quite hypothetical is quite clear from the fact that there is not a single well established case of the existence of such electrical isomers as we are constantly being asked to assume in great numbers. We must at least ask that the hypotheses involved shall be made very explicit.

Summary.

In the above paper the following objections are raised to the electron conception of valence:

1. The chemical evidence advanced in support of this hypothesis, in as far as it deals with simple phenomena is quite unconvincing.
2. Any application of the theory involves the constant use of assumptions that render it too elastic to be proved or disproved by these applications.
3. The electromeric formulas assigned to chemical cmpounds are inconsistent with any rule that can be proposed.
4. No single well-established case of electroisomerism is yet known.
5. The evidence of physical experiments is at present opposed to the assumptions on which it is based.
6. The conception necessarily involves assumptions regarding the attractive force between atoms, the attraction of various atoms for electrons, and the relation of this last property to chemical affinity. A number of questions are proposed which should be answered—at least, the hypotheses to be adopted regarding them should be explicitly stated—before the theory is applied to the most perplexing problems of organic chemistry.

[Contribution from the Chemical Laboratory of the University of Illinois.]

A METHOD FOR THE CALCULATION OF THE HYDRATION OF THE IONS AT INFINITE DILUTION, AND THE IDEAL DIFFUSION COEFFICIENT AS APPLIED TO THE HYDRODIFFUSION OF ELECTROLYTES.

By George McPhail Smith.

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Introduction.

If, in the formula for the diffusion coefficient, $dS = -Dq\, dc/dx\, dt$, we regard D as the quantity of the dissolved substance in grams or mols which in unit time, t, passes through the unit distance x in unit cross-section, q, with unit fall of concentration,—c, occurring in this distance, likewise expressed in grams or mols, and if we divide D by M, the molecular weight of the compound in question, then D/M ($= I$, the ideal diffusion coefficient) indicates the quantity of the substance which would pass under the above conditions, provided that each molecule while retaining its size, configuration, and free-path velocity, had its molecular weight reduced to unity, and, therefore, its momentum reduced to a corresponding degree.[1] By dividing the diffusion coefficients, determined at 20° in aqueous solution for nonelectrolytes, by the respective values of M, and plotting $\log D/M$ against $\log M$, the points so obtained have been found to lie on a straight line not passing through the origin, and whose equation must be, $\log D/M + n \log M = \log K$, where n is the slope of the line, and K proves to have practically the same value for a great variety of substances. By taking the antilog of both sides, a new fundamental law of diffusion, $DM^{n-1} = K$, has been obtained, according to which we can write $M = (K/D)^{1/n-1}$, and determine M for nonelectrolytes for which D has been measured experimentally.[2]

With the available data concerning the diffusion of the metals in liquid mercury, it has been found possible by means of this law to study the constitution of certain dilute, liquid amalgams, and it has been shown that, at ordinary temperatures, the metals indicated exist in mercurial solution in molecular forms corresponding to the formulas: Zn, Cd, Sn, Pb, $AuHg_2$, $TlHg_2$, $LiHg_3$, $NaHg_5$, $CaHg_5$, KHg_6, $RbHg_6$, $SrHg_6$, $CsHg_6$, $BaHg_6$.[3]

It is the object of the present paper to show that an analogous method can be applied in the study of the question concerning the hydration of the ions, the ionic mobilities in this case being treated in the same manner as were the diffusion coefficients of the metals in the study of the constitution of the dilute liquid amalgams. Such a method in the case of the ionic mobilities is justified by the following considerations.

Since at each moment, during the passage of electricity through the solution of an electrolyte, the individual (univalent) ions are under the influence of equal forces, the velocities of the individual ions, both positive and negative, are proportional to their equivalent conductances (mobilities). Also, the magnitude of the impelling force, which results from the potential gradient, and which acts upon the ions, is, under like external conditions, equally great for all univalent ions.[4] And, moreover, the conductance of a solution of a binary electrolyte, in which there is present a

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[1] In the original paper (THIS JOURNAL, **36**, p. 848, l. 38) the expression "to the reciprocal value" was used. The passage should read: "but the momentum of each such imaginary molecule of unit molecular weight would be equal only to $1/M$ times that of a molecule of the real compound." This correction should also be applied to the definition of the ideal diffusion coefficient given on p. 849, l. 10.

