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THE LAWS OF "CONCENTRATED" SOLUTIONS: II.[1] THE ESTIMATION OF THE DEGREE OF IONIZATION OF ELECTROLYTES IN MODERATELY CONCENTRATED SOLUTIONS.[2]

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1. Introduction.

The greatest obstacle with which we are confronted, when we attempt to apply, quantitatively, the principles of the Ionic Theory to any except the most dilute solutions, is the lack of a satisfactory method for computing the degree of ionization of an electrolyte in a concentrated solution. Until some method is found or adopted for this purpose no progress into the region of concentrated solutions is possible. It is the purpose of the present paper to examine critically the different methods which are at present in use for calculating the degree of ionization of electrolytes in dilute solutions with the view of deciding what, in the present state of our knowledge, is the best method to employ for this purpose in the more concentrated ones.

For dilute solutions two general classes of methods are employed at present. To the first class belong the so-called "Osmotic" methods—better called the Colligative Property Methods[3]—which involve the knowledge of some colligative property of the solution, such as the freezing point lowering, the boiling point raising, the relative vapor pressure lowering, etc. To this class belongs also the method based upon the e. m. f. of a concentration cell and involving the assumption that the ions are normal solutes.

The second class comprises only the conductivity method of Arrhenius.

2. The Colligative Property Methods for Calculating Degree of Ionization.

The calculation of the degree of ionization of an electrolyte from any one of the colligative properties of its solution is based upon the assumption that both the ions and the unionized molecules are *normal solutes*, that is, that each produces upon the colligative property in question (*e. g.*, the f. p. lowering) the same effect as would be produced by an equal number of molecules of an ordinary non-electrolyte, such as alcohol,

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[1] In the first contribution of this series (THIS JOURNAL, 32, 653 and 1636 (1910); also *Z. physik. Chem.*, 74, 537 (1910) and *J. chim. phys.*, 8, 538 (1910)) is presented the outline of a theory of solutions which is free from the assumption that the solution must be dilute. From the point of view of this theory, a systematic investigation of the subject of concentrated solutions has been undertaken in this laboratory and will be pushed as rapidly as the means at our disposal will permit.

[2] Presented at the Indianapolis meeting of the Society, June 29, 1911.

[3] Cf. THIS JOURNAL, 32, 496 (1910) and *Ibid.*, 32, 659 (1910).

for example; or, in other words, that their active masses, or "Activities"[1] are, in dilute solutions, proportional to their concentrations. This assumption, we know, however, cannot be true, for if it were, the Mass Action Law would be a thermodynamic necessity for a strong electrolyte, that is, failure to obey this law would constitute a real exception to the Second Law of Thermodynamics. This important point, which was emphasized by Jahn[2] in 1904 and to which attention has been recently called by G. N. Lewis,[4] is often overlooked. *When values for the degree of ionization calculated from some colligative property of the solution (e. g., the f. p. lowering) agree with those computed from the conductivity ratio, this agreement is frequently cited as evidence of their correctness. Such a conclusion is, however, not justified, for the colligative property method can only give correct value by an accidental compensation of errors,* the deviations of the ions from the behavior of a normal solute in the one direction being exactly compensated by the deviations of the unionized molecules in the opposit direction.[3]

All the evidence at present available[4] seems to indicate that the ions, of uni-univalent salts, at least, do not deviate widely from the behavior of normal solutes in dilute solution, but that the unionized molecules are very abnormal in this respect. In sufficiently dilute solutions, therefore, where the unionized molecules constitute only a *few per cent.* of the total number of solute molecules, the freezing point lowering should correspond, within a *few per cent.*, with the value calculated by using the conductivity ratio as a measure of the degree of ionization. Whenever, however, the unionized molecules begin to form an appreciable part of the total number of solute molecules, we can no longer estimate correctly the degree of ionization from the freezing point lowering or from any of the other colligative properties thermodynamically connected with it; and this would still be true, even if the complication due to hydration could be eliminated. For the purposes of the present paper, therefore, this method will have to be rejected.

It may be mentioned, in passing, that even in the case of *dilute* solutions of certain electrolytes of a high ionic type, where the degree of ionization is not large, very abnormal results may be obtained. A number of salts of this character have been investigated recently by A. A. Noyes and J. Johnston.[5]

3. The Conductivity Method.

The customary method for calculating the degree of ionization, γ,

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[1] Lewis, *Proc. Amer. Acad.*, 43, 288 (1907).

[2] *Z. physik. Chem.*, 50, 152 (1904).

[3] Cf. THIS JOURNAL, 32, 492 (1910).

[4] This evidence is presented by A. A. Noyes in various publications (cf. THIS JOURNAL, 30, 351 (1908).

[5] THIS JOURNAL, 31, 1008 (1909).

of an electrolyte from conductivity data by means of the equation, $\gamma = \Lambda/\Lambda_0$, is based among others upon the two assumptions: (1) that the physical dimensions of the ions and (2) that the resistance offered to their motion through the solution are constants, not affected by changes in the concentration of the electrolyte.

These two assumptions are justified if the solution be "sufficiently dilute,' but the expression, "sufficiently dilute," frequently means much more dilute than are many of the solutions which we are accustomed to regard as "dilute solutions." For example, the above equation is quite generally applied to 0.1 molal solutions and the value for γ expressed to tenths of a per cent. and yet the viscosity of a 0.1 molal solution may differ from that of pure water by *several per cent.*, even in the case of the simplest type of electrolytes. Some examples of the relative viscosities (η/η_0), of some 0.1 molal aqueous solutions are shown in Table I. It is evident from this table that *the neglect of the viscosity influence may introduce errors as high as 7 and 8 per cent. in the degree of ionization of a 0.1 molal solution as calculated from the conductivity ratio.*[2] *In fact it may be stated as a general rule that the equation $\gamma = \Lambda/\Lambda_0$ cannot be safely employed for solutions of greater concentrataions than 0.01 molal, if an accuracy of a few tenths of a per cent. is desired.*

TABLE I.[1]—RELATIVE VISCOSITIES OF SOME 0.1 MOLAL AQUEOUS SOLUTIONS.

