THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

THE ION MOBILITIES, ION CONDUCTANCES, AND THE EFFECT OF VISCOSITY ON THE CONDUCTANCES, OF CERTAIN SALTS.

BY DUNCAN A. MACINNES.

The change of the value of the equivalent conductance, Λ, of a salt with change of concentration may be due (a) to a variation in the number of ionic carriers, $i.\,e.$, to a change of the degree of dissociation, or (b) to changes of the values of the mobilities of the ions, or (c) to a combination of these two factors. This is indicated by the formula: $\Lambda = \gamma F(U^+ + U^-)$ in which γ, U^+ and U^- are the degree of dissociation, the mobilities of the positive and negative ions, respectively, and F is the faraday equivalent. Up to the present, the tendency has been to ascribe the observed changes of conductance entirely to variation of the number of carriers, and to ignore the possibility of changes of mobility. This paper is to a large extent an account of an investigation of the possible magnitude of such changes and their influence upon the question of the dissociation of electrolytes.

That relatively large changes of ion mobilities occur in narrow ranges of concentrations is indicated by an examination of the transference numbers. The transference number of the negative ion, T, is, of course, equal

to the ratio $T = U^-/(U^- + U^+)$. A variation of this number, with concentration, can take place through a change of U^- or U^+, or through changes, at different rates, of both these quantities. (An additional apparent change of the transference number, due to differences in the hydration of the ions, will be considered below.) As a matter of fact, the transference number changes considerably in the case of every electrolyte, except potassium chloride, upon which measurements have been made over a range of concentrations. Transference numbers, at 18°, for monovalent chlorides at a series of concentrations are given in Col. 4 of Table I. The anion transference number for hydrochloric acid for instance, is seen to vary from 0.167 to 0.156 between 0.01 and 1.0 N and that of lithium chloride from 0.668 to 0.694 in the same range. With but few exceptions, papers dealing with the ionic theory have ignored this change of the transference number. Lewis[1] has, however, published computations (based on a derivation by Tolman) showing, from conductance and transference data, that hydrochloric acid, and potassium, sodium, and lithium chlorides are dissociated to the same extent in 0.1 N solutions, if the assumption is made that the mobility of the chloride ion has the same value in all these solutions. The fact on which these conclusions are based is that the product $T_{Cl} \Lambda$ (in which T_{Cl} is the transference number, at 0.1 N of the chloride ion) is the same for all the electrolytes mentioned. Now if we were certain that the mobilities of the ions of potassium chloride do not change with the concentration from 0.1 N to infinite dilution, it would be possible to compute the degree of dissociation of this salt from the simple conductance ratio $1, \Lambda/\Lambda_o$. This ratio for potassium chloride would be, of course, also a measure of the ionizations of the other substances mentioned, since we are only assuming that the mobility of the chloride ion is constant. As potassium chloride is the only salt with a constant transference number, it is the only substance for which we can possibly assume that its ions do not vary in mobility with concentration.

Since the product $T_{Cl}\Lambda$, which is the contribution of the chloride ion to the total conductance, is constant at least up to 0.2 N in all solutions of monovalent chlorides, the chloride ion is, in all probability, identical in concentration and properties in each solution, at any one concentration. This was discussed in a previous paper[2] and additional evidence is given later in this article. If, however, we assume that the mobilities of the chloride and potassium ions are constant, a simple computation indicates that comparatively large changes of mobilities must be assigned to all the other ions in order to account for the observed conductances and transference numbers. From 0.01 to 0.1 N, for instance, the mobility of

[1] Lewis, THIS JOURNAL, **34**, 1631 (1912).

