains the values so derived. Isolated results of small weight and a few sets of values which are obviously inaccurate are omitted. The scattering results for the 24 salts grouped together at the end of Table IV are also not reproduced in Table V, in order to avoid unnecessary repetition.

The weights assigned refer, in general, to the values given for concentrations between 0.01 and 0.1 normal. They are based on the number and concordance of the separate data involved and on the weights assigned to them in Table IV.

TABLE V.—BEST VALUES OF THE CATION-TRANSFERENCE-NUMBER × 10^3.

Substance.	Temp.	Wt.	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5	1.0
NaCl	0	2	387	387	387	386	385	...	...	...	...
	18	4	396	396	396	395	393	390	388	382	369
	30	2	404	404	404	404	403	...	...	...	...
	96	1	...	...	...	442	442	442	...	...	...
KCl	0	2	493	493	493	493	492	491	...	...	...
	10	1	...	495	495	495	495	...	...	...	...
	18	3	496	496	496	496	495	494	...	...	...
	30	2	498	498	498	498	497	496	...	...	...
LiCl	18	2	...	332	328	320	313	304	299	...	...
NH_4Cl	0	2	...	489	489	...	...	...	...	...	...
	18	3	...	492	492	492	...	...	...	...	...
	30	2	...	495	495	...	...	...	...	...	...
NaBr	18	2	395	395	395	...	...	...	...	...	...
KBr	18	2	...	495	495	...	...	...	...	...	...
$AgNO_3$	0	2	...	...	461	...	...	...	...	...	...
	18	2	...	471	471	471	471	...	...	...	...
	25	2	...	477	477	477	...	...	...	...	...
	30	2	481	481	481	481	481	481	481	481	...
HCl	0	1	847	846	844	839	834	...	...	...	...
	10	6	840	840	841	...	...	...	...	...	...
	18	15	832	833	833	834	835	837	838	840	844
	30	9	...	822	822	822	...	...	...	...	...
	50	2	...	801	...	...	...	...	...	...	...
	76	2	...	...	...	...	781	...	...	...	...
	96	2	...	748	...	...	...	...	...	...	...
HNO_3	20	6	839	840	841	844	...	...	...	...	...
$BaCl_2$	0	2	439	437	432	...	...	...	...	...	...
	11	2	...	441	...	...	...	...	...	...	...
	16	2	...	...	...	...	420	408	401	391	...
	25	3	...	...	...	438	427	415	...	...	...
	30	2	445	444	443	...	...	...	...	...	...
	50	1	...	475	...	...	...	...	...	...	...

TABLE V (*continued*).

Substance.	Temp.	Wt.	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5	1.0
$CaCl_2$	20	2	440	432	424	413	404	395	389	...	...
	25	2	...	...	...	418	409	...	...	...	...
$SrCl_2$	20	1	...	441	435	427	...	...	...	...	...
$CdCl_2$	18	2	430	430	430	430	430	...	...	...	...
$CdBr_2$	18	2	430	430	430	430	429	410	389	350	222
CdI_2	18	2	445	444	442	396	296	127	46	3	...
Na_2SO_4	18	2	...	392	390	383	...	...	...	...	...
K_2SO_4	18	2	...	494	492	490	...	...	...	...	...
	25	3	...	...	...	496	494	493	...	...	...
Tl_2SO_4	25	4	...	...	...	478	476	...	...	...	...
H_2SO_4	8	4	...	...	835	835	835	...	...	...	...
	20	6	...	...	822	822	822	820	818	816	812
	32	5	...	...	808	808	808	...	...	...	...
$Ba(NO_3)_2$	25	6	...	...	...	456	456	456	...	...	...
$Pb(NO_3)_2$	25	4	...	...	...	487	487	...	...	...	...
$MgSO_4$	18	2	388	385	381	373	...	...	...	...	...
	30	2	...	388	386	380	...	...	...	...	...
$CdSO_4$	18	2	...	389	384	374	364	350	340	323	294
$CuSO_4$	18	2	...	...	375	375	373	361	348	327	...

Table VI contains the results obtained by Denison and Steele and by Denison by the moving-boundary method. The concentrations are given in equivalents of substance per liter of solution.

TABLE VI.—VALUES OF THE CATION-TRANSFERENCE-NUMBER × 10^3 OBTAINED BY THE MOVING-BOUNDARY METHOD.