Salt.	$CsNO_3$.	$LiIO_3$.	NaOH.	Na_2HPO_4.	NaH_2PO_4.	Na_3PO_4.	Na benzoate.	Na hydrocinnamate.	Na isovalerate.
t	0°	18°	18°	18°	18°	18°	25°	25°	25°
η/η_0	0.98	1.03	1.025	1.07	1.03	1.08	1.05	1.07	1.06

Even in the case of a 0.01 molal solution the influence of the viscosity effect is sometimes surprizingly large. The error from this source is about one-tenth of the error in the case of the 0.1 molal solution and may therefore in some cases amount to nearly one per cent., as is evident from Table I.

It is clear therefore that, in the case of all solutions of higher concentrations than 0.01 molal, it is necessary to take into account the viscosity of the solution in computing the degree of ionization of the electrolyte. The remainder of this communication will be devoted chiefly to the consideration of the best method of applying the viscosity correction. The influence of changes in the physical dimensions of the ions will also re-

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[1] Compiled from existing data in the literature.

[2] The very high viscosities of the solutions of the sodium salts of the phosphoric acids are of especial importance in connection with the investigation by Abbott and Bray (THIS JOURNAL, 31, 729 (1909)) of the equilibria and ionization relations in solutions of these acids and their salts. For a 0.1 molal solution of Na_2HPO_4 Abbott and Bray calculate the degree of ionization to be 0.596, *a result which is probably in error by more than per cent.* Their calculations are in need of revision, owing to the unusually large influence of the viscosity factor for these solutions.

ceive consideration in Section 7. This latter influence is one of the chief determining factors in very concentrated solutions and is closely connected with the cause of the minima frequently observed in the equivalent conductance curves.[1] There is at present no known method of estimating and correcting for this effect so that any method for computing degree of ionization in concentrated solutions must be restricted to solutions of moderate concentrations, say not exceeding normal, where this influence may be safely neglected.

4. The Viscosity Correction.

The ions and unionized molecules of a dissolved electrolyte, both directly by their own presence and indirectly through their effect upon the degree of association of the water, produce a medium whose viscosity is different from that of pure water. The change in viscosity may be either an increase or a decrease but for nearly all solutions of salts of inorganic acids, the magnitude of this change will not be greater than 40 per cent., for concentrations not exceeding one equivalent of salt per liter.[2] The relative viscosities of such solutions will be included between the limits 0.8 and 1.4.

In order to correct for the change in the mobilities of the ions produced by a change in the viscosity of the medium, the simplest assumption to make is that the mobility of an ion is inversely proportional to the viscosity, η, or directly proportional to the fluidity, f, of the medium. On the basis of this assumption the equation for the degree of ionization becomes

$$\gamma = \frac{\Lambda\eta}{\Lambda_0\eta_0} \text{ or } \gamma = \frac{\Lambda f_0}{\Lambda_0 f}. \qquad (1)$$

This equation has been proposed and employed by several authors[3] as a measure of ionization, a procedure which is unquestionably more logical than the entire neglect of the viscosity influence. Moreover, if we make certain assumptions, equation (1) can be derived theoretically from Stokes' equation for the motion of a small sphere through a viscous medium. The necessary assumptions are those which Stokes made in deriving his equation from the principles of the kinetic theory; namely, that the moving body (the ion in the present instance) must be a sphere and that its volume

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[1] See, for example, Sloan's curve for potassium iodide solutions at 0° (THIS JOURNAL, 32, 946 (1910).

[2] In addition to their effect upon the viscosity, the presence of unionized molecules in sufficient number may increase the conductivity through a kind of Grotthus-Chain action, but if their number does not exceed those present in a normal solution of a strong electrolyte, this effect will probably be very small. At all events it will be neglected in what follows, as there is at present no way of applying any correction for it.

[3] Cf. Sutherland, *Phil. Mag.*, [6] 3, 161 (1902); Bousfield and Lowry, *Phil. Trans. Roy. Soc. London* (*A*), 204, 256 (1905); Bousfield, *Z. physik. Chem.*, 53, 257 (1905) and *Phil. Trans.* (*A*), 206, 101 (1906).

must be large in comparison with the volume of the molecules of the medium through which it moves.

Neither of these conditions is in general fulfilled by the ions of electrolytes, so that exact proportionality between ionic mobility and fluidity is not to be expected and although the deviations should not be very great they may nevertheless be quite appreciable and should, if possible, be taken into account in correcting for the viscosity influence. That appreciable deviations are to be expected has been demonstrated theoretically by Cunningham,[1] and Millikan[2] has recently succeeded in demonstrating such deviations experimentally in the case of gaseous ions collected on very minute oil drops.

These considerations together with certain relationships discovered by W. H. Green[3] and by J. Johnston[4] have led the writer to adopt provisionally the following principle as furnishing, for the formulation of the viscosity correction, for moderately concentrated solutions, a more logical basis than Stokes' law.

The mobility of an electrolytic ion is in the case of salts[5] *proportional to the mth power of the fluidity of the medium through which it is moving, the coefficient, m, being not far from unity.*

The evidence in favor of the adoption of this principle is contained in or can be obtained from the papers of Green and Johnson above mentioned. We shall proceed to the consideration of the work of each investigator separately.

The Experiments of W. H. Green.—The purpose of these experiments is sufficiently evident from the title of the paper[3] and they constitute the most valuable direct contribution to the problem which has yet been made. "The problem was attacked experimentally by adding a non-electrolyte to a solution of a good electrolyte so as to cause artificially a considerable decrease in the fluidity. Simultaneous observations of both conductivity and fluidity were made." The solutes employed were lithium chloride and sucrose.

The measurements include a wide range of concentrations of both lithium chloride and sucrose, and were sufficiently extensive to enable extrapolations to be made in such a way as to give a set of equivalent conductance data for solutions of various fluidities (and therefore of dif-

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[1] Cunningham, *Proc. Roy. Soc. London* (*A*), 83, 357 (1910).

[2] Millikan, *Physic. Rev.*, 32, 349 (1911).

[3] W. H. Green, "Studies on the Viscosity and Conductivity of Some Aqueous Solutions........A Contribution towards the Elucidation of the Connection between Ionic Mobility and the Fluidity of the Solution" (*J. Chem. Soc.*, 93, 2049 (1908)).

