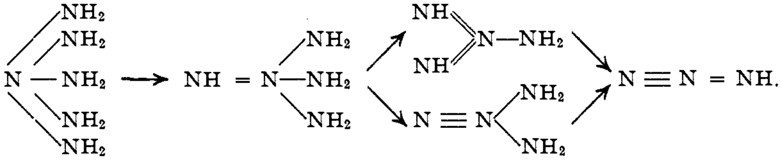
on the matter under discussion in the present paper, the following quotation from Franklin[1] is of especial interest:

"More perfect analogs of the aquo acids, however, would be compounds entirely devoid of oxygen, and in which all the functions of oxygen in the aquo acids are performed by nitrogen.

"If, after the familiar manner, acetic acid, carbonic acid, and nitric acid, and their anhydrides are assumed to be derived from the normal acids of the respective formulas, $CH_3C(OH)_3$, $C(OH)_4$, and $N(OH)_5$ by successive dehydration, the formulas for strictly analogous ammono acids and their anammonides may be deduced from the hypothetical ammono acids of the formulas, $CH_3C(NH_2)_3$, $C(NH_2)_4$ and $N(NH_2)_5$.*****

"Normal ammono nitric acid and its deammonation products [are then represented] by the formulas



"The indicated successive deammonation of nitrogen pentamide is especially interesting in view of the fact that the formula of the final product is identical with that recently proposed********for hydronitric acid. The experimental work*****shows very clearly the analogy between hydronitric acid and nitric acid as acids, respectively, of the ammonia and water systems, and proves to a practical certainty the correctness of the formula $HN=N\equiv N$ for hydronitric acid."

[Contribution from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 97.]

ON THE RELATION BETWEEN THE CONDUCTANCE AND THE VISCOSITY OF ELECTROLYTIC SOLUTIONS AND ITS BEARING ON THE THEORY OF THESE SOLUTIONS.

By Charles A. Kraus.

Received October 11, 1913.

1. Introduction.[2]

That the conductance of an electrolytic solution is dependent on its viscosity was first suggested by G. Wiedemann(1)[3] in 1856. The ex-

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[1] "The Organic Acid Amides and their Metallic Derivatives as Acids and Salts of the Ammonia System of Acids, Bases and Salts," *Trans. 8th Intern. Congr. Appl. Chem.*, 6, 119 (1912).

[2] This investigation was assisted by a grant made to Prof. A. A. Noyes by the Carnegie Institution of Washington. I wish to express my indebtedness for this assistance whereby the completion of this work was made possible.

[3] References to earlier papers will be found in the collected list of references at the end of this paper.

periments on which Wiedemann based his conclusions are not decisive in the light of our present knowledge; nevertheless, he correctly inferred that if the conductance of solutions is a simple function of their viscosity, then the conduction process must consist in a migration of carriers through the solution under the influence of the impressed potential gradient and against the opposing frictional resistance of the surrounding molecules.

Grotian(2) subsequently adduced conclusive evidence connecting the conductance with the viscosity of solutions, by showing that the temperature coefficients of conductance and fluidity are practically identical. Stephan(3) studied the conductance and viscosity of solutions in mixtures of alcohol and water and found that, with increasing dilution, the ratios of the products of conductance and viscosity in these mixtures to that in pure water approach approximately the same limiting value. He also found that for these solutions the temperature coefficients of conductance and fluidity are substantially the same.

The law of the independent motion of the ions was discovered by Kohlrausch(4) as a result of the consideration that in dilute solutions the motion of the ions is entirely controlled by the frictional resistance due to the solvent. He accounted for the increase in conductance with temperature, by assuming a decrease in the frictional resistance due to the solvent as a result of its greater fluidity. Kohlrausch also pointed out the important fact that, with increasing temperature, the difference in the conducting power of different electrolytes diminishes.[1]

Arrhenius(5) finally established the ionic theory of electrolytic conduction on a quantitative basis, and thereafter it was possible to study the relation between conductance and viscosity under widely varying conditions. Ostwald(6), after having shown that the law of mass-action applies to solutions of the weak acids, attempted to harmonize discrepancies arising between the measured and the calculated conductance values of concentrated solutions of butyric acid in water, by correcting the observed conductances in direct proportion to the fluidity change of the solution.

Arrhenius(7) made an extensive investigation of the influence of various non-electrolytes on the conductance of electrolytic solutions in water. He found that, for a given percentage addition of various non-electrolytes to solutions of a given electrolyte, the conductance change varies, being greater for substances of high molecular weight. For a given non-electrolyte, the conductance change was found to vary with the nature of the dissolved electrolyte, being in most cases greater for electrolytes with slow ions. From the results of Arrhenius it appears that, for a given viscosity change, the change in conductance is greater the smaller the dimensions of the molecules of the added non-electrolyte, and the greater

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[1] Kohlrausch(4) p. 196.

the dimensions of the ions of the dissolved electrolyte. Arrhenius recognized the fact that different ions experience different changes in the resistance to their motion as a result of viscosity change, and he suggested that the observed change in the transference numbers of various electrolytes with concentration is due to the specific influence of the accompanying viscosity change on the speed of the anion and the cation, respectively.

In recent years many investigations have been carried out on the relation between the conductance and the viscosity of solutions. Walden(8) has pointed out that for a given electrolyte in various solvents the Λ_0 values are very nearly proportional to the fluidities of these solvents. Martin and Masson(9), Jones and his associates(10), Fawsitt(11), Hartley, Thomas and Appleby(12), Green(13), and others have studied the relation between the conductance of electrolytic solutions containing nonelectrolytes and the viscosity of these solutions. Bousfield(14), R. Lorenz(15), Herzog(16), and others have attempted to apply to solutions of electrolytes the laws which have been found to hold between the dimensions and the mobilities of colloidal particles in solution.

Johnston(17) investigated the relation between the conductance and fluidity of dilute aqueous solutions at temperatures as high as 156°, employing the conductance data obtained by Noyes(18) and his associates in this laboratory. Johnston found that this relation may be expressed by the equation:

$$\Lambda_0 = kf^p. \qquad (I)$$

When k and p are constants, Λ_0 is the limiting conductance of a given electrolyte at any temperature and f is the fluidity of water at the same temperature. Johnston showed that p does not differ greatly from unity,[1] generally being less, and that it has a specific value for the individual ions. Recently, Washburn(19) has proposed to apply a correction for viscosity to the conductance of each ion, assuming that the change in speed which an ion experiences, as a result of a given viscosity change with concentration, is the same as that which it experiences for the same viscosity change due to temperature change. In other words, in making corrections for the viscosity effect due to concentration change, he employs the exponent p of Equation I, determined by Johnston from temperature change. How far this assumption is justified will appear below.

2. General Considerations.

It is the purpose of this paper to investigate the conditions under which corrections may be applied to conductance values for the influence of viscosity and to interpret the results in the light of the ionic theory, but, before examining the experimental data, it will be well to inquire into the principles underlying viscosity change in order that the data

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[1] With the exception of the case of the hydrogen and hydroxyl ions.

may be correctly interpreted. The slipping of the particles of a fluid with respect to one another or the motion of a particle through a collection of other particles is peculiarly dependent on the relative dimensions of the various particles concerned. This is shown by the work of Millikan(20) who investigated the motion of small charged particles of oil through air. If the moving particles are small with respect to those of the surrounding medium, their speed will undoubtedly be greater than would be that of larger particles in the same medium.

It is evident that, in interpreting the influence of viscosity on conductance, the relative dimensions of the ions and of the various molecules which resist the motion of the ions, are of primary importance.

Change in viscosity is, in general, brought about in one of three ways, namely: first, change in concentration, which may be due either to the addition of a new substance or of a larger amount of one already present in solution; second, change in pressure; and, third, change in temperature.

The influence of the viscosity change on the speed of an ion in a solution will, in general, differ with the nature of the process by means of which the viscosity change is brought about. I shall consider below, and in order, the relation between the change of ionic speed and the change of viscosity as it is brought about in the different ways suggested above.

3. Experimental Material.

A. Viscosity Change Produced by Concentration Change.

In many respects the most important case to be considered is that in which the viscosity change is due to the electrolyte itself, the speed of whose ions are under consideration; for this case arises whenever the concentration of a solution approaches normal, and in many cases at much smaller concentrations. If we are to determine the concentration of the ions at higher concentrations by the conductance method, it is essential that the law be known connecting the speed of the ions with the concentration of the solution. It is not obvious that the viscosity factor is the only one influencing the speed of the ions as the concentration increases. I shall, however, show below that this is the case in some instances.

The greatest difficulty which it has been necessary to overcome, in attacking this problem, has been the lack of a law connecting the conductance and concentration of solutions. As is well known, the law of mass action does not apply, even approximately, to solutions of strong electrolytes in water. Other relations than the mass-action law have been suggested, notably the law of Storch(22) which may be expressed by the following equation:

$$(c\gamma)^n/c(1 - \gamma) = D. \qquad \text{(II)}$$

Where n and D are constants, c is the concentration and γ is the degree of ionization. γ is determined by the equation:

$$\gamma = \Lambda/\Lambda_0. \qquad \text{(III)}$$

where Λ is the conductance at concentration c, and Λ_0 is the equivalent conductance which is approached as the concentration of the solution approaches zero. It is obvious that, if the speed of the ions changes, the value of Λ_0 for each ion must be corrected proportionately.

