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THE EXTENSION OF THE DILUTION LAW TO CONCENTRATED  
SOLUTIONS.

BY JAMES KENDALL.

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The dilution law of Ostwald:

$$\gamma^2/(1 - \gamma).v = K; \text{ or } c_i^2/c_u = K, \quad (1)$$

( $\gamma$  = fraction ionized,  $v$  = dilution,  $c_i$  = ionic concentration,  $c_u$  = concentration of un-ionized part,  $K$  = dissociation constant), is apparently securely based upon the principle of mass action, and yet has definite limits in its *exact* applicability to aqueous solutions of electrolytes. The law is found, on examination,<sup>1</sup> to break down in two directions.

In the first place, it is followed exactly only if the *ionic concentration* is small. When a certain limiting ionic concentration (approximately 0.01  $N$ ) is exceeded,  $K$  begins to increase, and increases steadily with  $c_i$ . Divergences from the dilution law in this direction are, therefore, met with in all strong electrolytes, and also in many of the transition electrolytes<sup>2</sup> at the higher concentrations. (Anomaly of strong electrolytes.)

In the second place, the law is followed exactly only if the *total concentration* of the electrolyte is small. The limit of exact applicability is

<sup>1</sup> Wegscheider, *Z. physik. Chem.*, **69**, 603 (1909).

<sup>2</sup> Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

fixed by Wegscheider<sup>1</sup> as lying between  $v = 32$  and  $v = 16$ , for typical weak electrolytes. In more concentrated solutions  $K$  shows a *decreasing* value, and the decrease becomes more and more rapid with increase of concentration. (Anomaly of concentrated solutions.) It is usual to connect this decrease with the increased viscosity of these concentrated solutions.

In concentrated solutions of strong and transition electrolytes, both disturbing influences are present and will partially counterbalance one another. Such cases have been investigated in a previous communication,<sup>2</sup> where it is shown that the ionic concentration influence is more important in relatively dilute solutions, and the total concentration influence in more concentrated solutions. A maximum value for  $K$  is thus observed at a certain concentration, the exact point being dependent upon the strength of the electrolyte.

It will be evident that the limits stated above for the exact applicability of the dilution law are only approximate. More exact experimental determinations will establish divergences in solutions still more dilute.<sup>3</sup>

The partial failure of the dilution law has led to the proposal of many alternative formulae for the expression of the dissociation equilibrium. Empirical equations for strong electrolytes have been put forward, among many others, by Rudolphi,<sup>4</sup> van't Hoff,<sup>5</sup> and Storch.<sup>6</sup> None of these is exactly applicable in all cases, and none has been shown to possess a definite theoretical basis. Similarly, no satisfactory formula has been found to apply to all concentrated solutions.

Recently, a number of formulae of a more general type have been proposed, expressing in one equation the dissociation equilibrium of all electrolytes. Such are the equations of Kraus and Bray,<sup>7</sup> and of MacDougall,<sup>8</sup> which are intermediate between the dilution law and Storch's equation, and may be written in the form:

$$c_i^2/c_u = K + D.c_i^n \quad (2)$$

( $K$ ,  $D$  and  $n$  are constants varying with the electrolyte.) Simultaneously, the present author<sup>9</sup> put forward a similar equation:

$$\gamma^2/(1 - \gamma)v = K + c.(1 - \gamma)/\gamma \quad (3)$$

( $K$  and  $c$  are constants varying with the electrolyte.) This equation is intermediate between the dilution law and van't Hoff's formula, and is

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Kendall, *Meddel. från K. Vet. Akads. Nobelinstitut*, Band 2, No. 38 (1913).

<sup>3</sup> Kendall, *J. Chem. Soc.*, 101, 1288 (1912).

<sup>4</sup> Rudolphi, *Z. physik. Chem.*, 17, 385 (1895).

<sup>5</sup> Van't Hoff, *Ibid.*, 18, 300 (1895).

<sup>6</sup> Storch, *Ibid.*, 19, 13 (1896).

<sup>7</sup> Kraus and Bray, *THIS JOURNAL*, 35, 1315 (1913).

<sup>8</sup> MacDougall, *Ibid.*, 34, 855 (1912).

<sup>9</sup> Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

less general than equation (2) only because of the absence of a third variable constant. The equation represents satisfactorily the dissociation equilibrium of acids of *all strengths* in aqueous solutions of lower concentration than  $v = 16$ .

In a second communication,<sup>1</sup> more concentrated solutions of acids of widely divergent strengths have been examined. Here equation (3) fails to apply, and gives—just as does the dilution law for weak electrolytes—values greater than the experimental value for  $\gamma^2/(1 - \gamma)v$ . The present paper continues the investigation of these concentrated solutions. For simplicity, typical weak electrolytes are first considered. Here it is possible to deal with the “anomaly of concentrated solutions” alone, since  $c_i$  is always exceedingly small. Subsequently, the transition electrolytes are briefly examined; the case of strong electrolytes is reserved for a future communication.

The Ostwald dilution law, as it stands, fails to represent accurately the dissociation equilibrium of *concentrated* solutions of a weak electrolyte. This failure, however, is easy to comprehend, since from thermodynamical considerations it is evident that the law can apply *exactly* only to dilute solutions, and must, of necessity, break down when the concentration of the solute is increased beyond certain limits. In the following pages a modified form of the dilution law is deduced, which is found to be exactly applicable even at high concentrations, and a possible theoretical basis for this modified law is indicated. It is then shown that, with the assumption of this theoretical basis, a thermodynamic investigation leads to the result that the modified law, unlike the original dilution law, would indeed hold exactly at all concentrations. Its agreement with the experimental data at high concentrations is demonstrated for several typical weak electrolytes, and its applicability to equation (3) for transition electrolytes is exemplified. Finally, the arguments in favor of the theoretical conclusions drawn are summarized.

*The Anomaly of Concentrated Solutions.*—A good illustration of the decrease in the dissociation constant of a weak electrolyte at high concentrations is given by the figures for acetic acid in Tables I and II, below.

TABLE I.—ACETIC ACID, 25° (KENDALL).

$v$ .	A.	100 K.	$\eta$ .	100 K <sub>1</sub> .	$d$ .	100 K <sub>2</sub> .
0.989	1.443	0.00140	1.112	0.00174	1.0084	0.00184
1.977	2.211	0.00165	1.056	0.00183	1.0043	0.00188
3.954	3.221	0.00176	1.028	0.00186	1.0022	0.00188
7.908	4.618	0.00181	1.014	0.00187	1.0011	0.00188
15.816	6.561	0.00184	1.007	0.00187	1.0006	0.00187
31.63	9.260	0.00185	1.003	0.00186	1.0003	0.00186
63.26	13.03	0.00185	1.002	0.00186	1.0002	0.00186
$\infty$	387.9	.....	...	.....	.....	.....