[4] J. Johnston, "The Change of the Equivalent Conductance of Ions with the Temperature" (THIS JOURNAL, 31, 1010 (1909)).

[5] This principle does not seem to hold for the mobilities of hydrogen- or hydroxyl-ions so that acids and alkalies are not included in what follows. See Section 9.

ferent sucrose concentrations) but of infinit dilution with respect to lithium chloride. It is with these results that we are chiefly concerned, since they permit of a direct comparison of ionic mobility and fluidity without the interference of an unknown ionization factor.

The data necessary for this comparison are shown in Table II. With the exception of column VII, these figures are taken directly from Table VII of Green's paper; with reference to the figures in columns V and VI Green says: "It will be observed that Λ is by no means proportional to f but more nearly to $f^{0.7}$." This latter "proportionality" is not a very satisfactory one, however. This is evident from the figures in column VI and can be seen graphically if values of $\log \Lambda$ are plotted against values of $\log f$, since if $\Lambda = kf^m$, then $\log \Lambda = \log k + m \log f$, and the graph should be a straight line. Such a plot was made on a large scale, and showed clearly that the relation between $\log \Lambda$ and $\log f$ is not a linear one.

TABLE II.

Temperature 25°.

I. Number.	II. Mols. of sucrose per liter of solution. N.	III. Fluidity in absolute units. f.	IV. Equivalent conductance of LiCl at infinit dilution. Λ_0.	V. Λ_0/f.	VI. $\Lambda_0/f^{0.7}$.	VII. $\Lambda_0/f^{0\ 94}$.
1	0	111.67	114.0	(1.020)[1]	...	1.37
2	0.02	109.75	111.84	1.019	4.169	1.37
3	0.05	107.00	108.85	1.017	4.132	1.36
4	0.1	102.40	104.15	1.017	4.078	1.36
5	0.2	93.42	95.80	1.025	4.000	1.35
6	0.4	76.43	81.05	1.060	3.895	1.39
7	0.6	61.06	68.67	1.125	3.862	1.44
8	0.8	47.51	56.85	1.197	3.811	..
9	1.0	35.91	46.62	1.298	3.802	..
10	1.2	26.28	37.38	1.422	3.793	..
11	1.4	18.57	29.50	1.588	3.815	..
12	1.6	12.54	22.72	1.812	3.870	..
13	1.8	8.017	16.83	2.099	3.920	..
14	2.0	4.826	12.02	2.490	3.993	..

The deviation from linearity is in the direction of a too rapid increase in Λ with increasing concentration of sucrose. A deviation in this direction in the more concentrated solutions, however, might be expected. Owing to the high degree of hydration of both the chloride and the lithium ions, especially the latter,[2] their volumes would decrease with increasing concentration of sucrose, owing to the decrease in their degrees of hydration. This would cause an increase in their mobilities for a given viscosity and a consequent too rapid increase in Λ exactly as observed.

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[1] This value not given in Green's table.

[2] Green seems inclined (*Loc. cit.*, p. 2061) to reject the theory that ions are hydrated.

It should be further noted that between pure water and the twice molal sucrose solution, there is a decrease of 96 per cent. in the fluidity of the medium. Over such an enormous range as this the simple exponential law may be insufficient to express the relationship between ionic mobility and fluidity, even if the ionic volumes remain constant. For the purposes of the present paper it will be sufficient if we can show that the simple exponential law is sufficiently exact for the range of fluidities included between that of pure water and those of normal salt solutions.

In order to test this for LiCl, using Green's data, the large scale plot of *log* Λ against *log* f was employed. The first six points (numbers 1 to 6 inclusive of Table II), that is up to and including the 0.4 normal sugar solution, involve a decrease of about 32 per cent. in the fluidity. Through these six points the "best straight line" was drawn. The location of this line was established independently by five different men and the following values for its slope were obtained: $m = 0.940, 0.939, 0.934, 0.918, 0.958$; mean[1] 0.94 ± 0.01.

The relation between Λ and f is, therefore, $\Lambda = k\ f^{0.94}$. In column VII of Table II are shown values of $\Lambda / f^{0.94}$ for the first seven solutions.[2]

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[1] If the first five points only are used, the value $m = 0.97$ is obtained. An uncertainty in m, of this magnitude (0.03), would mean an error of only 0.4 per cent. in the value of γ, for a normal LiCl solution at 25° (see p. —).

[2] With reference to the bearing of his experiments upon the question of calculating the degree of ionization, Green's final conclusion is that: "No trustworthy method has as yet been established whereby the true ionization coefficients of a salt in solution can be determined." His basis for this conclusion seems to have been chiefly the fact that the ionization-coefficients which he obtained seemed to indicate that the degree of ionization of lithium chloride is "enormously increased" by the addition of sucrose. His ionization coefficients were obtained by dividing the equivalent conductance of the solution by the equivalent conductance of a solution infinitly dilute with respect to lithium chloride but which contained sufficient sucrose to give it the same fluidity as the first solution. The following examples will illustrate the character of the results thus obtained:

1. A 0.5 normal solution of LiCl in water contains 108 mols. of H_2O per mol. of LiCl and has $\Lambda = 82.28$ and $f = 104.35$. A sucrose solution which has this fluidity contains 0.08 mol. of sucrose per 1000 grams or 0.17 mol. per 108 mols. of water and has $\Lambda_0 = 106.2$. The ionization coefficient of the first solution is therefore $82.3/106.2 = 0.775$.

2. A solution 0.5 normal with respect to LiCl and 0.1 normal with respect to sucrose contains 107 mols. of water and 0.2 mol. of sucrose per mol. of LiCl and has $\Lambda = 77.3$ and $f = 94.8$. A sucrose solution which has this fluidity contains 0.37 mol. of sucrose per 107 mols. of water and has $\Lambda_0 = 97.2$. The ionization-coefficient for the second solution is therefore $77.3/97.2 = 0.795$.