It has been found that the law of Storch does not apply strictly in dilute solutions, where the viscosity effect is negligible, and, therefore, any extrapolation to more concentrated regions is rendered uncertain. It has recently been shown by Kraus and Bray(23)[1] that, for a large number of electrolytes in various solvents, the following equation holds:

$$(c\gamma)^2/c(1-\gamma) = D(c\gamma)^m + K, \qquad \text{(IV)}$$

where m and K are constants and the other symbols possess the same significance as above. At high concentrations K becomes negligible in comparison with $D(c\gamma)^m$ and the equation reduces to the form of Equation II. The wide range of applicability of this equation justifies its application as an extrapolation function to more concentrated solutions. The influence of viscosity may then be determined by comparison with the extrapolated values from this equation.

Any arbitrariness in this procedure may be overcome by studying a system in which the solution possesses a minimum viscosity. In such solutions the viscosity at first decreases with concentration, then increases again, and finally becomes greater than that of the pure solvent. The point at which the viscosity of the solution becomes equal to the viscosity of the solvent thus furnishes a reference point, by means of which the validity of the extrapolation may be checked without any arbitrary assumptions.[2]

By way of illustration, the results of such a calculation are given for potassium iodide dissolved in water at 0°, in which case the viscosity change is very large. The conductance data in concentrated solutions are due to Sloan(24). Those in dilute solution are due to Kahlenberg(25).

The last five of Kahlenberg's values in dilute solutions were employed in determining the value of Λ_0 for KI. These last five points agree with the data of Sloan. They do not, however, agree with the remainder of Kahlenberg's determinations, which appear to be uniformly low. The value of Λ_0 obtained, and employed throughout these calculations, is 81.12. This value is in good agreement with the Λ_0 value employed by Washburn and MacInness(26) for KCl, which is 81.0. A small error in Λ_0 will not affect the extrapolation function in concentrated solutions to a marked degree. The experimental data are shown graphically in Fig. 1, where values of Λ are plotted as ordinates and those of $\log c$ as abscissas. Sloan's determinations are represented by circles and Kahlenberg's by crosses. It will be observed that in concentrated solutions the conductance curve

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[1] See also Kraus and Bray(49).

[2] This condition is partially fulfilled in the case of solutions of KI in water.

exhibits a distinct minimum and maximum. As we shall see below, this peculiar trend of the curve is due to viscosity change.[1]

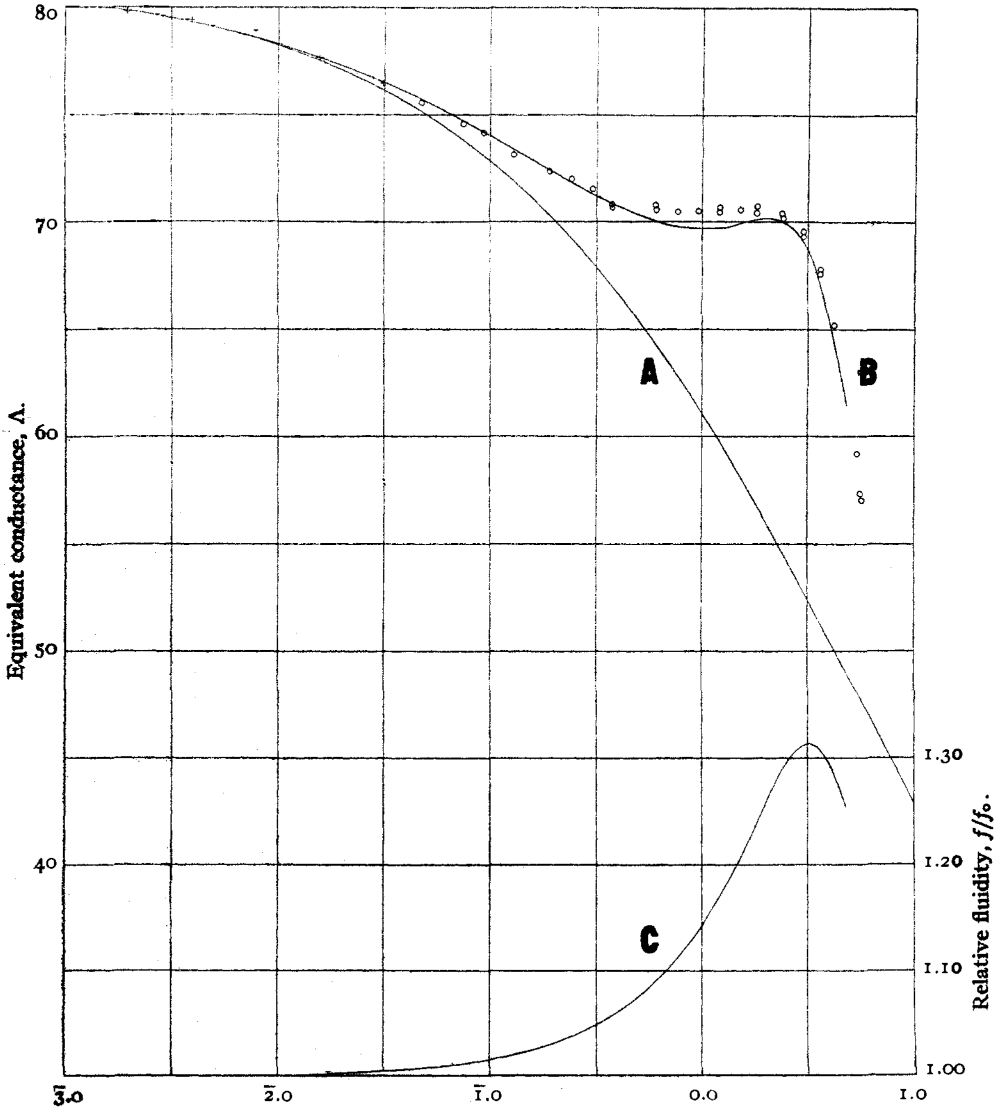

Fig. 1.—Fluidity and conductance curves for KI in water at 0°.

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[1] Washburn(42, p. 1464) has suggested that the maxima and minima frequently observed in the conductance curves of solutions, are due to viscosity change. In the case of non-aqueous solutions, in which this phenomenon occurs most frequently, the minimum is not due to viscosity change, as has been shown by Kraus and Bray (49). Only in the case of aqueous solutions are both the maximum and minimum due to viscosity.

The viscosity data are due to Sprung(27). The fluidity curve of potassium iodide at 0° is represented graphically in Fig. 1 (Curve C), values of f/f_0 being plotted as ordinates, f_0 being the fluidity at zero concentration and f the fluidity at concentration c. The lowest temperature at which Sprung measured the viscosity of KI was 5°. The values at 0° were obtained by graphical extrapolation. In Table I the concentration c of the solution is given in the first column; Λ, the conductance, as determined by Sloan and Kahlenberg, is given in the second column; and in the third column are given the values of n, the viscosity, as obtained by extrapolation.

TABLE I.—CONDUCTANCE AND VISCOSITY DATA FOR POTASSIUM IODIDE IN WATER AT 0°.

C.	Λ.	η.
5.662	57.30	0.8330
5.420	59.17	0.8145
4.818	64.33	0.795
4.218	65.20	0.777
3.623	67.83	0.765
3.614	67.65	0.765
3.012	69.31	0.763
2.410	70.40	0.777
1.807	70.40	0.809
1.506	70.43	0.831
1.205	70.61	0.856
0.7528	70.46	0.900
0.6025	70.65	0.9185
0.3772	70.83	0.946
0.3012	71.56	0.9565
0.2410	72.03	0.965
0.1884	72.36	0.9725
0.1280	73.13	0.981
0.09417	74.13	0.986
0.07528	74.55	0.989
0.04706	75.60	0.9927
0.03125	76.5	0.995
0.01563	77.7	0.9975
0.007812	78.9	0.9987
0.003907	79.4	..
0.001953	79.8	..

Since the fluidity of the solutions in question is greater than that of pure water, it seemed reasonable to assume that, whatever the mechanism to which the fluidity change may be due, the ions in their motion will not meet with molecules or molecular aggregates that are larger than those in pure water. Accordingly, the several conductance values were corrected in direct proportion to the viscosity change, each value of Λ being multiplied by the corresponding value of the viscosity ratio η/η_0.

These values were then tested by means of the extrapolation Function II which is a special case of the more general Function IV as already explained. Equation II may be written in the form:

$$n \log (c\Lambda) = \log [c(\Lambda_\circ - \Lambda)] + \log D\Lambda_\circ^{n-1}, \qquad \text{(V)}$$

which is the equation of a straight line when log $(c\Lambda)$ and log $[c(\Lambda_\circ - \Lambda)]$ are considered as variables.

In Fig. 2 this function is plotted for solutions of potassium iodide in water at 0°, values of log $(c\Lambda)$ being plotted as abscissae and values of log $[c(\Lambda_\circ - \Lambda)]$ as ordinates. The scale, in each case, is indicated on the lower and left hand margins, respectively. The circles represent points in which the conductance has been corrected for viscosity, while the crosses represent the same points without any viscosity correction. The distance between the two series of points gives a fair idea of the extent of the viscosity correction, which at its maximum is a little over 30%.

It is apparent, on inspection, that the circles all lie on a straight line and that the points in the more dilute solutions, where the correction for viscosity is small or negligible, also follow this line. It is thus demonstrated that, in the case of solutions of potassium iodide in water, Equation II, and by consequence also the more general Equation IV, is obeyed up to a concentration as high as 5.66 normal, and that the speed of the ions over this range is a linear function of the fluidity within the limits of experimental error.

