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III. *Ionic Size in Relation to the Physical Properties of Aqueous Solutions.*

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PART I.—INTRODUCTION.

THE electrical conductivity of a solution depends upon the rates of transference of the ionised portions of the solute in opposite directions under the influence of the applied electro-motive force. These rates of transference under a given potential gradient are conditioned by the viscosity of the medium and the sizes and possibly the shapes of the ions. Increase of viscosity of the solution and increase in the sizes of the migrating ions both tend to diminish the rates of transference of the ions, and thus to lower the conductivity. If the ion enters into combination with one or more molecules of water, its size is necessarily increased, and the motion of the water-logged ion becomes more sluggish as the amount of water in combination increases. To separate the elements which determine the conductivity of an electrolytic solution, and to analyse the joint effect of variations in ionisation, viscosity and water combination is a matter of great difficulty, but of much importance to the theory of solution.

In a former paper (BOUSFIELD on "Ionic Sizes in Relation to the Conductivity of Electrolytes"*) was proposed a method for effecting such an analysis based upon the expression evaluated by STOKES for the terminal velocity of a small sphere moving in a viscous medium. A consideration of the influence of the water in combination with the ion upon its mobility was used to obtain a correction of the coefficient of

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ionisation, which made VAN 'T HOFF's law (in a slightly modified form) an *accurate* expression of the relation between ionisation and dilution, down to twice decinormal solutions of KCl. This method of procedure gave for the radius of the hydrated ion an expression of the form

$$r = r_{\infty}(1+\mathrm{B}h^{-2/3})^{-1},$$

which indicated that the average radius of the ion steadily increased with dilution, owing to increasing hydration of the ion, up to "infinite dilution." Whether the resulting expression for r did in fact represent the average radius of the ion was tested by a consideration of the density law which would thence result. The volumes of the ions would be proportional to r^3, and it was found that a rational density formula could be constructed upon this basis which accurately corresponded with the observed densities of the solutions.

In the present paper the necessary experimental determinations for applying the method to solutions of NaCl are given, together with some other determinations for collateral purposes, and the hypothesis is further tested by reference to other physical properties of solutions. These results are independently of some value, apart from the hypothesis by which they are reached, and it has been thought well to designate the function r, which, according to our view, expresses the average radius of the ion, by the term "radion." Whilst this term connotes our hypothesis, it may, if necessary, be merely considered as expressing a certain function of the dilution. But it has a further convenience, as it enables us readily to extend the conception to denote the average molecular radius of any group of ions or molecules, or even of the whole of the ions and molecules both of solvent and solute in any given solution. The utility of this extended conception will appear more clearly in the section relating to a consideration of ionic size with reference to the viscosity of a solution.

The volume of the ion, according to our hypothesis, is proportional to the cube of the radion, and the volume of a pair of ions to the sum of the cubes. These cubes and their sums we refer to as "ionic volumes." But except where the context indicates the contrary, the term "radion" may be taken as merely denoting the function

$$r = r_{\infty}(1+\mathrm{B}h^{-2/3})^{-1},$$

and the term "ionic volume" as denoting the cube of the radion or sum of the cubes of the radions, apart from the hypothesis as to size.

As in our former paper, with reference to KCl, it is shown that the "solution volume" of NaCl solutions is a linear function of the ionic volumes. Hence the densities of KCl and NaCl solutions can both be accurately expressed by the same formula as simple functions of the radions.

A theoretical consideration of the relation of the Hittorf migration numbers to the sizes of the ions is given, and it is shown that our hypothesis as to the influence of

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ionic sizes upon rates of transference would theoretically lead to the result that the reciprocals of the Hittorf migration numbers should be expressible as a linear function of the ratio of the radions. This turns out in fact to be the case, and we incidentally arrive at a useful method of extrapolation to determine the value of the Hittorf number for an electrolyte at "infinite" dilution.

These considerations enable us to determine the coefficients B for the separate ions in the expressions for the radions. These coefficients B we refer to as the "hydration numbers," the relation between the hydration numbers and the migration numbers at infinite dilution being of the form

$$B = B_1N_1 + B_2N_2.$$

Turning now to a consideration of the viscosities of the KCl and NaCl solutions, it is shown that the viscosity of these solutions can be represented approximately as a linear function of the radions, as can also the viscosity of mixtures of normal KCl and NaCl solutions.

Passing to a consideration of the general relation of viscosity to ionic size, the extended conception of the radion is introduced, and an approximate value is given to the radion of water, which expresses the average radius of the water molecules reckoned upon the same scale as the radions of the solute. Using this value of the water radion in conjunction with the values of the radions of the solute determined from the conductivities, it is shown that the viscosity of the solutions can be expressed with a fair approach to accuracy by the expression

$$\eta = C\Sigma\beta r,$$

where r stands for the radion of a given species of molecules, and β for the fraction of the total volume occupied by such species. Since $\Sigma\beta r$ is, upon the extended conception of the radion, the average molecular radius of the whole solution, we may express this result by saying that the viscosity of an aqueous solution is proportional to its radion.

In order to correlate ionic sizes with osmotic pressure, a prolonged attempt was made to measure the vapour pressure of dilute KCl solutions at 18° C. A large barometer tube was used, closed by a small tap at the bottom, so that minute differences of level could be determined by removing and weighing the mercury cistern. A similar arrangement was used to determine simultaneously the variations of atmospheric pressure during each observation. It was found, however, that the variations of atmospheric pressure were often larger than the differences of vapour pressure to be measured, and no sufficiently accurate results could be obtained. Recourse was therefore had to the freezing-point determinations of JAHN with KCl and NaCl solutions. The variations of ionic size with temperature are probably serious

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and at present* unknown, and hence a consideration of ionic sizes at 18° C. in relation to osmotic data at another temperature might lead to error. But it seemed probable that the ionic sizes at different dilutions might have the same *relative* values at 18° C. and 0° C., and in the absence of other data it was decided to use these.

Defining the "effective molecular freezing-point depression" as the ordinary so-called molecular freezing-point depression divided by $(1+\alpha)$, where α is the ionisation, and denoting it by the letter D, it was found that D was a linear function of the ionic volume, and that it could be expressed both for KCl and NaCl as

$$D = 1{\cdot}86 + C\,(I_\alpha - I_v),$$

where I_v stands for the ionic volume at the given dilution and I_α for the ionic volume at infinite dilution, the value of the constant C being nearly the same for both substances.

In addition to the confirmation thus afforded to our view as to the fundamental importance of the radion in the theory of solutions, we are further led to a useful formula for obtaining by extrapolation the value of the molecular freezing-point depression at "infinite" dilution. For this purpose we are able to dispense with our hypothesis, and obtain from it a new result quite independent of it—one of the recognised tests of the validity of a hypothesis, though not a conclusive one.

We saw that the solution volume was a linear function of the ionic volume, and we have now the effective molecular freezing point-depression also as a linear function of the ionic volume. Hence the effective molecular freezing-point depression should be a linear function of the solution volume, and in this case the reference to ionic sizes which correlated the two sets of phenomena can be dispensed with. In order to test this matter, measurements of the densities of KCl and NaCl solutions at 0° C. were made. This is a little above the freezing point of dilute solutions, but it was considered to be near enough to make the desired comparison. Density measurements were made upon solutions of strengths of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$ normal, and empirical formulæ (based on the lines of the rational formulæ for 18° C.) were constructed to obtain the solution volumes at the concentrations at which JAHN'S freezing-point determinations were made.

The result was that the effective molecular freezing-point depression both for KCl

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* In my former paper I attempted to calculate the variation of ionic size with temperature by reference to the conductivity temperature coefficients of the ions at infinite dilution which were given by KOHLRAUSCH. I have, however, since come to the conclusion that these results are unreliable. KOHLRAUSCH'S values were largely based on determinations of the conductivities of $\frac{1}{1000}$ normal solutions. Dissociation being incomplete in such solutions, any variation of conductivity due to change of ionisation with temperature would be included in his temperature coefficients and might entirely vitiate the deductions which I drew. This portion of my former paper must therefore be withdrawn, and I propose to pursue the matter further experimentally.

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and NaCl solutions could be expressed by one formula with the same constants for both substances, viz. :—

$$D = 1{\cdot}86 + 3{\cdot}3\,\delta V_s,$$

where δV_s is the change in the solution volume for different dilutions. This formula would also include a non-electrolyte such as sugar, in which δV_s is almost zero. Furthermore, by correcting the concentration for the amount of water abstracted by and combined with the solute, a constant value was obtained for the effective molecular freezing-point depression of KCl solutions down to a concentration of twice decinormal.

The equivalent refractive power of KCl and NaCl solutions was similarly shown to be a linear function of the ionic volume, and, consequently, also of the solution volume.

In the sketch of the course of the present paper we have passed over some matters arising incidentally which may call for mention. But it must be observed that the main purpose kept in view throughout is to show the interpenetration of the theory of ionic sizes with the theories of the various phenomena of solutions, and to test the theory as far as possible in its relation to such phenomena. In this process various side avenues have been opened up, which we have forborne to follow if they carried us too far from the main track.

One incidental matter of importance is the correction of the coefficient of ionisation which is afforded by the theory, according to which the true value of the coefficient of ionisation is

$$\alpha = \frac{\lambda}{\Lambda} \cdot \frac{\eta}{1 + Bh^{-2/3}}.$$

The result of this correction is to make the values of α for KCl and NaCl very nearly the same for equimolecular solutions, down to twice decinormal concentration. In confirmation of this it was found that the observed densities of mixtures of normal solutions of KCl and NaCl were correctly given by the "law of mixtures" within very narrow limits.

The conductivities of these mixtures were also determined and a mixture law for the conductivities based upon the consideration of viscosities and ionic sizes was formulated. The agreement thus obtained between observed and calculated values also tends to show that the hypothesis upon which the calculations were made is correct.

The increase in the ionic volumes which takes place with increasing dilution must be nearly proportional to the increasing volume of water combined with the ion. The development of this matter quantitatively, so as to determine the number of molecules of water in combination with the ion under different circumstances, is a matter of great importance, but it cannot be dealt with in this paper. The effect of water

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combination as a sufficient and possibly the only cause of ionisation is dealt with, to some extent, in the former paper (see the revised version published in the 'Zeitschrift f. Phys. Chem.,' *loc. cit.*) and has also recently been considered by LOWRY ("An Application to Electrolytes of the Hydrate Theory of Solution," 'Trans. Farad. Soc.,' I., 197, 1905).

PART II.—EXPERIMENTAL DETERMINATIONS.

(*a*) *Density and Viscosity of* NaCl *Solutions at* 18° C.—The material used for the earlier determinations was purest fused NaCl (obtained from BAIRD and TATLOCK). A stock solution of a strength of 21·673 per cent. was prepared, the density of which at 15° C. was found to be 1·1638. MENDELÉEF ('Principles of Chemistry,' ed. 1905, vol. 1, p. 451) gives for the density of NaCl solutions at 15° C. the formula

$$S_{15} = 9991{\cdot}6 + 71{\cdot}17P + 0{\cdot}214P^2 \qquad \text{(water = 10,000).}$$

This formula gives for 21·673 per cent. the density 1·1635.

A further sample of material was purified by precipitation with HCl, recrystallised and fused (specially prepared by MERCK). A stock solution of 20·000 per cent. was made from this sample, the density of which at 15° C. was 1·1502. MENDELÉEF'S formula gives 1·1501. No substantial difference between these solutions manifested itself, but for any range of values the same solution was used.

The densities were determined in all cases in duplicate, by means of a pair of pyknometers, each having a capacity of about 100 cub. centims. The viscosities were determined for the most part by means of the simpler type of viscosimeter described in the former paper. The results from this instrument are indicated in the diagram by black circles. A few determinations which were made with another instrument are indicated by open circles.

The viscosities were calculated from a differential formula derived from the formula

$$\eta = \rho t\,(A - B/t^2).$$

By differentiating we have

$$\delta\eta = \frac{\eta}{\rho}\,\delta\rho + \rho\left(A + \frac{B}{t^2}\right)\delta t.$$

For water, $\eta_{18} = 0{\cdot}010514$, $\rho_{18} = 0{\cdot}99866$; and for the instrument chiefly used, $A = 0{\cdot}000017703$, $B = 0{\cdot}28294$, with a small correction for variations when the time of flow of water at 18° C. varied from 621 seconds.

These constants were determined by the time of flow of water at various temperatures, as derived from THORPE and RODGERS' determinations ('Phil. Trans.,' A, vol. 185, p. 397, 1894), by means of the formula given in a former paper (BOUSFIELD and LOWRY, 'Roy. Soc. Proc.,' vol. 71, p. 47, 1902), viz. :—

$$\eta_{18} = \eta_t\left[1 + 0{\cdot}0251\,(t-18) + 0{\cdot}000115\,(t-18)^2\right].$$

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The differential formula becomes on substituting for η, ρ, A, B and t,

$$\delta\eta = 0{\cdot}01053\ \delta\rho + 0{\cdot}000018406\ \delta t.$$

It was found by trial with a series of water values at different temperatures that the differential formula remained sufficiently accurate even when δt amounted to as much as 50 seconds.

The values determined for the less dilute solutions of NaCl are given in the following table:—

TABLE I.—Density and Viscosity of NaCl Solutions at 18° C.

P.	m.	Density.	Viscosity.	Viscosity referred to water as unity.
6	1·068	1·04200	0·01150	1·093
4	0·7024	1·02749	0·01112	1·058
3	0·5232	1·02027	0·01098	1·042
2	0·3463	1·01308	0·01083	1·030
1	0·1720	1·00592	0·01068	1·016
0	0	0·99866	0·010514	1·000

The duplicate density determinations in no case differed by more than a unit in the fifth place of decimals. The air corrections were determined from observation of barometer pressure and laboratory temperature, and it is considered that the densities may be taken to be relatively correct within ± 1 in the fifth place of decimals. The viscosity determinations have not the same order of accuracy.

For the purposes of this paper it was a matter of considerable importance to determine the viscosities of more dilute solutions, but this proved to be a matter of the greatest difficulty. Other observers of viscosities have had the same experience, but whether owing to the same cause is not clear.

In the former paper it was pointed out that the constants of the apparatus, as tested by the time of flow of water at 18° C., vary from time to time in an irregular manner. No amount of washing will bring the apparatus to a steady condition. In dealing with very dilute solutions the variations of the water constant are often of the same order of magnitude as the variations due to variation of concentration of the solution. Hence the only safe method of operation is to interpose between the observations of salt solutions observations of water, which, of course, involves a thorough rinsing of the apparatus, which may in itself introduce some change in its condition.

When a series of observations of solutions with interposed observations of water shows no material change in the water constant, it is assumed that the conditions were the same throughout, and that the observations are therefore accordant. But this assumption is not always true. A very large number of observations on dilute

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NaCl solutions were made, many of which had to be rejected in whole or in part, on account of variations in the water constant. Particulars of the best and most accordant set of observations on very dilute solutions are given in Table II.*

TABLE II.

P.	m.	Time of flow.	δt.	$\delta\rho$.	η.	Viscosity referred to water as unity.
Water	—	619 618·8	—	—	—	—
0·01	0·00174	619·3 619·4 619·4	0·5	0·00007	0·010524	1·0010
Water	—	619·1 619·5	—	—	—	—
0·04	0·00683	620·0 620·2	1·2	0·00029	0·010539	1·0024
0·0915	0·0156	620·6 620·8	1·8	0·00066	0·010554	1·0038
Water	—	619 618·6 619	—	—	—	—
0·131	0·0223	620·7 620·7	1·8	0·00094	0·010557	1·0041
0·335	0·0573	622·4 622·0	3·3	0·00242	0·010601	1·0083
0·60	0·1025	623·5 623·3	4·5	0·00433	0·010643	1·0123
1·00	0·1720	623·8 624·0	5·0	0·00726	0·010683	1·0161
Water	—	619 618·8	—	—	—	—

In this series the mean value for the time of flow of water at 18° at the beginning and end of the observations remains constant at 618·9. At one point there was a variation in the water constant, but it returned afterwards to the same value, and

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* As my viscosity determinations for very dilute solutions differ materially from GRÜNEISEN'S, which are given below, I have thought it well to set out fully the data from which my results are calculated, though very little use has been made of data for solutions below 1 per cent. strength in this paper, except for the initial process of correcting α. The effect of the solute in dilute solution upon the water itself, for which accurate measurements of dilute solutions are required, is left over for the time.

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there appears to be no break in the values for the solutions. δt is therefore calculated throughout from the value for water of 618·9. $\delta\rho$ is calculated from the density at 1 per cent. by a linear formula.

The series of observations set out in the two foregoing tables are plotted in Diagram I., and shown by black circles. A series of observations given in a recent paper by GRÜNEISEN ('Wiss. Abhand., Phys. Tech. Reichs.,' 4, 239, 1905), to which fuller reference will later be made, is also plotted. They are indicated by double open circles, and the values are set out below.

TABLE III.—GRÜNEISEN'S Determination of the Viscosity of NaCl Solutions at 18° C.

m.	Viscosity referred to water as unity.
1	1·0858
0·5	1·0410
0·2	1·0167
0·1	1·0086
0·05	1·0046

It will be observed that in the more concentrated solutions there is a fair agreement. But at the dilute end of the curve the present observations show a considerably greater viscosity than GRÜNEISEN'S observations.

It hardly seems possible that the difference can be due to changes in the apparatus constant during the series, as the water constant is the same at the beginning and end. No other series so coherent as the one set out above was obtained, but the following observations, made with another instrument, tend to show that the difference is slightly greater than is indicated by the above series.

TABLE IV.—Other Determinations of Viscosity of Dilute NaCl solutions.

m.	Viscosity referred to water as unity.
0·00085	1·0025
0·0090	1·0050
0·0120	1·0054
0·01563	1·0054
0·0286	1·0070
0·0343	1·0064
0·0491	1·0077

These determinations have only the value of isolated observations, but they are entitled to some weight, and they are indicated on the diagram by small open circles. The curve drawn on the diagram indicates the line of values actually adopted for the

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purpose of this paper. It was drawn on a larger scale for the very dilute end, and the values adopted for the different concentrations for very dilute solutions were taken from this curve.