Sub-stance.	18°			25°	Sub-stance	18°			25°
	0.02	0.05	0.1	0.1		0.02	0.05	0.1	0.1
NaCl	...	387	383	...	K_2SO_4	488	...	485	479
KCl	493	...	492	493	H_2SO_4	833	...	828	...
RbCl	497	...	494	...	$BaCl_2$	435	...	419	416
CsCl	504	...	500	...	$CaCl_2$	413	...	398	396
NH_4Cl	492	...	489	...	$SrCl_2$	412	...	400	404
NaBr	...	381	376	...	$MgCl_2$	...	368	352	...
KBr	482	...	481	480	$BaBr_2$	422	...	408	...
RbBr	495	...	492	...	$CaBr_2$	409	...	396	...
CsBr	497	...	493	...	$SrBr_2$	410	...	392	...
NH_4Br	483	...	481	...	$MgBr_2$	385	368	350	...
NaI	...	381	376	...	BaI_2	426	...	415	...
KI	487	...	486	483	CaI_2	416	...	400	...
RbI	498	...	497	...	SrI_2	416	...	393	...
CsI	497	...	497	...	MgI_2	388	...	350	...
NH_4I	489	...	484	...	....	...	...	....	...
KNO_3	502	...	502	501	....	...	...	...	...
$KClO_3$	534	...	536	537	....	...	...	...	...
$KBrO_3$	567	...	570	570	....	...	...	...	...
$KClO_4$	...	...	523	...	....	...	...	...	...
NaOH	...	...	158	...	....	...	...	...	...
KOH	...	...	257	...	....	...	...	...	...
HCl	835	...	835	...	....	...	...	...	...
HNO_3	846	...	855	...	....	...	...	...	...

9. Comparison of Transference Numbers Derived by the Three Different Methods

Before discussing the general significance of the results, it seems desirable to show the degree of concordance of the transference numbers obtained by the three independent methods—the gravimetric method, the moving-boundary method, and the conductance method. The well-known principles involved in these methods have been discussed in Section 6.

In Table VII are placed side by side the values obtained by these three methods at 18° and 25° at various equivalent concentrations up to 0.2 normal. The results by the conductance method are those given under the concentration-heading 0.0. They were calculated by equation (22) of Section 6 from the values of the equivalent conductances of the separate ions, which will be tabulated in the third paper of this

TABLE VII.—COMPARISON OF TRANSFERENCE NUMBERS DERIVED BY THE DIFFERENT METHODS.

VALUES AT 18°.

Substance.	0.0		0.005	0.02	0.05	0.10	0.20
NaCl	399	Gr(4)	396	396	395	393	390
		MB	...	...	386	383	...
KCl	496	Gr(3)	496	496	496	495	494
		MB	...	493	...	492	...
LiCl	337	Gr(2)	...	328	320	313	304
NH_4Cl	497	Gr(3)	...	492	492	...	...
		MB	...	492	...	489	...
RbCl	508	MB	...	497	...	494	...
CsCl	509	MB	...	504	...	500	...
NaBr	391	Gr(2)	395	395	...	...	...
		MB	...	...	381	376	...
KBr	488	Gr(2)	...	495	...	...	...
		MB	...	482	...	481	...
RbBr	499	MB	...	495	...	492	...
CsBr	501	MB	...	497	...	493	...
NH_4Br	489	MB	...	483	...	481	...
NaI	395	MB	...	...	381	376	...
KI	492	MB	...	487	...	486	...
RbI	503	MB	...	498	...	497	...
CsI	505	MB	...	497	...	497	...
NH_4I	493	MB	...	489	...	484	...
KNO_3	511	MB	...	502	...	502	...
$AgNO_3$	466	Gr(2)	...	471	471	471	...
$KClO_3$	539	MB	...	534	...	536	...
$KBrO_3$	575	MB	...	567	...	570	...
HCl	828	Gr(15)	832	833	834	835	837
		MB	...	835	...	835	...
HNO_3	836	Gr(6)	839	841	844	...	...
		MB	...	846	...	855	...

TABLE VII (*Continued*).

VALUES AT 18°.