In Fig. 1, the continuous curve marked *B*, passing through the experimental points, represents the equation

$$(c\Lambda')^2/c\Lambda_\circ(\Lambda_\circ - \Lambda') = D(c\Lambda'/\Lambda_\circ)^{n-1},$$

where $D = 2.62$, $\Lambda_\circ = 81.12$, $n = 1.51$, and $\Lambda' = \Lambda\eta/\eta_0$. The branch-curve marked *A* represents the conductance curve of KI on the assumption that no change in speed has taken place. The points on Curve *B* are thus obtained by multiplying the conductance values of Curve *A* by the viscosity factor η/η_0.

The agreement between the experimental and the calculated values is fully as good as the experimental data lead us to expect. The maximum and minimum of the conductance curve are perfectly reproduced in the calculated curve. A comparison with the fluidity curve (*C*), which appears on the same figure, shows clearly how the minimum and maximum result from the peculiar form of the fluidity curve.

The negative viscosity effect in potassium iodide at 0° is the largest for which both conductance and viscosity data are available. The correction has likewise been applied to potassium iodide, ammonium chloride, and potassium chloride at 18°,[1] all of which give solutions having a viscosity smaller than that of water. In all of these cases the agreement

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[1] For KCl see Kraus and Bray (49), p. 1407, *et seq.*

with Equation II, after correcting for viscosity in proportion to the viscosity change, is within the limits of experimental error. The viscosity correction in these cases is much smaller than it is in the case of potassium iodide at 0°.

Solutions of salts whose viscosities are greater than that of water have also been investigated. In the case of sodium nitrate, when corrected for viscosity in direct proportion to the viscosity change, the resulting curve agrees with Equation II as well as could be expected, since the data are not very consistent among themselves. In the case of sodium chloride and sodium acetate, the corrected conductance is greater than it should be according to Equation II.

The behavior of salts of this type is well illustrated in the case of lithium chloride at 0°. The viscosity change for this salt is very great. At normal concentration the viscosity of a lithium chloride solution is 12.4% greater than that of water. Up to this concentration the very excellent conductance and viscosity measurements of Washburn and MacInness(26) are available. I have, therefore, selected this salt as a typical example whereby to illustrate the relation between conductance and viscosity where the latter is larger than that of pure water.

In Fig. 2, the upper plot represents the Function V for lithium chloride. Curve *A* represents the function before any correction has been applied for viscosity. Curve *B* represents the function after multiplying the conductance by the viscosity ratio. It is evident that in the first case the deviation from a straight line is due to the influence of viscosity. On the other hand, the pronounced departure of Curve *B* from the experimental points shows that the speed of the ions is affected far less than the viscosity of the solution as a whole. For reasons which I shall elucidate more fully below, I have constructed a third curve, *C*, on the assumption that the speed of the lithium ion varies in direct proportion to the change in the fluidity of the solution, but that the speed of the chlorine ion remains unaltered. As may be seen by inspection, the Function II gives an excellent straight line when the conductances are corrected in this manner.

At higher concentrations than normal, the correction of the conductance of one ion alone will not suffice; although even up to 9 normal the correction factor is always less than corresponds to the viscosity change of the solution. Beyond 9 normal the correction factor again begins to decrease rapidly.[1] In obtaining the results discussed in this paragraph, the conductance and viscosity data of Green were employed. Green's conductance data, in dilute solutions, are not entirely satisfactory, and only

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[1] This is shown by an increase in the ratio Λ/f, at this point, which is clearly brought out in Fig. 5, page 2045 of Green's paper(13). The increase in Λ/f beyond 9 normal is doubtless due to increasing speed of the ions in consequence of dehydration.

a qualitative result can be obtained as to the general trend of the change in conductance with viscosity. There is, however, no question as to its general character.

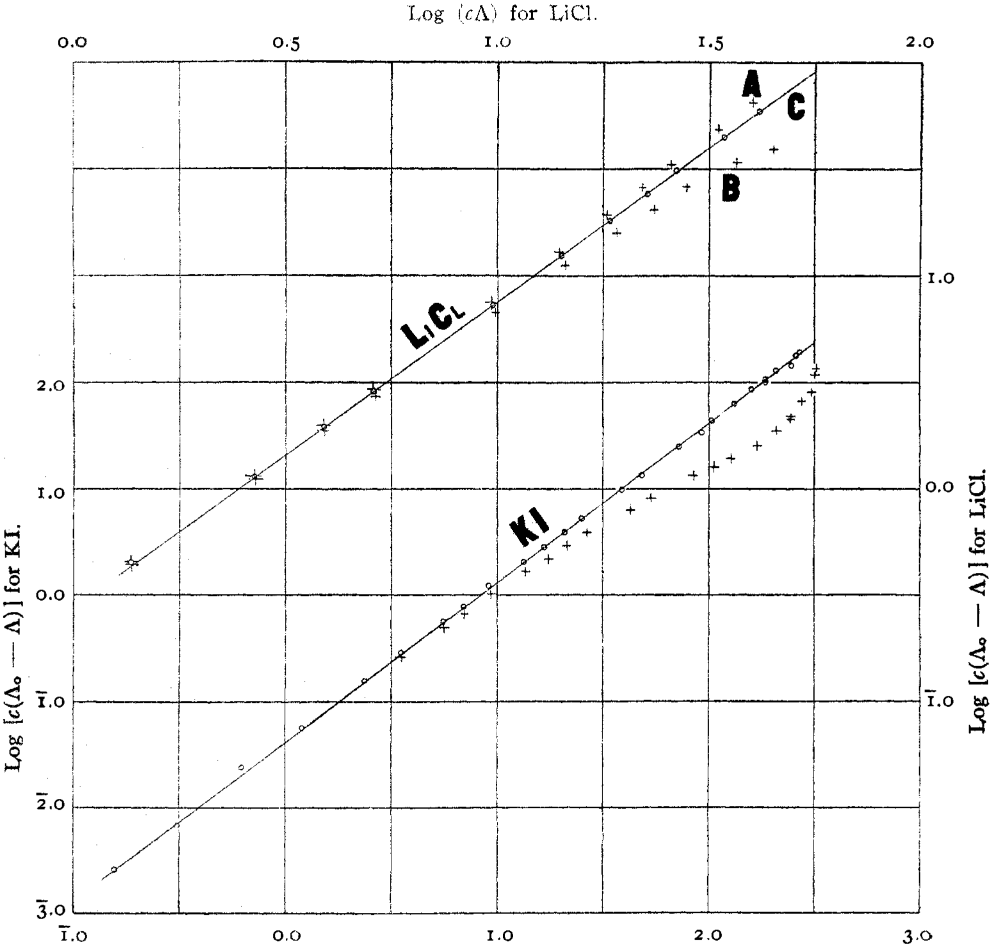

Fig. 2.—Plots for KI and LiCl in water as 0°.

Data relating to the conductance and viscosity of non-aqueous solutions are very meagre. In the case of ammonia solutions, however, the conductance data of Franklin and Kraus(28), and of Franklin(29) and the viscosity measurements of Fitzgerald(30) make it possible to determine the general character of the relationship between conductance and viscosity in the case of this solvent. Kraus and Bray have recently shown that Equation IV holds for ammonia solutions within the limits of experimental error up to concentrations which, in some cases, are above normal. In general, this concentration is higher the smaller the molecular weight of the electrolyte and the greater the speed of its ions. For potassium iodide the equation holds to normal concentration. At higher concentrations, the conductance values calculated from Equation IV are greater than the experimental ones.

This phenomenon appears to be a very general one and is particularly evident in the case of solvents of relatively low dielectric constants, in which case the exponent *m* of Equation IV is greater than unity. When *m* is greater than unity the conductance curve passes through a minimum, usually in the neighborhood of 1.0 to 0.10 normal concentration, to both sides of which the conductance rises. The experimental values, however, after passing through the minimum, reach a maximum in the more concentrated solutions, after which they continue to decrease indefinitely. Franklin and Gibbs(31) and Franklin(32) have suggested that this final drop in the conductance curve, in concentrated solutions, is due to in-

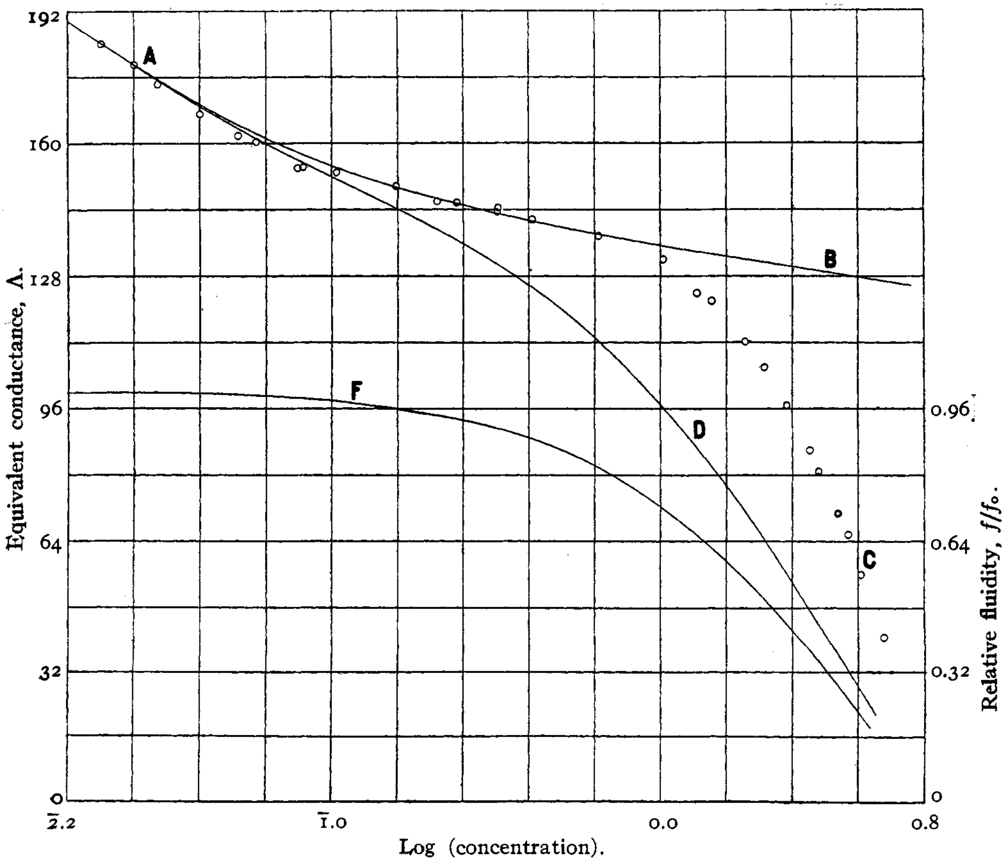

Fig. 3.—Conductance and fluidity curves for KI in NH_3 at —33.5°.

creasing viscosity of the solution. In case *m* is not greater than unity, the conductance curve does not pass through a minimum and a maximum, but the curve exhibits double curvature, indicating that the same factors are operative in this case as in the one in which *m* is greater than unity.