[2] G. McP. Smith, THIS JOURNAL, **36**, 847 (1914).

[3] G. McP. Smith, *Z. anorg. Chem.*, **88**, 161 (1914); cf. also E. Beckmann and O. Liesche, *Ibid.*, **89**, 171 (1914).

[4] For ions of the valence n the impelling force is, of course, n times as great. But polyvalent ions, owing to their tendency to enter into the formation of intermediate ions and other complexes, which renders uncertain the extrapolated values obtained for their mobilities at infinite dilution, will not be considered in this paper.

given concentration of free univalent ions, is proportional to the sum of the mobilities of the latter; and, since the quantities of electricity transported by the anion and cation are directly proportional to their individual mobilities, it follows that the velocities of the individual ions, and therefore the numbers that pass in unit time through unit distance are proportional to their mobilities.

When an ion of the mass M is subjected to the action of a constant force, F, it receives a certain acceleration, a, such that we have the relationship expressed by the equation, $F = Ma$. At the same time, the ion is retarded in its motion by the resistance which it must overcome in its passage through the liquid. If the force continues to act, the ion finally acquires the limit velocity, c, that can be imparted to it by that force; and this velocity is independent of the mass of the ion, but depends upon the viscosity of the liquid and upon the size and configuration of the ion. After having acquired this limit velocity, the ion continues to move at a constant rate of speed, and the resistance R, which it then encounters is exactly equal to the force F, or, what is the same thing, the positive acceleration which the ion acquires from the force F is exactly equal to the negative acceleration which it receives from the resistance R. If, therefore, a given ion, while retaining its charge, size, and configuration, could have its mass, M, reduced to unity, the force F would still impart to it the limit velocity c, but its positive or negative acceleration would then be equal to $M \times a$.

If, now, the original ion of the mass M and the corresponding ideal ion of unit mass were both traveling at the limit velocity c, and the force F should suddenly cease to act, the resistance R would initially obtain in both cases; the ion of the mass M would meet with an initial negative acceleration equal to a, while the corresponding ideal ion of unit mass would encounter an initial negative acceleration equal to $M \times a$; or, the kinetic energy of the real ion would be equal to $^1/_2Mc^2$, while that of the imaginary ion would be equal to $^1/_2c^2$. That is to say, the periods of time, t, in which the forward progress of the two ions would be brought to a standstill, and the distances s traversed by them, would bear to one another the approximate relationships:

$$t_1 : t_M = s_1 : s_M = {}^1/_2c^2 : {}^1/_2Mc^2 = c/M : c = l/M : l; \text{ and } s_1 = s_M/M.$$

Now, in the case of diffusion, according to the kinetic theory, the dissolved molecules (and what is said of the molecules applies equally well to the ions present in a salt solution) are incessantly moving about in irregular zig-zag paths, *with continually changing velocities*, and these are dependent not only upon the resistances encountered by the molecules, but also upon the masses of the latter; the mean free-path velocities of the molecules vary inversely as the square roots of their masses. Therefore, if a molecule of the mass M has the free-path velocity c_M, and if, with its mass reduced to unity, it would have the free-path velocity c_1, then, according to the kinetic theory, $c_1 = c_M\sqrt{M}$; the kinetic energies E of the respective molecules are $E_M = {}^1/_2 M c_M^2$, and $E_1 = {}^1/_2 c_1^2$, and these are equal. But if the corresponding ideal molecule, in addition to having its mass reduced to unity, be supposed also to retain its original free-path velocity c_M, then its kinetic energy $E'_1 = {}^1/_2 c_M^2$, and this is equal, not to E_M, but to E_M/M. In that case, provided that the real and the ideal molecules make the same number of movements,[1] we should have for the two neutral molecules the relationships:

$$E'_1 : E_M = {}^1/_2 C_M^2 : {}^1/_2 M c_M^2 = c_M/M : c_M = s_M/M : s_M = D/M : D,$$

in which D is the diffusion coefficient of the compound in question; or, in the case of a similarly related pair of univalent ions, the relationships:

$$E'_1 : E_M = c_M/M : c_M = s_M/M : s_M = l/M : l,$$

in which l is the mobility of the ion in question.