3. A solution 0.5 normal with respect to LiCl and 1 normal with respect to sucrose contains 86 mols. of water and 2 mols. of sucrose per mol. of LiCl and has $\Lambda = 37.06$ and $f = 34.30$. A sucrose solution which has this fluidity contains 2 mols. of sucrose per 86 mols. of water and has $\Lambda_0 = 43.1$. The coefficient of ionization of the third solution is therefore $37.06/43.1 = 0.86$.

Similarly a 0.05 normal solution of LiCl in water is about 88.5 per cent. ionized, *The Change of the Equivalent Conductance of Ions with the Temperature.*—Instead of altering the fluidity of the medium by the addition of a third substance to the solution, as in Green's experiments, we can bring about the change in fluidity by simply altering the temperature. In attempting to find a function connecting ionic conductances and temperature, which could be used advantageously for interpolation, J. Johnston noticed that if the logarithms of the Λ_0 values (for a given ion or for a given salt) were plotted against the logarithms of the fluidity of water corresponding to each temperature, the resulting graph was a straight line. In other words when the fluidity of the medium is altered by a change in temperature, the mobility of an ion changes according to the law, $\Lambda_0 = kf_0{}^m$.

Johnston found that this relation was satisfied for the temperature range 0° to 156° in the case of fourteen different ions. In Table III are shown the values of the exponent *m* for the univalent ions. With the exception of the values for Cs and Li. which have been computed by the writer, these figures are taken from Table 4 of Johnston's paper.

TABLE III.

Ion.	Cs.	K.	NH_4.	Na.	Li.	Ag.	NO_3.	Cl.	$C_2H_3O_2$.
m..........	0.842	0.887	0.891	0.97	1.05	0.949	0.807	0.88	1.008

The values for Cs and Li are based upon conductance and viscosity data at 0° and 18° only, no measurements at higher temperatures being available.

A glance at this table suggests several interesting relations: (1) In no instance does the value of *m* differ from unity by as much as 0.2. (2) In the case of the alkali ions the exponent *m* increases with increasing ionic volume being smallest in the case of the (probably) unhydrated Cs ion and greatest in the case of the highly hydrated Li ion. (3) K-ion and Cl-ion which have nearly the same ionic volumes have also the same value for *m*. (4) The value for the very large Li-ion is greater than unity. These ions probably resemble most nearly the minute spheres studied by Millikan, and the deviation from Stokes' law is in the same direction as that which he observed. In the case of the other ions their possibly unsymmetrical shape and their much smaller size in comparison with the water molecules combine to produce a smaller increase of mobility with increasing fluidity, than Stokes' law requires.

Using the data of Dutoit and Duperthuis[1] on the fluidity and the con-

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while the presence of 0.01, 0.1 and 1 mols. respectively of sucrose per liter of solution apparently increases the per cent. of ionization to 89.4, 92.6 and 97.5 respectively.

When we consider the high degrees of hydration of both the lithium chloride and the sucrose and the variations in the vapor pressure of the water in the above cases, it does not seem to the writer that Green's conclusion is unavoidable. A similar investigation with caesium nitrate or iodide as the electrolyte would be very valuable, because the complications due to hydration would be eliminated.

[1] *J. chim. phys.*, 6, 726 (1908).

ductances at zero concentration of sodium iodide in a number of solvents at a series of temperature between 0° and 80°, Johnston applied the equation $\Lambda_0 = kf_0^m$, and found that it agreed with the observations in every instance. The values of m for the different solvents were as follows: Ethyl alcohol, 0.935; propyl alcohol, 0.974; isobutyl alcohol, 0.955; isoamyl alcohol, 0.806; acetone, 1.086; and pyridine, 0.99.

In the opinion of the writer the foregoing evidence justifies the adoption of the relation, $\Lambda = kf^m$, as a basis for applying the viscosity correction in calculating the degree of ionization of univalent salts, up to a concentration of one equivalent per liter, at least. In the next section the method of applying this correction in practice will be discussed.

5. Application of the Viscosity Correction in Practice.

The method of applying the viscosity correction in practice is based upon the fact that if the equation $\Lambda = kf^m$ is applicable to the equivalent conductance of an ion it may, in very many cases, be applied to the equivalent conductance of a salt as well. Johnston found this to be the case for the salts investigated by him, and we have seen that it is also true in the case of Green's experiments with lithium chloride. It can also be shown to follow mathematically, as will be evident from the following derivation of the expression for the degree of ionization, γ.

Consider a salt of the type KA in aqueous solution at a concentration not greater than normal. Let the fluidity of the solution be f, the degree of ionization be γ, and the equivalent conductance, $\Lambda = \Lambda_K + \Lambda_A$. Similarly at zero concentration we have the fluidity f_0 and the equivalent conductance, $\Lambda_0 = \Lambda_{0_K} + \Lambda_{0_A}$. We have also for the individual ions the two equations $\Lambda_{0_K} = k_K f_0^{m_K}$ and $\Lambda_{0_A} = k_A f_0^{m_A}$ from which it follows that

$$\Lambda_K = \gamma \Lambda_{0_K}\left(\frac{f}{f_0}\right)^{m_K} \quad (2) \qquad \text{and} \quad \Lambda_A = \gamma \Lambda_{0_A}\left(\frac{f}{f_0}\right)^{m_A} \quad (3)$$

Adding these last two equations together and solving for γ we obtain the equation

$$\gamma = \frac{\Lambda}{\Lambda_{0_K}\left(\frac{f}{f_0}\right)^{m_K} + \Lambda_{0_A}\left(\frac{f}{f_0}\right)^{m_A}} \quad (4)$$

which, by a simple algebraic transformation, may be written as follows:

$$\gamma = \frac{\Lambda}{\Lambda_0}\left(\frac{f}{f_0}\right)^m \left[\frac{\Lambda_0}{\Lambda_{0_K}\left(\frac{f}{f_0}\right)^{m_K-m} + \Lambda_{0_A}\left(\frac{f}{f_0}\right)^{m_A-m}}\right] \quad (5)$$

where m has a value intermediate between m_K and m_A. Now if f/f_0 lies between 0.8 and 1.4 (as it does in the case of nearly all salt solutions of concentrations not greater than normal) and since m, m_A and m_K are not far from unity, the expression in the brackets will in most instances also be equal to unity within about 0.1 of a per cent. Two examples will serve to illustrate this.