<sup>1</sup> Kendall, *Meddel. från K. Vet. Akads. Nobelinstitut*, Band 2, No. 38 (1913).

TABLE II.—ACETIC ACID, 25° (RIVETT AND SIDGWICK).

1/v.	$\Lambda/v.$	100 K.	$\eta.$	100 K <sub>1</sub> .	$d.$	100 K <sub>2</sub> .
2.9771	1.854	0.00077	1.347	0.00139	1.0235	0.00165
2.0060	1.789	0.00106	1.230	0.00161	1.0162	0.00180
1.4886	1.671	0.00125	1.169	0.00172	1.0122	0.00186
1.3374	1.620	0.00131	1.150	0.00173	1.0109	0.00186
1.0029	1.474	0.00144	1.112	0.00179	1.0084	0.00189
0.8917	1.415	0.00150	1.098	0.00181	1.0074	0.00190
0.6687	1.264	0.00160	1.073	0.00184	1.0036	0.00191
0.3722	0.9722	0.00170	1.041	0.00184	1.0032	0.00188
0.1861	0.7079	0.00181	1.021	0.00188	1.0017	0.00190
0.0930	0.4986	0.00180	1.010	0.00184	1.0009	(0.00185)
0.0402	0.3372	0.00192	1.004	0.00195	1.0004	(0.00195)

The experimental data in Table II are selected from a series of determinations by Rivett and Sidgwick;<sup>1</sup> the density and viscosity results in both tables are also obtained from the same paper, by interpolation from the figures there given. ( $\Lambda$  = equivalent conductivity,  $\eta$  = relative viscosity (water unity),  $d$  = relative density.)

It will be seen, from the third column of these tables, that the dissociation constant 100  $K$  is a true constant for solutions less concentrated than  $v = 16$ , but that for higher concentrations the value obtained decreases, first slowly and afterwards more rapidly. (In Table II the constancy of the values at high dilutions is rather obscured by the relatively greater experimental error.)

There is, however, a viscosity correction to be applied to these results. The exact relation between conductivity and viscosity has been investigated and established by the researches of Green,<sup>2</sup> Johnston,<sup>3</sup> Washburn,<sup>4</sup> and Noyes and Falk.<sup>5</sup> The general conclusion drawn is that the simple equation,

$$\Delta\eta/\Lambda_0\eta_0 = \text{constant}, \quad (4)$$

( $\Lambda_0$  = equivalent conductivity and  $\eta_0$  = viscosity at zero concentration of solute) is not exactly followed; but rather the equation,

$$\Lambda/\Lambda_0 = \text{constant} (\eta_0/\eta)^n, \quad (5)$$

( $n$  is a constant varying with the electrolyte.) Nevertheless,  $n$  is in most cases so nearly equal to unity, and its exact determination is a matter of such difficulty, that we may assume, with Noyes, that the safest correction we can make is by the use of equation (4) above. In any case, the residual error will be small, unless very high concentrations (above normal) are considered.

Hence we obtain the corrected values for the dissociation constant by

<sup>1</sup> Rivett and Sidgwick, *J. Chem. Soc.*, **97**, 734 (1910).

<sup>2</sup> Green, *J. Chem. Soc.*, **93**, 2049 (1908).

<sup>3</sup> Johnston, *THIS JOURNAL*, **31**, 1010 (1909).

<sup>4</sup> Washburn, *Ibid.*, **33**, 1461 (1911).

<sup>5</sup> Noyes and Falk, *Ibid.*, **34**, 454 (1912).

employing the expression  $\Lambda\eta$  instead of the experimental value  $\Lambda$  for the equivalent conductivity in the above tables. These corrected values are given under the heading  $100 K_1$ . The application of the viscosity correction has not destroyed the divergences at the highest concentrations, where a steady decrease in the dissociation constant is still evident. Further examination into the cause of these divergences is therefore necessary.

In the following section, the dilution law itself is critically examined and its exact theoretical basis tested. A modified form of the dilution law is tentatively proposed, which is subsequently applied to the above experimental data and found to account for the divergences up to very high concentrations.

*A Modification of the Dilution Law.*—The exact significance of the Ostwald dilution law will first be studied from the simple kinetic standpoint.

We have, for a uni-univalent electrolyte of the type  $RX$ , the dissociation equation,



from which, by the application of the law of mass action, the dilution law is immediately obtained in the form

$$c_i^2/c_u = K. \quad (7)$$

The right-hand side of equation (6) presents no difficulty from the kinetic standpoint.<sup>1</sup> The concentration of each ion is  $c_i$ , and by the impact of two ions of opposite charge the undissociated salt is formed, with the mutual neutralization of the charges. The mechanism of the equilibrium reaction on the other side of the equation, however, is by no means so clear. *A definite conception of the nature of the reaction on the left-hand side of the equation has not yet been obtained, and, in spite of the importance of the question, it does not seem to have attracted any great attention, or to have been answered in any but the vaguest manner.*

The above statement may be further emphasized by an extract from a recent communication by Walden:<sup>2</sup> "The greater the dielectric constant of the interposed solvent, the less is the electrostatic attractive force [be-

<sup>1</sup> That is, so long as the ionic concentration is small. If  $c_i$  exceed a certain limit, then the electrostatic forces existing between the charged ions become of importance in the equilibrium, and we have the "anomaly of strong electrolytes."

<sup>2</sup> Walden, *THIS JOURNAL*, **35**, 1649 (1913). This communication first reached the author's notice after the present investigation was practically completed. Walden has attacked the subject from precisely the opposite direction to that here followed, namely, by a consideration of the "anomaly of strong electrolytes" from the increase in the dielectric constant of the solvent due to the dissolved salt. The view is expressed that "the process of disaggregation of the polymerized salt molecules also causes and induces the process of ionic cleavage." The conclusions drawn in the present paper are not necessarily in opposition to those advanced by Walden, but may rather be considered as confirming and supplementing them, as will be shown later.

tween ions of unlike charge], and with the greater difficulty does the recombination to electrically neutral molecules take place. Nevertheless, the neutral molecules will be formed in the solution. Why then do they again break up into ions? *For what reason does the neutral salt molecule break up into ions at all, as soon as it enters into solution?* This fundamental question has, up to the present, not been answered. Strangely enough, we do not even make a serious attempt at its solution."