The values of D/M are the ideal diffusion coefficients of the compounds, and those of l/M are proportional to the ideal diffusion coefficients of the ions in question. It should especially be noted that, in the foregoing discussion, ideal counterparts of the molecules of each separate compound (or ion) are imagined to exist, which, while retaining the exact size, configuration, and free-path velocity of the real molecules and ions, and while performing the same number of movements, differ from them only in that their masses are equal to unity.

Viewed in this light, the values of l/M assume a real physical significance, and we obtain in them a common denominator, to which the mobilities of the different ions might be reduced, if only their absolute hydration (*i. e.*, their ion-weights) were known. Since the l/M values are proportional to the ideal diffusion coefficients of the independent hydrated ions, we should expect in this case also to find the law to hold, that $lM^{n-1} = K$.

A. The Relative Hydration of the Ions.

During the last twenty-five or thirty years, there has been accumulated along various lines a great deal of evidence in favor of the view that the ions are more or less hydrated in aqueous solution.[2] Among the strongest

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[1] After each movement, the ideal molecule is supposed to pause and wait until the real molecule has finished its movement, whereupon they both start out again together, and so on, over and over again.

[2] Cf. G. Bredig, "Beiträge zur Stöchiometrie der Ionenbeweglichkeit," *Z. physik. Chem.*, **13**, 191–288 (1894); W. R. Bousfield, "Ionengrössen in Beziehung zur Leitfähigkeit von Elektrolyten," *Ibid.*, **53**, 257–313 (1905); E. H. Riesenfeld and B. Reinhold, "Berechnung der Ionenhydratation aus der Überführungszahl und der Beweglichkeit," *Ibid.*, **66**, 672–86 (1909); and, especially, E. W. Washburn, "Hydrates in Solution: A Review of Recent Experimental and Theoretical Contributions," *Technology Quarterly*, **21**, 360–449 (1908).

evidence in favor of this view is that which has been deduced from the results of transference experiments which have been carried out with various salt solutions in the presence of different nonelectrolytic reference substances. If at the end of such an experiment the ratio of water to nonelectrolyte has changed at the electrodes, then it follows either that the ions have carried water in the one direction, or that they have carried the nonelectrolyte in the opposite direction. Buchböck,[1] who was the first to obtain satisfactory quantitative results with this method, electrolyzed hydrogen chloride solutions, using mannite or resorcinol, at widely differing concentrations, as the reference substance; and, more recently, Washburn[2] has electrolyzed sodium chloride solutions with three different reference substances, sucrose, raffinose, and arsenious acid. These experiments all harmonize well together, and, unless we are prepared to assume that all of the different reference substances are capable of combining with the ions in the same way, the conclusion would seem to be justified that the changes in the ratio of water to nonelectrolyte at the electrodes are due, at least in the main, to the transfer of water from one part of the solution to another by the ions.

The relative degrees of hydration of chloride, hydrogen, potassium, sodium, and lithium ions, at 25°, in solutions containing about 1.25 formula weights of the metallic chlorides, and 0.1 formula weight of raffinose, to 1000 g. of water, or 1–1.5 formula weights of hydrogen chloride and up to 0.3 formula weight of mannite to 1000 g. of water, have been determined experimentally by E. W. Washburn,[3] according to whom, if we assume that the hydrated chloride ion contains on the average 9 molecules of water, we have for these ions the degrees of hydration which are indicated in the first column of Table I.

TABLE I.

No.	Hydrated ion.	Mobility.[4] l_0 25°.	log l.	M.	log M.	log $10l/M$.	$lM^{n-1} = K$.
1......	$[H(OH_2)_{2.0}]^+$	350	2.54407	37.04	1.56867	1.97540	8773
2......	$[Cl(HOH)_{9.0}]^-$	75.8	1.87967	197.6	2.29579	0.58388	8458
3......	$[K(OH_2)_{10.5}]^+$	74.8	1.87390	228.3	2.35851	0.51539	9472
4......	$[Na(OH_2)_{16.6}]^+$	51.2	1.70927	322.1	2.50799	0.20128	8848
5......	$[Li(OH_2)_{25.3}]^+$	...	...	462.7	...	...	
						Mean,	8888

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

[2] THIS JOURNAL, **31**, 322 (1909); *Z. physik. Chem.*, **66**, 513 (1909).