For 0.5 N lithium chloride at 0° the expression in the brackets becomes

$$\frac{60.30}{19.2(0.9)^{[1.05-0.94\,=\,0.11]} + 41.1(0.9)^{[0.88-0.94\,=\,-0.06]}} = 0.9995$$

and for 0.5 N cesium nitrate at 0° it becomes

$$\frac{84.0}{43.7(1.1)^{[0.482-0.826\,=\,0.016]} + 40.3(1.1)^{[0.807-0.826\,=\,-0.02]}} = 1.00008.$$

The expression for γ may therefore be written

$$\gamma = \frac{\Lambda}{\Lambda_0}\left(\frac{f_0}{f}\right)^m \tag{6}$$

or in terms of viscosity

$$\gamma = \frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^m \tag{7}$$

Stated in words, *the degree of ionization is equal to the equivalent conductance ratio multiplied by the relative viscosity of the solution raised to the m-th power.*

Equation (6) also means that the relation $\Lambda = kf^m$ holds for the equivalent conductance of a *salt* as well as for the equivalent conductance of an *ion*. In the case of some salts, however, in which a high viscosity of the solution is accompanied by a comparatively large difference between m and either m_K or m_A, this may not be true. In such a case it would be necessary to determin the separate values of m_A, m_K, Λ_{0_A} and Λ_{0_K} and employ the more exact equation, (4), for calculating γ. This will be seldom necessary, however.

The most convenient way in which to determin the numerical value of the fluidity exponent, m, for any given salt is to make use of Λ_0 and f_0 values for the salt at two temperatures, preferably two temperatures equally distant from and not very far from the temperature at which γ is desired. This latter stipulation is not very essential, however, in most cases, since the value of m for most salts will be nearly independent of the portion of the temperature scale employed, as Johnston's calculations show. In the case of a highly hydrated salt, however, it is desirable to use as small a temperature interval as possible and to restrict it to the neighborhood of the temperature at which γ is desired.

The Accuracy Necessary in the Value of m.—If γ is desired with a percentage accuracy of $100\delta\gamma/\gamma$ then the accuracy with which m must be known is obtained as follows:

$$\gamma = \frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^m \tag{8}$$

$$\delta\gamma = \frac{\Lambda}{\Lambda_0}\log_e\frac{\eta}{\eta_0}\cdot\left(\frac{\eta}{\eta_0}\right)^m\delta m \tag{9}$$

and

$$\frac{100\delta\gamma}{\gamma} = 100 \log_e \left(\frac{\eta}{\eta_0}\right)\delta m \tag{10}$$

Expanding the logarithm and rejecting all except the first term, we have,

$$\frac{100\delta\gamma}{\gamma} = 100\left[\frac{\eta}{\eta_0} - 1\right]\delta m \tag{11}$$

or

$$\delta m = \frac{100\delta\gamma}{\gamma} \Big/ 100\left[\frac{\eta}{\eta_0} - 1\right] \tag{12}$$

If η/η_0 lies between 0.8 and 1.4, m need not be determined with an accuracy of more than 1/40 ($100\delta\gamma/\gamma$) units and usually an accuracy of 1/20 ($100\delta\gamma/\gamma$) units will be sufficient. For example, if γ is desired to 0.1 per cent., then an error in m of 1 in the second decimal place will usually be allowable and sometimes a much larger error is permissible. The following examples illustrate this. A desired accuracy of 0.1 per cent. in γ is assumed.

(1) For a half normal cesium nitrate solution at 0°, $\eta/\eta_0 = 0.9$, and $m = 0.826$ with an allowable error of 1 in the second decimal place.

(2) For a normal potassium chloride solution at 18°, $\eta/\eta_0 = 0.985$, and $m = 0.905$ with an allowable error of 7 *in the second decimal place.*

(3) For a normal lithium chloride solution at 25°, $\eta/\eta_0 = 1.15$ and $m = 0.940$ with an allowable error of 7 in the third decimal place.

Since m is determined from Λ_0 values and f_0 values at two different temperatures, $t_1°$ and $t_2°$, it is important to know how far apart these two temperatures must be taken in order to give m with sufficient accuracy. This problem can be solved as follows.

The Temperature Interval Necessary for Computing m.—For m we have the expression

$$m = \frac{\log \Lambda_{0_1} - \log \Lambda_{0_2}}{\log \dfrac{f_{0_1}}{f_{0_2}}} \tag{13}$$

in which the subscripts 1 and 2 refer to the two temperatures $t_1°$, and $t_2°$.

f_1 and f_2 may be assumed to be known to any desired accuracy, since the error in m will be due almost entirely to the errors in the Λ_0 values. By the method of Least Squares we have therefore

$$\delta m = \frac{1}{\log \dfrac{f_{0_1}}{f_{0_2}}}\sqrt{\left(\frac{\delta\Lambda_{0_1}}{\Lambda_{0_1}}\right)^2 + \left(\frac{\delta\Lambda_{0_2}}{\Lambda_{0_2}}\right)^2} \tag{14}$$

and assuming the same fractional accuracy in both of the Λ_0 values

$$\delta m = \frac{\delta\Lambda_0}{\Lambda_0}\,\frac{\sqrt{2}}{\log \dfrac{f_{0_1}}{f_{0_2}}} \tag{15}$$

Combining with equation (10) on page 1471 we obtain

$$\log \frac{f_{o_1}}{f_{o_2}} = \frac{\sqrt{2}\,\frac{\delta\Lambda_o}{\Lambda_o}\left(\frac{\eta}{\eta_o}-1\right)}{\frac{\delta\gamma}{\gamma}}. \qquad (16)$$

Thorpe and Rodger found that their results for the viscosity of water at temperatures up to 100° could be expressed by a formula which may be written in the following form:

$$\log f = 1.5423 \log (43.252 + t) + \text{const.} \qquad (17)$$

from which follows the equation

$$\log \frac{f_{o_1}}{f_{o_2}} = 1.5423 \log \frac{43.3 + t_1}{43.3 + t_2}. \qquad (18)$$