[2] MacInnes, *ibid.*, **41**, 1086 (1919).

the hydrogen ion would have to increase 4.83% and the mobilities of the sodium, lithium and cesium ions decrease 3.76, 7.22 and 2.09%, respectively.[1]

It seems very improbable, therefore, that the ions of potassium chloride are exceptions and have constant mobilities. A far more credible explanation is that the mobilities of the ions of this salt vary with concentration at the same rate. If, on the other hand, we assume that these salts are completely dissociated *all* the changes of the values of the equivalent conductances with dilution must be due to changes in ion mobility. On the basis of total ionization, the necessary percentage changes of mobilities between 0.01 and 0.1 N are: $H^+ = -4.16$; $K^+ = Cl^- = -8.26$; $Na^+ = -11.9$; $Li^+ = -15.1$; and $Cs^+ = -10.4$. It will be noticed on comparing these figures with those given in the foregoing paragraph, first, that the changes of mobilities are, for the lithium ion, only slightly more than twice as great for total as for minimum ionization, and, in the second place, that for the assumption of total dissociation, the mobility changes are all in one direction. If, as seems probable.[2] the change of the velocities of the ions with the increase of concentration is due to the approach of the charged ions toward one another, the effect would be expected to be in the direction of a decrease of mobilities for all the ions.

So far as conductance and transference data are concerned it appears, therefore, that the assumption of complete dissociation results in a simplification of the theory of monovalent strong electrolytes, since one variable, ion mobility, is substituted for two, *i. e.*, the number and mobilities of the ions. The phenomena can otherwise only be explained by more or less indefinite distribution of the effects observed between these two variables.

Further, it follows from the conception of substantially complete dissociation that the properties of the salt solution should be *additive*. Lewis, in his paper on "The Use and Abuse of the Ionic Theory" has as a matter of fact, pointed out (in 1908) that the additivity of most of the properties of strong electrolytes may be interpreted as indicating complete dissociation.[3] It is of real interest, therefore, in connection with the study of the

[1] This computation was made as follows. Since the conductance of the positive ion Λ_+ equals $\gamma F U_+$ and also equals $\Lambda (1-T_{Cl})$ values of U_+ can be computed for various assumptions as to γ. In these figures γ was placed equal to Λ/Λ_0 for KCl for each concentration; for the computation in the next paragraph γ was assumed to be 1.

[2] See Milner, *Phil. Mag.*, **35**, 214, 354 (1918).

[3] Lewis, *Science*, **30**, 1–6; *Z. physik. Chem.*, **70**, 212–9 (1909). A paragraph from this paper is of interest in this connection. "The additivity of the properties of electrolytic solutions, striking as it is, seems to prove too much. If it is an argument for the dissociation of electrolytes, it seems to be an argument for complete dissociation. Why should the properties of a normal solution of potassium chloride be simply those of potassium and chloride ions if, as measurements of conductivity show, it is 25% undissociated? Why should the undissociated part have no individual properties of its own? It is easy to see why completely dissociated acids and bases should give the

dissociation of these monovalent chlorides, to see whether their conductivities are additive.   In a limited sense this has been found to be the case, for, although the conductance is not directly proportioned to the concentration of the salts, its value, at each concentration, can be found accurately from a sum of the effects of the separate ions.   In other words, as was shown in an earlier paper,[1] the conductance due to a chloride ion is independent, at least up to 0.1 N, of the (monovalent) ion with which it is associated.   The accuracy with which this holds can be observed in Col. 5 of Table I, which contains the product $T_{Cl}\Lambda$, (i. e., the conductance due to the chloride ion) for a series of chlorides.   Above 0.1 N, however, the $T_{Cl}\Lambda$ value is no longer constant (see data for 0.2 and 1.0 N in Table I).   Appreciable changes of the medium or environment of the chloride ion have occured with the increasing concentrations of the salts, as indicated by the changes of the relative viscocities, η, of the solutions, Col. 3.   It is important to note that at these higher concentrations the *chloride ion conductance, $T_{Cl}\Lambda$, is small when the viscosity is large, and vice versa.*   This is what would be expected if the chloride ion is the same substance in each of the solutions, since, under the same potential gradient, the velocity of the ions would be decreased by a high viscosity and the reverse effect would accompany a low viscosity.   If Stokes' law were followed, the conductances would be found to be inversely proportional to the first power of the values of the relative viscosities.   However, in these salt solutions, this strict proportionality is not to be expected, since the ions are not large in comparison with the particles through which they move, as is necessary for Stokes' law to hold, and the change of viscosity is due to the addition of the salt itself.   I have found, empirically, that by multiplying the $T_{Cl}\Lambda$ product by the relative viscosity, η, to the 0.7 power a constant is obtained (Col. 6) which is, presumably, the conductance of chloride ion in a solution whose relative viscosity is 1.   W. H. Green[2] has obtained the same exponent, 0.7, for the effect of viscosity on the conductance of lithium chlor-