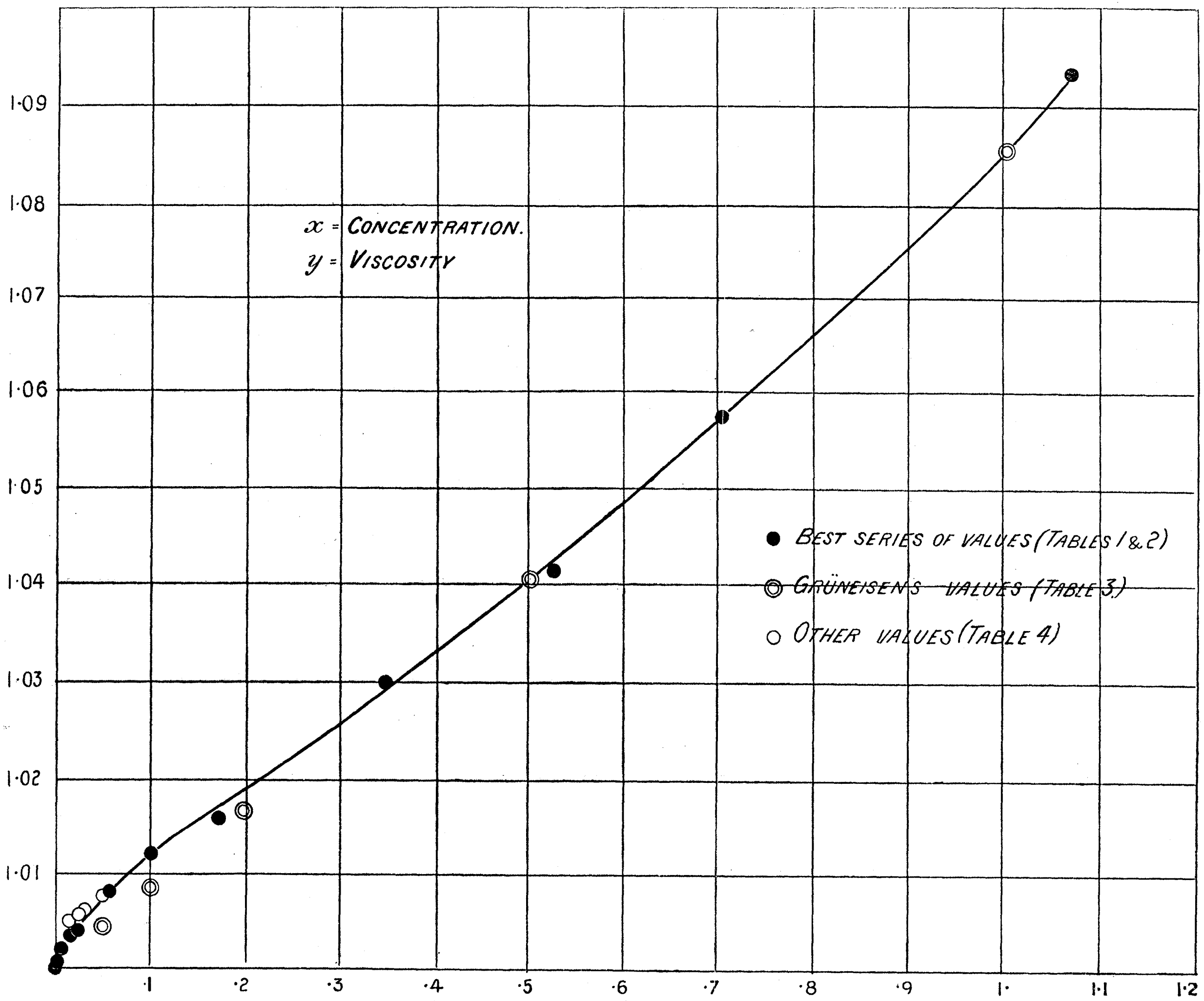

Diagram I. Viscosity of NaCl Solutions at 18° C.

(*b*) *Density, Viscosity and Conductivity of Mixtures of Normal Solutions of* KCl *and* NaCl.—In this series of experiments, stock normal solutions of KCl and NaCl were made up, and the density, viscosity and conductivity of these solutions and of mixtures thereof were determined at 18° C. The mixtures were made by means of 100- and 200-cub. centim. flasks (stamped at the P.T.R.). The densities and viscosities were determined as before described. The conductivities were measured by KOHLRAUSCH's method with wheel bridge and telephone with the special variations described in a former paper (BOUSFIELD and LOWRY, 'Phil. Trans.,' A, vol. 204, p. 286, 1905). The platinum pot containing a glass-shielded electrode was used as the conductivity vessel—resistance capacity = 16·310. The conductivities observed are given in Table X., Part III. (*e*).

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The duplicate density measurements corrected for differences of laboratory temperature and barometric pressure were as follows:—

TABLE V.—Densities at 18° C. of Normal KCl and NaCl Solutions and Mixtures thereof.

Volume KCl.	Volume NaCl.	Density.		Mean density.
		Pyknometer No. 1.	Pyknometer No. 2.	
4	0	1·044955	1·044981	1·04497
3	1	1·043555	1·043530	1·04354
2	2	1·042114	1·042109	1·04211
1	3	1·040668	1·040691	1·04068
0	4	1·039203	1·039217	1·03921

The viscosity measurements were made in two groups, with an interval of three days between. The water constant appears to be steady in each set, but differs by a second for the two sets. The order of accuracy obtained is about ±1 per thousand.

TABLE VI.—Times of Flow of KCl and NaCl Solutions at 18° C.

Volume KCl.	Volume NaCl.	Water test.	Time of flow.	Mean time.	η.
—	—	Water	622·2 622·2	622·2	—
4	0	—	589·2 589·0	589·1	0·010374
0	4	—	647·6 647·4	647·5	0·011433
2	2	—	616·8 616·6	616·7	0·010884
—	—	Water	622·2	622·2	—
—	—	Water	623·2 622·8 623·2	623·1	—
3	1	—	604·2 604·3	604·2	0·010633
1	3	—	633·5 633·6	633·5	0·011164
—	—	Water	623·4 623·2	623·3	—

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The viscosities are calculated from the formula

$$\eta = \rho t\,(A - B/t^2),$$

where for the first series

$$A = 0{\cdot}00001766, \qquad B = 0{\cdot}2819,$$

and for the second series

$$A = 0{\cdot}00001763, \qquad B = 0{\cdot}2811,$$

the constants being corrected for the change of the time of flow of water at 18° in the manner before indicated.

(*c*) *Determination of density of dilute solutions of* KCl *and* NaCl *at* 0° C.—It was necessary for our purpose to determine accurately the solution volumes of dilute solutions of KCl and NaCl at the freezing-point. A pair of pyknometers of large capacity (about 330 cub. centims.) was therefore used for this purpose. The solutions were made up by dilution at 18° C. from normal solutions, and ranged from N/2 to N/32. The pyknometers were packed in ice in a refrigerator for two or three hours in order to secure a correct temperature adjustment. The air corrections for the weighing operation were calculated from the temperature and pressure in the laboratory from time to time. The observed densities are given to the sixth place of decimals, though the sixth place is only of value as fixing the fifth place more accurately.

The "observed" solution volumes are calculated from the densities by means of the formula

$$V_s = \frac{1}{\rho_0} - \frac{1000}{m E \rho_0}(\rho - \rho_0),$$

where ρ_0 is the density of water at 0° C., m is the concentration in gram-molecules per litre of solution, E is the equivalent weight of the solute.

In order to obtain expressions for the solution volume in terms of the hydration h, a formula of the same form as is shown to hold for 18° C. was used (*vide post*, Part IV. (*a*)), viz., $V_s = c - b\gamma$, where $\gamma = (1 + Bh^{-2/3})^{-3}$.

For densities at 18° C. we were able to determine B from the conductivities by the method stated in Part III. (*g*). But no sufficiently accurate series of conductivity values at 0° C. was available for determining B in this manner. Hence the value of B was determined by taking trial values of B until, on setting out the resulting values of V_s upon the resulting value of γ, the points ranged approximately in a straight line. A considerable difference in the value of B makes little difference in the values of V_s, or in the limiting value which is obtained by putting $\gamma = 1$.

The value of B was taken as 6 in the case of KCl, and 4 in the case of NaCl, and with these values of B the values of γ were calculated.

The values of h (the number of molecules of water per molecule of solute) are not

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quite the same for solutions of KCl and NaCl of equal concentration, but this again makes no appreciable difference, and the mean values of h were taken for both. The empirical formulæ thus derived for the solution volumes were

for KCl . . . . $V_s = 0{\cdot}3658 - 0{\cdot}059\,\gamma$,
for NaCl . . . . $V_s = 0{\cdot}3015 - 0{\cdot}089\,\gamma$.

In the following table are set out the observed densities, the "observed" values of the solution volumes (calculated from the observed densities), the values of $h^{-2/3}$ and γ, the solution volumes calculated from the above formulæ and the differences. The values of the solution volumes at infinite dilution (obtained from the above formula by putting $\gamma = 1$) are for KCl 0·3068, for NaCl 0·2125.

Table VII.—Densities and Solution Volumes of KCl and NaCl at 0° C.

Concentration.	$h^{-2/3}$.	γ.		Densities.		V_s for KCl.			V_s for NaCl.		
		KCl.	NaCl.	KCl.	NaCl.	Observed.	Calculated.	Difference.	Observed.	Calculated.	Difference.
N/32	0·0068	0·887	0·923	1·001479	1·001305	0·3133	0·3135	− 2	0·2194	0·2194	±
N/16	0·0108	0·820	0·881	1·003061	1·002717	0·3174	0·3174	±	0·2236	0·2231	+ 5
N/8	0·0172	0·745	0·819	1·006203	1·005520	0·3217	0·3218	− 1	0·2285	0·2286	− 1
N/4	0·0274	0·633	0·732	1·012410	1·011058	0·3281	0·3284	− 3	0·2356	0·2363	− 7
N/2	0·0436	0·498	0·617	1·024633	1·021920	0·3364	0·3364	±	0·2465	0·2466	− 1

Part III.—Ionic Size in Relation to Conductivity.

(*a*) *Theoretical Considerations.*—Some confusion still exists in the use of terms employed in relation to the theory of conductivity, which makes it desirable to state the fundamental equations with precision, and to define the terms used with exactness. It will be convenient to set out together the meanings of the symbols employed.

U = absolute velocity of kation (expressed in centimetres per second) under a potential gradient of 1 volt per centimetre.
V = absolute velocity of anion.
q = quantity of electricity liberated by 1 gramme equivalent of any monad ($q = 98360$ coulombs).
m = concentration of solute in gramme equivalents per litre.
h = hydration (number of molecules of water per molecule of solute).
$u = qU$, $v = qV$, mobilities of the ions.

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κ = specific conductivity of solution reckoned in units such that κ^{-1} = resistance in ohms of a centimetre cube of the solution between its opposite sides.
$\lambda = 1000\kappa/m$, the "equivalent conductivity."
Λ = equivalent conductivity at "infinite" dilution.
$l_1 = u_\infty$, $l_2 = v_\infty$, so that $\Lambda = l_1+l_2$.
α = true coefficient of ionisation.
r = radius of an ion.
$\mathrm{R} = r_\infty$ = radius of ion at infinite dilution.
η = viscosity in absolute units.
n_2 = Hittorf migration number for anion; $n_1 = 1-n_2$.

Confining ourselves to the case of binary electrolytes composed of monovalent ions, we have

$$\kappa = \frac{\alpha m}{1000} \cdot q \cdot (\mathrm{U}+\mathrm{V}) \quad \text{. . . . .} \quad (1),$$

$$\lambda = \alpha\,(u+v) \quad \text{. . . . .} \quad (2),$$

and at infinite dilution

$$\Lambda = l_1+l_2 \quad \text{. . . . .} \quad (3).$$

It is important to note that u and v are the true "mobilities" of the ions, being really proportional to the velocities. The numbers usually tabulated as "mobilities" are αu and αv, whose sum makes up λ. At infinite dilution the distinction ceases to exist, since $\alpha = 1$, but it is important to keep it in mind for less dilute solutions.

According to STOKES' theorem (*vide* former paper), the limiting velocity of a small sphere of radius r in a medium of viscosity η under an applied force P is proportional to $\mathrm{P}/r\eta$. Assuming that the ions are spherical and that they are water-coated, so that the friction is always water on water, we should have, if STOKES' theorem is applicable to ionic movements under the electromotive force,

$$r = \mathrm{C}/v\eta \quad \text{. . . . .} \quad (4),$$

where C is a constant for monovalent ions.*

Assuming the validity of the application, the sizes of the ions can be ascertained in absolute units, as is done in Professor POYNTING'S calculation in reference to the former paper.† But for our present purpose we are concerned with comparative

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* Considerations derived from viscosity measurements of divalent ions render it doubtful whether the same value of C could be applied to them. It may be that divalent ions differ notably from a spherical shape. It is also possible that the H and OH ions, being little, if at all, hydrated, might require a different constant.

† I have set out this calculation in the paper as published in the 'Zeitschrift für Phys. Chem.,' 53, 1905, p. 302.

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sizes, and are at liberty to simplify the equations by choosing a suitable unit radius. This we do by making C = 1 in equation (4), so that we have always

$$r = 1/v\eta \quad \text{or} \quad 1/r = v\eta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

or, at infinite dilution,

$$R = 1/l.$$

In other words, our unit radius is the radius of an imaginary monovalent water-coated ion which has unit mobility at infinite dilution. All ionic radii will be given in ionic units, as we may shortly term this unit. Moreover, for reasons which will more fully appear hereafter, we shall speak of the ionic radius as the "radion." This will be specially convenient, first, because the radion will be shown to be an important physical quantity, quite apart from our theory that it represents the radius of the hydrated ion; secondly, because, as was shown in the former paper, the value of the ionic radius which we obtain is the *average* value for the whole of the ions, and not the value for any individual ion; and, thirdly, because the conception of the radion is useful, not only in reference to ions, but also to other hydrated molecules, and even to water itself.

Slightly modifying the notation given in the former paper, we have

$$u = \frac{1}{r_1\eta}, \quad v = \frac{1}{r_2\eta}, \quad \lambda = \frac{\alpha}{\eta}\left(\frac{1}{r_1} + \frac{1}{r_2}\right),$$

and writing

$$\frac{R_1}{r_1} = 1 + \phi_1, \quad \frac{R_2}{r_2} = 1 + \phi_2,$$

where ϕ_1 and ϕ_2 are written as abbreviations for $\phi_1(h)$ and $\phi_2(h)$, so that

$$\frac{1}{r_1} = l_1(1+\phi_1), \quad \frac{1}{r_2} = l_2(1+\phi_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6),$$

we get for the true value of α

$$\alpha = \frac{\lambda}{\Lambda} \cdot \frac{\eta}{1+\Phi}, \quad \text{where} \quad \Phi = \frac{l_1\phi_1 + l_2\phi_2}{\Lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7).$$

In the case of KCl it was shown that Φ was of the form $Bh^{-2/3}$. It will be hereafter shown that a function of the same form can be applied with a close approximation to the truth to the case of NaCl. Assuming that ϕ_1 and ϕ_2 are of the same form as Φ, we get

$$B\Lambda = B_1 l_1 + B_2 l_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8),$$

when B_1 and B_2 are the constants for the separate ions, and we get for the radions the expressions

$$\frac{1}{r_1} = l_1(1 + B_1 h^{-2/3}), \quad \frac{1}{r_2} = l_2(1 + B_2 h^{-2/3}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

It will be convenient to designate B, B_1, B_2, &c., as the hydration numbers.

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By direct determination of the quantities of each kind of ion which pass in opposite directions a given section of a solution in a certain time under the influence of a given current, HITTORF and others have obtained various series of values known as "migration numbers." These are tabulated for the anions, and are often represented by the letter $\mathfrak{n}$, so that

$$\mathfrak{n} = \frac{\text{so-called "mobility" of anion}}{\text{sum of so-called "mobilities" of anion and kation}}.$$

In order to make this fit in with the present nomenclature, it will be convenient to designate the Hittorf number by n_2 and the corresponding number for the kation by n_1. Then we have

$$n_1 = \frac{\alpha u}{\lambda}, \quad n_2 = \frac{\alpha v}{\lambda}, \quad n_1+n_2 = 1,$$

and for the values of n_1, n_2 at infinite dilution

$$N_1 = l_1/\Lambda, \quad N_2 = l_2/\Lambda.$$

Then, from equations (5), (6), and (7), we get

$$n_1 = \frac{l_1(1+\phi_1)}{\Lambda(1+\Phi)}, \quad n_2 = \frac{l_2(1+\phi_2)}{\Lambda(1+\Phi)},$$

or

$$\frac{n_1}{N_1} = \frac{1+\phi_1}{1+\Phi}, \quad \frac{n_2}{N_2} = \frac{1+\phi_2}{1+\Phi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10).$$

In the case of KCl and NaCl, equation (8) may be written in the form

$$B = B_1N_1+B_2N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11),$$

which is the relation between the hydration numbers and the migration numbers, and equation (10) gives us

$$n_2 = N_2+N_2(B_2-B)(B+h^{2/3})^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

There arises thus from our theory a simple linear relation between the series of Hittorf numbers n_2 for an electrolyte and the corresponding series of values of $(B+h^{2/3})^{-1}$. We shall see that this in fact holds, and that equation (12) gives us a ready means for obtaining N_2, the value of the Hittorf numbers at infinite dilution, a quantity of great importance in the theory of electrolytes.

(*b*) *Deduction of Constant for* NaCl.—In the former paper it was shown that in the case of KCl the function Φ was of the form $\Phi = Bh^{-2/3}$, and that the value of B was 3·33. This function was evaluated for KCl upon the hypothesis that the modified Van 't Hoff equation,

$$\log\frac{h}{\alpha} - \tfrac{2}{3}\log\frac{h}{1-\alpha} = C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13),$$

would hold accurately if the coefficient of ionisation were corrected for viscosity and

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variations of ionic size.* The coefficient of ionisation thus corrected according to our theory takes the form given above in equation (7).

In the case of NaCl it is now found that a similar accord with the law expressed in equation (13) can be obtained with a function of the same form and a value of $B = 2{\cdot}8$. This is shown in the following table in which are given corresponding values of m, λ, $\log h$, η, and the other magnitudes involved. The values of η are derived from large scale diagrams of the observed values. For obtaining the values of α there is taken the series of values of λ given by KOHLRAUSCH ('Sitz. der K. Preuss. Akad. der Wiss. zu Berlin,' 1900, p. 1002), $\Lambda = 108{\cdot}99$. The corrected values of α are calculated by means of equation (7) with the value for $\Phi = 2{\cdot}8h^{-2/3}$. The column headed C gives the value of the constant C in equation (13) as calculated from these data. The column headed ΔC shows the difference of C from the mean value 0·5049 (which is arrived at without reference to the value for $m = 0{\cdot}0001$, for the reasons given in the former paper).