Combining this equation with equation (16), we obtain

$$\log \frac{43.3 + t_1}{43.3 + t_2} = \frac{\sqrt{2}}{1.54}\left(\frac{\eta}{\eta^\circ} - 1\right)\frac{\delta\Lambda^\circ}{\Lambda_o}\Big/\frac{\delta\gamma}{\gamma}. \qquad (19)$$

Expanding the logarithm and rejecting negligible quantities, we obtain the expression

$$\frac{t_1 - t_2}{43 + t_2} = 0.92\,(\eta/\eta_o - 1)\,\frac{\delta\Lambda_o}{\Lambda_o}\Big/\frac{\delta\gamma}{\gamma}. \qquad (20)$$

Now the value of $\delta\gamma/\gamma$ can never exceed that of $\delta\Lambda_o/\Lambda_o$, so that since we desire a minimum value for $t_2 - t_1$, we may place $\delta\gamma/\gamma = \delta\Lambda_o/\Lambda_o$. Also the temperatures t_2 and t_1 should preferably be equidistant from the temperature, t, at which γ is desired, so that for t_2 in the denominator of the left-hand member of the above equation, we may write $t + 1/2(t_2 - t_1)$. Making these changes our equation becomes, finally,

$$t_2 - t_1 = \frac{(86 + 2t)(\eta/\eta_o - 1)}{1.2 + \eta/\eta_o}. \qquad (21)$$

Thus, if t is in the neighborhood of 0°, the temperature interval necessary to determin m need not exceed 13°, if $t = 25°$ it need not exceed 20°, and if $t = 50°$ it need not exceed 30°. In most cases a much smaller interval will be sufficient.

In this calculation we have assumed that the Λ_o values at t_1° and t_2°, the two temperatures employed for calculating m, are known with the same percentage accuracy as the Λ_o value at t°, the temperature at which γ is desired. If such is not the case the value of $t_2 - t_1$, obtained from equation (21), must be multiplied by

$$\sqrt{\left(\frac{\delta\Lambda_{o_1}}{\Lambda_{o_1}}\right)^2 + \left(\frac{\delta\Lambda_{o_2}}{\Lambda_{o_2}}\right)^2}\Big/\frac{\delta\gamma}{\gamma}.$$

6. Examples Illustrating the Results Obtained from the Equation, $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$.

In order to illustrate the character of some of the results obtained by the use of the above expression in the case of moderately concentrated aqueous salt solutions, it will be applied to solutions of caesium nitrate, potassium chloride and lithium chloride at 0°. The conductance and viscosity data necessary for these calculations have been obtained in this laboratory by Dr. D. A. MacInnes and will be published in full in the November Journal in connection with the third paper of this series.

In order to calculate values for the fluidity exponent, m, for these three salts, conductance and fluidity data at 0° and 18° were employed. They are shown in Table IV, together with the values for m which they give. The values of f_0 at the two temperatures are those of Thorpe and Rodger as corrected by Green.[1] The values of Λ_0 for cesium nitrate and lithium chloride at 0° were determined by MacInnes.

Table IV.

	0°.		19°.		
	Λ_0.	f_0.	Λ_0.	f_0.	m.
$CsNO_3$	84.0	...	129.9	...	0.826
KCl	81.0	...	130.2	...	0.900
LiCl	60.3	...	98.93	...	0.940
H_2O	..	0.01792	..	0.01058	...

The Λ_0 value for potassium chloride is from an extrapolation based upon the data of several observers. The Λ_0 values for 18° are those of Kohlrausch corrected to the basis of the 1910 atomic weights.

In Tables V to VII are shown values of η/η_0, Λ, Λ/Λ_0, $\Lambda\eta/\Lambda_0\eta_0$, and $\Lambda/\Lambda_0(\eta/\eta_0)^m$ for these three salts at 0° for a number of concentrations up to $n' = 0.5$ equivalent per 1000 grams of water. These illustrate the magnitude and direction of the viscosity correction in the case of typical uni-univalent salts of inorganic acids. Thus, the values for the per cent. of ionization of cesium nitrate, potassium chloride and lithium chloride, respectively, are altered by the following amounts: for $n' = 0.025$ by 0.1, 0.1 and 0.3 per cent.; for $n' = 0.1$ by 1.2, 0.3 and 1 per cent.; and for $n' = 0.5$ by 6.8, 3.8 and 4.6 per cent., respectively.

Table V.—Cesium Nitrate Solutions at 0.000°.

n.	η/η_0.	Λ.	Λ/Λ_0.	$\Lambda\eta/\Lambda_0\eta_0$.	$\Lambda/\Lambda_0 (\eta/\eta_0)^{0.826}$.
0	1.0000	84.0 ± 0.2	1.000	1.000	1.000
0.025	0.9960	75.19	0.8948	0.8912	0.8939
0.050	0.9905	72.94	0.8680	0.8597	0.8651
0.10	0.9796	69.32	0.8249	0.8080	0.8148
0.20	0.9613	65.18	0.7757	0.7456	0.7543
0.50	0.9138	59.31	0.7058	0.6449	0.6582

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[1] Green, *J. Chem. Soc.*, **93**, 2029 (1908).

TABLE VI.—POTASSIUM CHLORIDE SOLUTIONS AT 0.000°.

n.	η/η_0.	Λ.	Λ/Λ_0.	$\Lambda/\Lambda_0\ \eta/\eta_0$.	$\Lambda/\Lambda_0\ (\eta/\eta_0)^{0.90}$.
0.00	1.000	81 ± 0.2	1.00	1.00	1.00
0.025	0.9986	75.6	0.934	0.933	0.933
0.05	0.9974	73.9	0.911	0.908	0.909
0.10	0.9946	71.5	0.882	0.878	0.879
0.20	0.9865	69.1	0.853	0.842	0.842
0.50	0.9571	66.6	0.822	0.786	0.791

TABLE VII.—LITHIUM CHLORIDE SOLUTIONS AT 0.000°.

n.	η/η_0.	Λ.	Λ/Λ_0.	$\Lambda/\Lambda_0\ \eta/\eta_0$.	$\Lambda/\Lambda_0\ (\eta/\eta_0)^{0.94}$.
0	1.000	60.3 ± 0.3	1.000	1.000	1.000
0.025	1.0028	54.54	0.9043	0.9068	0.9067
0.050	1.0056	52.96	0.8781	0.8830	0.8828
0.10	1.0116	51.07	0.8468	0.8565	0.8559
0.20	1.0256	48.39	0.8023	0.8232	0.8219
0.50	1.0694	44.00	0.7296	0.7802	0.7771

7. The Influence of Changes in the Physical Dimensions of the Ions.

At a sufficiently high temperature (209°) and pressure water and liquid silver nitrate are miscible in all proportions and it is, therefore, possible to pass continuously from an infinitly dilute solution of this salt in water to an infinitly concentrated one, that is, to the pure fused salt. As the concentration of the aqueous salt solution increases, the ions gradually lose their water of hydration and take on the character of the ions of the fused salt. These latter may, of course, be surrounded by an envelope of the unionized salt molecules.