In Fig. 3 are shown the conductance and fluidity curves for solutions of potassium iodide in ammonia. Values of log c are plotted as abscissae and values of Λ as ordinates. The scale is indicated on the lower and left hand margins. Curve *AB* is the conductance curve calculated on the assumption that the mobility of the ions does not change with concentration. Curve *AC* is the experimental curve, the various points being indicated by circles. Curve *AD* is the conductance curve, calculated on the assumption that the mobility of the ions is proportional to the fluidity of the solution. The viscosity data are due to Fitzgerald; the fluidity curve (F) is shown in the lower portion of Fig. 3, values of the relative fluidity, f/f_0, being plotted as ordinates and of log c as abscissas. The scale of ordinates is indicated on the right hand margin of the figure, while the scale of abscissae is the same as that of the conductance curves.

B. Change in Viscosity and Conductance Due to Added Non-electrolytes.

When the viscosity change is brought about by the addition of a non-electrolyte, a conductance change takes place in the direction of the viscosity change, but in most cases the conductance change is smaller than the corresponding viscosity change. The experimental material is very incomplete. It is fairly evident, however, that the smaller the molecules of the added non-electrolyte and the larger the ions, the more nearly does the conductance change in direct proportion to the fluidity change.

It has been found that, for small additions of non-electrolytes, the relation between conductance and fluidity may be represented by an equation of the form of Equation I, in which p and k are constants, Λ_0 is the limiting conductance of the electrolyte in the solution containing the non-electrolyte, and f is the fluidity of the solution. The less the conductance of the electrolyte is influenced by the fluidity change, the smaller will be the value of p. Table II, which is reproduced from Green's paper(13), shows the value of p for various solutions.

TABLE II.—CHANGE OF CONDUCTANCE OF ELECTROLYTES DUE TO ADDED NON-ELECTROLYTES.

Electrolyte.	Non-electrolyte.	p.
HCl	Sucrose	0.55
KCl	Sucrose	0.70
LiCl	Sucrose	0.70
$CuSO_4$	Glycerol	1.0
NaOH	Carbamide	1.0
KCl	Carbamide	1.0
$LiNO_3$	Pyridine	1.0–1.3

An inspection of the table shows that, in the case of sucrose, the conductance of hydrochloride acid is affected much less than that of KCl or LiCl. In the case of $CuSO_4$, the conductance change is proportional to the viscosity change due to the added glycerol. The molecular weight of glycerol is much smaller than that of sucrose, while the dimensions of the Cu^{++} and SO_4^{--} ions are doubtless greater than those of the K^+, Cl^-, or H^+ ions. Carbamide, with a molecular weight of only 60, influences the conductance of both NaOH and KCl in direct proportion to the fluidity change.

C. The Influence of Pressure on Viscosity and Conductance.

So far as our present knowledge goes, water is the only solvent whose viscosity decreases with increasing pressure. The viscosity does not, however, continue to decrease indefinitely, but passes through a minimum after which it begins to increase rapidly. The minimum lies in the neighborhood of 1000 atmospheres. At higher temperatures the minimum becomes less and less pronounced and finally disappears altogether. The viscosity-pressure curve bears a striking resemblance to the viscosity-concentration curve of electrolytes which exhibit negative viscosity. Tammann[1] has shown that certain properties of solutions are comparable to the properties of water under pressure. He thus ascribes the influence of salts on the properties of water to the influence of internal pressure. However, we may look at the phenomenon, there can be no doubt that the negative viscosity effects, exhibited by water under pressure and by aqueous solutions under the influence of an added solute, are due to the same kind of molecular changes.

Tammann(33) has investigated the conductance of solutions of strong electrolytes in water under pressure. Some of his results for sodium chloride are reproduced in Fig. 4, where values of the relative resistance, R/R_0, are plotted as ordinates and the pressures in kilograms per square centimeter as abscissae. The continuous curves are drawn to pass through these points. The upper curve represents the results at 20° and the lower those at 0°. The concentration of the sodium chloride solution was 0.1 normal. It is unlikely that the trend of the conductance-pressure curve is materially influenced by change in ionization at this concentration. The circles represent the fluidity of pure water as determined by Cohen(34), the upper points representing the results at 15° and the lower those at 1°, respectively.

It is evident that the conductance curve of the NaCl solution corresponds very closely with the fluidity curve of pure water as determined by Cohen, coinciding within the limits of experimental error. This result is of great importance, since it shows that, while the conductance of a sodium chloride solution is affected far less than the viscosity by concentration

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[1] Tammann, *Eigenschaften der Lösungen*, Göttingen, 1906.

change of the electrolyte, the conductance of the same ions is affected in proportion to the fluidity by the pressure change.

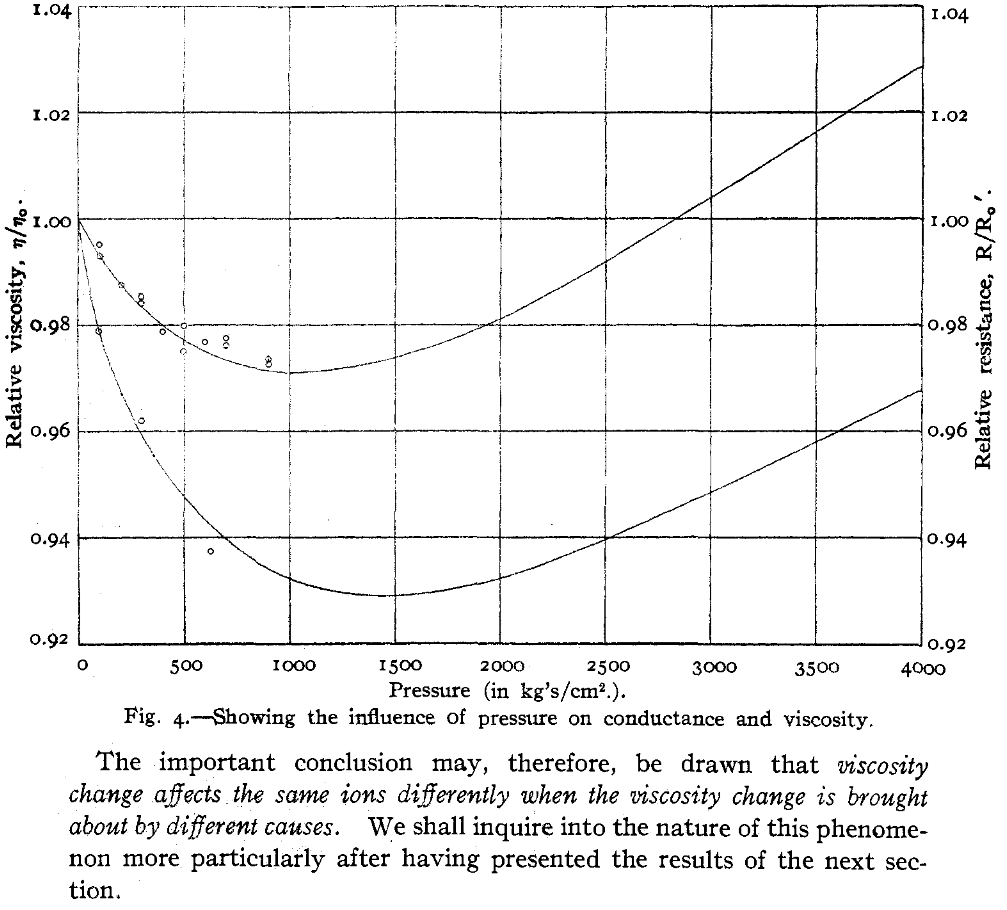

Fig. 4.—Showing the influence of pressure on conductance and viscosity.

The important conclusion may, therefore, be drawn that *viscosity change affects the same ions differently when the viscosity change is brought about by different causes.* We shall inquire into the nature of this phenomenon more particularly after having presented the results of the next section.

D. The Influence of Temperature on Conductance and Viscosity.

As regards the influence of temperature, various electrolytes exhibit great uniformity in their behavior, although differing greatly in degree. Kohlrausch(35) was the first to point out the relation between the ionic conductance and the temperature coefficient of ionic conductance. A paper by Johnston has already been mentioned in which he showed that the Λ_0 values of different ions may be expressed as a simple exponential function (Equation I) of the fluidity[1] of the pure solvent. The following table gives the values of p for univalent and bivalent ions:

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[1] Kohlrausch(47) first showed that the conductances of the ions in water follow the fluidity curve of water at different temperatures, particularly in the case of the larger ions. His conclusions, however, were based on the results for a much smaller temperature interval than Johnston's.