[3] *Loc. cit.* The relative hydration of hydrogen and chloride ions are calculated by Washburn from a portion of the experimental data of Buchböck, who does not state the temperature at which he worked. Washburn, himself, did not work with hydrogen chloride solutions.

[4] The mobilities given in the table are taken from a paper by A. A. Noyes and K. G. Falk, THIS JOURNAL, **34**, 479 (1912). The mobility of lithium ion at 25° has never been determined; the approximate value may, however, be calculated by means of the formula: $l_{0}\ 25^\circ = K/M^{n-1} = 8888/(462.7)^{0.892} = 37.3$.

If, now, we plot the values of log l/M against those of log M, we obtain the points shown in Fig. 1, which are seen to lie on the straight line AB. The slope of this line, n, is equal to $140 \div 74 = 1.892$.

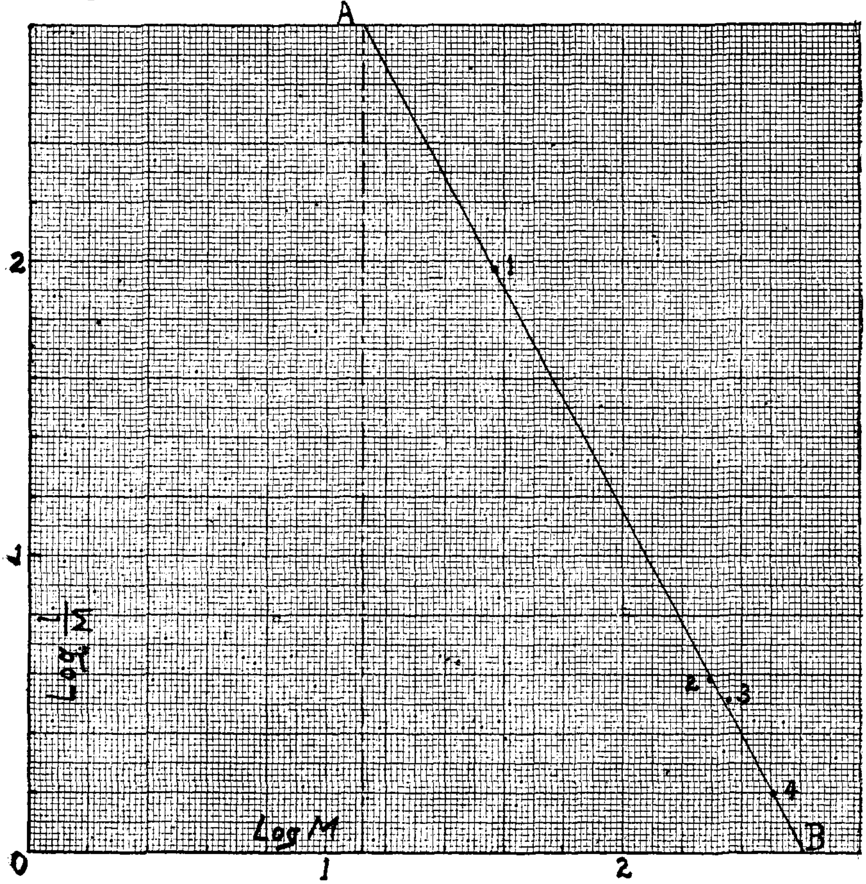

Fig. 1.

On the basis of the assumption that 2 and 3 are the respective maximum coördination numbers of hydrogen and oxygen,[1] and that these ions there-

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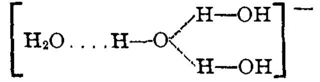
[1] The maximum coördination number of oxygen, according to Werner ("Neuere Anschauungen a. d. Gebiete d. anorgan. Chemie, ed. 1913, pp. 257–61) is 3, and from this it would seem to be likely that that of hydrogen is 2; upon this basis, assuming nonpolymerized water molecules, these hydrated ions correspond to the formulas,


$$\left[H_2O....H{-}O\begin{matrix}\diagup H{-}OH\\ \diagdown H{-}OH\end{matrix}\right]^-$$

and $[H_2O....H....OH_2]^+$. In these formulas, the dashes represent principal valences, and the dotted lines secondary valences. The polymerization of water can be interpreted as a necessary preliminary step in its ionization; *e. g.*,

$$HOH + 5H_2O \rightleftharpoons \underset{\text{Interpolation compound.}}{[(H_2O)_2H][OH(H_2O)_3]} \rightleftharpoons [(H_2O)_2H]^+ + [OH(H_2O)_3]^-.$$

fore contain at infinite dilution 2 and 3 molecules of water of hydration, the degrees of hydration of the other univalent ions whose mobilities have been determined can be calculated for infinite dilution at 18°, as follows:

For the line *AB*, in Fig. 1, we have the equation,

$$\log l/M + n \log M = \log K;$$

whence,
$$lM^{(n-1)} = K, \tag{1}$$

and
$$M = (K/l)^{1/n-1}. \tag{2}$$

Assuming that the same law holds at 18° for zero concentration, we have only to substitute in (1) the values of $l_{0\ 18°}$, and of M, for the two ions, and we get the relationships:

$$314.5 \times 37.04^{(n-1)} = K = 174 \times 71.05^{(n-1)};$$

whence
$$n = 1.9087,$$

and
$$K = 8378.$$

And, in order to calculate the hydrated-ion weights of the other univalent ions, we then substitute these values in (2):

$$M = (K/l)^{1/n-1} = (8378/l)^{1.1004}.$$

The values thus obtained, together with the numbers of hydrated water molecules, are given in Table II, and, in addition, the last column of the table contains the degrees of hydration calculated by Washburn from the experimental data at 25°, on the assumption that the chloride ion carries 9 molecules of water (cf. Table I).[1]

It is very noteworthy that, starting with the data obtained at 25° by means of transference experiments with mixtures containing about 1.25 mols of electrolyte, 0.1 mol of reference substance, and 55.5 mols of water, assuming chloride ion to be combined with 9 molecules of water and taking the resulting experimental values for the other four ions, the law is found to hold, that $l_{0\ 25°} \times M^{n-1} = K$; and that, starting with the assumptions that hydrogen and hydroxide ions at infinite dilution, respectively, contain, at 18°, 2 and 3 hydrated molecules of water, and that the law, $l_{0\ 18°} \times M^{n-1} = K$, holds in this case, we obtain upon calculation practically identical values for the degrees of hydration of the same ions under these widely differing conditions. This fact furnishes confirmatory evidence that in each of the above mentioned transference experiments with electrolyte and nonelectrolytic reference substance, the changes in ratio between reference substance and water at the elec-

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[1] In his paper, Washburn determines the relationship which exists between the degree of hydration of each of the four positive ions and that of chloride ion, and in a table he gives the number of molecules of water which are combined with each of these ions for different assumptions regarding the number combined with the chloride ion. In the present paper, those of Washburn's values are taken which are based upon the assumption that chloride ion is combined with 9 molecules of water; since in that case it results that 2 molecules of water are assigned to the hydrogen ion.

trodes were due almost wholly to the transfer of water, and not to that of reference substance, by the ions.

TABLE II.

Ion.	Mobility.[1] l_0 18°.	log l.	log M.	M.	Molecules of hydrated water calculated for zero concentration at 18°.	Washburn's corresponding values at 25°. based on $[Cl(OH_2)_9]^-$ for mixtures of 1.25 mols salt and 55.5 mols water.
H.........	*314.5*	...	...	*37.04*	*2.0*	2.0±0.04
OH........	*174*	...	...	*71.05*	*3.0*	..
Cs.........	68.0	1.83251	2.30051	200	3.7	[9.9 (E. B. Millard)][2]
Br.........	67.7	1.83059	2.30262	201	6.7	..
Rb........	67.5	1.82930	2.30404	201	6.4	..
I..........	66.6	1.82347	2.31045	204	4.3	..
Tl.........	65.9	1.81889	2.31549	207	0.15	..
Cl.........	65.5	1.81624	2.31841	208	9.6	*9.00*
NH_4.......	64.7	1.81090	2.32426	211	10.7	..
K..........	64.5	1.80956	2.32576	212	9.6	10.5±0.2
NO_3.......	61.8	1.79099	2.34619	222	8.9	..
SCN.......	56.7	1.75358	2.38736	244	10.3	..
ClO_3.......	55.1	1.74115	2.40104	252	9.3	..
Ag........	54.3	1.73480	2.40803	256	8.2	..
BrO_3.......	47.6	1.67761	2.47096	296	9.3	..
F..........	46.7	1.66932	2.48008	302	15.7	..
Na........	43.4	1.63749	2.51511	327	16.9	16.6±0.2
IO_3.......	34.0	1.53148	2.63176	428	14.1	..
Li.........	33.3	1.52244	2.64171	438	24.0	25.3±0.4