These changes in the nature of the ions will, of course, produce corresponding changes in their mobilities and consequently in the conductance of the solution. These will be superimposed upon those resulting from the variation of the viscosity of the medium and, in so far as they are appreciable, will produce an error in the value of γ as calculated from the relation $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$. The magnitude of this error will vary with the nature of the salt and with its concentration, being greatest in the case of the highly hydrated salts and increasing with the concentration. For normal solutions of most inorganic salts the evidence at present available, although rather meager, indicates that the error from this source will not amount to more than about one per cent., except possibly in the case of a highly hydrated salt such as lithium chloride.

In order to be more certain upon this point, it will be necessary to determin the value of the fluidity exponent, m, for a number of salts both by the method of altering the temperature and by the method of adding different non-electrolytes to the solution, as in Green's experiments with lithium chloride and sucrose. Alteration of the pressure at constant temperature also offers a method for calculating m. If the value of m is found to be reasonably independent of the nature of the non-electrolyte used to produce the viscosity change, and is also found to be substantially identical with the value obtained by the method of altering the temperature or the pressure, then we may feel reasonably certain that the relation $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$ will give correct results.

At present, data for making such a comparison are available only for one salt, lithium chloride. We have seen above (p. 1469 and Table II) that if the Λ_0 value of this salt is altered by adding sucrose to the solution, the relation between Λ_0 and the fluidity can be satisfactorily expressed by the equation $\Lambda_0 = kf^m$. This equation was found to hold over a range involving a decrease of 32 per cent. in the fluidity and the value of m was found to be 0.94 ± 0.01. We can also calculate the value of m for this salt by the method of changing the temperatures. Between 18° and 0° the fluidity of water decreases 41 per cent. If we calculate the value of m from Λ_0 and f_0 values at 18° and 0° we obtain the result $m = 0.940$, as given in Table III.

The relation $\Lambda = kf^m$ may be also studied by comparing the value of the true transference number calculated from it with the value obtained by direct measurement.

8. The Calculation of True Transference Numbers by Means of the Relation $\Lambda = kf^m$.

The true transference number n of an ion may be defined as equal to the equivalent conductance of the ion divided by that of the ionized salt, or more generally by the sum of the equivalent conductances of all the ions present in the solution. Thus the transference number of the anion of a salt is expressed by the equation

$$n_A = \frac{\Lambda_A}{\Lambda_A + \Lambda_K}. \tag{22}$$

Since the equivalent conductances of different ions change with the viscosity at different rates, it is obvious that the transference number will be a function of the viscosity and if the relation $\Lambda = kf^m$ is correct, we can obviously calculate the true transference number of an ion in any given solution, provided we know its value in any other solution whose relative viscosity with respect to the first solution is known.

To illustrate this we will derive the expression which connects the true transference number of the anion of a salt in a solution whose relative viscosity is η/η_0 with its value at infinit dilution at the same temperature.

The relation $\Lambda = kf^m$ gives us the two equations

$$\Lambda_A = \Lambda_{0A}\left(\frac{f_0}{f}\right)^{m_A} \tag{23}$$

and

$$\Lambda_K = \Lambda_{0K}\left(\frac{f_0}{f}\right)^{m_K} \tag{24}$$

Dividing the first of these equations by their sum, we have

$$n_{\text{A}} = \frac{\Lambda_{\text{A}}}{\Lambda_{\text{A}} + \Lambda_{\text{K}}} = \frac{\Lambda_{\text{o A}}}{\Lambda_{\text{o A}} + \Lambda_{\text{o K}}\left(\frac{\eta}{\eta_0}\right)^{m_{\text{A}}-m_{\text{K}}}} \qquad (25)$$

By an algebraic transformation this equation may be written

$$n_{\text{A}} = \frac{\Lambda_{\text{o A}}}{\Lambda_{\text{o A}} + \Lambda_{\text{o K}}}\left(\frac{\eta}{\eta_0}\right)^{m_{\text{A}}-m}\left[\frac{\Lambda_0}{\Lambda_{\text{o A}}\left(\frac{f}{f_0}\right)^{m_{\text{A}}-m} + \Lambda_{\text{o K}}\left(\frac{f}{f_0}\right)^{m_{\text{K}}-m}}\right] \qquad (26)$$

in which m, as before, is the fluidity exponent for the salt. The expression in brackets is identical with that in equation (5), which we have seen may be placed equal to unity if (η/η_0) is not very far from unity. For most cases, therefore, equation (26) may be written

$$n_{\text{A}} = n_{\text{o A}}\left(\frac{\eta}{\eta_0}\right)^{m_{\text{A}}-m} \qquad (27)$$

or in words: *The true transference number of an ion in a solution of concentration C is equal to the transference number at infinit dilution multiplied by the relative viscosity of the solution raised to a power equal to the difference between the fluidity exponent of the ion and the fluidity exponent of the salt.*

Since the value of m lies between m_{A} and m_{K}, the exponent in the above equation will be positive for the slower ion and negative for the faster ion, so that with decreasing viscosity the transference numbers tend to approach 0.5, a well known tendency which is observed as the temperature increases.