TABLE III.—INFLUENCE OF TEMPERATURE ON ION CONDUCTANCES.

Univalent Ions.

Ion.	Cl^-.	K^+.	NH_4^+.	NO_3^-.	Ag^+.	Na^+.	$C_2H_3O_2$.
p......	0.88	0.887	0.891	0.807	0.949	0.97	1.008
Λ......	65.4	64.7	64.4	61.8	54.0	43.5	34.6

Bivalent Ions.

Ion.	$^1/_2SO_4^{--}$.	$^1/_2C_2O_4^{--}$.	$^1/_2Ba^{++}$.	$^1/_2Ca^{++}$.
p....................	0.944	0.931	0.986	1.008
Λ....................	68.7	63.8	55.9	52.1

In Table III, the different ions are arranged in order of decreasing conducting power. It will be seen that, in the case of the univalent ions, this order corresponds with the order of increasing values of p, with one exception in the case of the NO_3^- ion. The same relation holds for the bivalent ions with one exception in the case of the $C_2O_4^{--}$ ion (which, however, is probably within the limits of experimental error). It is evident that there is an intimate relation between the conductance of an ion, and the change of its conductance with fluidity change, due to change in temperature.

Only two of the ions have an exponent greater than unity. These are $C_2H_3O_2^-$ and Ca^{++}. Both of these ions have very low conductance values, being, respectively, the final members of the two series. Whether the exponent is actually greater than unity is doubtful; for the Λ_0 values under the best conditions are probably not accurate to more than 2%.[1] At higher temperatures the values may be expected to be correspondingly less certain. As the size of an ion increases, it is probable that, ultimately, its speed will become a linear function of the viscosity. That its speed should change more rapidly than viscosity does not seem probable unless the dimensions of the ion change. In order to bring out this relation, and to show that it holds at high temperatures as well as at low, the conductances of the different univalent ions have been compared with that of the $C_2H_3O_2^-$ (acetate) ion. Johnston has shown that this ion changes its speed proportionally to the fluidity of water. The ratios of the conductances of the different ions to that of the $C_2H_3O_2^-$ ion are given in Table IV and are shown graphically in Fig. 5. Under f' are given values of the fluidity divided by the conductance of the $C_2H_3O_2^-$ ion. Since the conductance of this ion is proportional to the fluidity of the solvent, the ratio of f to the conductance of the acetate ion remains constant and independent of temperature. At 306° the conductance of the acetate ion was approximated from that of the sodium ion.

In Fig. 5 the relative conductance of the various ions (with respect to the conductance of the acetate ion) are plotted as ordinates against temperatures as abscissae. On the left hand margin, the various curves

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[1] Compare Kraus and Bray(49), p. 1410, *et seq.*

TABLE IV.—INFLUENCE OF TEMPERATURE ON THE CONDUCTANCE OF VARIOUS IONS RELATIVE TO THAT OF THE ACETATE ION.

Ion.	0.0°.	18°.	25°.	50°.*	75°.	100°.	128°.	156°.	218°.	306°.
K^+	1.99	1.87	1.83	1.72	1.66	1.58	1.54	1.50	1.32	1.18
Na^+	1.28	1.26	1.25	1.22	1.20	1.19	1.19	1.18	1.15	1.11
NH_4^+	1.98	1.86	1.83	1.72	1.66	1.59	1.55	1.52	1.37	1.30
Ag^+	1.62	1.57	1.54	1.51	1.49	1.45	1.43	1.42	1.29	..
Cl^-	2.02	1.89	1.85	1.73	1.67	1.59	1.54	1.51	1.32	..
NO_3^-	1.99	1.78	1.73	1.55	1.46	1.37	1.30	1.25	1.21	..
H^+	11.82	9.08	8.58	6.95	5.88	4.95	4.23	3.68	2.79	1.82
OH^-	5.17	4.95	4.71	4.24	3.75	3.38	3.07	2.81	2.08	1.62
f'	2.73	2.72	2.73	2.71	2.72	2.71	2.71	2.71	..	..

are marked with the symbols of the ions to which they relate. The curves for potassium, ammonium and chloride ions differ so little that they are represented by a single curve, that of the K^+ ion. The curve for the NO_3^- ion is indicated by a broken line.

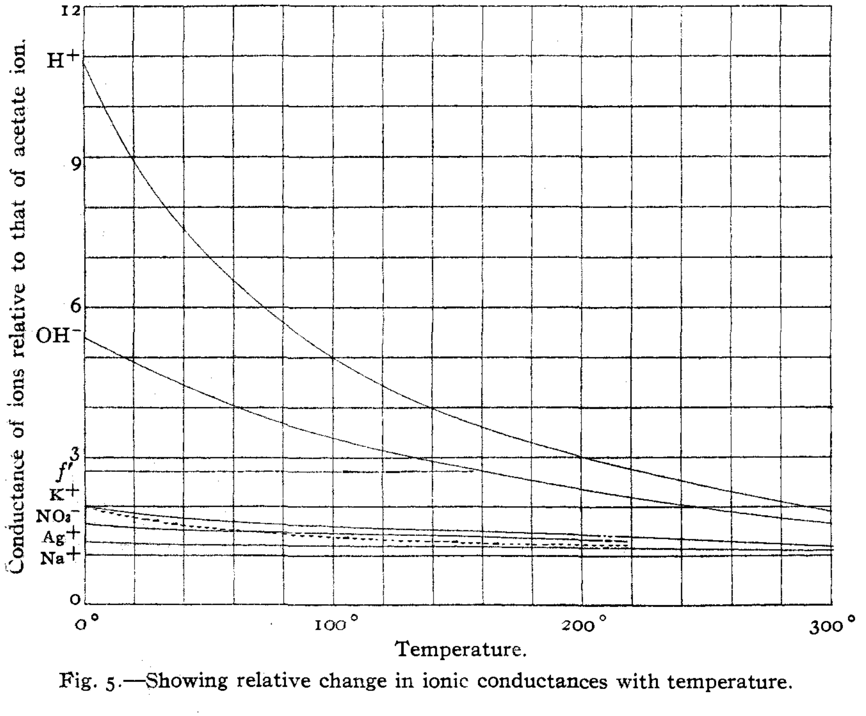

Fig. 5.—Showing relative change in ionic conductances with temperature.

It will be seen on inspection of the Table and the figure that the fluidity curve, f', is a horizontal straight line, and that the $C_2H_3O_2^-$ ion, therefore, changes its speed in proportion to the fluidity change. In the case of all the other ions the relative speed decreases with increasing fluidity and temperature. The relative decrease in speed is greater, the greater the conductance of the ion, it being greatest for the hydrogen ion and least for the sodium ion. The nitrate ion alone is exceptional, in that its relative speed decreases far more than that of other ions of the same conducting power.

From a consideration of the above results, we are led to conclude that, for very large ions, conductance and fluidity change in direct proportion to each other; but that, for ions of smaller dimensions, the speed undergoes a relatively smaller change than the fluidity of the solvent; and that this change is smaller the smaller the ion, *i. e.*, the larger the original speed of the ion.

4. Discussion.

A. Nature of the Molecular Changes Occurring in Water.

The dependence of the phenomena concerned in conductance and viscosity on the relative dimensions of the molecules of the solvent and of the ions has already been pointed out. Before proceeding farther it is necessary to consider the molecular state of water itself and the changes to which it is subject under various conditions. It is the accepted view that water consists not of single but of associated molecules, the complexity of which is a function of the temperature. As is well known, water exhibits a maximum of density in the neighborhood of 4°. This peculiar form of the density curve is readily explained on the assumption that, as the temperature falls, the volume change is the result of two factors:[1] first, a normal contraction, due to a diminution of the distance between the various molecules; and, second, an expansion due to an increase in the number and complexity of the molecular aggregates. The assumption that the aggregates occupy a space larger than that of the simple molecules is a logical one, since the density of solid water is much less than that of the liquid. These aggregates, which precipitate from solution—so to speak—when solidification occurs, are doubtless present in water even at high temperatures, although their complexity and their number is much decreased. In this connection, it may be recalled that in other cases than pure water it has been shown that crystalline aggregates persist in a liquid at temperatures far above that at which they are normally present.[2]

Since the volume of the aggregates is greater than that of the simple molecules, it follows, that if water be placed under pressure the percentage of aggregates present in water will be less than in pure water under normal pressure.

Now, the viscosity of a liquid is greatly increased by the presence of a few large aggregates. This is shown by the fact that the addition of a substance of large molecular weight increases the viscosity of a solution

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[1] Sutherland (36).

[2] Young and Mitchell (37).

enormously. Such, for example, is the case when sugar is added to water. The viscosity of water at ordinary temperatures is, therefore, for the most part due to the presence of highly complex aggregates. If pressure be applied to water at a temperature not too far removed from its freezing point, the percentage of the aggregates, or the average extent of aggregation, is reduced thereby. As a result, the fluidity of water is increased with increasing pressure and decreasing volume. Of course, if the pressure be carried high enough, the viscosity must ultimately increase again, because of the reduction of the mean distance between the molecules of the liquid. At temperatures, far removed from the freezing point where the largest aggregates have already disappeared, the viscosity will not be reduced by application of pressure.