same heat of neutralization, since we regard this heat as simply due to the union of hydrogen and hydroxide ions, but half normal potassium and sodium hydroxides give essentially the same heat of neutralization with an acid, although they are 20% undissociated.   Half-normal barium hydroxide gives the same, although 40% undissociated.   Copper sulphate as dilute as one-tenth normal is still more than half undissociated, but its color is practically the pure color of cupric ion.   Indeed in all the strong electrolytes the partial volume, heat capacity, internal energy, viscosity, refractive index, rotatory power, in fact, practically all the significant physical properties of the undissociated part of the electrolyte seem practically identical with the properties of the constituent ions.   If we had no other criterion for the degrees of dissociation, these facts would undoubtedly lead us to regard salts, up to a concentration of normal or half-normal, as completely dissociated."

  [1] MacInnes, THIS JOURNAL, **41**, 1086 (1919).

  [2] Green, *J. Chem. Soc.*, **93**, 2049 (1908).

ide solutions. From his work, it was found that the limiting values of the conductance, Λ_0, of lithium chloride, in a series of sucrose solutions of viscosity η can be expressed by the formula, $\Lambda_0\eta^{0.7} =$ const. From earlier work he finds the same value for the exponent expressing the effect of viscosity on the conductance of the ions of potassium chloride, but a lower value (0.55) holds for hydrochloric acid. The higher exponent probably represents the effect of viscosity on the conductance of potassium, lithium and chloride ions.

TABLE I.—ION CONDUCTANCES AT 18° OF THE CHLORIDE ION FROM VARIOUS ELECTRO-
LYTES.

Conc. 0.01 N.

	Λ.	η.	T_{Cl}	$T_{Cl}\Lambda$	$T_{Cl}\Lambda\eta^{0.7}$
HCl	369.3	1.0005	0.167	61.67	61.67
CsCl	125.07	0.9997	0.495	61.89	61.89
KCl	122.37	0.9996	0.504	61.68	61.68
NaCl	101.88	1.0009	0.604	61.55	61.55
LiCl	91.97	1.0016	0.668	61.46	61.48

Conc. 0.1 N.

HCl	351.4	1.005	0.161	56.6	56.80
CsCl	113.44	0.997	0.499	56.6	56.50
KCl	111.97	0.9982	0.504	56.45	56.40
NaCl	91.96	1.0086	0.616	56.67	57.0
LiCl	82.28	1.0161	0.684	56.35	56.95

Conc. 0.2 N.

HCl	342.0	1.010	0.159	54.4	54.8
KCl	107.9	0.9959	0.504	54.4	54.3
NaCl	87.7	1.0167	0.618	54.2	54.8
LiCl	77.8	1.031	0.691	53.8	54.9

Conc. 1.0 N.

HCl	301.0	1.050	0.156	46.95	48.6
KCl	98.22	0.982	0.504	49.50	48.8
NaCl	74.31	1.086	0.617	45.9	48.6
LiCl	63.27	1.150	0.694	43.9	48.5

In my computations, the "true transference numbers" of Washburn[1] and of Buchbock[2] were used at 1.0 N (corrected, in the case of Washburn's results, for the difference between 1.0 N and 1.25 N at which his determinations were made). Since the product $T_{Cl}\Lambda$ is intended to represent the actual conduction of electricity by the chloride ion, a short consideration will show that the true transference number should be used in the calculation. In the determination of the Hittorf number concentration changes are produced at an electrode, (a) by the movement of the ions and (b) by the movement of water with the ions. In Washburn's and in Buchbock's measurements (a) alone was found by the artifice of referring

[1] Washburn, THIS JOURNAL, 31, 322 (1909).
[2] Buchbock, Z. physik. Chem., 55, 563 (1906).