TABLE VIII.

m.	Log h.	λ.	η.†	$\alpha = \frac{\lambda}{\Lambda} \cdot \frac{\eta}{1+\Phi}$.	C.	ΔC.	Δλ.
0·0001	5·74374	108·10	1·0004	0·9918	0·5274	+0·0225	−0·07
0·0002	5·44271	107·82	1·0007	0·9893	0·5052	+0·0003	±
0·0005	5·04477	107·18	1·0011	0·9833	0·5041	−0·0008	±
0·001	4·74375	106·49	1·0014	0·9765	0·5056	+0·0007	−0·01
0·002	4·44271	105·55	1·0018	0·9672	0·5060	+0·0011	−0·01
0·005	4·04475	103·78	1·0029	0·9495	0·5038	−0·0011	+0·02
0·01	3·74368	101·95	1·0041	0·9309	0·5053	+0·0004	−0·01
0·02	3·44259	99·62	1·0055	0·9064	0·5044	−0·0005	+0·03
0·05	3·04444	95·71	1·0087	0·8632	0·5028	−0·0021	+0·09
0·1	2·74304	92·02	1·0126	0·8189	0·5064	+0·0015	−0·08
0·2	2·44131	87·73	1·0184	0·7680	0·5048	−0·0001	+0·01
0·5	2·04105	80·94	1·0408	0·6889	0·5041	−0·0008	+0·05
1·0	1·73592	74·35	1·0857	0·6198	0·5064	+0·0015	−0·12

The column headed Δλ shows the difference between the observed and calculated value of λ, worked out (as in the former paper) from ΔC. The differences are somewhat more uneven than in the case of KCl, owing partly to the fact that the viscosity correction is larger and probably less accurate, and partly to the fact that the function $Bh^{-2/3}$ does not quite so well represent the correction. But the accurate correspondence of the experimental values with the modified Van 't Hoff law is in this case brought down to normal solutions, within the limits of experimental error; and the divergence is nowhere so great as one per thousand except on the extreme figure. The following table shows the values of α for KCl and NaCl calculated in the ordinary way and the values of α calculated from equation (7) or equation (13).

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* As to this hypothesis, *vide* Appendix, p. 155.

† Referred to water as unity.

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It will be seen that whilst the ordinary values of α widely diverge at a concentration of twice decinormal, the corrected values of α are nearly the same. Beyond this point the values diverge.*

TABLE IX.—Values of α.

m.	$\alpha = \frac{\lambda}{\Lambda}$.			$\alpha = \frac{\lambda}{\Lambda} \cdot \frac{\eta}{1+\Phi}$.		
	KCl.	NaCl.	Difference.	KCl.	NaCl.	Difference.
0·0001	0·9921	0·9918	3	0·9916	0·9981	−2
0·0002	0·9898	0·9893	5	0·9890	0·9893	−3
0·0005	0·9847	0·9834	13	0·9833	0·9833	±
0·001	0·9788	0·9771	17	0·9765	0·9765	±
0·002	0·9709	0·9684	25	0·9673	0·9672	+1
0·005	0·9563	0·9522	41	0·9499	0·9495	+4
0·01	0·9411	0·9354	57	0·9311	0·9309	+2
0·02	0·9221	0·9140	81	0·9065	0·9064	+1
0·05	0·8897	0·8782	115	0·8622	0·8632	−10
0·1	0·8611	0·8424	187	0·8194	0·8189	+5
0·2	0·8298	0·8049	249	0·7687	0·7680	+7

A greater divergence in more concentrated solutions is to be expected, and it is important to point out the reason therefor.

(*c*) *Distinction between Autolytes and Heterolytes.*—In a recent paper (BOUSFIELD and LOWRY, 'Phil. Trans.,' A, vol. 204, p. 256, 1905) attention was drawn to the difference between autolytic and heterolytic conductivity,† and it was shown that an electrolyte, such as sodium hydroxide, which was a good conductor in the melted state, showed clear indications of autolytic conductivity in the more concentrated solutions. It may be supposed that, as in dilute solution, water combination is the effective force producing ionisation, so in the melted state self-ionisation (resulting in autolytic conduction) is produced by the combination of the ions with molecules of the melted salt. In concentrated solution, this action probably still persists, and though we have mainly heterolytic ionisation produced by combination of ions with the solvent, we may have also some autolytic ionisation produced by combination of the ions with molecules of the solute.‡ KCl and NaCl belong to the class of autolytes,

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* Since this paper was communicated, I have made an examination of a group of nine salts with reference to this matter, and have come to the conclusion that no stress should be laid upon the near approach to equality of the values of α for KCl and NaCl. If water combination be the efficient cause of ionisation, one would expect that the great differences in the amount of water combination with different salts would lead to corresponding differences in the values of α. This turns out to be probably the case.

† These words were adopted by Dr. LOWRY and myself at the suggestion of Professor ARMSTRONG, to indicate the phenomena to which attention was called.

‡ This theory has been recently developed in a paper by Dr. LOWRY, 'Trans. Faraday Society,' vol. 1, 1905, p. 197, "An Application to Electrolytes of the Hydrate Theory of Solutions."

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and if we took a concentrated solution of either salt at a suitable pressure and a temperature above the melting-point of the salt, and were gradually to drive off the water, we should come gradually to a condition of things in which the conduction was entirely autolytic. Hence we cannot expect the near equality of ionisation which we find in the case of KCl and NaCl at the dilute end of the range to persist at the concentrated end where the idiosyncrasies of self-ionisation may produce a marked effect.

(*d*) *Mixtures of* KCl *and* NaCl *Normal Solutions.*—If two solutions have the same ionisation, there should be no change of molecular aggregation upon mixture, since, according to our theory, change of ionisation and change of ionic hydration are necessarily concomitant. Density measurements afford a very sensitive test of changes of molecular aggregation, and the results in this instance show that the change of aggregation upon mixing normal KCl and NaCl solutions in various proportions is very small.

The question of the conductivities of such mixtures has a bearing upon the validity of our main hypothesis. If the conductivities of such mixtures are calculated according to the so-called "law of mixtures," they all come out about 0·0003 too high; but calculated as below they come within 0·0001 of the correct values. The residual difference, both with the densities and the conductivities, may be due to the slight difference in ionisation in normal solutions which we attribute mainly to a difference in autolytic ionisation.

According to our hypothesis we have, for the conductivity of the solutions of KCl and NaCl respectively,

$$\kappa_1 = \frac{m\alpha}{1000} \cdot \frac{1}{\eta_1 r_1}, \quad \kappa_2 = \frac{m\alpha}{1000} \cdot \frac{1}{\eta_2 r_2},$$

where $\frac{1}{r}$ stands for the sum of the reciprocals of the radions in each case.

If we mix a volume V_1 of the KCl solution with a volume V_2 of the NaCl solution, and there is no contraction, we have for the concentrations of KCl and NaCl, respectively, in the mixture

$$m_1 = \frac{mV_1}{V_1+V_2}, \quad m_2 = \frac{mV_2}{V_1+V_2}.$$

Hence, if η be the viscosity of the mixture, we get for the portions of the conductivity of the mixture due to the KCl and NaCl respectively, assuming the coefficients of ionisation to be equal,

$$\frac{\alpha}{1000} \cdot \frac{mV_1}{V_1+V_2} \cdot \frac{1}{\eta r_1} \quad \text{and} \quad \frac{\alpha}{1000} \cdot \frac{mV_2}{V_1+V_2} \cdot \frac{1}{\eta r_2}$$

or

$$\frac{V_1}{V_1+V_2} \cdot \frac{\kappa_1 \eta_1}{\eta} \quad \text{and} \quad \frac{V_2}{V_1+V_2} \cdot \frac{\kappa_2 \eta_2}{\eta}$$

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and the sum of these portions gives the combined conductivity

$$\kappa = \frac{\kappa_1\eta_1 V_1 + \kappa_2\eta_2 V_2}{\eta (V_1 + V_2)}.$$

This, then, should be the true formula for the conductivity of mixtures of equal ionisation.

The formula for calculating the densities of the mixture is, of course, simply

$$\rho = \frac{\rho_1 V_1 + \rho_2 V_2}{V_1 + V_2}.$$

In the following table are set out the observed values of the viscosities, densities, and conductivities, together with the calculated values for the densities and conductivities according to the above mixture formulæ. The calculated values for the viscosities of the mixtures are dealt with elsewhere.

TABLE X.—Mixtures of Normal KCl and NaCl Solutions.

V_1 (KCl).	V_2 (NaCl).	Viscosity observed.	Density.		Difference.	Conductivity.		Difference.
			Observed.	Calculated.		Observed.	Calculated.	
4	0	0·01037	1·04497	—	—	0·0983	—	—
3	1	0·01063	1·04354	1·04353	+1	0·0920	0·0919	+1
2	2	0·01088	1·04211	1·04209	+2	0·0860	0·0859	+1
1	3	0·01116	1·04068	1·04065	+3	0·0800	0·0799	+1
0	4	0·01143	1·03921	—	—	0·0743	—	—

(*e*) *Hittorf Numbers a Function of the Radions.*—From equations (10) and (6) we see that, according to our theory,

$$\frac{n_1}{n_2} = \frac{l_1(1+\phi_1)}{l_2(1+\phi_2)} = \frac{r_2}{r_1},$$

and therefore, since $n_1 + n_2 = 1$, we have

$$\frac{1}{n_2} = 1 + \frac{r_2}{r_1}.$$

Hence the reciprocal of the Hittorf number should be a linear function of the ratio of the radions, and the radions for the ions of a given solute are inversely proportional to the migration numbers of the ions.*

The most useful way of testing this relation for KCl and NaCl, since it gives us certain important results and verifies the result predicted by our theory in a form

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* This simple relation leads to a different method of arriving at the radions from that which is followed in this paper, but it cannot be developed here.

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independent of any hypothesis, is to take the relation in the form shown in equation (12), viz.,

$$n_2 = \mathrm{N}_2 + \mathrm{N}_2 (\mathrm{B}_2 - \mathrm{B}) (\mathrm{B} + h^{2/3})^{-1} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (12),$$

which gives n_2 as a linear function of $(\mathrm{B}+h^{2/3})^{-1}$, and to set out the values of n_2 as ordinates upon the values of $(\mathrm{B}+h^{2/3})^{-1}$ as abscissæ. This is done in Diagrams II. and III. In the following tables are set out the values of the Hittorf numbers

TABLE XI.—Hittorf Numbers for KCl, calculated from the Radions. B = 3·33.

m.	$h^{2/3}$.	$(\mathrm{B}+h^{2/3})^{-1}$.	n_2.		Difference.
			Observed.	Calculated.	
0·01	313·2	0·0031	0·506	0·506	±
0·02	197·2	0·0050	0·507	$0{\cdot}506_3$	+0·7
0·05	107·0	0·0090	0·507	0·507	±
0·1	67·4	0·0141	0·508	0·508	±
0·2	42·4	0·0219	0·509	0·509	±
0·5	23·0	0·0380	0·513	0·512	+1
1·0	14·4	0·0565	0·514	0·515	−1

TABLE XII.—Hittorf Numbers for NaCl, calculated from the Radions. B = 2·8.

m.	$h^{2/3}$.	$(\mathrm{B}+h^{2/3})^{-1}$.	n_2.		Difference.
			Observed.	Calculated.	
0·05	107·1	0·0091	0·614	0·614	±
0·1	67·4	0·0142	0·617	0·616	+1
0·2	42·4	0·0221	0·620	0·620	±
0·5	23·0	0·0387	0·626	0·627	−1
1·0	14·4	0·0581	0·637	0·636	+1

according to KOHLRAUSCH ('Leitvermögen der Elektrolyte,' Ed. 1898, p. 201). There are also set out the values of $h^{2/3}$ calculated from the values of m given by KOHLRAUSCH, and the values of $(\mathrm{B}+h^{2/3})^{-1}$, taking, for KCl, B = 3·33 and, for NaCl, B = 2·8. There are also given the values of the Hittorf numbers calculated from the expressions

for KCl . . . . $n_2 = 0{\cdot}5055 + 0{\cdot}16\ (\mathrm{B}+h^{2/3})^{-1}$,
and for NaCl . . . . . $n_2 = 0{\cdot}610 + 0{\cdot}45\ (\mathrm{B}+h^{2/3})^{-1}$.

It will be seen that the agreement between observed and calculated values is very close. This linear relation is quite independent of the theory, but predicted by it, and therefore affords strong support to our hypothesis.

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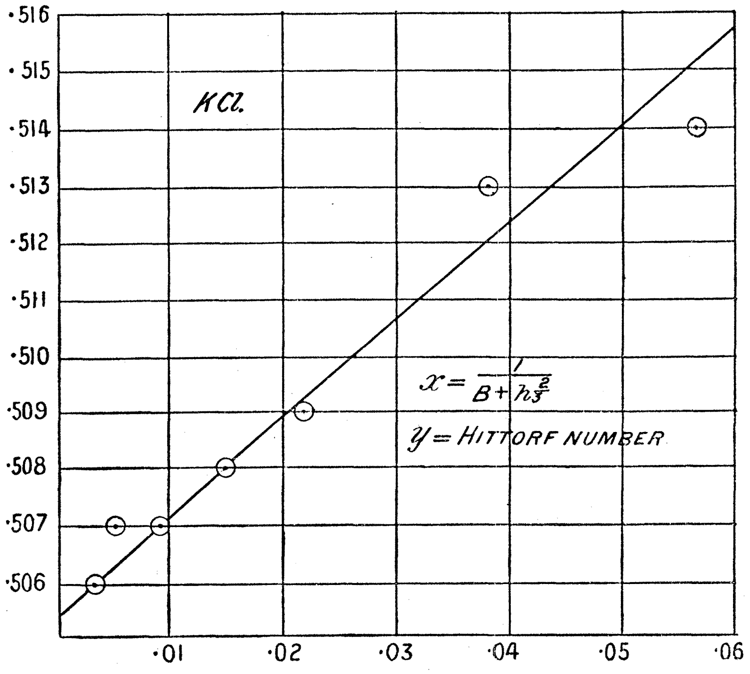

Diagram II.

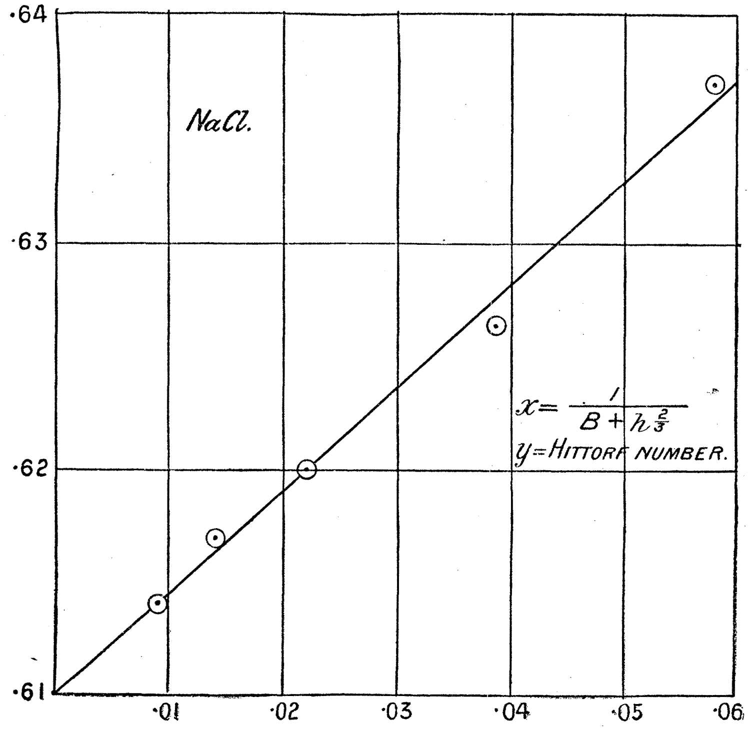

Diagram III.

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The value of these equations considered merely as empirical extrapolation formulæ, quite apart from the theory on which they are based, is clear. Putting $h = \infty$, they give us for the values of the Hittorf numbers at infinite dilution the figures 0·5055 and 0·610 respectively, and these are undoubtedly the numbers which must be obtained by extrapolation from the data given by Kohlrausch. But in Kohlrausch's 1900 paper (*loc. cit.*) he states, without giving further data, that he takes the value of the migration number for KCl as 0·503.

This paper is still the standard paper for the most accurate values of the conductivities of binary electrolytes with monovalent ions. The great accuracy of the values of λ is shown by their correspondence both with Kohlrausch's empirical formula and with the formula given in this paper—the modified Van 't Hoff law with the corrected coefficient of ionisation. Kohlrausch gives the values of the separate mobilities at infinite dilution as

$$\text{K}, \ l = 64{\cdot}67, \quad \text{Na}, \ l = 43{\cdot}55, \quad \text{Cl}, \ l = 65{\cdot}44,$$

and the values of Λ at infinite dilution as

$$\text{KCl}, \ \Lambda = 130{\cdot}10, \quad \text{NaCl}, \ \Lambda = 108{\cdot}99.$$

The Hittorf numbers which correspond to these mobilities should be

$$n_2 = \frac{65{\cdot}44}{130{\cdot}1} = 0{\cdot}5030 \quad \text{and} \quad \frac{65{\cdot}44}{108{\cdot}99} = 0{\cdot}6006.$$

Both of these diverge seriously from the actual values obtained by extrapolation from the data formerly given by Kohlrausch, especially the number for NaCl, which is 0·6004 as against 0·610. It might be well to reconsider the values of the mobilities of the separate ions, in the light of the above given extrapolation formulæ, unless it turns out that Kohlrausch had more accurate but unpublished data in his possession in 1900, since these numbers are of such fundamental importance in the theory of conductivities.

(*f*) *Deduction of Hydration Numbers and Values of Radions and Ionic Volumes.*—It remains now to deduce the hydration numbers for our present purpose.