Similarly, the cause for the negative viscosity of certain solutions in water is, doubtless, the dissociation of the molecular aggregates of the liquid, the ones to which the high viscosity of water is due; and it seems highly probable that this dissociation is due to an increase of the internal pressure on the liquid as suggested by Tammann.[1] The correspondence of the viscosity-pressure curve of water with the viscosity-concentration curve of certain electrolytes (Fig. 4), both as to form and to temperature range, leaves little room for doubting that the negative viscosity of solutions is due to disgregation of the solvent aggregates.

Even in the case of electrolytes which do not exhibit negative viscosity, the disgregation effect enters, but it is combined with an increase in viscosity due to the presence of large ions or un-ionized molecules. The resulting effect, therefore, is that initially (*i. e.*, at lower concentrations) the viscosity curve rises much less rapidly than it does at higher concentrations.

The foregoing considerations account for the fact that the conductance can be corrected proportionately to the viscosity change in the case of electrolytes which exhibit negative viscosity, but not in the case of electrolytes which exhibit a large positive viscosity effect. In the case of lithium chloride, for example, the viscosity change is due to the presence of very large neutral molecules of the salt and, probably, also to large lithium ions. Now, Washburn(39) has shown that the lithium ion is much more highly hydrated than the chloride ion. The lithium ion will, therefore, experience much greater opposition to its motion than the relatively small chloride ion. If the difference in the size of the ions is great enough, the smaller ion will, in the limit, experience no change whatever in resistance to motion; while the larger ion will experience an increased resistance, which is directly proportional to the fluidity change. It is obvious that the transference number of the ions will be affected, in this case, in correspondence with the change in the speed of the larger ion.

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[1] Compare, also Euler(38).

There are many experimental observations which bear out this hypothesis. According to Denison(40) the relative speed of the anion in gelatin solutions of $SrCl_2$ is greater than in pure water. In this case only the largest ions undergo any alteration in speed in consequence of the presence of the colloid. In the case of aqueous solutions, those electrolytes whose solutions exhibit a marked positive viscosity effect likewise exhibit a marked change of their transference numbers with concentration. This change corresponds to a smaller relative speed of the more slowly moving ion. Thus, with increasing concentration the transference number of the Li^+ ion in LiCl solutions decreases, while in HCl the transference number of the Cl^- ion decreases with concentration. The change in the relative speed of the ions is thus opposite in direction to what is to be expected on the assumption that the more highly hydrated ion is losing its hydrate molecules at higher concentration. On the other hand, if we assume that the more highly hydrated ion (the larger ion) experiences a greater diminution of speed, owing to the viscosity change, than does the smaller ion, the expected change in transference numbers is in agreement with the observed results.[1]

At 1.25 normal the viscosity of pure LiCl solution is approximately 1.14 times that of pure water. Assuming that the speed of the Cl^- ion remains unchanged with increasing viscosity, but that the speed of the much larger Li^+ ion decreases in proportion to fluidity, we may calculate the transference number of the Li^+ ion at 1.25 normal. Assuming the limiting conductance of the Cl^- and Li^+ ions to be 65.5 and 33.3, respectively, we have for the transference number of the Li^+ ion at 1.25 normal the value:

$$T^{Li^+}_{1.25} = \frac{33.3/1.14}{65.5 + 33.3/1.14} = 0.304.$$

The transference number of the Li^+ ion at infinite dilution is 0.337. The change in transference number of the Li^+ ion as calculated above is smaller than the change of the ordinary transference number. This discrepancy may be due to the influence of hydration on the transference results. The curve *C* of Fig. 2 has been calculated on the assumption that the lithium ion changes its speed in direct proportion to the viscosity change. On inspection, it is apparent that a straight line results and that it is in excellent agreement with the points in the more dilute solutions, where the correction for viscosity is either very small or negligible. So far as our available data go, the observed change of transference numbers with

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[1] The consideration of the influence of viscosity change on the transference numbers is greatly complicated, owing to uncertainties as to the influence of hydration on the results of transference measurements. In the case of transference measurements made in the presence of a non-electrolyte uncertainties arise in consequence of the influence of the viscosity due to the added non-electrolyte on the speed of the ions.

concentration may be accounted for on the hypothesis that the viscosity change, due to the presence of large molecules, affects the speed of large and small ions in different degree, causing the greater change in the case of the larger ion.[1]

It is at once apparent that it is not, in general, possible to correct for viscosity except in case the viscosity change is due to small molecules, as, for example, in the case of salts with negative viscosity. The changes due to hydrostatic pressure can also probably be corrected in this way. In other cases it is necessary to correct the conductance of each ion separately. From what has been said, it is obvious that the correction will be larger, the larger the ion. Washburn(42) suggested applying a viscosity correction in this manner. He assumes that the relation between viscosity and conductance for concentration change is the same as for temperature change, and employs, for the constant p of Equation I, the values for the several ions determined by Johnston from the change of conductance with temperature. It is obvious, from the preceding considerations, that the value of p deduced from temperature change is not necessarily applicable to a viscosity change due to some other agency. The constant p of Equation I is smaller, the larger the conducting power of the ion. Now it is in the case of these ions that we have solutions with negative viscosity, where the conductance change is proportional to the fluidity change, *i. e.*, p should be equal to unity as far as the concentration viscosity correction is concerned. On the other hand, in the case of a highly hydrated salt, such as LiCl, for example. The correction to be applied is much smaller than the viscosity ratio.

It is not possible to account for the change in transference numbers by assuming that the highly hydrated ions break down at higher concentrations. For, while it is true that a change in the transference number with concentration is found only in the case of highly hydrated salts, yet the change is always in a direction corresponding to a slowing up of the more highly hydrated ion, *i. e.*, the more slowly moving ion, and it is obvious that if the hydration of the larger ion decreased with increasing concentration, its speed would become relatively greater.

The fact, that the conductance of KI solutions may be corrected in direct proportion to the viscosity change up to a concentration of 5.66 normal, is practically conclusive evidence that the hydration of the K^+ and I^- ions does not change materially with concentration. This is not unexpected, since the activity of water in a normal solution is only about 2% less than that of pure water.

B. Change of Ionic Conductance with Temperature.

One of the most remarkable phenomena in connection with the conductance of aqueous solutions, and one for which no adequate explana-

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[1] Compare, Arrhenius(7), p. 500, *et seq.*

tion has heretofore been suggested, is the change of the conductance of the various ions with temperature. That the ionic conductances of the different ions are tending toward an approximately common value at higher temperatures was pointed out by Kohlrausch. The work of Noyes and his associates, in which the conductances of aqueous solutions were measured as high as 306°, has shown, beyond a doubt, that the relation pointed out by Kohlrausch at low temperatures holds equally well at high temperatures. The change of conductance with temperature is strikingly shown in Fig. 5. Whereas, at 0°, the ratio of the conductance of the hydrogen to that of the acetate ion is 10.6,[1] at 306° it is only 1.82. In other words, at 306°, the speed of the hydrogen ion, relative to that of the acetate ion, is less than that of the potassium ion, relative to the speed of the acetate ion at 0°. A change of this order can occur only as a result of some far-reaching and fundamental change of the conditions existing in the immediate neighborhood of the ions.

Before pursuing this subject farther, it will be well to point out some other significant facts. Foremost among these is the fact that the larger the ion, *i. e.*, the smaller its conductance, the more nearly does its change of conductance with temperature change approach a linear function of the fluidity of the solvent.[2] This is shown in Table IV, and also in Fig. 5, where the fluidity line f' of the acetate ion is practically a straight, horizontal line.

It is interesting to note, in this connection, that, while the ratios Λ_0/f of the conductances of the more rapidly moving ions to the fluidity of the solvent in aqueous solutions differ greatly from the same ratios in ammonia, the ratios for the slowly moving ions are practically identical. Thus, in water the ratio Λ_0/f for the acetate ion has the value 0.367. The conductance of the acetate ion in ammonia is not known, but, if we consider that of the negative ion in cyanacetamide, we find the ratio $\Lambda_0/f = 0.346$.[3]

If the considerations, regarding the relation between viscosity and conductance, in an earlier section of this paper are correct, then the approach of the conductance of the different ions toward a common limit at higher temperatures can be explained only on the assumption that at higher temperature the dimensions of all ions approach a common limit. Now, it might be suggested that as the temperature rises the more highly hydrated ions break down and thus approach the conducting power of the less hydrated ions. This hypothesis, however, is not in agreement with a number of important facts. Thus, if the highly solvated ions increased their

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[1] Johnston's value for the conductance of the H^+ ion gives 11.8. This number appears to be somewhat too large. The above value has been approximated from Fig. 5.

[2] Compare Kohlrausch(47).

[3] Kraus and Bray(49), p. 1343.

speed as a result of diminution of their dimensions, we should expect the conductance of these ions to increase more rapidly than in correspondence to the fluidity change of water. Such is not the case. The slowest univalent ion for which we have data over a large temperature range, namely the acetate ion, experiences a conductance change in exact proportion to the fluidity change. Similarly, the sodium ion, whose conductance is the smallest next to that of the acetate ion, experiences an increase in conductance which is smaller than that of the fluidity, but the higher the temperature the more nearly does its conductance change become proportional to that of the fluidity of pure water. The same considerations hold for all the other ions without exception, save that the smaller the ion, the less does its conductance increase in proportion to the fluidity of the solvent. If the phenomenon under consideration were due to a decrease in the hydration of the ions, we should expect the conductance of the rapidly moving ions to increase in proportion to the fluidity change, while the conductance of the larger ions should increase much more rapidly. The converse of this is actually true.