the concentration changes to an indifferent dissolved substance. It is clear that in computing the conducting power of an ion, the effect due to the movement of the water should be eliminated, since concentration changes due to the motion of the ions are modified by the transfer of water. For the concentrations below $1.0\ N$ the transference numbers are corrected in Table I, for hydration of the ions, by Washburn's[1] formula,

$$T - T_H = \Delta n \ . \ N_s/N_w$$

in which T and T_H are the true and Hittorf transference numbers, Δn is the number of mols of water transferred from anode to cathode per faraday of current, and N_s/N_w is the ratio of mols of salt to mols of water in the solution. For the values of Δn the original paper may be consulted. Washburn's determinations were, however, made at $25°$, and the remainder of the data of Table I for $18°$. That no serious error is involved by the assumption that the changes between two temperatures are small is shown by referring to the Hittorf transference numbers at lower temperatures and those obtained incidentally in Washburn's work.[2] For instance Hopgartner's value for T_{Cl} for sodium chloride at $16°$ (0.634) is nearly identical with Washburn's value (0.635) for $25°$. Also MacInnes and Beattie[3] have shown that the Hittorf numbers for lithium chloride do not change appreciably between $18°$ and $25°$. Buchbock does not give the temperature of his determination of the true transference numbers of hydrochloric acid. His value for the true transference number of this substance is identical with that of the Hittorf number at $18°$ as determined by Riesenfeld and Rheinhold, but the difference between the two values is small since the value of Δn (equation 2) is lower than that found for any other electrolyte. The assumption that the hydration of the ions is the same at the two temperatures is, of course, included in these computations. At the lower concentrations different assumptions as to the hydration have relatively little effect on the values of the true transference number. It is hoped, however, that data referring to one temperature can be obtained in the near future.

The transference numbers for the lower concentrations are taken, with some exceptions, from the "best values" in Noyes and Falk's compilation.[4] For hydrochloric acid solutions, the data of Riesenfeld and Rheinhold are preferred to the earlier and less concordant values. For sodium chloride, at intermediate concentrations, a study of the available data led to a revision of the "best values" just referred to. For instance, at $0.1\ N$, the compilation gives 0.606 for the transference number of the chloride ion.

[1] *Loc. cit.*

[2] See Noyes and Falk's compilation of transference numbers. THIS JOURNAL, **33**, 1436 (1911).

[3] MacInnes and Beattie, *ibid.*, **42**, 1117 (1920).

[4] *Loc. cit.*

This is based, almost entirely, on the work of Jahn, Schulz and Bogdan. However, Hopgartner's work at 16°, the moving boundary values of Steele and Dennison, and the early work of Hittorf all give the value 0.617 for the same number. The latter figure has been adopted in Table I.

The values for the relative viscosity have also been taken from Noyes and Falk's compilation[1] of conductance data, with the exception of the values for hydrochloric acid, which are based on Greene's work at 25° corrected by a temperature coefficient determined by Taylor.[2]

It is of interest to see whether the conductances of other ions ($T\Lambda$ values) of strong electrolytes show the constancy from compound to compound that is exhibited by the monovalent chlorides. It is unfortunate that so few data are available, but in nearly every case so far examined, the rule that the conductance of an ion is independent of its (monovalent) association has been found to hold within the limits of error of the transference work. In general, the numbers obtained by the moving boundary method give more concordant $T\Lambda$ values than those obtained by the Hittorf procedure. The reasons for this may be, first, that the former is a more direct method than the latter, and subject to less experimental error, and second, experimenters and compilers of data have shown a noticeable tendency to give most weight to Hittorf numbers that show little shift with concentration. The moving boundary measurements as carried out by Steele and Dennison involve an error, pointed out by Lewis.[3] However, at 0.1 N and below, this error is not serious, as is shown by Lewis' computations and by the agreement, in many cases, of the moving boundary numbers with those obtained by other methods. Data are given in Table II for the computation of $T\Lambda$ products for other ions than the chloride. As the concentrations involved are 0.1 N and below, hydration and viscosity effects are smaller than the probable error of the transference numbers. The agreement is certainly as close as could be expected.