In the dilution law, as it stands, it is tacitly assumed that the undissociated molecules  $RX$  break up *quite spontaneously* into the separate ions  $R^+$  and  $X^-$ . The whole equilibrium is taken to be exactly analogous to that existing in gaseous dissociation, and the analogy is indeed sufficiently striking. Nevertheless, there are fundamental differences between the two phenomena of gaseous and ionic dissociation, and one is the influence of the solvent medium upon the equilibrium in the latter case. *The nature of the solvent plays an important part in determining the degree of dissociation of the dissolved electrolyte.*

The role of the solvent in the dissociation equilibrium (except from the point of view of the dielectric constant) has been strangely neglected by the followers of the dissociation theory of Arrhenius.<sup>1</sup> The tendency has been to treat the solvent simply as so much "dead space." The upholders of the solvate theory, on the other hand, have referred all dissociation phenomena to interaction between solvent and solute.

A general, but indefinite, feeling of dissatisfaction with the present position (as is indicated above by Walden) has certainly existed among the followers of the dissociation theory, and this feeling has occasionally found its way into print in well-known text-books, where definitions of electrolytic dissociation may be found, which undoubtedly do not agree with the hypothesis of spontaneous dissociation of the undissociated molecule tacitly assumed above. For example, Stieglitz<sup>2</sup> states: "When an ionogen is dissolved in water, its molecules are immediately, more or less completely, *dissociated by the water* into smaller fragments or molecules of unlike composition." Similarly, Alexander Smith<sup>3</sup> writes: "The conducting power of the solution is indissolubly connected with the fact that the original molecules of the solute have been broken up by the solvent into smaller molecules containing one or more atoms." Nernst<sup>4</sup>

<sup>1</sup> Compare Lowry, *Science Progress* (1908).

<sup>2</sup> Stieglitz, "Qualitative Chemical Analysis," Part I, page 41. The italics are in the original. See also pages 61-66, where the ionizing power of solvents (as related to their dielectric behavior, the unsaturated condition of their simple molecules, and their power of association) is critically examined, and the above idea is repeatedly expressed.

<sup>3</sup> Alexander Smith, "Introduction to Inorganic Chemistry," page 317.

<sup>4</sup> Nernst, *Theoretische Chemie, Sechste Auflage* (1909), page 534. See also repeated statements on pages 378-80.

states: "Der Umstand, dass gerade das Wasser die ganz besondere Fähigkeit besitzt, gelöste Stoffe electrolytisch zu spalten, legt die Vermutung nahe, dass bei der Ionenspaltung chemische Verbindungen mit dem Wasser eine Rolle spielen." Here there is not only the statement that *the solvent* splits up the undissociated molecules into the separate ions, but the possibility also is noted that, in so doing, the solvent actually combines with the solute to form hydrates and hydrated ions.<sup>1</sup> Ostwald<sup>2</sup> himself goes so far as to say: "Das Wasser nimmt, in Bezug auf seine Fähigkeit electrolytische Lösungen zu bilden, oder Stoffe in Ionen zu spalten, eine ausgezeichnete Stellung ein." Arrhenius<sup>3</sup> also speaks of "die Fähigkeit der Lösungsmittel, Elektrolyte in Ionen zu zerlegen."

Now, if the molecules of the undissociated salt in the solution are indeed broken up *by the molecules of the solvent* into the separate ions, then the concentration of the solvent in the solution should appear in the equation of equilibrium, and the simple dilution law is not valid. The equation is modified into the form:

$$c_i^2/c_u \cdot c_s = K, \quad (7)$$

( $c_s$  = concentration of solvent in the solution.) At moderately high dilutions  $c_s$  becomes practically constant, and the equation reduces to the simple dilution law. At higher concentrations of solute,  $c_s$  begins to diminish, since molecules of solvent are being replaced in the solution by molecules of solute.

We may write equation (7) in the form:

$$c_i^2/c_u = Kc_s,$$

from which it is at once evident that the equation is *qualitatively* in accordance with the fact, shown by the results of experiment, that  $c_i^2/c_u$  is not constant at high concentration of solute, but exhibits a *decreasing* value. The validity of the equation at high concentrations may be tested *quantitatively* with the help of the density data.

This is done for acetic acid in the last columns of Tables I and II above. The values under  $100K$  are corrected by means of the ratio:

*weight of solvent in one liter of pure solvent/weight of solvent in one liter of solution*  
and the results are given under  $100K_2$ , which therefore represents  $100K$  in equation (7) above.

<sup>1</sup> The subject of the hydration of ions has recently attracted much attention; for a summary of the bearing of the subject on the present discussion see Wegscheider, *Z. physik. Chem.*, **69**, 605-6 (1909). Ciamician, reviewing the results obtained, makes the significant statement: "Alles scheint darauf hinzuweisen dass die Annahme, nach welcher die Dissociation in Lösungen durch das Lösungsmittel vermittelt und bedingt wird, heute an Berechtigung gewonnen hat und den bekannten Tatsachen am besten entspricht," *Z. physik. Chem.*, **69**, 100 (1909).

<sup>2</sup> Ostwald, *Lehrbuch der Allgemeinen Chemie*, Band 2, Teil 1 (1893), page 705.

<sup>3</sup> Arrhenius, *Lehrbuch der Elektrochemie* (1901), page 55. Also "Theories of Chemistry" (1907), page 83.

It will be seen that the values for the dissociation constant are now *really constant*, up to concentrations of solute well above normal. (In very highly concentrated solutions there is still a slight decrease; this is considered in a later section.) Equation (7) is therefore valid for the expression of the dissociation constant of acetic acid *in concentrated solutions*. In subsequent tables it is shown that it is similarly applicable to other weak electrolytes. Meanwhile, some theoretical consequences of the hypothesis put forward above will be considered and its legitimacy tested.

In one respect it will, at first sight, appear that the dilution law of Ostwald claims preference over the modified law advanced above, namely in its simplicity. In equation (7) a variable factor,  $c_s$ , has been brought into the equation for the dissociation equilibrium, and this factor varies with the concentration in the desired direction for improving the constancy of  $K$  at high concentrations. Hence it may seem that the introduction of the variable factor  $c_s$  into the equation is simply a mathematical trick, which improves the agreement with the experimental results only by destroying the original simplicity of the dilution law. If this were indeed so, then the generally accepted theoretical basis lying behind the dilution law of Ostwald (the assumption of spontaneous dissociation of the undissociated molecule) could not legitimately be called into question here.