But even were we to deny the force of this argument, there are other considerations of equal force which show that the hydration of the ions does not decrease with increasing temperature. If we consider a system of particles moving in a medium of molecular structure, the speed of the particles under a given impressed force will vary inversely as their diameter, *i. e.*, according to Stokes' law, provided the particles are large compared with the dimensions of the molecules of the medium. If, now, we were to reduce the dimensions of all the particles, the medium remaining the same, a point would ultimately be reached where the speed of the smaller particles would increase more rapidly than that of the larger particles, and this divergence of the speed of the particles would continue until the dimensions of all the particles were small compared to those of the molecules of the medium. Now the acetate ion, even assuming it to be unhydrated, is large in comparison with a water molecule. At high temperatures the association of water decreases and the acetate ion is relatively larger in comparison. If we were to assume that all the ions lost their combined solvent at high temperatures, the difference in the speed of the different ions at 306° should be very great. In other words, with increasing temperature we should expect the different ions to approach limiting values which, instead of being the same for all ions, should differ as much as or more than those at lower temperatures.

It is evident from an examination of the experimental data that the different ions are approaching a common limit of conductance; at any rate, this is true of ions whose complexity does not exceed that of the acetate or nitrate ion. Their dimensions must, therefore, be the same. Since they can approach this condition only by adding water molecules, it follows that, with increasing temperature, the water envelopes, which probably surround all ions in aqueous solution, increase, and that the ions ultimately are all surrounded by envelopes of the same dimensions. This may at first seem an unwarranted assumption, but a careful examination discloses nothing inconsistent with known facts. If we assume that the forces concerned in the hydration of the ions are electrical in their origin, it follows that the force acting between a charge and the molecules of its surrounding envelope must be relatively independent of temperature, or even increase with it. For, since the dielectric constant of water decreases with increasing temperature, it follows that the field of force about a charge increases. If, then, an equilibrium exists between the ions and the solvent, the degree of hydration of the ions will increase with temperature. Another way of looking at the same phenomenon is to consider the solvent as a highly associated liquid. Let us assume that the water molecules are added to an ion, not as aggregates, but as single molecules. At low temperatures, where the association of the liquid is high, the number of single water molecules present will be relatively small and the envelope surrounding an ion will be small. At higher temperatures, however, the association of the solvent decreases, the proportion of single molecules increases and the degree of solvation of the ions increases. At low temperatures only those ions will be highly hydrated which exhibit a strong tendency to form solvates in the free salt. At high temperatures, however, the purely electrical forces become more and more determinative of solvation and consequently all ions approach each other in size.

C. The Hydrogen and Hydroxyl Ions.

The preceding considerations have a bearing on questions regarding the large difference in the speed of the various ions in water. Non-aqueous solvents have much smaller dielectric constants and are much less associated than water. Therefore, the solvent envelope will, in general, be larger and the different ions will approach each other more nearly in speed. Because of the high degree of association of water, some ions lose their envelopes in a very large measure, the resulting ion becomes small in comparison with the solvent molecules and an abnormally high speed results. The hydrogen and hydroxyl ions are examples of ions of this type.

It has been a commonly accepted hypothesis that the abnormally high speed of the hydrogen and hydroxyl ions bears some relation to the fact that these ions result when water itself dissociates.[1] Kraus and Bray,[2] however, have shown that the NH_4^+ and the NH_2^- ions in ammonia, which bear the same relation to ammonia as the H^+ and OH^- ions do to

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[1] Danneel(48).

[2] Kraus and Bray(49), pp. 1368–9.

water, possess, in ammonia, a conductance far below the average. Further, and this is most important, the H^+ and OH^- ions in water exhibit exceptional speed in far smaller degree at high than at low temperature. If any relation existed between the abnormally high conductance of these ions and the dissociation of water, we should expect these ions to become more exceptional as the dissociation of water increases.

The conception underlying this hypothesis, which seeks to connect the high conductance values of H^+ and OH^- ions with the dissociation of water, embodies some elements of the so-called "Grotthuss Theory," according to which conductance takes place by an interchange of H^+ and OH^- ions with the water molecules between the electrodes along the lines of current flow. If this theory were true, we should certainly expect the effect to become more pronounced at higher temperatures, which it does not.

There has been a discrepancy between the values of the transference number for the H^+ ion, as determined by conductance and transference measurements. The value for the transference number of H^+ in hydrochloric acid has, in most cases, been found larger by transference than by conductance measurements, even in dilute solutions. Lewis(43) has recently cited this intance as showing that the speed of the ions may change with concentration, even in relatively dilute solutions. It is, of course, obvious that the conductance method can not give correct values of the ionization when the transference number changes. The reason for the observed changes in transference numbers I have already given. In the case of the hydrogen ion, certain circumstances have operated to lead to a seeming disagreement. In a recent paper, Kraus and Bray have shown that the Λ_0 value for KCl, as commonly accepted, is too high by several units.[1] This discrepancy is due to the uncertainty in correction for the conductance of the solvent in dilute solution, and likewise to the use of a method of extrapolation for Λ_0 which is inapplicable. In the case of the acids, these sources of error have not been operative to the same extent as in that of the salts. Therefore, the commonly accepted value for the conductance of the hydrogen ion is more nearly correct than it is for other ions. Kendall(44) has recently determined the conductance of the hydrogen ion at 25° to be 347.0. At 18° this gives a value of 312.6. If we take for the conductance of the chlorine ion, instead of the value 65.5, the lower value 64.4 deduced from the Λ_0 of KCl as found by Kraus and Bray, we obtain for the transference number of the H^+ ion in hydrochloric acid the value 0.830. This is in excellent agreement with the value obtained by Noyes and Kato(45), in dilute solutions by direct determination, and also with the results of Drucker(46). Actually, therefore, no discrepancy exists, and the transference number of the ions in HCl undergo only a small change even up to fairly high concentrations.

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[1] P. 1407, *et seq.* of reference 49.

D. Speed of the Ions in Different Solvents.

If the forces governing the solvation of the ions are electrical rather than chemical in their origin, we have a ready explanation for the fact, that in different solvents the ratio Λ_0/f of conductance to fluidity has approximately the same value in different solvents. For the electrical forces are in all cases approximately the same for different solvent media, as well as for different ions. The envelope will, therefore, be large in all cases and relatively independent of the nature of the solvent.

It is interesting to compare the speed of the ordinary ions in water and ammonia with that of the ions produced in hexane by radiations. In Table V the name of the solvent appears in the first column, that of the ion in the second column, the absolute speed, S, of the ion $\times 10^4$ in the third column, the fluidity f in the fourth column, and in the last column the ratio $S/f \times 10^6$. The values in hexane are due to Jaffé(21).

TABLE V.—SPEED OF IONS IN DIFFERENT SOLVENTS.

Solvent.	Ion.	$S \times 10^4$.	f.	$S/f \times 10^6$.
H_2O	Acetate	3.58	95.35	3.76
NH_3	Lithium	11.60	376	3.05
Hexane	Positive	6.03	312	1.98
Hexane	Negative	4.17	312	1.34

The speed of the positive and negative ions produced by radiations of radioactive substances in hexane is, therefore, a little less, relative to fluidity, than that of the slowest ions in ammonia or water. Since these ions in ammonia and water are very large, it follows that a single charge in hexane must be combined with a considerable number of solvent molecules.

E. Non-aqueous Solutions.

Examination of Fig. 3 shows that the mobility of the ions in ammonia changes less than the fluidity of the solvent. This is not surprising, since both the K^+ and I^- ions in ammonia possess relatively high mobilities. In this connection, it is of importance to note that the viscosity change due to the presence of the salt is enormously greater for non-aqueous solvents than for water. This is illustrated in Table VI.

TABLE VI.—VISCOSITY OF SOLUTIONS IN DIFFERENT SOLVENTS.

		Relative viscosity at concentration:		
Solvent.	Solute.	0.5.	1.0.	2.5.
Water	LiCl	1.05	1.10	1.42
Ammonia	KI	1.16	1.38	2.38
Methylamine	$AgNO_3$	1.40	1.96	6.38

In the first column appears the name of the solvent, in the second the name of the solute, and in the third, fourth and fifth columns, respectively, the relative viscosities of the solutions at 0.5, 1.0 and 2.5 normal. As aqueous solutions go, the viscosity of lithium chloride solutions is very large. Yet, as is apparent from the table, the viscosity of KI in ammonia is enormously greater than that of LiCl in water. Values are also given for the viscosity of solutions of $AgNO_3$ in methylamine. As may be seen, the viscosity of silver nitrate solutions in methylamine is far greater than that of KI in ammonia. The viscosities of other inorganic salts, in ammonia and methylamine, do not differ greatly from those of the salts given in the table.[1]

According to considerations already set forth in this paper, the relative dimensions of the ions and solvent molecules do not differ greatly in different solvents; although in water at low temperatures the ions are, relatively, somewhat smaller than in the solvents. It follows, therefore, that the viscosity change in ammonia solutions is due to molecules which are relatively very large. Probably the viscosity change is due to molecules of the un-ionized salt associated with a large number of solvent molecules.[2] If this is the case, then we should expect the speed of the ions in ammonia to be affected less, due to concentration change, than in water. This explains why Equation IV holds for non-aqueous solvents to such high concentrations, as Kraus and Bray have shown. The tendency of the dissolved salt to form large aggregates with the solvent apparently increases with decreasing dielectric constant. In non-aqueous solvents, then, we can not hope to apply a correction for the viscosity of the solvent. On the other hand, we are justified in assuming that no correction is necessary so long as Equation IV holds. The fall in the conductance curves of concentrated non-aqueous solutions, with increasing concentrations, is undoubtedly due to the influence of the increasing viscosity of the solutions.