TABLE II.—HYDROGEN-ION CONDUCTANCES AT 18°.

	0.01N			0.02N			0.01N	
	Λ.	$T_H\Lambda$.	$T_H\Lambda$.	Λ.	T_H.	$T_H\Lambda$.	Λ.	T_H.	$T_H\Lambda$.
HCl........	369.0	0.833	*307.3*	365.5	0.833	*304.0*	351.4	0.839	*294.8*
HNO$_3$.....	365.0	0.839	*306.2*	361.2	0.846	*305.5*	346.4	0.855	*296.2*

POTASSIUM-ION CONDUCTANCES AT 18°.

		0.02N			0.1N	
	Λ.	T_K.	$T_K\Lambda$.	Λ.	T_K.	$T_K\Lambda$.
KCl..............	119.90	0.496	*59.4*	111.97	0.496	*55.5*
KBr..............	121.78	0.482	*58.8*	114.14	0.481	*54.9*
KI	121.10	0.487	*59.0*	113.98	0.486	*55.4*

[1] Noyes and Falk, THIS JOURNAL, 34, 454 (1912).

[2] Greene, J. Chem. Soc., 93, 2023 (1908); Taylor, Proc. Royal Soc. Edinburgh, 25, 231. These references were kindly called to my attention by E. W. Washburn.

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

It appears, then, that the existing conductance and transference data for the alkali halides and for nitric and hydrochloric acids indicate that the conductance is, in the limited sense described, an additive property, at least at higher dilutions, and that in the case of the chlorides this property is modified in a quite definite manner by the change of relative viscosity with increasing concentrations.

Another test is possible of the additive nature of the conductances of uni-univalent salts in cases in which transference data are not available. By subtracting the ion conductances of the positive ions (which can be obtained from the data in Table I) from the corresponding conductances of two or more salts of the same acid, agreeing values of the conductance of the negative ion should be obtained. For instance, the same value for the bromide ion should be obtained by subtracting values of the conductances of the potassium and sodium ions, obtained as described, from the conductances, at the corresponding concentration, of potassium and sodium bromide. The data on the alkali halides fulfil this test reasonably well, although most of the available data are obtained from early work by Heydweiler, which must be corrected by a constant in order to compare it with Kohlrausch's more accurate determinations. The alkali nitrates and chlorates, however, show no such regularity, at 0.1 N, and must, therefore, be regarded as definite exceptions. The agreement of the data on these latter salts with the test just described is, on the other hand, excellent at 0.01 N so the variation can hardly be due to experimental error. These solutions should receive further study, including determinations of transference numbers and viscosities.

Since the conductance of the chloride ion, and, therefore, the number of ions, is the same at equivalent concentrations of the univalent chlorides, these substances must have the same degree of dissociation. This argument applies also to the hydrogen ion and to nitric and hydrochloric acids. It appears then that as diverse substances as lithium chloride and nitric acid have the same degree of dissociation in equimolar solutions. This similarity with regard to ionization seems, to the author at least, hard to account for unless the dissociation has reached a limit dependent only on the electrical fields due to the ions. There are a number of indications that this limit is complete, or substantially complete, dissociation.

For instance, a recent paper by Hill[1] describes experiments in which all but 1/45,000 of a strong electrolyte, silver perchlorate, left a benzene solution, in which it was non-conducting, when shaken with the same volume of water. This is evidence that there are no common substances in the benzene and water solutions. As pointed out in the paper referred to, this result can follow from (a) complete hydration of the salt in the aqueous

Hill, THIS JOURNAL, **43**, 254 (1921).

layer, (b) complete solvation in the benzene layer, or (c) complete ionization in the aqueous phase. With regard to the first possibility, it appears probable that, unless the hydrates are very stable, they will exist in equilibrium with at least a small amount of the anhydrous material, which would enter another phase in which it is soluble. The hydrates of the alkali halides and of silver perchlorate are, however, easily broken up; the latter salt can be dried completely at 110° and the salts separate from saturated solutions in the anhydrous form. The same considerations apply to solvation in the benzene phase. Though not decisive, the evidence is in favor of (c), i. e., complete, or substantially complete dissociation. As mentioned in a previous paper[1] hydrochloric acid does not have an appreciable partial pressure of HCl molecules, even up to 2 N, although, according to the earlier theories of dissociation a considerable portion of the substance is in an undissociated condition. HI and HBr solutions have still smaller partial pressure of the solutes, being just capable of determination at 6 N.[2]