Comparing the expressions for n_2 above given with equation (12) above set out, the KCl equation gives us for the Cl ion the value $B_2 = 3{\cdot}65$, and the NaCl equation gives us for the Cl ion the value $B_2 = 3{\cdot}54$. This is on the hypothesis that the values of the Hittorf numbers at infinite dilution are 0·5055 and 0·610 respectively. We shall assume, however, that Kohlrausch has data at his disposal which justify his taking the figure for KCl at 0·503 instead of 0·505, which makes the velocities of the K and Cl ions more nearly equal, and we shall provisionally fix the hydration number for Cl at the value 3·5. We then deduce the values for the K and Na ions from the equation

$$B\Lambda = B_1 l_1 + B_2 l_2,$$

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and thus get for the values for the K and Na ions,

$$B_{\rm K} = 3{\cdot}16, \quad B_{\rm Na} = 1{\cdot}75.$$

The complete series of hydration numbers is then as follows* :—

$$B_{\rm KCl} = 3{\cdot}33, \quad B_{\rm NaCl} = 2{\cdot}8, \quad B_{\rm Cl} = 3{\cdot}5, \quad B_{\rm K} = 3{\cdot}16, \quad B_{\rm Na} = 1{\cdot}75.$$

With the aid of the numbers for the separate ions the radions are calculated from the expression

$$r = l^{-1}\,(1+Bh^{-2/3})^{-1},$$

taking the values for l given by KOHLRAUSCH in his 1900 paper and above set out. The values so obtained are set out in the following tables :—

TABLE XIII.—Values of Radions and Ionic Volumes in KCl Solutions.

P.	$\frac{2}{3}\log h$.	$r_{\rm K}$.	$r_{\rm Cl}$.	$r_{\rm K}^3 \times 10^6$.	$r_{\rm Cl}^3 \times 10^6$.	I_v.
0	∞	0·01546	0·01528	3·692	3·569	7·261
1	$\bar{1}$·7418	0·01463	0·01437	3·128	2·968	6·096
2	$\bar{1}$·5382	0·01417	0·01387	2·843	2·671	5·514
3	$\bar{1}$·4178	0·01380	0·01348	2·627	2·448	5·075
4	$\bar{1}$·3315	0·01348	0·01314	2·448	2·268	4·716
6	$\bar{1}$·2081	0·01293	0·01256	2·163	1·981	4·144
Normal	$\bar{1}$·1542	0·01266	0·01227	2·029	1·852	3·881

TABLE XIV.—Values of Radions and Ionic Volumes in NaCl Solutions.

P.	$\frac{2}{3}\log h$.	$r_{\rm Na}$.	$r_{\rm Cl}$.	$r_{\rm Na}^3 \times 10^6$.	$r_{\rm Cl}^3 \times 10^6$.	I_v.
0	∞	0·02296	0·01528	12·107	3·569	15·676
1	$\bar{1}$·6714	0·02214	0·01422	10·848	2·876	13·724
2	$\bar{1}$·4678	0·02167	0·01365	10·177	2·545	12·722
3	$\bar{1}$·3474	0·02129	0·01321	9·648	2·303	11·951
4	$\bar{1}$·2611	0·02095	0·01282	9·198	2·137	11·335
Normal	$\bar{1}$·1573	0·02047	0·01229	8·578	1·852	10·430
6	$\bar{1}$·1377	0·02041	0·01218	8·506	1·806	10·312

In the above tables the values of the radions are given in ionic units as before defined. Expressed in the same unit the volume of an ion would be $\frac{4}{3}\pi r^3$. But we shall save trouble, with a gain of convenience, if we take the volume of the ions as $r^3 \times 10^6$. Our unit of ionic volume is therefore the volume of an ion whose radius measured in ionic units is 0·01. The volumes of the ions so calculated are also set

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* These numbers can only be regarded as approximately fixed. The existence of the discrepancies above indicated in the values of the HITTORF numbers introduces considerable uncertainty. This, however, is not of much consequence in the consideration of dilute solutions, since the magnitude of the radion is primarily fixed by the mobility at infinite dilution, and the hydration number affects only the rate of change of magnitude with dilution, which is small.

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out in the tables, together with the total volume of the pair of ions, which is indicated by the letter I_v, and is the sum of the volumes of the two ions.

The above are the figures which will most frequently be required. Where the values for other concentrations are wanted they can be calculated in the manner above indicated. It will be noticed that the volume of the sodium ion greatly exceeds that of either the K or Cl ion, indicating that the sodium ion is combined with about four times as much water as either of the other two ions.

PART IV.—IONIC SIZE IN RELATION TO DENSITY.

(*a*) *Solution Volume a Linear Function of Ionic Volume.*—As explained in the former paper, the solution volume derived from density observations is a measure of the amount of contraction which takes place on solution, and therefore a measure of the amount of water entering into combination with the solute. The ionic volumes at different dilutions should be nearly proportional to the amounts of water in combination with the ions, if the volume of water is large compared with the volume of the ionic nucleus. Hence, if our theory is correct, we ought to find the solution volume approximately a linear function of the ionic volume of the pairs of ions in dilute solutions.

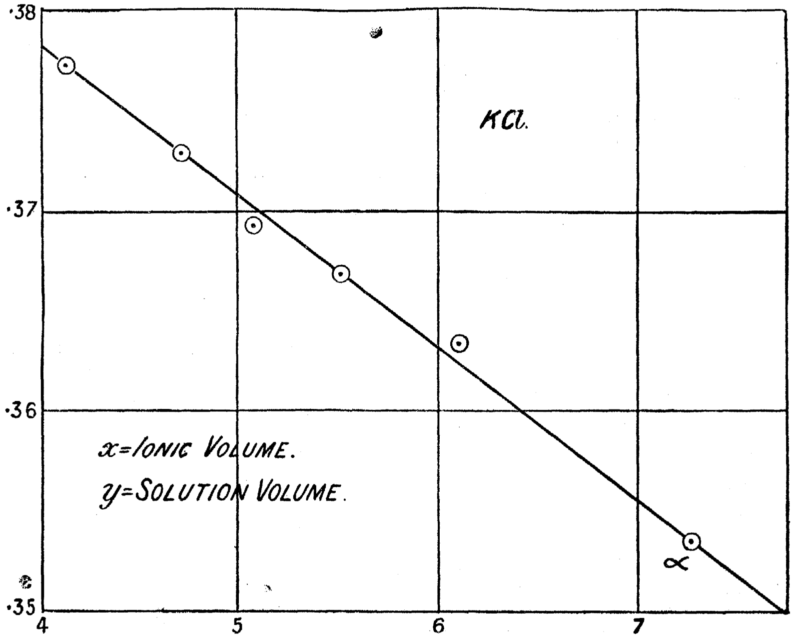

Diagram IV.

In the following tables are set out the solution volumes for KCl and NaCl solutions from 0 to 6 per cent., together with the ionic volumes taken from Tables XIII. and XIV. The solution volumes are calculated from the densities by means of the formula

$$V_s = \frac{1}{\rho_0} - \frac{100}{P}\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right),$$

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where ρ is the density of the solution at 18° C. and ρ_0 the density of water. The KCl densities used are given in the former paper. The NaCl densities used are those tabulated in Table I.

In diagrams IV. and V. the solution volumes are plotted as ordinates upon the ionic volumes as abscissæ. They give the following linear relations, from which the calculated values of V_s given in the tables are derived* :—

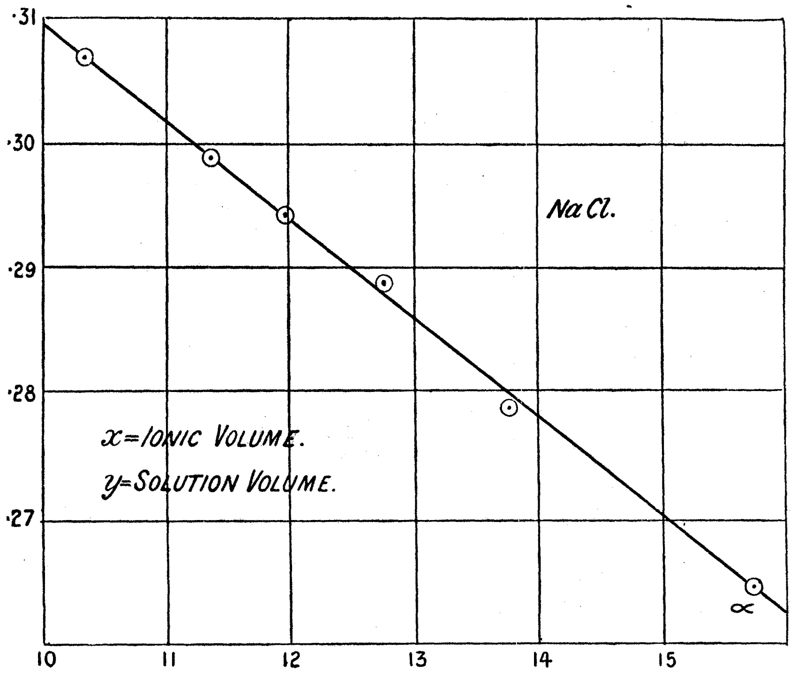

Diagram V.

For KCl . . . . . . $V_s = 0{\cdot}408 - 0{\cdot}0075\,I_v$,

for NaCl . . . . . . $V_s = 0{\cdot}390 - 0{\cdot}0080\,I_v$.

Table XV.—Ionic and Solution Volumes for KCl.

P.	I_v.	V_s (from density).	V_s calculated.	Difference.
6	4·144	0·377	0·377	±
4	4·716	0·373	0·373	±
3	5·075	0·369	0·370	−1
2	5·514	0·367	0·367	±
1	6·096	0·363	0·362	+1
0	7·261	—	0·354	—

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* In the former paper the hydration numbers B_1 and B_2 for K and Cl were taken as equal. The revised figures for KCl are therefore here given.

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TABLE XVI.—Ionic and Solution Volumes for NaCl.

P.	I_v.	V_s (from density).	V_s calculated.	Difference.
6	10·31	0·307	0·307	±
4	11·34	0·299	0·299	±
3	11·95	0·294	0·294	±
2	12·72	0·289	0·288	+1
1	13·72	0·279	0·280	−1
0	15·68		0·265	—

(*b*) *Density a Function of Radions.*—As in the former paper, we may now proceed to deduce a rational density formula for KCl and NaCl from the expressions for the solution volumes.

The densities are given by the expression

$$\frac{1}{\rho} = \frac{1}{\rho_0} - \frac{P}{100}\left(\frac{1}{\rho} - V_s\right).$$

As V_s has been expressed in each case as a function of the radions, we now have the densities expressed simply as a function of the radions. The agreement between observed values and values calculated from the radions is shown in the following tables :—

TABLE XVII.—Density of KCl, calculated from Radions.

P.	ρ observed	ρ calculated.	Difference.
6	1·03745	1·03747	−2
4	1·02437	1·02439	−2
3	1·01749	1·01792	+2
2	1·01148	1·01148	±
1	1·00507	1·00507	±

TABLE XVIII.—Density of NaCl, calculated from Radions.

P.	ρ observed.	ρ calculated.	Difference.
6	1·04201	1·04199	+2
4	1·02750	1·02748	+2
3	1·02027	1·02026	+2
2	1·01308	1·01309	−1
1	1·00592	1·00591	+1

In both cases the formulæ hold with great accuracy.

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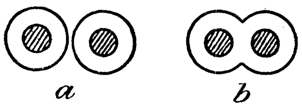
The above results are calculated as if the solution were fully ionised, the ionic volume for a pair of ions being taken as the sum of the volumes of the ions. Now, ionisation could only be complete for very dilute solutions, but we find that our formulæ hold without sensible loss of accuracy nearly up to normal solutions for which the coefficient of ionisation is less than 0·7. This is a matter of some practical importance hereafter, as it is an indication that we can take the ionic volume of the *un-ionised* molecules as being approximately equal to the sum of the volumes of pairs of ions with radii given by the formulæ obtained for the separate ions. This means that if we consider a pair of ions just after ionisation to be represented by *a* in the figure, we may consider a pair of ions just before ionisation to be represented by *b*. Hence, while a consideration of conductivities and mobilities only gave us a clue to the size of the ions themselves, the density formula indicates that in solutions of moderate dilution the volumes of the un-ionised molecules may be taken to follow approximately the same law.



Part V.—Ionic Size in Relation to Viscosity.

(*a*) *Viscosity a Function of the Radions.*—We discuss further on the general relation between the viscosity of a fluid and the sizes of the molecules of which it is composed. For the moment, it will suffice to say that it seems, *à priori*, probable that the *change of viscosity* caused by the introduction of foreign molecules

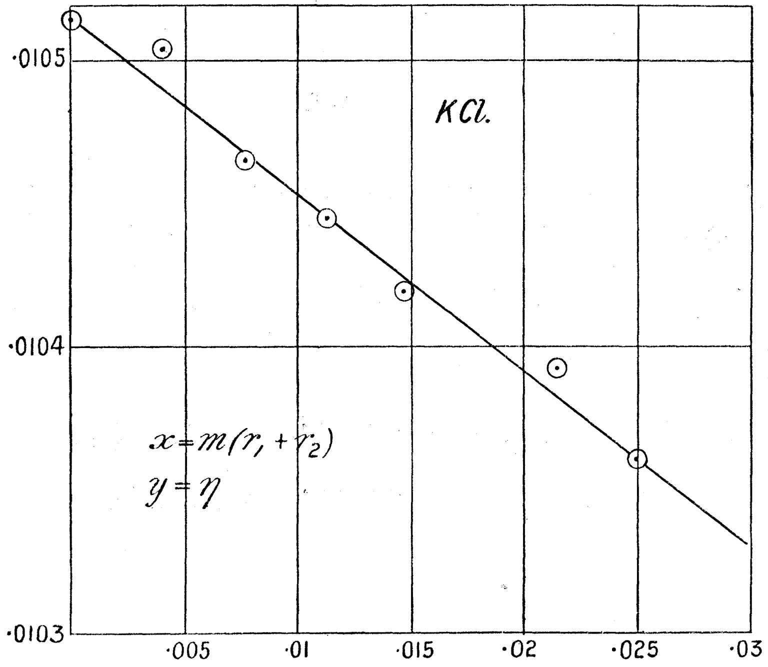


Diagram VI.

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into water would depend upon the number and size of the molecules so introduced. According to the theory postulated, an ion is a compound molecule consisting of the ionic nucleus with its envelope of water molecules, as are also the un-ionised molecules of the solute. Hence, if the theory be true, we should expect to find a close relation between the viscosity of the solution and the number and size of these aggregates. The number of molecules depends upon the concentration m, and the *size* upon the radions; the product $m(r_1+r_2)$ should therefore be a measure of the joint effect of the introduced ions upon the viscosity in dilute solutions.

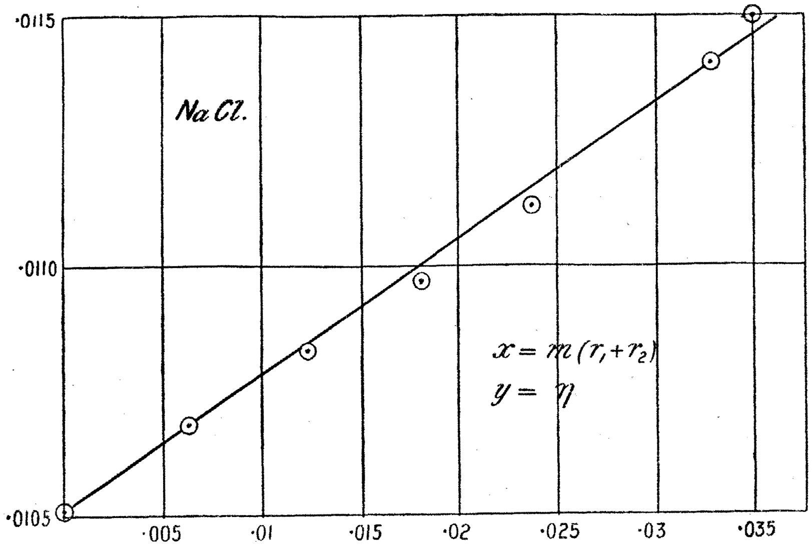

Diagram VII.

In the following tables are set out the concentrations, the sums of the radions, the products $m(r_1+r_2)$ and the observed and calculated viscosities for KCl and NaCl. In Diagrams VI. and VII. the viscosities are set out as ordinates upon the products $m(r_1+r_2)$ as abscissæ. It will be seen that the viscosity is approximately a linear function of $m(r_1+r_2)$, the expressions being

$$\text{for KCl} \quad . \quad . \quad . \quad \eta = 0{\cdot}010514 - 0{\cdot}00578\, m(r_1+r_2) \quad . \quad . \quad . \quad (14),$$

$$\text{for NaCl} \quad . \quad . \quad . \quad \eta = 0{\cdot}010514 + 0{\cdot}0272\, m(r_1+r_2) \quad . \quad . \quad . \quad . \quad (15).$$

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Table XIX.[*]—Viscosity of KCl Solutions, calculated from KCl Radions.

P.	m.	r_1+r_2.	$m(r_1+r_2)$.	η Observed.	η Calculated.	Difference.
0	0·0	0·03074	0·0	0·010514	0·010514	±
1	0·1347	0·02900	0·003906	0·010504	0·010491	+ 13
2	0·2712	0·02804	0·007605	0·010465	0·010470	− 5
3	0·4094	0·02728	0·011168	0·010445	0·010450	− 5
4	0·5493	0·02662	0·014623	0·010419	0·010430	− 11
6	0·8344	0·02549	0·021269	0·010393	0·010391	+ 2
Normal	1·000	0·02493	0·02493	0·010374	0·010374	±

Table XX.[*]—Viscosity of NaCl Solutions, calculated from NaCl Radions.

P.	m.	r_1+r_2.	$m(r_1+r_2)$.	η Observed.	η Calculated.	Difference.
0	0·0	0·03824	0·0	0·010514	0·010514	±
1	0·1720	0·03636	0·00625	0·01068	0·01068	±
2	0·3463	0·03532	0·01223	0·01083	0·01085	− 2
3	0·5232	0·03450	0·01805	0·01097	0·01100	− 3
4	0·7024	0·03377	0·02372	0·01112	0·01116	− 4
Normal	1·000	0·03276	0·03276	0·01143	0·01141	+ 2
6	1·068	0·03259	0·03480	0·01150	0·01146	+ 4

Moreover, if our reasoning is correct, the viscosities of mixtures of normal solutions of KCl and NaCl ought to be given by the formula (derived from the two preceding)

$$\eta = 0{\cdot}010514 - 0{\cdot}00578\alpha\, m(r_{\mathrm{K}} + r_{\mathrm{Cl}}) + 0{\cdot}0272(1-\alpha)\, m(r_{\mathrm{Na}} + r_{\mathrm{Cl}}) \quad . \quad . \quad . \quad (16),$$

where α represents the fraction of the volume of the mixture which consists of normal KCl, and $(1-\alpha)$ the fraction which consists of normal NaCl. m in this case is unity, since we are dealing with mixtures of normal solutions, and taking the sums of the radions at normal dilution from the preceding tables, the expression becomes

$$\eta = 0{\cdot}010514 - 0{\cdot}000144\alpha + 0{\cdot}000892(1-\alpha).$$

In the following table the observed values of the viscosity of mixtures of normal NaCl and KCl solutions are taken from Table VI. *ante*, and the calculated values are those given by the above equation.