It should also be mentioned that Buchböck,[3] who worked with solutions containing hydrogen chloride and reference substance at different concentrations, extrapolates his hydration values to zero concentration, both of hydrogen chloride and of the reference substance, and comes to the conclusion that, at infinite dilution, chloride ion is combined with 4 molecules of water for each water molecule that hydrogen ion is combined with; *i. e.*, if hydrogen ion carries 2 water molecules, chloride ion carries 8. This conclusion is in surprizing agreement with the calculated value for chloride ion (Table II).

It is further interesting to note that Washburn and MacInnes[4] have

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[1] The mobilities given in the table, with the exception of that of hydroxide ion, are taken from the paper by Noyes and Falk, *Loc. cit.* The value for hydroxide ion is that given in Landolt-Börnstein-Meyerhoffer's Tabellen, 4th ed. (1912), p. 1124; it is less accurately known than the others, and may be 2 or 3% in error, while that for hydrogen ion is less than 1% in error (Private communication from Dr. S. J. Bates), Owing to the lesser accuracy of the determined values of l_0 18° for hydrogen and hydroxide ions, *upon which the above table is based*, it was not considered worth while in the case of the salts to use the somewhat more accurate values of Bates (THIS JOURNAL, **35**, 519 (1913)).

[2] See below.

[3] *Loc. cit.*

[4] E. W. Washburn and D. A. MacIunes, THIS JOURNAL, **33**, 1686 (1911).

drawn the conclusion from their cryoscopic data that, in 0.5 *N* solution potassium chloride is combined with about 9, and lithium chloride with about 18 mols of water more than caesium nitrate is combined with. By means of the data in Table II, we arrive at relationships for 18° and zero concentration which are in as good agreement with these conclusions as could be expected; the figures so obtained are that potassium chloride is combined with 6.6, and lithium chloride with 21.0 mols of water more than caesium nitrate is combined with.[1]

In this connection, however, attention should be called to the fact that, by means of transference experiments, at 25°, with caesium chloride solution, with raffinose as the reference substance, E. B. Millard[2] has recently determined the relative degree of hydration of caesium ion; he concludes from his work that caesium ion carries 0.65 mol of water less than potassium ion does. According to him, if potassium ion combines with 10.5 mols of water, then caesium ion, under the same conditions, combines with 9.9 mols of water. This result is very surprizing, when it is viewed in the light of the good agreement obtained in all other cases. Furthermore, additional evidence in favor of the calculated values is furnished in the next section, where it is shown that these values may be used to advantage in connection with the ideal diffusion coefficient and the hydrodiffusion of electrolytes.

B. The Ideal Diffusion Coefficient and the Hydrodiffusion of Electrolytes.

L. W. Öholm[3] has determined, at 18° and 0.01 *N* concentration, the diffusion coefficients of the following highly dissociated electrolytes: NaCl, KCl, LiCl, KI, HCl, KOH, and NaOH. At infinite dilution—and the same would hold approximately at 0.01 *N* concentration—the ions of these electrolytes would diffuse independently, if it were not for their electrical charges; but the differences in potential, which result from the tendency of the lighter to precede the heavier ions, tend to hold the faster lighter ones back, while pulling the slower heavier ones forward. The net result, of course, is that the electrolytes diffuse upwards as a whole, virtually in the form of vibrating labile systems, each of which consists of one positive and one negative ion. Therefore, by taking as the molecular weights of the electrolytes the sums of the hydrated-ion weights of their positive and negative ions (Table II), it should be possible to successfully apply the conception of the ideal diffusion coefficient to the question of

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[1] Washburn and MacInnes assume in their paper that caesium nitrate is not at all hydrated.

[2] Thesis submitted to the Graduate Faculty of the University of Illinois in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry, 1914, p. 28.