It seems very probable, from the Lewis-Langmuir conception of the structure of the atoms of these electrolytic substances, that they are "polarized" even in the solid state, i. e., in silver perchlorate, for instance, the silver and perchlorate radicals have permanent positive and negative charges. The simple molecules thus remain polarized even when dissolved in a medium, such as benzene, in which they form a non-conducting solution. The arguments concerning conductivity given in the first portion of this paper prove only that there is, at moderate concentrations, a definite ratio between "polarized" and "ionized" molecules, the latter only being responsible for conduction of electricity. However, there seem to be no reasons why "polarized" molecules should not distribute between two phases if capable of existing in both. Here again, the evidence is not conclusive, since the "polarized" molecules in one phase or the other may form stable solvates. On the other hand, it is noteworthy that this nearly complete absence of "escaping tendency" (toward phases in which the solutes are not ionized but in which they are capable of existing in large concentrations) is found, so far as I am aware, only in connection with solutions of strong electrolytes.

Summary and Discussion.

The changes of the transference numbers with concentration indicate that variations of ionic mobility with concentration *must* be considered in any theory of strong electrolytes. Since changes in the transference numbers can indicate only *differences* of mobilities, it seems very probable that the actual changes are greater than these differences. As there is

---

[1] Noyes and MacInnes, THIS JOURNAL, **42**, 239 (1920).

[2] Bates and Kirshman, *ibid.*, **41**, 1991 (1919).

no way at present of distinguishing between variations of the equivalent conductance due to (a) changes of number of ions, (b) changes of mobilities of ions, it seems desirable to consider a group of these substances as completely dissociated and all variations of conductance as due to changes of mobility. These latter changes can, quite conceivably, arise from the increasing strength with concentration of the electrical field due to the ions. However, the evidence at present available is most nearly clear in the cases of the alkali halides, and hydrochloric and nitric acids. These substances fulfil a further condition of complete dissociation, i. e., additivity at each concentration, of the conductance, except as this property is modified by the changing viscosity.

It must be recognized, of course, that any degree of dissociation less than that represented by the limiting case considered above, can be found in solutions of electrolytes, particularly "weak electrolytes" and those with polyvalent ions. However, the degree of dissociation of the latter can hardly be computed from the relation Λ/Λ_0, since the changes of the transference numbers with concentration indicate that ion mobility changes also occur in these solutions.[1] With weak electrolytes, the conductivity ratio probably represents the degree of dissociation since with these substances the ion concentrations, and therefore, the electric fields around the ions, change but slightly with concentration.

In connection with strong electrolytes there does not appear to be any property of salt solutions that can be computed from the conductance ratio. The activity coefficients of the ions of the alkali chlorides and hydrochloric acid (to which the freezing-points, and other colligative properties are thermodynamically related) are first lower and then much higher than the corresponding ratios as the concentrations are increased.[2] On the other hand, so far as they have been measured, the "activities," or free energy contents of the ions of these substances have been found to be additive at each concentration[3] as would be expected if they were completely or substantially completely dissociated.

CAMBRIDGE 39, MASS.

[1] It has been usual to ascribe changes of the transference number, with concentration, of electrolytes containing polyvalent ions to the presence of ionic complexes and intermediate ions. The figures in Table I show that LiCl, whose transference numbers change rapidly. is quite normal in behavior, and not essentially different from KCl and NaCl. It appears, therefore, that while such intermediate and complex ionsundoubtedly exist in certain solutions, variation of transference numbers is not a certain indication of their presence.

[2] See compilation by Noyes and MacInnes, THIS JOURNAL, 42, 239 (1920).

[3] MacInnes, ibid., 41, 1086 (1919); Chow, ibid., 42, 497 (1920); Harned, ibid., 42, 1809 (1920).