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[*] The observed values of η for KCl from 0 to 6 per cent. are taken from the former paper. The values for the normal solutions of KCl and NaCl are taken from Table VI. Being taken from a different series of observations, they do not range well with the percentage series, but the discrepancy, for our present purpose, is not material.

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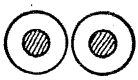
TABLE XXI.—Viscosity of Mixtures of Normal KCl and NaCl Solutions, calculated from the Radions.

α	η Observed.	η Calculated.	Difference.
1	0·01037	0·01037	±
0·75	0·01063	0·01063	±
0·5	0·01088	0·01089	− 1
0·25	0·01116	0·01115	+ 1
0·0	0·01143	0·01141	+ 2

The agreement between observed and calculated values in Tables XIX., XX., and XXI., is sufficient to show that the *chief element* which determines the viscosity of the solutions is the product $m(r_1+r_2)$. But the expressions (14), (15), and (16), are not put forward as true viscosity formulæ for KCl and NaCl. They are only intended to show that the viscosity of the solutions is *mainly dependent on the size of the radions.* The results tend strongly to confirm the fundamental hypothesis as to the character of the magnitudes which we have called "radions," and which we derived from the conductivities by the application of the Stokes theorem and the Van 't Hoff law.

It is surprising that the agreement with the observed values in Tables XIX. and XX. should be so close when we consider that at normal concentration the ionisation is less than 0·7. This may be explained on our theory in the following way. As indicated by the agreement upon the density formulæ (see Tables XVII. and XVIII.), *there appears to be no break in the hydration law as between ionised and un-ionised molecules.* Thus, if a represents the condition of things when the molecule is just sufficiently hydrated for ionisation, and (b) the condition of things shortly before ionisation, the same functions approximately express the ionic radii before and after ionisation. A little consideration will show that the expression $m(r_1+r_2)$ *takes the radion of the un-ionised molecule as* r_1+r_2. For if α be the ionisation, this would give us for the separate ions the products $\alpha m r_1$ and $\alpha m r_2$, and for the un-ionised molecule the product $(1-\alpha)m(r_1+r_2)$. The sum of the three products is simply $m(r_1+r_2)$. This seems to explain why the linear relation, which might be expected to obtain between $m(r_1+r_2)$ and η for dilute solutions, does in fact approximately persist up to normal solutions.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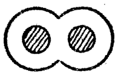
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(b) *References to Previous Theories.*—The results obtained in the last section suggest considerations which may tend to a great simplification of our ideas in reference to the internal friction of fluids. Hitherto, very diverse theories have been advanced in order to account for the *apparent* anomalies in the viscosity of liquids, and various general formulæ have been proposed in order to express the experimental

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facts. Arrhenius proposed a formula of the form $\eta = C^m$ ('Zeit. f. Phys. Chem.,' 1, 285, 1887) to express the viscosity of a solution in terms of the concentration. For a mixture he proposed $\eta = C_1^{m_1}C_2^{m_2}C_3^{m_3}\ldots$ This formula in the case of KCl, where the constants for the two ions could be taken as approximately equal, reduced to the form $\eta = C_1^{m_1}C_2^{2m_2}$. In this form Euler ('Zeit. f. Phys. Chem.,' 25, 536, 1898) further investigated the matter. Neither of these formulæ turned out to be of general validity.

Grüneisen* ('Wiss. Abh. der Phys.-Tech. Reichsanstalt,' 4, 239, 1905) has elaborated a very accurate formula which takes the form

$$\frac{\eta - \eta_0}{m} = A\alpha + B(1-\alpha) + Cm,$$

where α is the coefficient of ionisation. Grüneisen has given the constants A, B, and C for a large number of electrolytes, and the formula brings out the important fact that the equivalent viscosity increment for electrolytes has *a minimum value* at concentrations varying from normal to $\frac{1}{5}$ normal. But Grüneisen's results stop short of furnishing a theoretical explanation of the facts. He observes (*loc. cit.*, p. 250):—

"That the minimum found with electrolytes should result from experimental errors, I regard as impossible. The only doubt is whether it is peculiar to electrolytes. I held this idea at first, but further experiments are certainly desirable. This suggests the possibility that the phenomenon may be accounted for by the dissociation of the molecules. On this supposition, the increase of the equivalent viscosity increment at greater dilution would be most simply explained by assuming that the *dissociation of the molecule always increases the friction of the solution.*"

Other observers who have theorised on supposed viscosity anomalies have tendered widely differing explanations. Arrhenius ('Zeit. f. Phys. Chem.,' 1, 296, 1887), referring to the lowering of viscosity, or so-called "negative friction," which results from the solution of certain substances, such as KCl, suggests that the *lowering of the friction is a result of electrolytic dissociation.* Euler ('Zeit. f. Phys. Chem.,' 25, 541, 1898) suggests that the change of viscosity in a solution consists of two components, first, an increase which is in inverse proportion to the mobilities of the ions, and, secondly, a component depending upon the compression (electrostriction) of the water through the electric charge of the ions. Wagner ('Zeit. f. Phys. Chem.,' 46, 871, 1903) controverts both these views, and adumbrates the view (based upon mixtures of alcohol, nitro-toluol, and other organic compounds) that the viscosity of a mixture depends upon the viscosity of its components, and that this will account for "negative friction."

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* Grüneisen's paper came to my notice whilst the present paper was in progress. His results afford strong confirmation to the hypothesis with which this paper is concerned, and a fuller reference is made to them later.

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One matter of great importance has been established in relation to viscosity, viz., that it is an "additive" property. This is due, in the first instance, to the work of REYNER ('Zeit. f. Phys. Chem.,' 2, 744, 1888) and WAGNER ('Zeit. f. Phys. Chem.,' 5, 46, 1890), and finally has been placed on a very firm foundation by GRÜNEISEN (*loc. cit.*).

(*c*) *À priori Considerations leading to a General Viscosity Formula.*—The results obtained in section (*a*) appear to point to the simple view that the viscosity of a solution is in the main merely a function of the number and size of its component molecules. We there saw that the *change of viscosity* of a liquid could be approximately expressed in terms of the size and number of the molecules of the solute introduced, both in the case of simple salts and of mixtures. But the viscosity of the solvent itself should be capable of similar expression. According to STOKES' theorem, the resistance to a very small sphere moving in a viscous medium is proportional to its radius. *À priori* this would lead us to the hypothesis that the viscosity of the medium itself would be proportional to r, in the case of a simple homogeneous medium consisting of molecules of radius r. Furthermore, this, in conjunction with the result which appears in section (*a*), suggests the hypothesis that the viscosity of a heterogeneous medium, consisting of molecules of radii r_1, r_2, r_3, ..., in proportions m_1, m_2, m_3, ..., could be expressed as

$$\eta = \frac{C_1 m_1 r_1 + C_2 m_2 r_2 + \dots}{m_1 + m_2 + \dots}.$$

In the general case, the different sorts of molecules might have different coefficients of friction, so that the constants C_1, C_2, C_3 would have different values. But, in the case of aqueous solutions, supposing the ions and molecules to be sufficiently hydrated, we should have, both in the case of water molecules and molecules of the solute, the friction of water on water. We will confine ourselves to this case and take the constant as the same for the different molecules, so that our expression would be simply

$$\eta = C\Sigma mr/\Sigma m.$$

This would possibly exclude the case of H and OH ions, which are possibly little, it at all, hydrated. In case of molecules differing much from the spherical form either a special coefficient of friction would have to be assigned to them, or their radion would have to be taken as their largest or some mean dimension.

The numbers m_1, m_2 might be regarded as expressing either the relative numbers of the various molecular species or their relative amounts reckoned by the total volumes occupied by each species in the solution. In some cases it will make no difference which view we adopt, in others it may make a serious difference. It is easier to work with relative volumes, and we find that such a volume relation holds for the changes of viscosity of mixtures of normal KCl and NaCl solutions. We shall therefore adopt this alternative in order to test the hypothesis, bearing in mind,

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however, that this is merely a tentative selection from the alternatives. Hence, if β_1, β_2, β_3, ... represent the total volumes occupied in the solution by each species of molecules, we propose to represent the viscosity of the solution as

$$\eta = \mathrm{C}\Sigma\beta r/\Sigma\beta.$$

In order to simplify matters, we shall always take $\Sigma\beta = 1$, so that β_1, β_2, β_3, ... will be the fractions of the total volume of the solution occupied by each species of molecules, and the expression becomes

$$\eta = \mathrm{C}\Sigma\beta r.$$

(*d*) *Extended Conception of the Radion.*—The conception of the radion as the average molecular radius of any set or sets of molecules, basing the average on a volume reckoning, will greatly simplify the hypothesis. We adopted the term "radion" as a convenient contraction for the *radius of the ion*, which we supposed to be an aggregate consisting of the ionic nucleus and water molecules. The expressions which we obtained for the ionic radius in terms of hydration, which were of the form

$$r = r_\infty(1+\mathrm{B}h^{-2/3})^{-1},$$

clearly indicated that the radius so derived must be an *average* radius, since the hydration h is a *continuously* varying magnitude, whilst the actual numbers of molecules must be whole numbers and must vary *per saltum*. We may now generalise the conception of the radion and use the term to indicate the average radius of any group of molecules. Suppose, then, we have a liquid containing a volume β_1 of molecules of radius r_1, a volume β_2 of molecules of radius r_2, and so on, the radion of this liquid, taking the average on a basis of volumes, would be

$$\mathrm{R} = \Sigma\beta r/\Sigma\beta.$$

If we always consider a unit of volume so that $\Sigma\beta = 1$, and therefore β_1, β_2, ... are the fractions of the total volume occupied by each set of molecules, then we have for the radion, or average molecular size, simply $\mathrm{R} = \Sigma\beta r$.

It follows also that if r_1, r_2, r_3, ... be the radions of different volume fractions β_1, β_2, β_3 ... of the liquid (instead of the radii of the ultimate molecules) the radion of the liquid is still expressed as $\mathrm{R} = \Sigma\beta r$.

(*e*) *The General Viscosity Formula.*—The general viscosity formula for aqueous solutions in which the coefficients of friction between the molecules may be taken as constant throughout, to which we were led by *à priori* considerations, was $\eta = \mathrm{C}\Sigma\beta r$.

The conception of the radion enables us to express this simply as $\eta = \mathrm{CR}$, where R is the radion of the whole solution. Also if the liquid be composed of various composite constituents having radions r_1, r_2, r_3, ... for the respective volume fractions β_1, β_2, β_3, ..., the viscosity of the separate fractions (if they could be separated) would

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be Cr_1, Cr_2, Cr_3, ..., and the viscosity of the whole $\eta = C\Sigma\beta r = CR$, if R is the radion of the whole, since $R = \Sigma\beta r$.

We have determined the values of the radions for K, Na and Cl ions in Part III. (*g*) of this paper. In extending the conception of the radion to the molecules of the solvent or to other molecules, its magnitude in any particular case must be measured in the same ionic units, and by reference to the scale furnished by the ions whose radions we have determined. Thus we know, upon our theory, the radions of K and Cl ions, which are approximately equal, and we find that the introduction of such ions into water makes, speaking roughly, no change in the viscosity of the water. This tells us at once (if we neglect the small change in the water radion which is probably produced by the solute) that *the radion of water is of about the same magnitude as the radions of the* K *and* Cl *ions.* As a fact, the introduction of these ions slightly diminishes the viscosity of water and hence the radion of the uncombined water in the solution should be somewhat greater than the radions of K and Cl ions.

There is good reason for believing that the introduction of a solute into water somewhat lowers the radion of water, since the process of abstraction of water molecules by the solute breaks up some of the molecular complexes of the uncombined water and therefore lowers the average molecular size of the un-combined water. The investigation of the amount of this lowering is a complex matter, and we shall neglect it, as it does not seriously affect the general character of our results, though it involves a slight loss of accuracy.

The fundamental constant C of our viscosity equation is calculated from the experimental data in reference to water and KCl and NaCl solutions, but it is not necessary to give the details of the process. The justification of the value given and also of the theory involved is to be found in the correspondence between observed and calculated values given later. The value of C determined from the data at 18° C. is C = 0·54.

No closer adjustment of its value is at present attainable. This value gives the radion for pure water as

$$R = \eta/C = \frac{0 \cdot 010514}{0 \cdot 54} = 0 \cdot 01947.$$

(*f*) *Experimental Verification.*—We now proceed to test the hypothesis by reference to the experimental data before given. Taking first the simple case of mixtures of KCl and NaCl normal solutions, we have here solutions which do not materially change their state of aggregation upon mixing. We can therefore take the radions of the solutions before mixing as being identical with their radions when mixed. The radion of the normal KCl solution is

$$\eta/C = \frac{0 \cdot 010374}{0 \cdot 54} = 0 \cdot 01929.$$

The radion of the NaCl normal solution is

$$\eta/C = \frac{0 \cdot 011433}{0 \cdot 54} = 0 \cdot 02117.$$

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In this case the value of C makes no difference to our results. The water radion is not required, as we can take the radion of *the whole of each solution*, before mixing, as the basis of our calculation, thus accounting for the total number of molecules both of solvent and solute. The constant is here introduced as illustrating the procedure in the more complex case. Care must be taken to distinguish between the radion of a salt solution as a whole, and the radion of the salt in solution.

In the following table are set out the observed values of the viscosities for the mixtures, and the values calculated from the equation $\eta = 0{\cdot}54\ \Sigma\beta r$, where β_1, β_2 are the fractions of KCl and NaCl respectively in unit volume of the mixture.

TABLE XXII.—Viscosities of Mixtures of KCl and NaCl Normal Solutions, calculated from their Radions.

β_1.	β_2.	η observed.	η calculated.	Difference.
1	0	0·01037	0·01037	±
0·75	0·25	0·01063	0·01063	±
0·5	0·5	0·01088	0·01090	−2
0·25	0·75	0·01116	0·01117	−1
0	1	0·01143	0·01143	±

Let us now apply the equation to the general case of a salt in solution. Let r be the radion of the uncombined water in the solution (which may be different from the radion of water itself). Let r' be the radion of the hydrated solute (comprising both ions and molecules). Let β be the total fraction of unit volume of the solution which is occupied by the hydrated ions and molecules of the solute. Then $1-\beta$ will be the fraction which is occupied by uncombined water. Then the equation $\eta = \mathrm{C}\Sigma\beta r$ takes the form $\eta/\mathrm{C} = (1-\beta)\,r+\beta r'$, or

$$\eta/\mathrm{C}-r = \beta\,(r'-r) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17).$$

This may be regarded as the fundamental viscosity equation for a simple salt solution. It may be noted that if we take r as the radion for pure water, we have its viscosity $\eta = \mathrm{C}r$, so that for solutions so dilute that the value of the water radion is not sensibly changed by the addition of the solute we may say

$$\delta\eta = \mathrm{C}\beta\,(r'-r),$$

which indicates that if the radion of the solute is less than that of water $\delta\eta$ is negative. This is in fact the case for KCl, the solutions of which have a less viscosity than water. Cases of "negative friction" therefore are readily explicable upon the present hypothesis.

So far the matter is simple, but in applying the above equation in practice we

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meet with difficulties which are small for very dilute solutions, but increase with the concentration.

In considering what we are to take as the radion of the group of un-ionised molecules, our difficulties begin. But we saw that in our rough viscosity formula for KCl and NaCl no serious error up to 6 per cent. was introduced by taking the radion of the un-ionised molecule as the sum of the radii of the united ions. This would probably give too large a value, which would vitiate our equations at higher concentrations, but, within the range of concentration with which we are dealing, does not introduce a serious error.

The calculation of the *volumes* of the un-ionised molecules presents a further difficulty. The un-ionised molecules must be combined with less water than the pairs of ionised molecules, but a consideration of the density law showed us that we might without serious error up to 6 per cent. reckon the volumes of the molecules as though they were composed of pairs of spheres, the radii of which followed the same law as the ionic radii. We shall therefore continue to reckon the volume in this way, though it may give too much volume to the un-ionised molecule, in a proportion which will increase with increasing concentration.

The total fraction of volume of the solution occupied by any set of ions will be approximately proportional to the number and volume of the individual ions, but not exactly. If r_1, r_2 be the radions of the separate ions of an electrolyte (reckoned in ionic units), we reckoned the separate ionic volumes as $v_1 = r_1^3 \times 10^6$, $v_2 = r_2^3 \times 10^6$, leaving out the multiplier $\frac{4}{3}\pi$ and introducing the multiplier 10^6 for the sake of convenience. We also took the volume of *either a pair of ions or a molecule* as

$$I_v = V_1 + V_2 = (r_1^3 + r_2^3) \times 10^6.$$

In order to calculate the absolute volumes from the ionic volumes, we must introduce a suitable factor γ. The total volume occupied by the hydrated ions and molecules in a litre of solution being approximately proportional to mI_v, let us represent the fraction of a unit of volume of the solution which is occupied by the ions and molecules of the solute by $\gamma m I_v$. γ will be nearly the same for different molecules, but not quite, since molecules of different volumes do not exactly displace proportionate numbers of molecules of the solvent.

If α be the coefficient of ionisation, the volumes occupied by the ions and molecules respectively will then be

$$\alpha\gamma m V_1, \quad \alpha\gamma m V_2, \quad (1-\alpha)\gamma m (V_1 + V_2).$$

Therefore in unit volume of solution the total volume of the hydrated ions and molecules is $\gamma m (V_1 + V_2)$ or $\gamma m I_v$, and the volume of uncombined water is $(1 - \gamma m I_v)$.

Hence, if r is the radion of water, the general equation $\eta = C\Sigma\beta r$ becomes

$$\frac{\eta}{C} = (1-\gamma m I_v) r + \alpha\gamma m V_1 r_1 + \alpha\gamma m V_2 r_2 + (1-\alpha)\gamma m (V_1 + V_2)(r_1 + r_2),$$

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which reduces to

$$\frac{\eta/\mathrm{C}-r}{\gamma m\,(\mathrm{V}_1+\mathrm{V}_2)} = \mathrm{R}-r, \quad \text{where} \quad \mathrm{R} = r_1+r_2-\alpha\,\frac{\mathrm{V}_1 r_2+\mathrm{V}_2 r_1}{\mathrm{V}_1+\mathrm{V}_2}.$$

R is of course (*vide* equation *ante*) the radion of the solute, and the equation, when written in the form

$$\eta/\mathrm{C} = r+\gamma m\mathrm{I}_v\,(\mathrm{R}-r),$$

is seen to be identical with the general equation (17) before given.