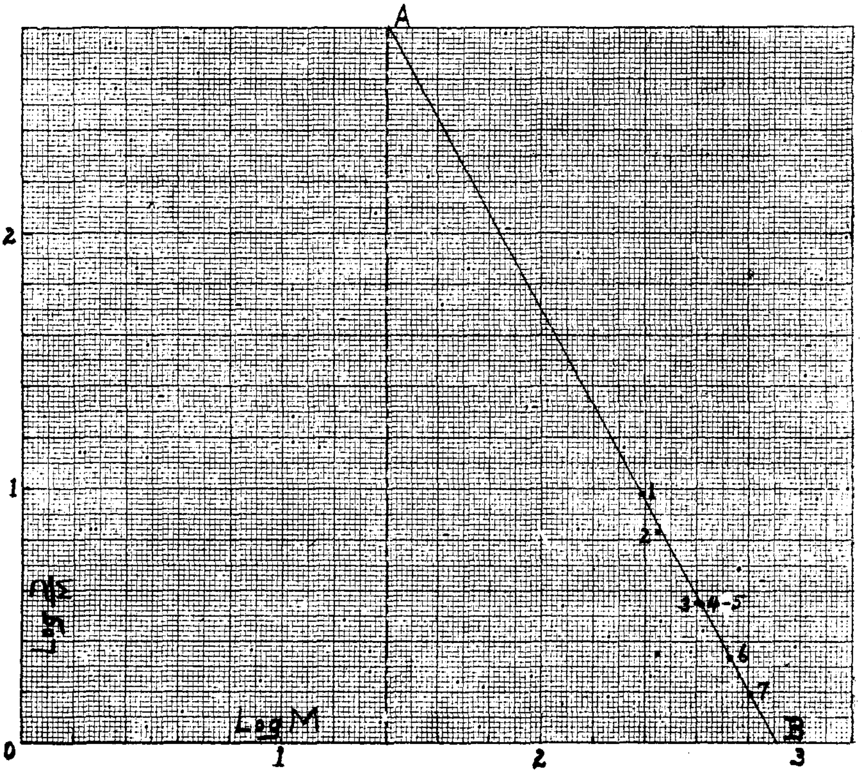
[3] *Z. physik. Chem.*, 50, 309 (1904–05).

the hydrodiffusion of these substances. The data listed in Table III, in which the $D_{18°}$ values are those determined experimentally at 0.01 N concentration, show in a convincing manner that this actually can be done.

TABLE III.

No.	Added formulas of hydrated ions (Table II).	$D_{18°}$.	log D.	Sum of hydrated-ion weights. (Table II). M.	log M.	log 10^3 D/M.	$DM^{n-1} = K$.
1.....	$HCl.11.6H_2O$	2.324	0.36624	245	2.38917	0.977	274
2.....	$KOH.12.6H_2O$	1.903	0.27944	283	2.45179	0.828	254
3.....	$NaOH.19.9H_2O$	1.432	0.15594	398	2.59988	0.556	257
4.....	$KI.13.9H_2O$	1.460	0.16435	416	2.61909	0.545	272
5.....	$KCl.19.2H_2O$	1.460	0.16435	420	2.62325	0.540	274
6.....	$NaCl.26.5H_2O$	1.170	0.06819	535	2.72835	0.340	271
7.....	$LiCl.33.6H_2O$	1.000	0.00000	646	2.81023	0.190	273

Upon plotting the values of log D/M against those of log M, the points shown in Fig. 2 are determined, and these are seen to lie upon the straight line AB, whose slope, n is equal to $140 \div 75 = 1.8667$. That is, upon taking into consideration the hydration of the ions, the diffusion of the highly dissociated electrolytes is found to be essentially no more com-



Fig, 2.

plicated than that of the nonelectrolytes; we have in this case also the law, $DM^{n-1} = K$. The values of K, which have been calculated for the different substances, are included in the last column of Table III. Their excellent agreement furnishes evidence which points almost convincingly to the correctness of the data calculated for ionic hydration at infinite dilution.

It will perhaps not be out of place also to note at this point that, by combining the two laws, $DM^{n-1} = K$, and $lM^{n-1} = K$, a diffusion formula can be obtained, which bears a striking resemblance to that developed along entirely different lines by Nernst.