In the following section, however, it will be demonstrated that the above objection is not valid. The equilibrium of ionic dissociation has, so far, been considered only from the simple kinetic standpoint. When an exact thermodynamic examination is made, it is found that the original simplicity of the dilution law is not sacrificed by the modified view taken of the nature of the dissociation equilibrium; but that the dilution law has, on the other hand, *actually become less complicated*, inasmuch as certain simplifying assumptions, necessary for the development of the equation in its original form, may now be dispensed with.

*Thermodynamic Investigation of the Dissociation Equilibrium.*—The dilution law is first developed below in its original form and examined from the thermodynamic view-point. The modified form of the law, as deduced from the theoretical considerations advanced above, is then similarly derived, and the results compared.

For the Ostwald dilution law, the line of argument followed is substantially that given by Partington<sup>1</sup> in an investigation on the ionic equilibrium in solutions of electrolytes.

“The thermodynamic investigations lead to the equilibrium isotherm:<sup>2</sup>

<sup>1</sup> Partington, *J. Chem. Soc.*, 97, 1159 (1910).

<sup>2</sup> It has been pointed out to the author by D. A. MacInnes that this is not a *purely* thermodynamic equation. From the laws of thermodynamics alone we arrive at the

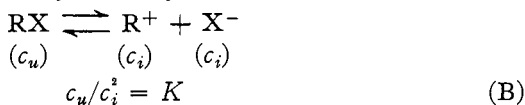


$$n' \log c' + n'' \log c'' + n''' \log c''' + \dots = \log K,$$

where  $K$  is a function of the temperature and total pressure for given components, but is constant at constant temperature and pressure.  $K$  is independent of the molecular concentration ( $c$ ) and numbers of molecular weights ( $n$ ) of the components. Thus:

$$c'^{n'} \cdot c''^{n''} \cdot c'''^{n'''} \dots = K \tag{A}$$

For the ionization of a binary electrolyte:



If  $n_u, n_i, n_s$  are the corresponding numbers of molecular weights of the components,

$$\begin{aligned} c_u &= n_u / (n_u + 2n_i + n_s); \\ c_i &= n_i / (n_u + 2n_i + n_s); \end{aligned}$$

where  $n_s$  refers to the solvent.

Substituting in (B), we obtain:

$$n_u(n_u + 2n_i + n_s)/n_i^2 = \text{constant} \tag{C}$$

This reduces, when  $n_u$  and  $n_i$  are small compared with  $n_s$ , to the form:

$$n_u \cdot n_s / n_i^2 = \text{constant}$$

Let  $v$  be the volume of solution containing one molecular weight of total salt, then (again only if  $n_u$  and  $n_i$  are small compared with  $n_s$ ), we have,

$$n_s = kv(n_u + n_i),$$

where  $k$  is a constant of proportionality.

Thus finally,

$$n_u(n_u + n_i)v/n_i^2 = \text{constant}. \tag{D}$$

This equation is as far as thermodynamic theory will proceed; to bring the result into a region accessible to experimental test, a further assumption is necessary. The determination of  $n_i$ , the ionic concentration, is made possible if we accept Arrhenius' fundamental theorem that the ratio of the number of "active" (or ionized) molecules of the electrolyte to the total number, active and inactive, present in a given portion of solution is equal to the ratio of the molecular electrical conductivity of the solution to the limiting value of this when the dilution is very great:

$$n_i / (n_u + n_i) = \Lambda / \Lambda_0 = \gamma \tag{E}$$

Substituting in (D) the value of  $n_i / (n_u + n_i)$  from (E), we obtain:

$$\Lambda^2 / \Lambda_0 (\Lambda_0 - \Lambda) v = \text{constant} = K \tag{F}$$

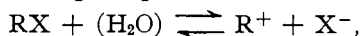
This is Ostwald's Dilution Law.

equation:  $n'v'd\pi' + n''v''d\pi'' + n'''v'''d\pi''' + \dots = 0$ . (Compare Washburn, THIS JOURNAL, 32, 484 (1910).) The equation given above is obtained by the integration of this and with the use of the further assumption that the relation  $c = k\pi$  holds. ( $\pi$  = osmotic pressure,  $c$  = molecular concentration,  $k$  = constant.)

The thermodynamic derivation shows that the formula can, in any case represent the course of ionization only in solutions of such dilution that the regions of solvent influenced by each molecule of solute are independent.

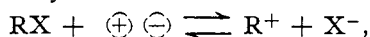
From the above argument it will be evident that the apparent simplicity of the Ostwald dilution law is obtained only at the sacrifice of its applicability to concentrated solutions. The changes necessary in the above thermodynamic derivation of the equation for the dissociation equilibrium, under the modified theoretical basis advanced above, may now be investigated.

The equation representing the process of ionization becomes:



corresponding with the view, expressed above, that the dissociation of the undissociated molecule RX into its component ions  $\text{R}^+$  and  $\text{X}^-$  is brought about by impact with molecules of the solvent.

It may appear at this point that the above equation is incorrectly stated, inasmuch as it does not balance. As a matter of fact, the corresponding equation for the original dilution law also does not balance, since the ionic charges appear only on one side. It will be shown, in a subsequent section, that the solvent is not to be considered as acting *chemically* in the ionization equation written above. The process of dissociation is regarded as entirely *physical* in its nature, the action of the solvent molecules being ascribed to their unsaturated character, *i. e.*, to the free valences or "neutrons" attached to them. Thus the above equation is more correctly to be written:



where  $\oplus \ominus$  represents a neutron. This equation balances exactly. Since, however, the ionic charges are supplied directly by the molecules of the solvent, the concentration of the latter is the factor that must appear in the equation. The matter is discussed more fully later, in connection with the results of Walden.

From the above equation we obtain:

$$c_u \cdot c_s / c_i^2 = K \quad (\text{B}')$$

For  $c_s$  we have the relation:

$$c_s = n_s / (n_u + 2n_i + n_s),$$

$c_u$  and  $c_i$  being transformed as before. We now obtain, in the next step, the equation:

$$n_u \cdot n_s / n_i^2 = \text{constant}, \quad (\text{C}')$$

which is *valid exactly at all concentrations*.

Let us now define  $v'$  as the number of *unit weights of solvent* employed to dissolve one equivalent weight of total salt. The change is thus made from volume concentration of the solute (equivalent weights per fixed

volume of solution) to weight or molecular concentration (equivalent weights per fixed weight of solvent). Then we have:

$$n_s = k'v'(n_u + n_i),$$

where  $k'$  is a constant of proportionality.<sup>1</sup> This equation is also *exactly true for all concentrations*.

We now obtain:

$$n_u(n_u + n_i)v'/n_i^2 = \text{constant}, \quad (\text{D}')$$

and finally, employing equation (E) as before, we have the modified dilution law,

$$\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda).v' = \text{constant} = K, \quad (\text{F}')$$

both of which equations are valid not only for small concentrations of solute, but *for all concentrations*.