Substance.	0.0		0.005	0.02	0.05	0.10	0.20
$BaCl_2$	458	Gr(2)	...	...	...	422[1]	410
		MB	...	435	...	419	...
$CaCl_2$	442	Gr(2)	438	422	411	402	393
		MB	...	413	...	398	...
$SrCl_2$	442	Gr(2)	...	433	425	...	...
		MB	...	412	...	400	...
$MgCl_2$	412	MB	...	...	368	352	...
$BaBr_2$	450	MB	...	422	...	408	...
$CaBr_2$	434	MB	...	409	...	396	...
$SrBr_2$	434	MB	...	410	...	392	...
$MgBr_2$	404	MB	...	385	368	350	...
BaI_2	454	MB	...	426	...	415	...
CaI_2	438	MB	...	416	...	400	...
SrI_2	438	MB	...	416	...	393	...
MgI_2	408	MB	...	388	...	350	...
Na_2SO_4	388	Gr(2)	...	390	383	...	...
K_2SO_4	485	Gr(2)	...	492	490	...	...
		MB	...	488	...	485	...
H_2SO_4	821	Gr(6)	...	824	824	824	822
		MB	...	833	...	828	...
$Ca(NO_3)_2$	456	Gr(2)	450	...	...	...	...
$MgSO_4$	401	Gr(2)	388	381	373	...	...
$CdSO_4$	404	Gr(2)	...	384	374	364	350
$CuSO_4$	401	Gr(2)	...	375	375	373	361
$CaSO_4$	431	Gr(2)	441	...	...	...	...

VALUES AT 25°.

Substance.	0.0		0.005	0.02	0.05	0.10	0.20
NaCl	403	Gr(3)	400	400	399	397	394
KCl	497	Gr(3)	497	497	497	496	495
		MB	...	...	...	493	...
NH_4Cl	497	Gr(3)	...	494	494	...	...
KI	494	MB	...	...	...	483	...
$AgNO_3$	473	Gr(2)	...	477	477	...	...
KNO_3	514	MB	..	...	...	501	...
HCl	822	Gr(12)	...	826	826	827	...
$KBrO_3$	577	MB	...	...	...	570	...
$BaCl_2$	462	Gr(3)	...	...	438	427	415
		MB	...	...	...	416	...
$CaCl_2$	442	Gr(2)	...	...	418	409	...
		MB	...	...	...	396	...
K_2SO_4	483	Gr(3)	...	...	496	494	493
		MB	...	...	...	479	...
Tl_2SO_4	487	Gr(4)	...	479[1]	478	476	...
H_2SO_4	814	Gr(6)	...	817	817	817	...
$Ba(NO_3)_2$	480	Gr(6)	...	...	456	456	456
$Pb(NO_3)_2$	502	Gr(4)	...	487[1]	487	487	...
$MgSO_4$	407	Gr(1)	...	384	377	...	...

[1] At 0.03 normal.

series.[1] The results by the gravimetric method are preceded by the letters Gr; those by the moving-boundary method by the letters MB. The figures, within parentheses following the letters Gr show the weights attributed to the results at the concentrations 0.02 to 0.1 normal.

An examination of Table VII shows that the values at 18° obtained by the gravimetric and moving-boundary methods are concordant within about 1 per cent. for hydrochloric, nitric and sulfuric acids, potassium chloride, ammonium chloride, and potassium sulfate, but that those by the gravimetric method are considerably larger (usually by 2.5 to 3.0 per cent.) for the other six substances that have been investigated by both methods. The values obtained by the conductance method with uni-univalent salts are also almost uniformly 1 to 3 per cent. higher than those by the moving-boundary method. These results, considered in connection with the fact that careful measurements by the moving-boundary method have thus far been made only by two investigators, Denison and Steele, indicate that the values obtained by that method require further confirmation before much confidence can be placed in them. It is to be hoped that the method will be further studied with respect to the sources of error involved and the reproducibility of the same values under varied experimental conditions, for it furnishes by far the most rapid means of determining transference numbers.

It will be seen that in the case of almost all the uni-univalent substances the values obtained by the conductance method at zero concentration agree within about one per cent. with those obtained by the gravimetric method at 0.005 to 0.02 normal. Lithium chloride seems, at first sight, an exception, but not when the rapid change with the concentration is considered.

In the case of uni-bivalent halides, the change with the concentration is so rapid that it is difficult to judge accurately of the correspondence between the results obtained by the two methods. But in the case of the other uni-bivalent salts that have been carefully investigated (potassium sulfate, thallous sulfate, barium nitrate, and lead nitrate at 25°), it is remarkable that though the "gravimetric" values do not change much with the concentration yet they differ by much more than the probable experimental error[2] (namely, by from 9 to 23 $\times 10^{-3}$ units) from the "conductance" values at zero concentration. Moreover, the diver-

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[1] These ion-conductances at 18° are nearly identical with those given by Kohlrausch (*Z. Elektrochem.*, 13, 333 (1907)). The small differences arise mainly from the adoption of 0.496 for the transference number of potassium chloride, in place of 0.497, which was used by Kohlrausch.