For the diffusion of the hydrated electrolytes, we have

$$D_{18^\circ} M^{0.8667} = 270,$$

or, since $M_{\text{Electrolyte}} = M_{\text{Cation}} + M_{\text{Anion}}$, we have,

$$D_{18^\circ} = 270/(M_K + M_A)^{0.8667} \tag{3}$$

In the case of the hydrated ions, we have,

$$M_K = (K/l_K)^{1/n-1} \quad \text{and} \quad M_A = (K/l_A)^{1/n-1};$$

or,

$$M_K = (8378/l_K)^{1.1004} \quad \text{and} \quad M_A = (8378/l_A)^{1.1004}.$$

Substituting in (3) these values of M_K and M_A, we obtain,

$$D_{18^\circ} = \frac{270}{[(8378/l_K)^{1.1004} + (8378/l_A)^{1.1004}]^{0.8667}} = 0.04896\left(\frac{l_K^{1.1004} \cdot l_A^{1.1004}}{l_K^{1.1004} + l_A^{1.1004}}\right)^{0.8667} \tag{4}$$

According to Nernst,[1] on the other hand, $D_{18^\circ} = 0.04485\left(\frac{l_K \cdot l_A}{l_K + l_A}\right)$ This formula furnishes values for infinite dilution.

By means of the formula, $D = K/M^{n-1} = 270/(M_K + M_A)^{0.867}$, it is of course possible to calculate the diffusion coefficients of other uni-univalent electrolytes, for 18°, at 0.01 N concentration. For nitric acid and sodium iodide, for example, we obtain the values 2.18 (2.13, at 0.13 N) and 1.17 (1.115, at 0.086 N).[2]

In conclusion, a summarized list of the cases in which the law, $DM^{n-1} = K$, has been found to hold, together with the corresponding values of n and K, is given in Table IV:

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[1] Theoretische Chemie, 5th ed. (1907), p. 371, Equation 8. For the diffusion coefficients of hydrogen chloride and sodium hydroxide, we obtain by means of Nernst's formula the values, 2.431 and 1.558; the writer's Formula 4, gives 2.294 and 1.505; Öholm's values are 2.324 and 1.432.

[2] The values in parenthesis are given by Öholm (*Loc. cit.*, p. 333), who obtains them by recalculation to 18° of Scheffer's value for nitric acid, and of Kawalki's value for sodium iodide.

TABLE IV.

Case.	Concentration.	Temperature.	n.	K.
Hydrodiffusion of nonelectrolytic organic compounds	0.25	20°	1.505	7.00
Hydrodiffusion of nonelectrolytic organic compounds	*zero*	20°	1.489	6.66
Hydrodiffusion of nonelectrolytic organic compounds[1]	0.25	10±1°	1.489	4.77
Hydrodiffusion of gases	*very* low	18±2°	1.533	10.0
Diffusion of metals and metallic compounds in mercury	*very* low	10±2°	1.458	13.9
Hydrodiffusion of highly ionized (hydrated) electrolytes	0.01	18°	1.867	270
Independent diffusion of hydrated univalent ions ($lM^{n-1} = K$)	*zero*	18°	1.909	8378

URBANA, ILL.

[COMMUNICATION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

THE INFLUENCE OF AN ALTERNATING CURRENT ON ELECTROLYSIS BY A DIRECT CURRENT.

[PART II.]

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In a previous communication[2] the action of an alternating current of high frequency on simple voltaic cells was studied. In this communication the influence of an alternating current on electrolytic cells will be described.

Löb[3] investigated the solution of metals in potassium cyanide solution under the influence of unsymmetrical alternating currents. Von Wartenburg and Archibald[4] investigated the formation of ozone at the anode in sulfuric acid solution by means of an alternating current impressed on a direct current. The object of this investigation, however, is to determine how an alternating current affects the phenomenon of electrolysis in general.

The poles of a four-volt lead accumulator were connected through the secondary circuit of an induction coil, and a suitable resistance, to the two electrodes of a voltameter. The induction coil used was a small one,

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[1] In the former paper, the values given for this case are erroneous. Only a portion of Öholm's data was available at that time, and upon taking into consideration also his later work at 10°, the values given in this table are found to be correct (cf. L. W. Öholm, *Z. physik. Chem.*, **70**, 393ff. (1910); Medd. k. Vetenskapskad. Nobelinst., Vol. **2**, No. 23 (1913)).

[2] THIS JOURNAL, **36**, 2333 (1914).

[3] *Z. Elektrochem.*, **12**, 79 (1906).

[4] *Ibid.*, **17**, 812 (1911).