Equation (F')—which is, of course, identical with the previous equation (7) above—therefore has, when compared with the dilution law in its original form, the two advantages of *simplicity* and of *agreement with the experimental data at high concentrations*. Several points in the above thermodynamic investigation, however, require more extended consideration; these are taken up in order below.

We have, first of all, the fact that it appears, on a first inspection of equation (F') above, that there are two units of concentration simultaneously employed, namely in the expression of  $\Lambda$  (the equivalent conductivity, *i. e.*, the specific conductivity divided by the *volume concentration* of the solute) and of  $v'$  (the reciprocal of the *weight or molecular concentration* of the solute). However, the equation can be expressed, in terms of weight concentration only, without change of form, since  $\Lambda$  has the same value for either unit of concentration.

This becomes evident from an examination of the experimental method followed in the determination of equivalent conductivity. The quantity directly measured in experimental work is the specific electrical resistance of the solution. The specific conductivity,  $\kappa$ , is the reciprocal of this, and is proportional to the number of dissociated molecules in *unit volume of the solution*.<sup>2</sup> The equivalent conductivity  $\Lambda$  is equal to  $\kappa v$ , where  $v$  represents the dilution in volume units.

If now, we change from volume concentration units to weight concentration units, thereby altering the dilution  $v$  to  $v'$ , we must also modify our definition of specific conductivity, and this will now be proportional to the number of dissociated molecules in *unit weight of the solvent*. Consequently, if the specific conductivity under weight concentration units is  $\kappa'$ , we have the relation:

<sup>1</sup>  $k'$  represents the number of equivalent weights of the solvent contained in the fixed weight of solvent chosen as unit. The equation consequently represents both molecular and weight ratios between solute and solvent.

<sup>2</sup> Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898), pages 102-3.

$$\kappa' = \kappa.(v/v').$$

Hence the equivalent conductivity under weight units,  $\kappa'v'$ , is equal to  $\kappa v$ . The equivalent conductivity  $\Lambda$  therefore has the same value, expressed in either unit of concentration.

A second point for examination is how far we are justified in considering the fundamental assumption of Arrhenius:

$$\Lambda/\Lambda_0 = \gamma, \text{ the degree of dissociation,}$$

as being applicable to concentrated solutions.

It is a much-debated question<sup>1</sup> whether this assumption is exactly true even at very high dilutions. In any case, it can be directly valid only if the ionic mobilities are not functions of the concentration. Now at high concentrations the ionic mobilities certainly are variable, since they are affected by the increased viscosity of the medium, and any correction (as for acetic acid in Tables I and II) can be only approximate. At high dilutions, however, the viscosity factor (that is, the change in the nature of the medium) may be neglected. Variation in ionic mobility at high dilutions, therefore, can occur only if mobility is a function of *ionic concentration*. That this is indeed the case was a view first advanced by Jahn,<sup>2</sup> in order to account for the "anomaly of strong electrolytes." Arrhenius,<sup>3</sup> however, showed that neither Jahn's theoretical work nor his experimental data were sufficiently reliable to warrant the conclusions drawn. The case of the hydrogen ion has been most frequently investigated, and here the majority of results<sup>4</sup> certainly point to the fact that the mobility is constant in dilute solutions.

The hypothesis of Jahn has recently been brought into prominence again by the work of Lewis.<sup>5</sup> The opposite view—that the ionic mobility is constant, and that the abnormality of strong electrolytes must be attributed to the change in the dissociating power of the solvent, due to the addition of solute—first advanced by Arrhenius,<sup>6</sup> has also been supported by the extended researches of Walden.<sup>7</sup>

Here a choice must be made between the two views, and since the assumption of varying ionic mobility in dilute solution must be regarded as not yet confirmed,<sup>8</sup> the simple hypothesis of Arrhenius and Walden

<sup>1</sup> For a review of the subject and a list of references see Wegscheider (*Z. physik. Chem.*, **69**, 603 (1909)) and Partington (*J. Chem. Soc.*, **97**, 1162 (1910)).

<sup>2</sup> Jahn, *Z. physik. Chem.*, **33**, 545 (1900); **35**, 8 (1900).

<sup>3</sup> Arrhenius, *Ibid.*, **36**, 28 (1901).

<sup>4</sup> For references see Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

<sup>5</sup> Lewis, *THIS JOURNAL*, **34**, 1631 (1912).

<sup>6</sup> Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899). See also Franklin and Kraus, *THIS JOURNAL*, **27**, 216 (1905); Lewis and Wheeler, *Z. physik. Chem.*, **56**, 179 (1906).

<sup>7</sup> Walden, *THIS JOURNAL*, **35**, 1649 (1913).

<sup>8</sup> Wegscheider, *Z. physik. Chem.*, **69**, 605 (1909).

will be followed in the present paper. It will be assumed that ionic mobility is not a function of ionic concentration.

When we consider higher concentrations, the mobilities of the ions undoubtedly vary. Also the different ions of an electrolyte are not equally affected by the change in the nature of the medium, since the transport numbers may vary appreciably with the concentration.<sup>1</sup> This variation is clearly connected with the phenomena of ionic hydration, and is important only in the case of electrolytes containing highly hydrated ions, where the variation in the degree of ionic hydration with the concentration will be greatest. For more normal electrolytes the change in the transport numbers of the ions, for solutions of less than normal concentration, may be regarded as of secondary importance.<sup>2</sup>

From the point of view taken above—that the ionic mobility is, in normal cases,<sup>3</sup> not a function of the ionic concentration—it follows that the degree of accuracy obtained in the determination of  $\gamma$ , as calculated from the experimental value for  $\Lambda$ , will be dependent primarily only upon the accuracy of the viscosity correction applied. This correction has already been discussed in an earlier section.

The fundamental assumption of Arrhenius, even if it does not lead us directly to conclusive results, yet enables us to attack problems which we should otherwise have to leave untouched. It has consequently been in general use in the investigation of concentrated solutions as our only means, until considerable advances have been made, of interpreting and using experimental results.<sup>4</sup>

*The Change from Volume to Weight Units of Concentration.*—From a purely thermodynamic and theoretical view point, there is no question as to the desirability of the change from volume to weight concentration units,<sup>5</sup> here as in other branches of physical chemistry. From the experimental side the use of the volume unit undoubtedly offers many advantages in simplicity and convenience of procedure, and these suffice to account for its general adoption for the expression of experimental data. However, since  $\Lambda$  has the same value expressed in either unit, the change

<sup>1</sup> Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898), page 201. In the case of two only of the simple uni-univalent electrolytes given is the variation in the transport number of the anion, between zero and half-normal concentration, greater than 0.01. These two electrolytes are the chlorides of lithium and sodium, the component ions of which are known to be highly hydrated.