[2] The probable error in the gravimetric values may be estimated at 2×10^{-3} units in the cases where a weight of 3 or more is assigned. The error in the values with a less weight than 3 is much more difficult to estimate.

gence is in the same direction for the last three salts; but in the opposit direction for potassium sulfate.

10. Change of the Transference Number with the Concentration and Temperature.

Table VII shows that the transference numbers obtained by the gravimetric method for the uni-univalent substances studied at 18° and at 25° do not vary more than 3×10^{-3} units between the concentrations 0.005 and 0.1 normal, except in the cases of nitric acid and of lithium chloride.

The transference numbers of the halides and sulfates of the bivalent metals (and of lithium chloride) obtained by the gravimetric and moving-boundary methods decrease steadily and rapidly with increasing concentration. This large change is probably due not to physical causes, but to changes in the composition of the ions; thus it may be accounted for by assuming that complex anions, such as $BaCl_4^{=}$ or $Mg(SO_4)_2^{=}$, are formed in considerable quantity at the higher concentrations.

The other uni-bivalent salts (potassium and thallium sulfates and barium and lead nitrates), as above noted, show little, if any, change at concentrations between 0.03-0.05 and 0.1-0.2 normal; but there is a difference of 2 to 5 per cent. between these values and those at zero concentration. This suggests the possibility that the conductance values extrapolated for zero concentration may be considerably in error in the case of these salts—a matter that will be discussed in detail in the third paper.

The fact that the transference numbers of these uni-bivalent salts, unlike the bivalent halides, show little, if any, progressive change with the concentration, makes it probable, though it does not prove,[1] that intermediate ions (such as KSO_4^- or NO_3Ba^+) and complex ions (such as $K_2(SO_4)_2^{=}$) are not present in large quantities in solutions of these salts, at concentrations up to 0.2 normal.[2]

Hydrochloric acid and sulfuric acid[3] also show a nearly constant transference number between 0.005 or (0.02) normal and 0.1 normal; but there is a considerable difference between the value at these concentrations

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[1] See the theoretical discussion of this matter near the end of Section 6 of this article; also Falk, THIS JOURNAL, 32, 1567–70 (1910).

[2] It is to be noted that, even if the difference between the values at zero and higher concentrations be regarded as real, the change lies (except in the case of potassium sulfate) in a direction opposit to that which would be produced by the presence of the intermediate ion (unless its equivalent conductance be even smaller than that required by equations (21) given in Section 6).

[3] For a full discussion of the transference relations of sulfuric acid, see Noyes and Stewart, THIS JOURNAL, 32, 1134, 1138 (1910).

and that at zero concentration. The latter fact becomes especially obvious when one considers the anion-transference numbers, which were the quantities obtained directly from the experiments; thus those for hydrochloric acid are —172 at 0.0 normal and —166 at 0.1 normal. This again suggests an error in the values of the equivalent conductance of the ions at zero concentration. It indicates more specifically, as pointed out by Noyes and Sammet[1] and Noyes and Kato,[2] that the hydrogen-ion at higher concentrations has a considerably higher conductance than that derived from conductance measurements with very dilute acids. The latter authors conclude that this was probably true only at the higher concentrations, and that the conductance of the hydrogen-ion increased markedly with increasing concentration. But in view of the approximate constancy of the transference number between 0.005 and 0.1 normal, which the now available data indicate, it seems more probable that the value for the hydrogen-ion at zero concentration is in error. The transference number of nitric acid, unlike those of hydrochloric and sulfuric acids, increases markedly with increasing concentration.

The change in the transference number taking place at concentrations above 0.1 normal has been carefully investigated for only a few substances. The results may best be seen by reference to Table V. The effect of concentration is pronounced only in the cases of the halides and sulfates of the bivalent metals and of lithium chloride, and is probably due mainly to complex anions, as is illustrated most strikingly by the negative transference of cadmium iodide at 0.5 normal and above. The smaller effects in the other cases are doubtless due, at least, in part, to hydration of the ions, since this has been definitly shown by Washburn to be true for the chlorides of potassium, sodium and lithium.

In regard to the effect of temperature the statement can be made that in the case of the substances investigated the transference number with rising temperature invariably decreases if larger than 500×10^{-3}, and increases if smaller than this quantity, showing that the transference and velocity of the various ion-constituents differ by a smaller fractional amount at the higher temperatures. The transference measurements at different temperatures are not numerous nor accurate enough to warrant other general conclusions of a quantitative character.

BOSTON, MASS.

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[1] THIS JOURNAL, 24, 967–8 (1902).

[2] *Ibid.*, 30, 332 (1908).