F. The Calculation of Molecular Dimensions.

A number of writers have attempted to determine the dimensions of ions and dissolved molecules from conductance and diffusion experiments. The equations which are employed for this purpose involve a knowledge of the molecular weight or the density of the particles in question. For this purpose the densities of the salts in the solid or liquid state have been employed. In the light of the present investigation, it is obvious that we have no knowledge of the density of the ions or of dissolved substances, in general; nor do we possess a knowledge of their molecular weights save in a few instances. Calculations of this kind are entirely futile and their results are misleading.

G. Deviation from the Mass-Action Law and Change of Ionic Mobilities.

One of the important problems confronting the further development of the theory of electrolytic solutions is the question whether the conduc-

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[1] Fitzgerald(30).

[2] It is to be noted that in solvents of lower dielectric constant, the proportion of un-ionized molecules is relatively much greater than in water.

tance method gives a correct measure of the ionization in dilute solutions, *i. e.*, where viscosity and other similar effects are negligible. As is well known, the ionization values, as calculated from conductance data, do not satisfy the law of mass action. This may be due to the fact that the mobility of the ions is not independent of the concentration, as was first pointed out by Ostwald. There has been much controversy regarding the applicability of the conductance method as a measure of ionization without, however, leading to any definite results. In a recent paper, Lewis(43) reverts to this question and suggests that in aqueous solution the mobility of the ions is a function of concentration, but he makes a reservation to the effect that in other solutions, particularly non-aqueous solutions, it may be necessary to make the additional hypothesis that a real deviation from the mass-action law exists.

The results of the present paper have an important bearing on this question, for it has been shown that solutions in water obey Equation II, which is a special case of Equation IV, to concentrations greater than 5.0 normal. Now, Kraus and Bray(49) have shown that this equation is quantitatively applicable to all non-aqueous solutions for which accurate data are available. It is clear, therefore, that the nature of the deviation of the actual conductance curve from that required by the mass-action law is precisely the same whether the solutions be aqueous or non-aqueous. Any explanation for the observed discrepancies must, therefore, be generally applicable to all solvents without exceptions, otherwise it must fall to the ground.

If the mass-action law holds at high concentrations, then Equation IV expresses the relation between the change of ionic mobility and concentration. On this hypothesis it is evident that according to equation IV the mobilities of both ions change with concentration in exactly the same manner. For, in Equation IV, Λ_o, the sum of the ionic conductances enters, and not the individual ionic conductances. When combined with a given positive ion, M^+, for example, the negative ion X^- follows the same law of change of speed as the ion M^+. When however, the ion X^- is combined with another positive ion M_1^+, it follows an entirely new law of conductance change which, in this case, is the same for M_1^+ and X^-; for the constants of Equation IV for the two salts MX and M_1X will, in general, be different and this difference is often large. If we grant the correctness of the law of the independent motion of the ions, then it is obvious that the hypothesis which assumes the mobility of the ions to change with concentration becomes untenable.

Other considerations, also, go to show that the hypothesis of increasing ionic mobilities is incorrect. If the speed of the ions increases with increasing concentration, then this increase in speed can only be ascribed to a diminution in the size of the ions; for the increase in speed can not be due to increased fluidity, since the fluidity in general decreases and ultimately reduces the speed of the ions, as has been shown above. Now the increase in speed which would have to be assumed in certain non-aqueous solutions is as much as 1000-fold. A diminution of the dimensions of the ions of a magnitude sufficient to account for this order of change in speed is too improbable to warrant serious consideration. Even if we were to grant that such change in dimensions took place, we would only meet with another inconsistency, since, if the dimensions of the ions were reduced to this extent, their motion should become practically independent of the viscosity of the solution, which is manifestly due to the presence of large molecules or aggregate. We have seen, however, that in all cases in concentrated solutions, the conductance ultimately decreases with increasing concentration, as a result of increasing viscosity. Finally, it should be noted that, although a large number of electrolytes have been investigated in many different solvents, no case has ever been discovered where the ratio Λ/Λ_0 exceeds unity in concentrated solutions. If the mobility of the ions increases with concentration, we might well expect to find, at least, some instances in which the speed increases to such extent that the ratio Λ/Λ_0 exceeded unity. This would indeed be a crucial test in favor of the hypothesis in question.

One other point remains to be considered; the mobility of the ions may remain unaltered with concentration change, the deviation from the law of mass action being due to the superposition on the normal ionic conduction process of another type of conduction which, for example, might be of the nature of a "Grotthuss chain" effect. Whatever the nature of such a process might be, it must manifestly be ionic in character, since, at the electrodes, Faraday's laws hold for the electrochemical change accompanying the current. That the solvent itself takes any direct part in the conduction process is extremely unlikely; for the deviation from the law of mass action is not a function of the chemical properties of the solvent, but rather of its physical properties, the dielectric constant in particular. We thus find deviations of the same order of magnitude in solvents having the same dielectric constant; whether the solvent be elementary in its nature, or whether a compound, whether the solvent be readily dissociable into ions, or whether it be a compound which is entirely neutral in its properties. The deviation, moreover, is a direct function not of the concentration of the un-ionized fraction, but of the ions. The observed results can not, therefore, be explained by means of a "Grotthuss chain" effect through the un-ionized molecules.

As we have seen, the hypotheses which seek to account for the deviations from the mass-action law by assuming that the ratio Λ/Λ_0 does not give the correct degree of ionization lead to conclusions which are not in accord with the facts. In contrast to these, the hypothesis, that the ratio Λ/Λ_0 gives the correct ionization, accounts for all the known facts in a simple manner and without conflict with any theoretical principle. In dilute solutions, as Kraus and Bray have shown, the mass-action law applies in all cases. That deviations from the mass-action law should arise at higher concentrations is a result which was to have been expected, since the applicability of this law postulates that the forces acting between molecules of different species or of the same species are negligible. That large forces come into play in the neighborhood of the ions is evidenced by the extent to which the ions are surrounded with solvent molecules. There is no consideration which, at the present time, would enable us to predict at what concentration the forces between the individual particles of an electrolytic system become negligible. The assumption that these disturbing forces would begin to become negligible in the neighborhood of 0.1 normal concentration as they do in non-electrolytic systems is entirely unwarranted. The only means we now have for determining at what concentration the disturbing forces between the particles become negligible is that of direct experiment. The results of such experiments have shown that the influence of the forces between the particles in an electrolytic system is, in most cases, appreciable even beyond a concentration of 0.001 normal, and that, as was to have been expected, the deviation from the mass-action law is, in general, smaller the higher the dielectric constant of the medium. The original assumption of Arrhenius that the ratio Λ/Λ_0 measures the true degree of ionization is borne out by the facts; and the future problem of the theory of electrolytic solutions is to develop an adequate theory for the equilibrium of charged systems.

5. Summary.

The general principles governing conductance as a function of viscosity change are discussed.

It is shown that in the case of aqueous solutions exhibiting negative viscosity, the conductance may be corrected for viscosity in direct proportion to the fluidity change. The same is probably true for viscosity change due to external pressure.

In the case of aqueous solutions exhibiting a positive viscosity, correction for viscosity can not in general be made, although in some instances, correction may perhaps be effected by considering the influence of viscosity on the individual ions.

The change in the true transference numbers of electrolytes with concentration is due to the different effect of viscosity on the speed of the two ions.

The viscosity change due to concentration change in non-aqueous solutions is positive and much greater than it is in water for inorganic electrolytes. The speed of the ions in non-aqueous solutions changes far less than the fluidity of the solutions, although at high concentrations a marked influence results. Correction for viscosity, so far, is not possible in these cases, and up to normal concentration a correction is in many cases unnecessary.

The influence of viscosity on the speed of the ions is governed by the relative dimensions of the ions and the molecules to which viscosity change is due. The characteristic relations observed in the case of aqueous solutions are due, in part at least, to the complexity of the molecules of liquid water.

At higher temperatures the speeds of different ions in aqueous solutions approach, approximately, a common limit, indicating that the ions, under these conditions, are approaching one another in size.

It is shown that the dimensional changes observed can not be accounted for on the assumption that the larger ions become smaller at higher temperatures; and it is suggested that the smaller ions increase in size (due to increasing hydration) with increasing temperature. This increase in dimensions is due to the decrease in the value of the dielectric constant with increasing temperature and probably also to decreasing complexity of the water molecules.

It is shown that the commonly accepted hypothesis, according to which the high speed of the hydrogen and hydroxyl ion is related to the fact that these ions are ions of the solvent itself, is not true.

The facts discussed in this paper corroborate the fundamental hypothesis of Arrhenius that the degree of ionization of electrolytes is correctly measured by the conductance ratio, Λ/Λ_0.

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CALIBRATION TABLES FOR COPPER-CONSTANTAN AND PLATINUM-PLATINRHODIUM THERMOELEMENTS.

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In view of the fact that chemists are making more and more extensive use of thermoelements as a means of measuring high temperatures, it seemed desirable to present two tables which save much trouble in converting microvolts into degrees. Nothing will be said here as to the precautions to be observed in the use of thermoelements,[1] further than that experience has shown the necessity of frequent recalibration in order to insure trustworthy results. The experimental work required for such a calibration involves comparatively little time or labor, but interpolation between the fixed points can be accomplished accurately only by means of an empirical equation expressing the relation between electromotive force and temperature, and repeated recalculation of such an equation

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[1] These precautions have been discussed by W. P. White, *Physic. Rev.*, **23**, 449 (1906); *Am. J. Sci.*, [4] **28**, 479 (1909).