<sup>2</sup> The accurate determination of transport numbers is extremely difficult, and in most cases a large variation in the transport number represents a relatively small change in the calculated value of  $\gamma$ .

<sup>3</sup> *i. e.*, where the variation in the degree of ionic hydration with concentration exercises no disturbing influence.

<sup>4</sup> Compare Lewis, *Z. physik. Chem.*, **70**, 217-8 (1910).

<sup>5</sup> Planck, *Wied. Ann.*, **32**, 489 (1887); Washburn, *THIS JOURNAL*, **32**, 668 (1910).

of units here involves no experimental difficulties to counterbalance its advantage for the expression and derivation of theoretical relations.

In several branches of physical chemistry, closely related to equivalent conductivity, the change to weight units has already furnished important results. A prominent example is afforded by the work of Morse and Frazer<sup>1</sup> on the osmotic pressures of solutions of sucrose. Results of experiments on the lowering of the freezing point, the raising of the boiling point, and the lowering of the vapor pressure of the solvent by dissolved salts have always been expressed in weight units of concentration.<sup>2</sup> In the application of the solubility-product principle, the concentrations of the dissolved electrolytes must be reduced to weight units to obtain comparable results.<sup>3</sup> Similarly, the viscosity of binary mixtures<sup>4</sup> (including solutions) has been shown to be a function of the molecular and not of the volume concentration of the two components. This is important in view of the close relation existing between viscosity and equivalent conductivity.

*Experimental Data.*—In the preceding section the modified form of the dilution law has been shown to be fundamentally more simple than the original dilution law, and to cover a more extended range, since it is exactly applicable to concentrated solutions. Hence it is, at this point, legitimate to emphasize the theoretical basis assumed above, namely, that the dissociation of the undissociated molecule in the solution is brought about, not spontaneously, but by the action of the solvent.

It is not asserted here that the above theoretical basis is definitely established by the results obtained. Several factors have been left out of consideration, which become of importance in concentrated solutions, as is discussed later; also the amount of *exact* experimental data that can be brought forward is, at present, extremely meagre.<sup>5</sup>

<sup>1</sup> Morse and Frazer, *Am. Chem. J.*, **34**, 1 (1905); see also Bancroft, *J. Phys. Chem.*, **10**, 319 (1906), and Morse, Frazer and Dunbar, *Am. Chem. J.*, **38**, 212–26 (1907).

<sup>2</sup> For example, in the freezing point data, collected by Noyes, *THIS JOURNAL*, **32**, 1026 (1910). In comparing the results obtained with those derived from conductivity experiments, however, Noyes has transferred these figures to volume concentrations without correction (*THIS JOURNAL*, **34**, 485 (1912)). Washburn and MacInnes, in a similar comparison of the freezing point and conductivity data for solutions of caesium nitrate, have, on the other hand, expressed all quantities in molecular concentrations, *THIS JOURNAL*, **33**, 1711 (1911).

<sup>3</sup> Kendall, *Proc. Roy. Soc., (A)* **85**, 200 (1911).

<sup>4</sup> Kendall, *Meddel. från K. Vet. Akads. Nobelinstitut*, Band **2**, No. 25 (1912).

<sup>5</sup> Only very weak acids and bases are of use for examination here, since even in acids a little stronger than acetic acid we shall have, in *concentrated* solutions, the "anomaly of strong electrolytes" beginning to appear. The substances examined must also be very soluble in water to give sufficiently concentrated solutions. These conditions cut out the majority of the ordinary organic acids, and only in a few of those remaining are all the necessary data available.

An extensive list of weak electrolytes has been tabulated by Wegscheider,<sup>1</sup> and the concentration fixed in each case at which divergence from the dilution law begin to become appreciable. For all these electrolytes, it may be asserted that the modified dilution law will give *qualitatively* better agreement with the experimental data at high concentrations, but the absence of reliable density and viscosity results precludes, at present, the possibility of establishing *quantitatively* exact agreement.

Experiments are already in progress to supplement the few instances given below.

For the series of normal fatty acids, the following results are available. The conductivity data are selected from the determination of White and Jones,<sup>2</sup> the results for viscosity and density are taken from the work of Reyher.<sup>3</sup> The various columns have the same significance as in Table I.

TABLE III.—FATTY ACIDS, 25° (WHITE AND JONES).

Acid.	<i>v.</i>	$\Lambda$ .	$\eta$ .	<i>d.</i>	100 <i>K</i> .	100 <i>K</i> <sub>2</sub> .
Acetic.....	2	2.089	1.060	1.0042	0.00169	0.00194
	8	4.342	1.017	1.0013	0.00183	0.00191
	32	8.699	1.004	1.0003	0.00186	0.00188
Propionic.....	2	1.700	1.099	1.0035	0.00116	0.00145
	8	3.704	1.026	1.0011	0.00138	0.00147
	32	7.436	1.007	1.0003	0.00141	0.00143
<i>n</i> -Butyric.....	2	1.730	1.132	1.0022	0.00120	0.00161
	8	3.891	1.031	1.0006	0.00153	0.00164
	32	7.902	1.008	1.0002	0.00159	0.00162
<i>iso</i> -Butyric.....	2	1.633	1.129	1.0016	0.00108	0.00152
	8	3.821	1.032	1.0004	0.00147	0.00158
	32	7.621	1.008	1.0001	0.00148	0.00150

Considering the accuracy of the data employed, the degree of concordance in the values shown under 100 *K*<sub>2</sub> in the above table is satisfactory throughout. Hence the modified dilution law may be held to apply, for the above acids, up to solutions of at least half-normal concentration.

In Table IV the figures for a typical weak base—ammonia—are given.

TABLE IV.—AMMONIA, 25° (OSTWALD).

<i>v.</i>	$\Lambda$ .	$\eta$ .	<i>d.</i>	100 <i>K</i> .	100 <i>K</i> <sub>2</sub> .
2	1.56	1.012	0.995	0.00193	0.00203
4	2.24	1.006	0.997	0.00199	0.00204
8	3.21	1.003	0.998	0.00205	0.00208
16	4.55	1.001	0.999	0.00207	0.00208
∞	(252)	...	...	.....	.....

<sup>1</sup> Wegscheider, *Z. physik. Chem.*, **69**, 611-13 (1909).

<sup>2</sup> White and Jones, *Am. Chem. J.*, **44**, 159 (1910).