In the following tables are set out the values of R and η, calculated from the above expressions, together with the necessary data for the calculations. The ionic data are taken from Tables XIII. and XIV. The values of α are obtained by setting out the corrected values of α (given in Table IX.) on a large-scale curve and taking off the values for the different values of m. The observed values of the viscosities are the same as in Tables XIX. and XX. The values of γ used for the calculation were 0·032 for KCl and 0·030 for NaCl. These are mean values calculated from the separate sets of figures for the two salts. The value of r, the radion of the uncombined water, is taken as 0·01946 in both cases. The value of C was worked out from these two sets of figures and the mean value 0·54 was obtained, as before mentioned.

Considering the various slight inaccuracies involved in the approximations above detailed, the correspondence between observed and calculated values appears to be sufficiently close to support the general character of the hypothesis as to the relation between the radions of the various species of molecules and the viscosity of the solution. The two sets of viscosities are calculated from *the same formula, with practically the same constants*, the only difference in the constants employed being that the factor γ is taken as 0·032 for KCl and 0·030 for NaCl.

It must be borne in mind that the purpose was not to construct an accurate empirical formula, which is fairly easy where plenty of constants are available. But in the cases examined the simple formula $\eta = \mathrm{C}\Sigma\beta r$ is found to be adequate to express, with a near approach to accuracy, the viscosities of the solutions up to normal strength in the case of KCl and 5 per cent. in the case of NaCl, *showing that, with such aqueous solutions, the viscosity depends mainly upon the average size of all the molecules present.*

The departure of the calculated values from the observed values for the NaCl solutions at about normal strength may be partly due to our approximations breaking down before normal strength is reached. But we are more inclined to attribute this departure to a cause which was considered in Part III. (c) of this paper. With an autolytic solute, it is probable that there is some *association of the molecules of the solute in* more concentrated solutions. In the case of KCl, with its comparatively small ions and molecules, this does not appear. But in the case of NaCl, with its larger hydrated molecules, the radion of the solute might be notably increased by the

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TABLE XXIII.—Viscosity of KCl Solutions, calculated from the Radions.

P.	m.	r_{K}.	r_{Cl}.	V_{K}.	V_{Cl}.	I_v.	α.	R.	η observed.	η calculated.	Difference.
0	0	0·01546	0·01528	—	—	7·261	1·0	0·01537	0·01051	0·01051	±
1	0·1347	0·01463	0·01437	3·128	2·968	6·096	0·798	0·01743	0·01050	0·01048	+2
2	0·2712	0·01417	0·01387	2·843	2·671	5·514	0·745	0·01760	0·01047	0.01046	+1
3	0·4094	0·01380	0·01348	2·627	2·448	5·075	0·7095	0·01761	0·01045	0·01044	+1
4	0·5493	0·01348	0·01314	2·448	2·268	4·716	0·6805	0·01757	0·01042	0·01042	±
6	0·8344	0·01293	0·01256	2·163	1·981	4·144	0·639	0·01759	0·01039	0·01040	−1
Normal	1·000	0·01266	0·01227	2·029	1·852	3·881	0·620	0·01720	0·01037	0·01036	+1

TABLE XXIV.—Viscosity of NaCl Solutions calculated from the Radions.

P.	m.	r_{Na}.	r_{Cl}.	V_{Na}.	V_{Cl}.	I_v.	α.	R.	η observed.	η calculated.	Difference.
0	0	0·02296	0·01528	12·107	3·569	15·676	1·0	0·02121	0·01051	0·01051	±
1	0·1720	0·02214	0·01422	10·848	2·876	13·724	0·7805	0·02397	0·01068	0·01068	±
2	0·3463	0·02167	0·01365	10·177	2·545	12·722	0·7245	0·02427	0·01083	0·01085	− 2
3	0·5232	0·02129	0·01321	9·648	2·303	11·941	0·685	$0\cdot02438_5$	0·01097	0·01100	− 3
4	0·7024	0·02095	0·01282	9·198	2·137	11·335	$0\cdot656_5$	0·02435	0·01112	0·01114	− 2
Normal	1·000	0·02047	0·01229	8·578	1·852	10·430	0·620	0·02424	0·01143	0·01132	+11
6	1·068	0·02041	0·01218	8·506	1·806	10·312	0·619	0·02416	0·01150	0·01135	+15

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presence of a small fraction of the solute in the form of associated molecules. This, in our view, probably accounts for the observed viscosity values for NaCl in the neighbourhood of 6 per cent. coming out notably higher than the calculated values.

It would be going too far from the purpose of this paper to follow up the considerations which are suggested by the view of the relation of viscosity to molecular size which is here presented. It must suffice to point out that to all the various speculative questions as to the meaning of "negative friction," as to the effect of dissociation in increasing or decreasing friction, and so on, this theory has but one reply—the change in viscosity in aqueous solutions under varying conditions is mainly dependent upon the change in the average molecular size which takes place, that is, to the change in the radions of the components of the solution.

(*g*) *Comparison with* GRÜNEISEN'S *Results.*—The important paper by GRÜNEISEN, which came to hand during the progress of this paper, to which reference has already been made, tends strongly to confirm the propositions here advanced. GRÜNEISEN gives viscosity measurements for some nineteen solutions of electrolytes, and finds that in all cases, as dilution increases, the equivalent viscosity increment comes to a minimum, and then increases with further dilution. This is in accord with our results, according to which, as dilution takes place, ionisation at first *diminishes* the viscosity by breaking up the molecules and afterwards *increases* it, owing to the increase of the ionic radii with further dilution.

Moreover, GRÜNEISEN has dissected the equivalent viscosity increments due to the separate ions at infinite dilution, and has found values of the equivalent viscosity increments for hypothetical "normal solutions of the separate ions." For monovalent ions he finds that these viscosities may be approximately expressed by the equation

$$\eta - 1 = -0\cdot207 + 13\cdot3/l,$$

where η is the viscosity of a "normal solution of ions" and l is the mobility of such ions. The viscosity of water is reckoned as unity.

This result is not exactly comparable with the present results, but an approximate comparison may be made. If r be the radion of the uncombined water, r' the radion of a set of ions of mobility l, β the fraction of unit volume of the solution occupied by 1 gram-molecule of the ions, we should have, according to our theory, for the viscosity of the hypothetical "normal solution of ions,"

$$\eta = \mathrm{C}\{(1-\beta)\,r + \beta r'\}.$$

If r_0 be the radion of pure water, we should have $\eta_0 = \mathrm{C}r_0$, and therefore, for the change in viscosity caused by the introduction of 1 gram-molecule of the ions, we should have (remembering that according to our theory $r' = 1/l$)

$$\Delta\eta/\mathrm{C} = (1-\beta)\,r - r_0 + \beta/l.$$

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Grüneisen's expression, for the purpose of comparison, may be written

$$\Delta\eta = -a + b/l.$$

But according to our view, the value of β differs for each ion, and hence Grüneisen's expression, in which a and b are given constant values for *all* monovalent ions, could only approximately represent the general result, and in fact it does not profess to do more. But the important point is that Grüneisen's empirical result, which brings out the equivalent viscosity increment of a "normal solution of ions" as approximately a linear function of the reciprocal of the mobility, is in complete accord with and so far confirms the general theory of ionic sizes herein set forth.*

Part VI.—Ionic Size in Relation to Freezing-point Depression.

(*a*) *General Considerations.*—As is well known, the so-called "molecular" freezing-point depression, which is normally nearly constant for dilute solutions of non-electrolytes, varies with the concentration in the case of dilute solutions of electrolytes, and tends at great dilution to a value which is for binary electrolytes about double the value for a dilute solution of non-electrolytes. This may partly be attributed to the ionisation of the electrolyte, upon the theory that the ionisation of a molecule of a binary electrolyte breaks up one molecule into two ions, each of which ions produces the effect of a molecule in the depression of the freezing-point.

Hence, if

Δ = observed freezing-point depression,
N = gram-molecules of solute per 1000 grammes of solvent,
α = ionisation coefficient,

the *effective* number of gram-molecules per 1000 grammes of solvent is $N(1-\alpha)+2N\alpha$, that is to say, $N(1+\alpha)$.

Hence, upon this theory, the true molecular freezing-point depression is $\Delta/N(1+\alpha)$, instead of Δ/N, the ordinary so-called molecular depression. In order to distinguish the fraction $\Delta/N(1+\alpha)$ it will be convenient to refer to it as the "effective molecular freezing-point depression," or more shortly by the initials E.M.D., since upon the ionisation theory $N(1+\alpha)$ is proportional to the actual or *effective* number of molecules present.

When we have evaluated the E.M.D. for any electrolyte, we still find it not constant but variable with the concentration, and it is probable that this variation is intimately connected with the varying ionic volume of the solute, which represents, upon our hypothesis, the varying amount of water in combination with the ions.

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* Grüneisen's relation for divalent ions is $\eta - 1 = -0{\cdot}207 + 24/l$. This appears to indicate that divalent ions have a different coefficient of friction from monovalent ions, possibly because they are not approximately spherical.

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Now, in order to make a just comparison, we ought to consider the value for the E.M.D. in relation to the ionic volumes in the neighbourhood of the freezing-point. But the data at or near 0° C. necessary for making the comparison accurately do not exist. We have for KCl and NaCl obtained the ionic volumes and the ionisation coefficients at 18° C., and it is probable that the *ratios* of these values will not be sufficiently different at 0° C. to vitiate our comparison, though the values themselves will be sensibly different. We will therefore make a comparison on this basis.

(*b*) *Freezing-point Depression a Linear Function of Ionic Volume.*—Jahn (' Zeit. Phys. Chem.,' 1904, 50, p. 136) gives a series of values of the molecular freezing-point depression for KCl and NaCl which we will use as the basis of our comparison. All his observations are taken in pairs, on solutions of nearly equal concentration. In most cases we have taken the mean of his duplicate observations, but in a few cases the separate results are taken, in order to indicate the order of his maximum errors of observation.

In the following tables are set out for KCl and NaCl the following data :—

N, the number of gram-molecules of the solute per 100 grammes of water,

h, the hydration, *i.e.*, the number of gram-molecules of water per gram-molecule of solute,

r, the radions, of which the cube is calculated from h, as described in Part III. (f),

I_v, the ionic volume, which in our units is equal to the sum of the cubes of the radions $\times 10^6$,

Δ/N, the molecular depression of the freezing-point as given by Jahn,

α, the true ionisation coefficient at 18° C.,

$D = \Delta/N(1+\alpha)$, the effective molecular depression of the freezing-point.

Table XXV.—KCl.

N.	$h^{-2/3}$.	$r_K^3 \times 10^6$.	$r_{Cl}^3 \times 10^6$.	I_v.	Δ/N.	α.	D observed.	D calculated.	Difference.
0·3395	0·03345	2·736	2·561	5·297	3·337	0·727	1·93	1·94	−1
0·3377	0·03333				3·344		1·94		±
0·259	0·02790	2·870	2·698	5·568	3·37	0·749	1·93	1·93	±
0·201	0·02357	2·981	2·813	5·794	3·385	0·769	1·91	1·92	−1
0·151	0·01945	3·092	2·929	6·021	3·41	0·790	1·90	1·91	−1
0·100	0·01483	3·223	3·066	6·289	3·472 3·457	0·819	1·91 1·90	1·90	+1 ±
0·076	0·01231	3·298	3·145	6·443	3·485	0·837	1·90	1·89	+1
0·0504	0·00938	3·387	3·239	6·626	3·50	0·863	1·88	1·89	−1
0·0378	0·00774	3·439	3·294	6·733	3·55	0·878	1·89	1·88	+1
0·02552	0·00596	3·511	3·370	6·881	3·547	0·896	1·87	1·875	±
0·02527	0·00592				3·562		1·88		
∝	—	—	—	7·261	—	—	—	—	

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TABLE XXVI.—NaCl.

N.	$h^{-2/3}$.	$r_{Na}^3 \times 10^6$.	$r_{Cl}^3 \times 10^6$.	I_v.	Δ/N.	α.	D observed.	D calculated.	Difference.
0·301	0·03087	10·339	2·623	12·96	3·40	0·737	1·96	1·96	±
0·2528	0·02748	10·516	2·709	13·23	3·41	0·751	1·95	1·95	±
0·2011	0·02359	10·723	2·813	13·54	3·43	0·769	1·94	1·94	±
0·1505	0·01945	10·952	2·929	13·88	3·44	0·790	1·92	1·93	− 1
0·1004	0·01485	11·210	3·065	14·28	3·46 3·48	0·819	1·90 1·91	1·91	− 1 ±
0·07581	0·01231	11·358	3·144	14·50	3·49	0·837	1·90	1·90	±
0·05035	0·00937	11·531	3·239	14·77	3·50	0·863	1·88	1·89	− 1
0·03798	0·00765	11·634	3·297	14·93	3·55	0·878	1·89	1·89	±
0·02520	0·00591	11·739	3·356	15·10	3·52 3·57	0·896	1·86 1·88	1·88	− 2 ±
∞	—	—	—	15·68	—	—	—	—	—

In the last columns are given the calculated values of D and the differences from the observed values.

In diagrams VIII. and IX. are set out the values of the effective molecular depression as ordinates, upon the values of $(I_\infty - I_v)$ as abscissæ. I_∞ stands for the value of the ionic volume at infinite dilution (see Tables XIII. and XIV.). The values of I_∞ are

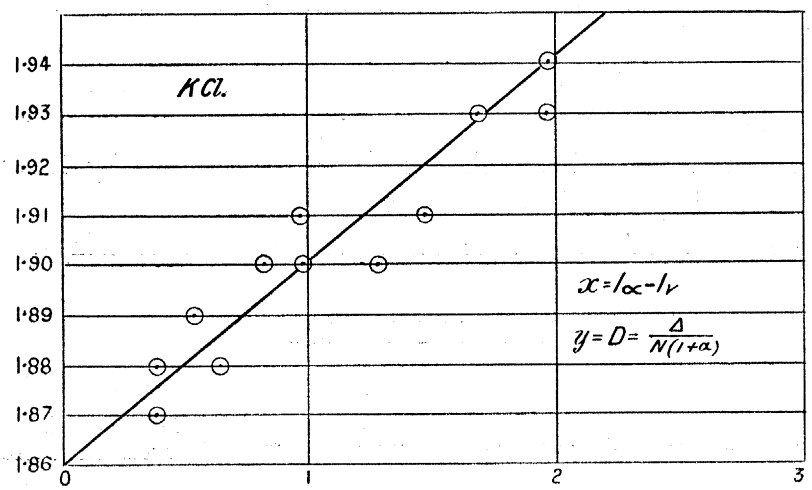

Diagram VIII.

for KCl . . . . $I_\infty = 7·261$,
for NaCl . . . . $I_\infty = 15·68$.

It will be seen at a glance that we have a linear relation between the E.M.D. and the ionic volume, and that *the limiting value of the E.M.D. at infinite dilution is* 1·86, the same value as has been determined for non-electrolytes such as sugar.

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The deviations from the straight line are within the limits of experimental error. These limits are indicated by the duplicate values at the dilute ends, which differ by 0·01 in the case of KCl and by 0·02 in the case of NaCl. The expressions which give the values of the E.M.D. are :—

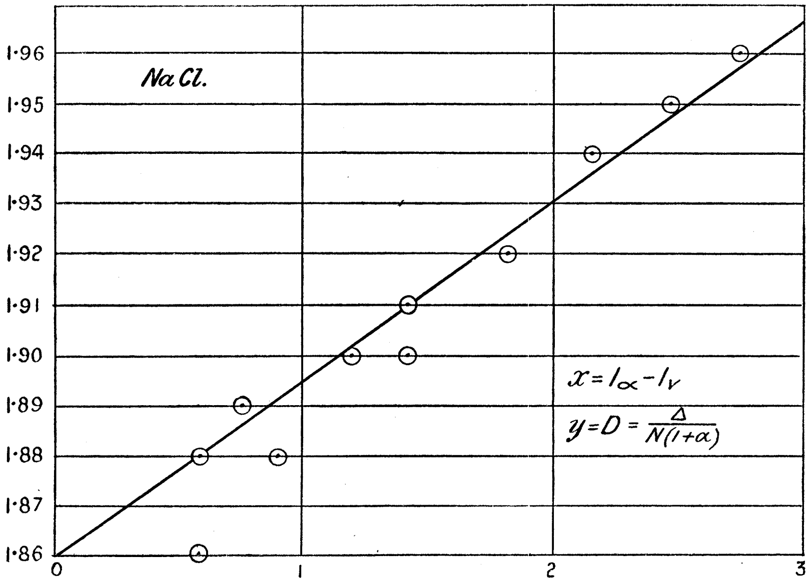

Diagram IX.

For KCl . . . . $D = 1·86+0·041\,(I_\infty - I_v)$,

,, NaCl . . . . $D = 1·86+0·037\,(I_\infty - I_v)$.

The values of D calculated from these expressions, together with the differences from the observed values, are set out in the last columns of the above tables. The maximum difference in the case of KCl is 0·01, and in the case of NaCl, 0·02, and these are the same as the duplicate experimental differences.

It thus appears that the freezing-point depression, both for electrolytes such as KCl and NaCl, and for non-electrolytes such as sugar in dilute solution, may be expressed by one formula, viz. :—

$$\frac{\Delta}{N\,(1+\alpha)} = 1·86 + C\,\delta I_v,$$

since in the case of a non-electrolyte like sugar the ionisation is nil, so that $\alpha = 0$, and the molecular volume is nearly constant in dilute solution,* so that $\delta I_v = 0$.

---

* We are justified in saying that the molecular volume of sugar is nearly constant in dilute solution owing to the facts :—

(*a*) That the solution volume of sugar in dilute solution is nearly constant.

(*b*) That the viscosity of dilute sugar solutions is almost a linear function of the concentration.

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Moreover, the value of C is nearly the same for both KCl and NaCl, though the ionic volumes are very different.

(*c*) *Effective Molecular Freezing-point Depression a Linear Function of Solution Volume.*—In Part IV. (*a*) it was shown that the solution volume was a linear function of the ionic volume, that is the sum of the cubes of the radions, and it has now been shown that the effective molecular freezing-point depression is also a linear function of the ionic volume. If this be so, we can dispense with our hypothesis and obtain the effective molecular freezing-point depression as a linear function of the solution volume.