We will now compare the values of the true transference numbers calculated from our equation (27) with those obtained by direct measurement in concentrated solutions. In a previous investigation[1] by the writer, the true transference numbers for 1.2 molal solutions of potassium chloride, sodium chloride and lithium chloride at 25° were measured by transference experiments in the presence of raffinose as a reference substance. Each solution was 0.1 molal with respect to raffinose and the solutions had the following[2] relative viscosities at 25°; LiCl, 1.4; NaCl, 1.3; KCl, less than 1.3. For the transference number of the anion at infinit dilution at this temperature we have,[3] for KCl,

[1] THIS JOURNAL, 31, 322 (1909).

[2] Recent measurements in this laboratory by Mr. L. F. Nickell.

[3] With the exception of the value 38.3 for Li-ion all of these conductance values are taken from the table computed by Johnston (THIS JOURNAL, 31, 1015 (1909)). The value for Li-ion was computed from the data of Green (*J. Chem. Soc.*, 93, 2060 (1908)) and those of Hartley, Thomas and Appleby (*J. Chem. Soc.*, 93, 552 (1908)). For LiCl at 25° Green found $\Lambda_0 = 114$. This gives for the conductance of Li-ion, $\Lambda_{0\text{Li}} = 114 - 75.5 = 38.5$. Hartley, Thomas and Appleby found for $LiNO_3$ at 25.08°, $\Lambda_0 = 109.4$ which for 25° would be 108.8. Using Johnston's Λ_0 value for NO_3-ion at this temperature we have $\Lambda_{0\text{Li}} = 108.8 - 70.6 = 38.2$.

$$n_{0A} = \frac{\Lambda_{0A}}{\Lambda_{0A} + \Lambda_{0K}} = \frac{75.5}{75.5 + 74.5} = 0.504; \qquad (28)$$

for NaCl,

$$n_{0A} = \frac{75.5}{75.5 + 50.9} = 0.597; \qquad (29)$$

and for LiCl,

$$n_{0A} = \frac{75.5}{75.5 + 38.3} = 0.664. \qquad (30)$$

The fluidity exponent for Cl-ion is 0.88 (see Table III) and for the three salts it has the following values: for KCl, 0.88; for NaCl, 0.92; and for LiCl, 0.94. Substituting all of the foregoing values in equation (27), we obtain for the true transference number of the chloride ion in the solutions with which direct transference experiments were made by the writer, the following values:

$$\text{For KCl,} \quad n_{\mathrm{Cl}^-} = 0.504\ (\eta/\eta_0)^{[0.88 - 0.88 = 0.00]} = 0.504. \qquad (31)$$

$$\text{For NaCl,} \quad n_{\mathrm{Cl}^-} = 0.597\ (1.3)^{[0.92 - 0.88 = 0.04]} = 0.604. \qquad (32)$$

$$\text{For LiCl,} \quad n_{\mathrm{Cl}^-} = 0.664\ (1.4)^{[0.94 - 0.88 = 0.06]} = 0.678. \qquad (33)$$

The values obtained in the transference experiments were: (1) for KCl, 0.505 and 0.505; (2) for NaCl, 0.617 (one result only); (3) for LiCl, 0.694 and 0.699.

Comparison of the two sets of values shows perfect agreement in the case of KCl. In the case of the other two salts the change of the transference number with the change in viscosity is in the right direction but is apparently not large enough. What significance, if any, is to be attached to this difference is a question which must await the accumulation of further experimental data.

The value of the fluidity exponent, *m*, may, for example, be dependent somewhat upon the nature of the molecules composing the medium through which the ions are moving and although as we have seen above that small changes in *m* do not greatly affect the calculation of the degree of ionization, they have a much larger influence upon the calculation of the transference number. If, for example, the value of *m* for LiCl were 0.98 instead of 0.94, this would change the value of γ calculated for a normal LiCl solution at 25°, only from 73.0 to 73.4 per cent. The value for the transference number calculated in equation (33) above, would, however, become 0.687, which is in good agreement with the one obtained by direct measurement.

9. The Viscosity Correction in the Case of Acids and Alkalies.

Johnston found that the relation, $\Lambda = kf^m$, did not hold in the case of hydrogen and hydroxyl ions. If the molecules of water influence the conductance of an acid, or an alkali solution by a kind of Grotthus-chain action as suggested by Daneel,[1] then anything which alters the degree of association of the water would influence the magnitude of this effect. In order, therefore, to estimate the degree of ionization of strong acids or alkalies in concentrated solutions, the best procedure would probably be to make use of the equation

$$\gamma = \Lambda/\Lambda'_0 \qquad (34)$$

in which Λ is the equivalent conductance of the solution for which γ is desired, and above which the vapor pressure of the water is p. Λ'_0 is the equivalent conductance of the electrolyte at infinit dilution in a solution to which a suitable non-electrolyte has been added, so as to give it the same viscosity and the same vapor pressure, p, as the first solution. In the absence of any experimental data, however, equation (34) must be regarded merely as a suggestion.

Summary.

1. It is pointed out that in calculating the degree of ionization of an electrolyte by the conductivity method, the neglect of the viscosity effect may produce errors as high as 7 and 8 per cent., even at such low concentrations as 0.1 normal and for such simple electrolytes as uni-univalent salts.

2. The relation $\Lambda = kf^m$ (in which Λ is the equivalent conductance of an ion, f is the fluidity of the solution, m is a constant not far from unity and dependent chiefly upon the nature of the ion, and k is a proportionality constant) is proposed, provisionally as the most logical basis for formulating the viscosity correction in calculating the degree of ionization, γ, in moderately concentrated solutions.

3. The above relation is shown to lead to the following expression for the degree of ionization: $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$. Examples illustrating the results obtained with this equation are given and methods for determining the "fluidity exponent," m, are discussed.

4. The relation $\Lambda = kf^m$ is shown to lead to the following expression for the true transference number n_A of the ion A in any solution: $n_A = n_{0A}(\eta/\eta_0)^{m_A - m}$. n_{0A} is the transference number at infinit dilution in pure water, (η/η_0) the relative viscosity of the solution, and m_A and m are the "fluidity exponents" for the ion and for the salt, respectively. Values calculated from this equation are compared with those determined experimentally.

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THE ACTION OF NITROGEN ON LITHIUM CARBIDE.

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Although particular attention has been given by many investigators

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[1] *Z. Elektrochem.*, 11, 249 (1905).