<sup>3</sup> Reyher, *Z. physik. Chem.*, **2**, 749 (1888). The viscosity results are liable to (relatively) considerable error, as will be evident by inspection of the original.

The conductivity results are those of Ostwald,<sup>1</sup> the viscosity and density data are interpolated from the figures given in Landolt-Börnstein.

The agreement of the values given under  $100 K_2$  is again satisfactory, in view of the nature of the experimental data. For example, an error of 0.01 in the value of  $\Lambda$ , at the first concentration given, corresponds to a difference of 3 units in  $100 K_2$ .

The above tables may be amplified by extending the modified form of the dilution law to the author's equation for transition electrolytes, shown in equation (3), (which also fails in concentrated solutions) and testing its applicability there also. Equation (3) is modified to the form:

$$\gamma^2/(1 - \gamma)v' = K + c(1 - \gamma)/\gamma. \quad (9)$$

The results for a typical transition electrolyte—dichloroacetic acid—are given in Table V. The viscosity and density figures are taken from the determinations of Kanitz.<sup>2</sup>

TABLE V.—DICHLOROACETIC ACID, 25° (KENDALL).

v.	A.	$\eta$ .	d.	$100\{K + c(1 - \gamma)/\gamma\}$		$100\{K + c_2(1 - \gamma)/\gamma\}$	
				Expt.	Calc.	Expt.	Calc.
2	114.9	1.1318	1.0263	6.33	7.68	8.92	8.93
4	151.7	1.0640	1.0139	6.38	6.70	7.57	7.52
8	190.2	1.0287	1.0067	6.00	6.08	6.60	6.62
16	231.6	1.0143	1.0033	5.64	5.65	5.96	6.00
32	273.1	1.0071	1.0016	5.38	5.34	5.57	5.55
64	309.7	1.0035	1.0008	5.12	5.14	5.23	5.26
128	338.7	1.0018	1.0004	4.96	5.02	5.04	5.09
256	359.2	1.0009	1.0002	4.94	4.94	5.02	4.99
$\infty$	385.6	....	....	..	4.85	..	4.85

$$K = 0.0485, c = 0.0120, c_2 = 0.0173.$$

The agreement of equation (3) in its original form with the experimental results is shown by the figures under  $100\{K + c(1 - \gamma)/\gamma\}$  in Table V, the agreement of the equation in its modified form (9) is given by the figures under  $100\{K + c_2(1 - \gamma)/\gamma\}$ . It will be seen that the equation holds exactly, in its original form, only for dilute solutions; while the modified form gives agreement throughout the entire series.

Additional experimental results will be given in a future communication, where the application of the above changes to solutions of strong electrolytes will also be considered. In conclusion here, the limits of the applicability of the modified dilution law proposed are briefly examined, and the results obtained in this paper compared with those of Walden.

*Limits of Applicability of the Modified Dilution Law.*—It has been shown that the dilution law, in its modified form, is exactly applicable up

<sup>1</sup> As transposed to the modern units in Kohlrausch and Holborn, "Leitvermögen der Elektrolyte" (1898), page 167.

<sup>2</sup> Kanitz, *Z. physik. Chem.*, **22**, 336 (1897).



to concentrations of at least half-normal for typical weak electrolytes. In the case of acetic acid, the values obtained for  $K$  with the aid of the modified law are constant up to concentrations well above normal, then follows a decrease when still higher concentrations are considered.

It will be evident, on examination, that the modified law *must* break down at these very high concentrations of solute, since many complicating factors arise which have not been taken into account. The chief of these are enumerated below.

In the first place, the viscosity correction to  $\Lambda$  becomes larger, and the probable error of its application greater, with increase of concentration. Also the likelihood that the fundamental assumption of Arrhenius, discussed previously, will be true even if an exact viscosity correction could be applied, decreases as the concentration of solute is increased.

At high concentrations, further, the hydration of the solute—both in its undissociated and in its dissociated state—complicates the equilibrium in the solution. The undissociated solute, if hydrated, will withdraw a considerable quantity of solvent from the equilibrium, and the concentration of “free” solvent in the solution will be greatly reduced. If the ions are hydrated, their mobilities may vary considerably in concentrated solutions, owing to the variations in the degree of hydration with the concentration of the solvent.

More important still, the change in the *nature* of the solvent at high concentrations of solute will be considerable. A highly associated solvent, such as water, will tend to dissociate more and more into simpler molecules as its concentration in the solution decreases.<sup>1</sup> Also the change in the dielectric constant of the medium, for high concentrations of solute, is of importance.

Finally the variation in the heat of dilution with the concentration (which affects the constancy of  $K$ ) has not been taken into consideration.

The modified form of the dilution law, as expressed in the simple equations (7) and (F'), cannot be expected to hold in general, therefore, for *highly concentrated* solutions. Only up to (approximately) normal concentration of solute is it exactly valid. Even so, this represents a con-

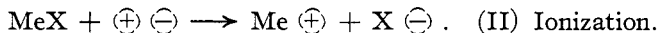
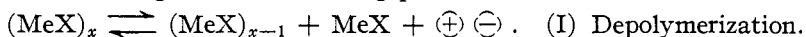
<sup>1</sup> The ionizing power of a solvent is intimately connected with its *power of association* into large molecules. The best ionizing solvents are unsaturated, *e. g.*, water contains an unsaturated oxygen atom with two free valencies, and the simple molecule may be written  $\text{H}_2\text{O}\ddagger$ . Hence, by the loss of two free valences (the positive charge on one oxygen atom being neutralized by the negative charge on another) two simple molecules can combine to form a complex molecule,  $+\text{OH}_2\cdot\text{H}_2\text{O}-$ . Such association can evidently continue further, each step being accompanied by the loss of two free valences. “One can readily see that such molecules would be electrically polarized, and their charges might easily have the power to cause electrolytic dissociation or ionization.” Stieglitz, “Qualitative Chemical Analysis” (1912), Part 1, page 65. Compare also Arrhenius, “Theories of Chemistry” (1907), page 83.

siderable advance upon the previous limit of  $v = 32$  (approximately) for the dilution law in its original form.

*Comparison with the Results of Walden.*—It is of interest at this point to compare the conclusions of the present investigation with those drawn by Walden from the study of the dielectric constants of dissolved salts, and to examine how far the results may be combined.

The hypothesis advanced here as an explanation of the immediate cause of the dissociation of the undissociated molecule in the solution of an electrolyte is that the simple undissociated molecules are broken up into their component ions by impact with the molecules of the solvent.