With the object of testing this relation, the density measurements of KCl and NaCl at 0° C. were made. From these have been already derived formulæ expressing the solution volume in terms of hydration (see Part II. (*c*)). If we denote by δV_s the difference between the solution volume at a given concentration, and the solution volume at infinite dilution, the expressions we obtained in Part II. (*c*) may be written

for KCl . . . . $\delta V_s = 0{\cdot}059\,(1-\gamma)$,
for NaCl . . . . $\delta V_s = 0{\cdot}089\,(1-\gamma)$,

where $\gamma = (1+Bh^{-2/3})^{-3}$, B having the value 6 for KCl and 4 for NaCl. At infinite dilution for KCl, $V_s = 0{\cdot}3068$, and for NaCl, $V_s = 0{\cdot}2125$.

By means of these formulæ we can calculate the solution volumes corresponding to the concentrations at which JAHN's freezing-point observations were made, and we find, as our theory led us to anticipate, that the effective molecular freezing-point depression is in fact a linear function of the solution volume calculated from the densities.

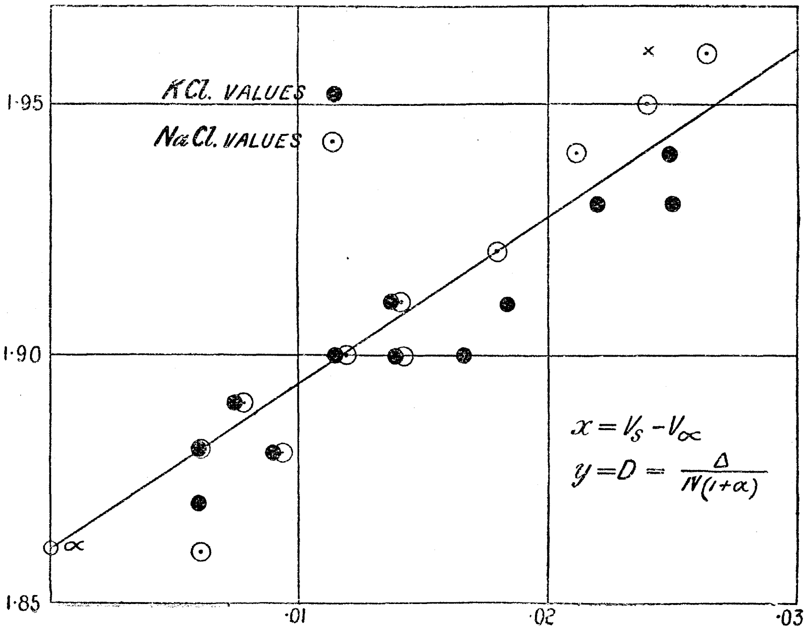

Diagram X.

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In the following tables are set out the figures given by JAHN for KCl and NaCl, side by side with the solution volumes calculated from the densities. In Diagram X. are set out the values of the E.M.D., both for KCl and NaCl, as ordinates upon the values of δV_s as abscissæ. The maximum experimental error in the values of the E.M.D. is 0·02, so that within the limits of experimental error we have the E.M.D. a linear function of δV_s. The values of the E.M.D. appear to range a little higher for NaCl than for KCl, as was the case when they were set out upon the ionic volumes. This may represent a real difference, as there is reason to suppose that the density of the water, in combination with the ions and molecules, is slightly different in the two cases. In the comparison with ionic volumes we gave two different expressions, with constants of slightly different value. In the present case we will take one single formula to represent the E.M.D. for both KCl and NaCl, viz., $D = 1·86 + 3·3\ \delta V_s$.

The calculated values of D are set out in the tables, and the differences from the observed values given in the last columns.

TABLE XXVII.—KCl.

$h^{-2/3}$.	V_s.	δV_s.	D observed.	D calculated.	Difference.
0·03345 0.03333	0·3317	0·0249	1·93 1·94	1·94	− 1 ±
0·02790	0·3287	0·0219	1·93	1·93	±
0·02357	0·3251	0·0183	1·91	1·92	− 1
0·01945	0·3234	0·0166	1·90	1·91	− 1
0·01483	0·3206	0·0138	1·91 1·90	$1·90_5$	±
0·01231	0·3182	0·0114	1·90	1·90	±
0·00938	0·3157	0·0089	1·88	1·89	− 1
0·00774	0·3142	0·0074	1·89	1·88	+ 1
0·00596 0·00592	0·3127	0·0059	1·87 1·88	1·88	− 1 ±

TABLE XXVIII.—NaCl.

$h^{-2/3}$.	V_s.	δV_s.	D observed.	D calculated.	Difference.
0·03087	0·2388	0·0263	1·96	1·95	+ 1
0·02748	0·2364	0·0239	1·95	1·94	+ 1
0·02359	0·2336	0·0211	1·94	1·93	+ 1
0·01945	0·2304	0·0179	1·92	1·92	±
0·01485	0·2266	0·0141	1·90 1·91	1·91	− 1 ±
0·01231	0·2244	0·0119	1·90	1·90	±
0·00937	0·2218	0·0093	1·88	1·89	− 1
0·00765	0·2202	0·0077	1·89	1·88	+ 1
0·00591	0·2185	0·0060	1·86 1·88	1·88	− 2 ±

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If, as in the comparison with ionic volumes, we take two slightly different constants for KCl and NaCl, we obtain differences between observed and calculated values which are substantially identical with those given in Tables XXV. and XXVI.

Since, in the case of non-electrolytes such as sugar, we have in dilute solutions the solution volume practically constant and the ionisation nil, we arrive again at an expression which is valid both for electrolytes such as KCl and NaCl, and non-electrolytes such as sugar, viz. :

$$\Delta/\text{N}\,(1+\alpha) = 1{\cdot}86+\text{C}\;\delta\text{V}_s.$$

This result is, of course, quite independent of the hypothesis which it is the purpose of this paper to test, and gives us a ready means of extrapolation for arriving at the true molecular freezing-point depression at infinite dilution based on simultaneous density observations.

Whether expressed in terms of ionic volumes (according to our hypothesis) or in terms of solution volumes, the meaning of the relation seems to be clear. Both δI_v and δV_s are proportional to the decrease in the amount of water in combination with a given weight (say a gramme equivalent) of the solvent as concentration increases. Hence we get the result that in dilute solutions *the increment of the effective molecular depression of the freezing-point above* 1·86 *as concentration increases is proportional to the decrement of the amount of water in combination with a gram-molecule of the solute.* To discuss the physical meaning of this relation would carry us too far from the main lines of the present paper.

(*d*) *Correction of Freezing-point Depression by Reference to Ionic Volumes.*—In Part V. (*f*) our experimental results were shown to lead to the view that the viscosity of an aqueous solution was proportional to the average molecular size of all the molecules. We were able also to calculate approximately from the viscosity data the actual volume occupied by a gramme equivalent of the solute at a given concentration. If I_v be the ionic volume at a given concentration, and the volume in litres of a gramme equivalent of ions be taken as γI_v, it was found in the case of KCl, from the viscosity data, that $\gamma = 0{\cdot}032$. Hence the volume of a gramme equivalent of KCl in solution is 32I_v, reckoned in cubic centimetres.

To find the volume of the KCl itself, we have the density of solid fused KCl which is given by QUINCKE as 1·87, which gives for the volume of 1 gramme of liquid KCl 0·551 cub. centims., allowing 3 per cent. for expansion from the solid to the liquid state. This gives the volume of a gramme equivalent of liquid KCl as 41·1 cub. centims., and therefore the volume of water combined with 1 gramme equivalent of KCl is

$$32\text{I}_v-41{\cdot}1 \text{ cub. centims.}$$

Hence, if we have a solution of KCl containing N gram-molecules dissolved in 1000 grammes water, we have approximately for the amount of free water

$$w = 1000-\text{N}\,(32\text{I}_v-41{\cdot}1).$$

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Let us now calculate the effective molecular freezing-point depression, not upon the *total* amount of water present but upon the amount of *free* water obtained from the above expression. The expression for the E.M.D. calculated in this way is

$$D' = \frac{\Delta}{N'(1+\alpha)},$$

where N′ is the number of gram-molecules of the solute in 1000 grammes of *free* water. We have then

$$N' = \frac{1000N}{w} \quad \text{and} \quad D' = D \cdot \frac{w}{1000}.$$

In the following table are set out the values of D resulting from Jahn's data (taken from the column "D calculated" in Table XXV.), together with the other data necessary for the calculation of D′, the effective molecular depression of the freezing-point calculated on the amount of free water. It will be seen that we obtain *a constant value* for D′, up to about twice decinormal solutions, the mean value of the constant being 1·867.

Table XXVIIIa.

N.	I_v.	*w*.	D.	D′.	Difference from mean.
		grammes.			
0·201	5·794	971	1·92	1·864	− 3
0·151	6·021	977	1·91	1·866	− 1
0·100	6·289	984	1·90	1·869	+ 2
0·076	6·443	987·5	1·89	1·866	− 1
0·0504	6·626	991	1·89	1·873	+ 6
0·0378	6·733	993	1·88	1·867	±
0·0254	6·881	995	1·875	1·866	1

We may recapitulate the method by which the above figures are obtained. The ionic volumes measured in arbitrary units having only relative values were deduced from the corrected conductivity data. The factor γ which was required to give us the absolute volume for a gramme equivalent of KCl in solution, with its combined water, was deduced from the viscosity data. The volume of free water so deduced, when applied to calculate the effective molecular freezing-point depression, gives us for this *a constant value*, which is in correspondence with the value obtained for non-electrolytes. We thus obtain a striking confirmation of the validity of the hypothesis and of the method pursued, and at the same time illustrate the dependence of the various physical properties considered upon the varying size of the hydrated ions caused by the varying amount of water with which they combine.*

---

* The corresponding values for NaCl solutions give the constant as 1·860 for high dilutions, but for lower dilutions the value is too low, indicating over-correction. This may indicate that either the ionic volumes deduced for NaCl, or the value 0·030 for γ, may be slightly too high. The larger ionic volume for the Na ion renders any error much more effective in disturbing the constant.

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PART VII.—IONIC SIZE IN RELATION TO REFRACTIVE POWER.

The refractive power of a medium is known to be closely related to the state of aggregation of its components. According to the hypothesis which we are discussing, the combination of water with the ions and molecules of a solute changes the state of aggregation of the fraction of the water which is so combined, and also, to some extent, of the uncombined water. Hence we should expect to find a close relation between ionic volume and refractive power.

If n = refractive index of a solution at 18° C.,
n_0 = refractive index of water at same temperature,
m = concentration (gramme equivalents per litre of solution),

the simplest measure of the refractive power is $(n-n_0)/m$, say $\Delta n/m$, which we may refer to shortly as the equivalent refractive power of the solute.

A recent paper by DINKHAUSER ('Sitz.-Ber., Wien. Akad. Wiss.,' July, 1905, p. 1001) gives the values of this equivalent refractive power for solutions of KCl and NaCl. The values for KCl appear to be a little rough, but the values for NaCl seem to be particularly accurate.*

In the following tables are given the concentrations, the values of log h and of the radions and ionic volumes calculated therefrom, together with the values of the equivalent refractive power given by DINKHAUSER. In Diagrams XI. and XII. are set out the values of the equivalent refractive power as ordinates upon the values of the ionic volumes as abscissæ. It will be seen that a linear relation appears, which may be expressed by the equations

for KCl . . . . $\Delta n/m = 0{\cdot}009145 + 0{\cdot}0001845\ \mathrm{I}_v$,
for NaCl . . . . $\Delta n/m = 0{\cdot}00855\ + 0{\cdot}0001271\ \mathrm{I}_v$.

The values calculated from these expressions and the differences from observed values are also given in the tables. If I_∞ be the value of I_v at infinite dilution (see Tables XIII. and XIV.), and we put $\Delta\mathrm{I}_v = \mathrm{I}_\infty - \mathrm{I}_v$, the expressions may be written

for KCl . . . . $\Delta n/m = 0{\cdot}01048 - 0{\cdot}0001845\ \Delta\mathrm{I}_v$,
for NaCl . . . . $\Delta n/m = 0{\cdot}01054 - 0{\cdot}0001271\ \Delta\mathrm{I}_v$.

---

* For KCl, DINKHAUSER gives the value 9·80 for m = 1·234 (p. 1020) and the same value for m = 1 (p. 1025). The whole series shows that the latter value must be inaccurate. For m = 0·812 he gives the value 10·06 (p. 1020) and for m = 0·5 the value 10·05. The former of these values is rejected. The values for concentrations less than one-fiftieth normal are also rejected, since the large factor by which the observed value of n must be multiplied to get the equivalent refractive power greatly magnifies any error. These discrepancies are partly due to the fact that DINKHAUSER has combined his own results with those of other observers.

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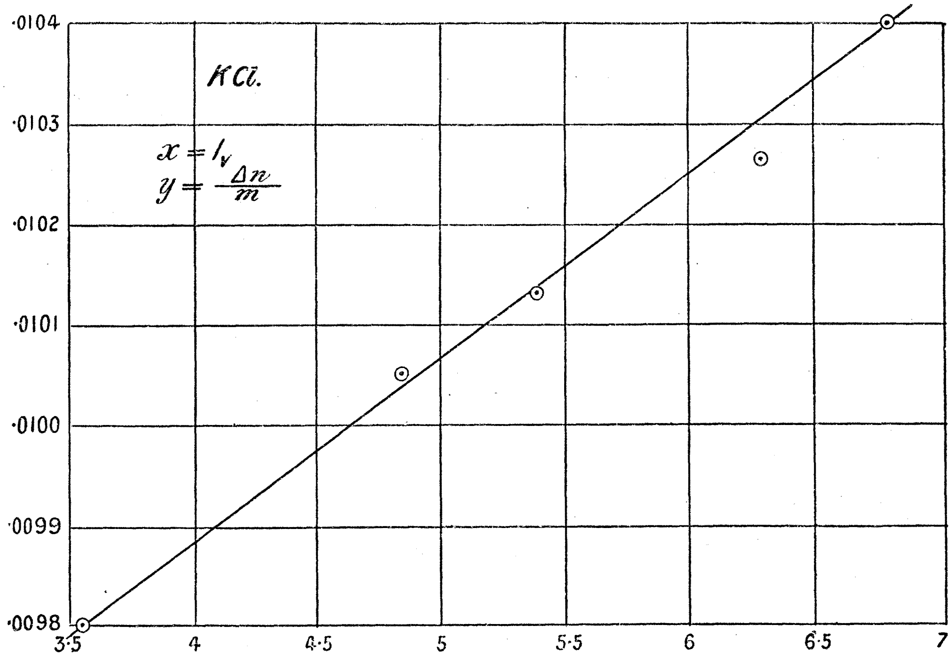

Diagram XI.

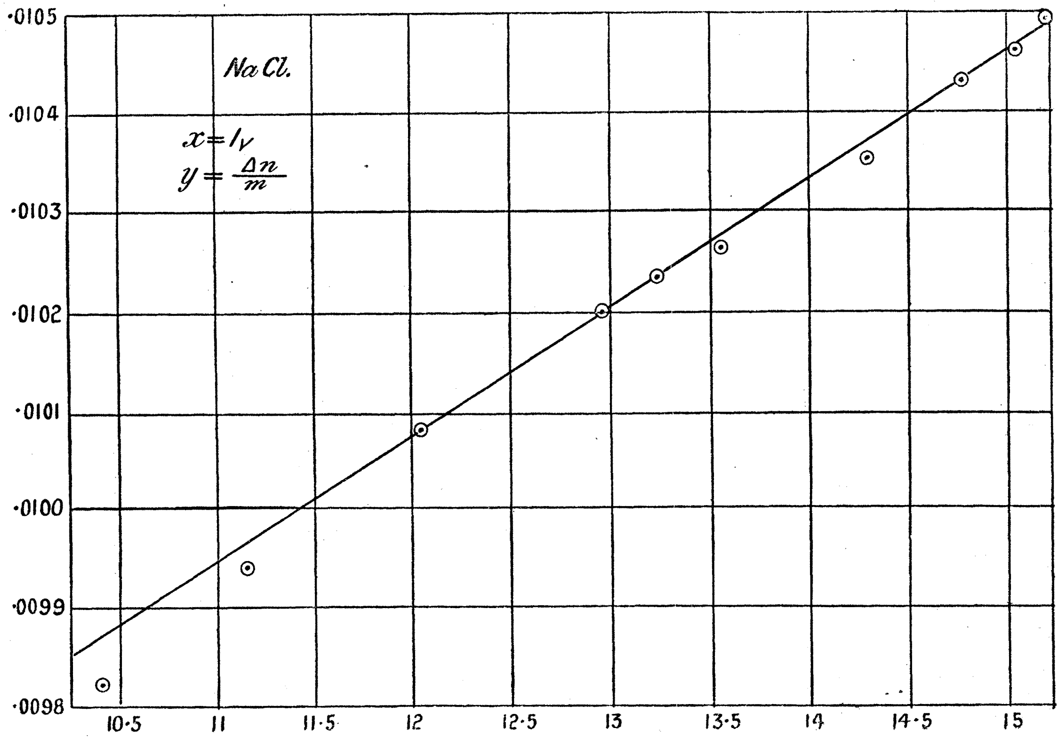

Diagram XII.

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TABLE XXIX.—KCl.

m.	log h.	r_K^3.	r_{Cl}^3.	I_v.	$\Delta n/m$ observed.	$\Delta n/m$ calculated.	Difference.
0·03	3·26629	3·474	3·331	6·805	0·0104	0·0104	±
0·1	2·74257	3·222	3·065	6·287	0·01026	0·01030	− 4
0·311	2·24734	2·775	2·601	5·376	0·01013	0·01014	− 1
0·5	2·03874	2·508	2·328	4·836	0·01005	0·01004	+ 1
1·234	1·63710	1·866	1·687	3·553	0·00980	0·00980	±

TABLE XXX.—NaCl.

m.	log h.	r_{Na}^3.	r_{Cl}^3.	I_v.	$\Delta n/m$ observed.	$\Delta n/m$ calculated.	Difference.
0·02	3·44259	11·798	3·385	15·18	0·01049	0·01048	+ 1
0·03	3·26646	11·694	3·331	15·03	0·01046	0·01046	±
0·05	3·04444	11·532	3·240	14·77	0·01043	0·01043	±
0·1	2·74304	11·211	3·066	14·28	0·01035	0·01036	− 1
0·2	2·44131	10·725	2·813	13·54	0·01026	0·01027	− 1
0·25	2·34404	10·521	2·712	13·23	0·01023	0·01023	±
0·3	2·26451	10·336	2·622	12·96	0·01020	0·01020	±
0·5	2·04105	9·711	2·331	12·04	0·01008	0·01008	±
0·75	1·86290	9·089	2·062	11·15	0·00994	0·00997	− 3
1·0	1·73590	8·578	1·852	10·43	0·00982	0·00988	− 6

Table XXX. shows that the relation in the case of NaCl down to half normal solutions is particularly accurate.