Walden,<sup>1</sup> on the other hand, concludes that "the process of disaggregation of the polymerized salt molecules also causes, and induces, the process of ionic cleavage." The following processes are assumed.<sup>2</sup>



$(\text{MeX})_x$  is the polymerized salt,  $x$  the extent of association,  $\text{MeX}$  the simple salt molecule.  $\oplus$  and  $\ominus$  represent a positive and a negative electron, respectively,  $\oplus \ominus$  a neutral electron (neutron),<sup>3</sup>  $\text{Me} \oplus$  a cation,  $\text{X} \ominus$  an anion.

Now the depolymerization of the solid salt  $(\text{MeX})_x$ , which takes place in its solution, must be regarded as due to the bombardment of the complex and unstable molecules of the salt by the molecules of the solvent. The reaction is specific in each case, and the natures of both solute and solvent are factors in the degree of depolymerization. That this is so is shown by the two facts that different substances are depolymerized to different degrees in the same solvent, and that the same substance is depolymerized to different degrees in different solvents.

In this depolymerization of the solute, neutrons are formed in the solution, as is indicated by the first equation of Walden above. These neutrons will attach themselves to molecules of the solvent,<sup>4</sup> and the dielectric constant of the medium will be changed.

The process can be studied from another point of view with similar re-

<sup>1</sup> Walden, *THIS JOURNAL*, **35**, 1661 (1913).

<sup>2</sup> The depolymerization process (Equation I) consists, of course, of successive stages from  $(\text{MeX})_x$  to  $\text{MeX}$ , of which one only is given above.

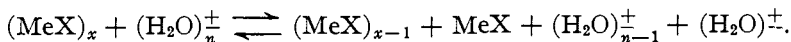
<sup>3</sup> Walden's conception of "neutral electrons" is retained in the discussion merely for convenience in the comparison of results. It will become evident below that the argument could be more logically expressed in terms of *free valences*, without the use of the indefinite expression "neutron."

<sup>4</sup> This statement is, of course, an assumption, since the neutrons might attach themselves directly to the simple undissociated molecule  $\text{MeX}$ . (Compare A. A. Noyes, *Carnegie Institute Publication*, No. **63**, 351 (1907).) The change in the degree of association of the solvent with the concentration of solute necessitates, however, at least *some* transfer of neutrons to the solvent.

sults. After the addition of the salt, the concentration of the solvent in the solution will have been diminished, hence its degree of association will also have diminished. That is, some complex molecules of the solvent will have broken down into simpler molecules, and this process is essentially *the taking-up of neutrons*.<sup>1</sup> For example, in water,



We may therefore rewrite the first equation of Walden in the form:



It is evident from this equation that *the process of depolymerization is common to both solvent and solute*,<sup>2</sup> and is accompanied by an increase in the number of neutrons in the solution and by a change in the dielectric constant. The change in the dielectric constant will be greater, the more neutrons the solvent has taken up, that is, the greater the degree of depolymerization.<sup>3</sup> This is in accordance with the results of Walden, and is of importance in the consideration of the "anomaly of strong electrolytes."

It is now evident that the second equation of Walden, for the expression of the ionization equilibrium, can be at once made identical with the equation given on page 1078 of the present paper by transformation as below:



the solvent acting *simply as the carrier of the "neutron."* Hence also the equation

$$c_u \cdot c_s / c_i^2 = K \quad (7)$$

for the dissociation process can hold only so long as the concentration of neutrons in the solution is proportional to the concentration of the solvent. At high concentrations this can no longer be assumed to be the case, and the modified dilution law consequently cannot apply exactly, as has already been pointed out in the previous section.

We have now a simple means of expressing the mechanism of electrolytic dissociation. By impact of an undissociated molecule of the solute, MeX, with a molecule of the solvent, a neutron is transferred from the latter to the former, and the undissociated salt breaks up into its separate ions Me<sup>⊕</sup> and X<sup>⊖</sup>. Similarly, by impact between ions of unlike

<sup>1</sup> See note on page 1085. A neutron is equivalent to *two free valences*, and is used in this sense throughout the present discussion.

<sup>2</sup> Hence, also, non-associated solvents do not depolymerize dissolved salts. Consequently salts are highly ionized only by associated liquids; for example, hydrochloric acid, which is almost entirely dissociated in water, gives practically a non-conducting solution in benzene (Kablukoff, *Z. physik. Chem.*, 4, 430 (1889)).

<sup>3</sup> It is possible that the dielectric constant is *directly* a function of the concentration of neutrons on the solution. This will account for the low dielectric constants of non-associated liquids, and for the great increase in the dielectric constant of a feebly ionizing solvent on the addition of an electrolyte.

charge,  $\text{Me}^{\oplus}$  and  $\text{X}^{\ominus}$ , a molecule of the undissociated salt  $\text{MeX}$  is formed, with the liberation of a neutron, which attaches itself to a molecule of the solvent. The solvent molecules thus lose and gain neutrons alternately, as expressed by equation (10). The above view is evidently consistent with the fact that ionizing solvents possess the two characteristic properties of *unsaturation* (presence of neutrons) and *association*.

By comparison of the results of Walden with those of the present paper and by combination of the conclusions drawn we are able to obtain, therefore, a simple view of the whole mechanism of the dissociation equilibrium in the solution of an electrolyte.

### Summary.

A modified form of the dilution law has been proposed, which is found to be in accordance with the data of experiment throughout a region in which the dilution law, in its original form, fails to apply, namely in concentrated solutions of weak electrolytes.

The theoretical basis underlying this modification of the dilution law is that the dissociation of the undissociated molecule  $\text{RX}$  in the solution of a binary electrolyte, into its component ions  $\text{R}^+$  and  $\text{X}^-$ , takes place not spontaneously but by impact with the molecules of the solvent.

With the use of this hypothesis the dilution law, as derived thermodynamically, is found to be fundamentally simpler in form than previously, since it is applicable exactly not only to dilute but also to concentrated solutions without any simplifying assumptions.

The advantage of a change from volume units of concentration to weight or molecular units, for the expression of equivalent conductivities and the calculation of dissociation constants, has been pointed out.

The conclusions of the present investigation have been compared and combined with those of Walden, with the result that a simple view of the mechanism of the ionization equilibrium is obtained. It is shown that the dissociating power of the solvent molecules is to be ascribed to their unsaturated character, *i. e.*, to the presence of free valences.

Additional experimental results will be given, and the case of strong electrolytes examined, in a future communication.

The above investigation was commenced at the Nobel Institute of Physical Chemistry, Experimentalfaltet, Sweden. It is a pleasant duty to me to express here my gratitude to Professor Svante Arrhenius for his hospitality, and for his helpful criticism of the initial stages of the research.