In Part IV. (*b*) it was shown that the ionic volume might be calculated from the radions of the separate ions with fair accuracy down to nearly normal solutions. It is obvious, however, that, as the proportion of un-ionised solute becomes greater, it becomes more and more inaccurate to take the ionic volume of a molecule as the sum of the volumes of a pair of ions. It is probable that the divergence of the calculated values in Table XXX. for the last two observations tabulated is due to this error in the calculation of the ionic volumes. Now, as in the case of freezing-point depression, so here, having shown previously that solution volume is a linear function of ionic volume, we deduce that the equivalent refractive power, which is shown above to be a linear function of ionic volume, must therefore also be a linear function of solution volume. The series of values given by DINKHAUSER for KCl is not sufficiently good to make this comparison useful. But the series for NaCl shows clearly the remarkable fact that the equivalent refractive power is *accurately a linear function of the solution volume right through the range of dilute and concentrated solutions.*

In Table XXXI. are set out the solution volumes, calculated from the density data

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given by DINKHAUSER,* the values of the equivalent refractive power as given by him, together with the values calculated from the linear relation

$$\Delta n/m = 0{\cdot}01643 - 0{\cdot}0215\,V_s.$$

It will be seen that the difference between observed and calculated values nowhere exceeds more than a unit in the last place of decimals, from a concentration of one-tenth normal to five times normal.

It may be noted that we have here a clue which may enable us to obtain the ionic volume in concentrated solutions.† In dilute solutions we have shown that the ionic volume, as derived from the radions, is a linear function of the solution volume. It seems probable that this linear relation persists through concentrated solutions, and that the solution volume may therefore enable us to calculate accurately the ionic volume in concentrated solutions. But we cannot follow up this clue in the present paper.

TABLE XXXI.—NaCl.

m.	V_s.	$\Delta n/m$ observed.	$\Delta n/m$ calculated.	Difference.
0·1	0·2831	0·01035	0·01034	+1
0·25	0·2888	0·01023	0·01022	+1
0·5	0·2960	0·01008	0·01007	+1
0·75	0·3016	0·00994	0·00995	−1
1·0	0·3071	0·00982	0·00983	−1
2	0·3235	0·00946	0·00947	−1
3	0·3350	0·00922	0·00923	−1
4	0·3461	0·00898	0·00899	−1
5	0·3567	0·00876	0·00876	±

PART VIII.—CONCLUDING OBSERVATIONS.

Let us now briefly review the main course of the argument, as developed in this and the former paper, in relation to our fundamental hypothesis.

As our starting point we took the Van 't Hoff dilution law, which we may express by saying that if D represents the concentration of the dissociated portion of a solute and U the concentration of the undissociated portion, reckoned by means of the

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* DINKHAUSER gives the values of $\Delta\rho/m$, where $\Delta\rho$ is the difference of the density ρ of the solution from the density ρ_0 of water at the same temperature, and m is the concentration. The solution volumes can be calculated from the expression

$$V_s = \frac{1}{\rho_0}\left(1 - \frac{\Delta\rho}{m}\cdot\frac{10^3}{E}\right),$$

where E is the weight of a gram-molecule of the solute.

† It would be more accurate in concentrated solutions to use the term molecular volume instead of ionic volume, but unfortunately the term molecular volume has been already misapplied to indicate the product of the solution volume by the weight of a gram-molecule—a use which has led to much confusion of ideas.

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ordinary value of α, there exists a linear relation between log D and log U, leading to a relation of the form $K = D/U^n$, where n is for various electrolytes nearly but not quite two thirds. (See Appendix.)

This suggested that if we could find a suitable correction for α, which is usually taken as λ/Λ, the Van 't Hoff dilution law would turn out to be an *exact* relation for dilute solutions of binary electrolytes such as KCl.

The materials for such a correction were sought in the known fact that the viscosity of the solution produced aberrations in the mobilities of the ions, but viscosity differences alone were inadequate to give an account of such aberrations.

Kohlrausch's observations on the temperature coefficients of the ions had already led him to the general view that the ions must be considered to be water-coated. This water combination necessarily altered the sizes of the ions, and it was considered that the joint effect of changes of viscosity and changes of size might adequately account for changes in the mobility.

To reckon these effects quantitatively, Stokes' theorem as to the motion of a small sphere in a viscous medium was available, and though the actual motion of the ions through an electrolyte under the influence of a potential gradient is probably extremely erratic, it was thought that, nevertheless, the effect of size and viscosity upon the average rectilinear drift under the influence of the electro-motive force might be amenable to exact treatment, just as the average rectilinear drift itself can be accurately calculated.

Assuming, then, that the aberrations of the mobilities which made the Van 't Hoff law inexact were due to such causes and could be dealt with in this way, corrections were applied to the mobilities, and corrections for α were calculated, the nature of which was determined by the Stokes theorem, and the amount of which was determined by the Van 't Hoff law (expressed in terms of the hydration h instead of the volume V of the solution).

The result of this process was to give us the expression

$$r = r_{\infty}\left(1 + Bh^{-2/3}\right)^{-1}$$

for the relation betwen the radius of an ion and the dilution of the solution.

Up to this point, if one may compare small things with great, the process followed is similar to that of the astronomer who sought to locate the position of a new planet by considering the irregularities produced in the movements of the old ones. In that case the result could be tested by turning a telescope to the spot indicated by the calculations.

In the present case the result could only be tested by considering how far the hypothesis as to the changing sizes of the ions owing to the changes in the amount of water combination could be rationally related to the various physical phenomena of solutions, and how the quantitative results were functionally related to existing data. In the case of each set of phenomena it was necessary to consider *à priori* how the

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changing size of the ions would be likely to affect it. *À priori* it seemed probable that the Hittorf transference numbers, and the viscosities of the solutions themselves, would depend merely upon the linear dimensions of the ions, whilst the densities of the solutions and the variations of effective molecular freezing-point depression and refractive power would depend upon the amounts of combined water, and therefore upon the cubes of the ionic dimensions.

These *à priori* considerations have, in fact, turned out to be justified, not merely qualitatively, but with considerable numerical accuracy, having regard to the difficulty of some of the approximations involved. We are able to express the Hittorf numbers, the densities, the effective molecular freezing-point depressions and the equivalent refractive power within the limits of experimental error, as simple functions of the radions, and to express the viscosities, with a fair approach to accuracy, not merely as a function of the radions of the solute, but also upon the extended conception of the radion as being simply proportional to the radion, or average molecular radius, of the whole solution. Our hypothesis has also enabled us to discover new relations which are independent of the hypothesis, viz., the fact that the Hittorf migration numbers are a linear function of $(B+h^{2/3})^{-1}$, and the fact that the effective molecular freezing-point depression and the equivalent refractive power are linear functions of the solution volume.

It is submitted that the above considerations justify the working hypothesis, that the function which we have named the radion, derived as above described, may in fact be taken to be a measure of the actual sizes of the ions. In any case, the radion turns out to be of fundamental importance in correlating the various phenomena of solution.

APPENDIX.

Note on the Van 't Hoff Law.

Reasons for Supposing that the Van 't Hoff Law with Index exactly $\frac{2}{3}$ is an Accurate Law for certain Binary Electrolytes with Monovalent Ions.

1. A large number of such electrolytes follow the Van 't Hoff law with close approximation over a considerable range of dilution. (See Bancroft, 'Zeit. Phys. Chem.,' 31, 191, 1899, and for KCl see Bousfield, 'Zeit. Phys. Chem.,' 53, p. 268, 1905, where diagram for KCl is given.)

For KCl the value of the index is $\frac{2 \cdot 2}{3 \cdot 2}$ for uncorrected α.

2. In order to test the law with great accuracy, we ought to examine it over a range of dilutions so high that the viscosity is practically constant and the increase of ionic size (if any) is practically complete. In such a case we might expect to find the value of n practically constant and equal to $\frac{2}{3}$, if the Van 't Hoff law holds accurately. It is impossible to make such a test, owing to the fact that the error introduced by the uncertainty as to the correction for the conductivity of the solvent, multiplied by the

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large factor necessary to obtain the equivalent conductivity, entirely swamps the small difference (if any) from the exact value of the index which we desire to detect.

Hence the only available means of investigation is to get the true value of n at high dilutions, by extrapolation from lesser dilutions where the errors to which reference is made above become almost inappreciable. For this purpose a range of dilutions is chosen between $\frac{1}{10}$ normal and $\frac{1}{1000}$ normal. As we descend through this range of dilutions (from higher to lower dilution) we necessarily get an increasing divergence from the true value of n, owing to changes of viscosity and changes of ionic size, but we can extrapolate into the desired region where viscosity and ionic size are nearly constant.

According to the Van 't Hoft law, in the modified form adopted in this paper, if $x = \log \frac{h}{1-\alpha}$, $y = \log \frac{h}{\alpha}$, we ought to have $dy/dx = \frac{2}{3}$.

In the following tables are set out the values of α (uncorrected, that is to say

TABLE XXXII.—KCl.

m.	$\alpha = \frac{\lambda}{\Lambda}$.	log h.	$y = \log \frac{h}{\alpha}$.	$x = \log \frac{h}{1-\alpha}$.	$\frac{\Delta y}{\Delta x}$.	$\frac{\Delta y}{\Delta x} - \frac{2}{3}$.
0·0005	0·9847	5·04477	5·0515	6·8601	0·674	0·007
0·001	0·9788	4·74374	4·7531	6·4174	0·678	0·011
0·002	0·9709	4·44270	4·4555	5·9788	0·681	0·014
0·005	0·9563	4·04474	4·0642	5·4043	0·683	0·016
0·01	0·9411	3·74367	3·7700	4·9736	0·691	0·024
0·02	0·9221	3·44248	3·4777	4·5509	0·697	0·030
0·05	0·8897	3·04419	3·0950	4·0016		

TABLE XXXIII.—NaCl.

m.	$\alpha = \frac{\lambda}{\Lambda}$.	log h.	$y = \log \frac{h}{\alpha}$.	$x = \log \frac{h}{1-\alpha}$.	$\frac{\Delta y}{\Delta x}$.	$\frac{\Delta y}{\Delta x} - \frac{2}{3}$.
0·001	0·9771	4·74375	4·7538	6·3839	0·674	0·007
0·002	0·9684	4·44271	4·4566	5·9430	0·676	0·009
0·005	0·9522	4·04475	4·0660	5·3653	0·679	0·012
0·01	0·9354	3·74368	3·7727	4·9335	0·684	0·017
0·02	0·9140	3·44259	3·4816	4·5081	0·693	0·026
0·05	0·8782	3·04444	3·1009	3·9588		

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$\alpha = \lambda/\Lambda$), the values of x and y calculated therefrom and the values of $\Delta y/\Delta x$. In diagram XIII. are set out the values of $\Delta y/\Delta x - \frac{2}{3}$ as ordinates, upon the values of α as abscissæ. Each value of $\Delta y/\Delta x$ belongs to a value of α intermediate between the two values of α from which it is reckoned. As this intermediate value is uncertain, each value of $\Delta y/\Delta x - \frac{2}{3}$ is set out *twice*, *i.e.*, to say upon the two values of α which lie one on each side of it. It will be seen from the diagrams that when $\alpha = 1$, *i.e.*, at infinite dilution, the extrapolated value of $\Delta y/\Delta x - \frac{2}{3}$ is in each case zero, *i.e.*, $dy/dx = \frac{2}{3}$ accurately.

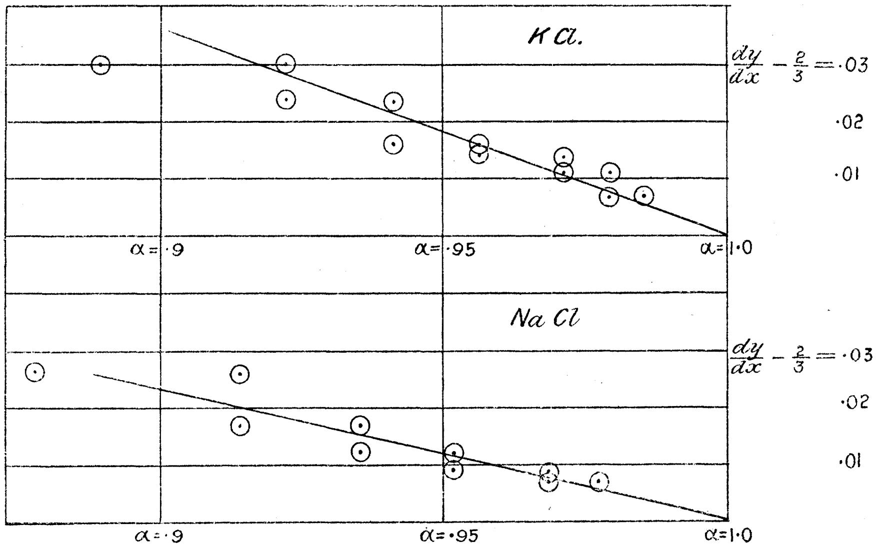

Diagram XIII.

This enables us to say that in the region of dilution where change of viscosity and ionic size become negligible the Van 't Hoff law holds accurately for KCl and NaCl.

If we were to follow out the same process for (say) acetic acid, we should find that the limiting value of dy/dx was accurately $\frac{1}{2}$, *i.e.*, we should get OSTWALD's law.

3. OSTWALD's law, with its accurate index, can be easily derived from the law of mass action. There is, therefore, reason to suppose that the Van 't Hoff law should also be capable of being based upon the law of mass action, which would necessarily give us, for high dilution, some definite and exact value for the index, since the index is the ratio of certain small numbers of molecules, which are necessarily whole numbers. In the former paper (see 'Zeit. Phys. Chem.,' 53, p. 266, 1905) this matter was discussed, and a hypothesis was set out upon which the law of mass action gives the Van 't Hoff law with exact index. This hypothesis may be unsound, but it shows the possibility of basing the Van 't Hoff law upon the law of mass action when the nature of the equilibrium between the molecules of solvent and solute is better understood.

MORGAN and KANOLT ('Journ. Amer. Chem. Soc.,' 26, p. 635, 1904) have arrived

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at a similar result, based upon the law of mass action, with a wholly different hypothesis as to combination of ions and water molecules.

Again, this hypothesis may not be accurate, but it strengthens the view that the Van 't Hoff law can, in some way, be based on the law of mass action, which would give an exact instead of an approximate index.

The above sets of considerations point to the view, that if α, the coefficient of ionisation, be corrected for viscosity and ionic size, the Van 't Hoff law would hold accurately in the lower range of dilution. It is found that such a correction can be made by the aid of STOKES' theorem, according to which the velocity of transportation is inversely proportional to the linear dimensions of the ionic complex, which gives the ionic size as a simple function of dilution.

The relation above indicated should be expressible by the equation

$$\frac{dy}{dx} - \tfrac{2}{3} = k(1-\alpha),$$

when $1-\alpha$ is small. This equation can be compared with the relation

$$h(1-\alpha)^2/\alpha^{3(1+n)} = \mathrm{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

Since for considerable dilution h is proportional to $1/m$, the relation may be written as

$$(1-\alpha)/\alpha^p = \mathrm{B}m^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

This is the relation given by KOHLRAUSCH as an empirical result ('Sitz. Akad. Wiss. Berlin,' 1900, p. 1006). It is shown by him to hold with great accuracy from decinormal to infinite dilution for a series of nine binary electrolytes with monovalent ions, and is used by him to deduce the values of Λ_∞.

As equation (1) is thus established as an adequate empirical relation, we may use it by a reverse process to examine the more exact relation which the diagram indicates when the curve is prolonged.

Equation (1) may be written

$$3\log\frac{h}{\alpha} - 2\log\frac{h}{1-\alpha} = \log \mathrm{C} + 3n\log\alpha.$$

Using Napierian logarithms and writing μ for the modulus of common logarithms,

$$\frac{x}{\mu} = \log\frac{h}{1-\alpha}, \quad \frac{y}{\mu} = \log\frac{h}{\alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

and we may write the relation as

$$3y - 2x = \log \mathrm{C} + 3\mu n \log \alpha.$$

By differentiation we get

$$\frac{dy}{dx} - \tfrac{2}{3} = n \cdot \frac{\mu}{\alpha} \cdot \frac{d\alpha}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Also from (3) we get by eliminating the variable h and differentiating

$$\frac{\mu}{\alpha} \cdot \frac{d\alpha}{dx} = \left(1 - \frac{dy}{dx}\right)(1-\alpha),$$

whence by substituting in (4) and writing

$$\frac{dy}{dx} - \tfrac{2}{3} = z, \qquad 1 - \alpha = \beta,$$

we obtain the equation

$$z = n\beta\left(\tfrac{1}{3} - z\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

This, then, is the more exact equation of the curve which has been indicated as a straight line in the diagram on p. 157. The curve starts from the origin, and has a horizontal asymptote.

To compare the constants with KOHLRAUSCH'S figures, we note that

$$p = \tfrac{3}{2}(1+n), \quad \text{or} \quad n = \tfrac{2}{3}p - 1.$$

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For p KOHLRAUSCH gives the values

$$\text{KCl},\ p = 3\cdot280,\quad \text{NaCl},\ p = 2\cdot649,$$

which gives for n the values

$$\text{KCl},\ n = 1\cdot187,\quad \text{NaCl},\ n = 0\cdot766.$$

For the tangent of the inclination of the curve at and near the origin we have for KCl the value 0·39, and for NaCl the value 0·25.

These agree well with the diagram.

The accurate empirical law deduced by KOHLRAUSCH is, in fact, not sensibly different in the part near the origin $\alpha = 1$ from the Van 't Hoff law for which $p = \frac{3}{2}$. That is, in the region where, from the present point of view, ionic size and viscosity may be regarded as constant, VAN 'T HOFF'S law, there equivalent practically to $1 - \alpha = \text{const} \times m^{1/2}$, is to be taken as the starting point for substances of the class here considered.