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THE DIELECTRIC CONSTANTS OF DISSOLVED SALTS.[1]

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As may be remembered, J. J. Thomson, as well as W. Nernst, independently of each other, (as a result of theoretical considerations) formulated the rule that the electrolytic dissociation of an electrolyte increases with the dielectric constant of the solvent. Proceeding from this point, experimental research has followed along two lines. The dielectric constants of various solvents have been redetermined (Nernst, Drude, Ratz, Thwing, Philip, Schlundt, Walden and others), and the connection between this and other physical properties has been sought (*e. g.*, Ph. A. Guye, Walden); on the other hand, the validity of the rule of Thomson-Nernst for various solvents and electrolytes has been investigated (*e. g.*, Carrara, Kahlenberg and Lincoln and most exhaustively by Walden since 1905). This connection between the dielectric constant and dissociating effect of the solvent, for which new facts were discovered and new equations were formulated by the author, found further rigorous examination and theoretical application in the investigations of Malmstroem (1905), Baum (1906), Sutherland (1907), J. J. Van Laar (1907), McCoy (1908), F. A. Kjellin (1911), F. Krueger (1911). If, then, the one component of the solution, the solvent, has been investigated exhaustively, the role of the second component, the dissolved substance (especially the dissolved binary salts), has, strangely enough, not received sufficient attention. And yet, solvent and undissolved substance act reciprocally, one upon the other, and both may readily exchange their functions. What

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[1] Abstract from the writer's publications in *Bull. de l'Acad. Impér. des Sciences, St. Petersburg*, pp. 305–332, 1055–1086 (1912). Acceding to the kind request of Prof. W. A. Noyes I take pleasure in preparing this report particularly for THIS JOURNAL, Translated from the German by H. C. P. Weber.

is true for the dissociating effect of the solvent—*mutatis mutandis*—is true of the dissolved substance. In short, the following question arises; Is the dielectric constant of the solvent, and hence its dissociating effect, changed or not changed by dissolving an electrolyte (for instance a binary salt) in it?

The question is not new. As early as 1892 it was raised by E. Cohn and was answered experimentally in the manner that the increase of the dielectric constant of water "is surely indicated" upon dissolving salt (*e. g.*, NaCl) in it. Similar results were obtained by G. Udny Yule (1893) in the case of aqueous zinc sulfate solutions. On the other hand, W. Nernst (1894) maintained that "according to the present knowledge, an addition of small quantities of foreign substances to a dielectric, which very markedly increases its electrical conductivity, is without effect upon its dielectric conductance." In the same manner, so well known an authority as P. Drude (1896–97) came to the conclusion that it "undoubtedly follows from the results (aqueous solutions of NaCl and $CuSO_4$) that, even up to the conductivity $\alpha = 11 \times 10^{-3}$, the dielectric constant of water is certainly not increased through solution of an electrolyte." Forrest Palmer (1902) reached similarly negative results (KCl and $CuSO_4$) with water. As a result of these decided negations, the observations of F. J. Smale (1897) remained unnoticed, or at least doubtful, and yet this investigator had shown by the electrometric method that a decided increase of dielectric conductivity is produced by small additions of salts (KCl, HCl, $CuSO_4$, manite boric acid).

This unsettled, and according to the writer's opinion, important problem, it has (since 1910) been my object to solve, in that I replaced the strongly ionizing water (with its high dielectric constant $\mathbf{K} = 80$) by weakly ionizing solvents. For this purpose chloroform ($\mathbf{K} = 4.95$), methylene chloride ($\mathbf{K} = 8.3$), and formic ethylester ($\mathbf{K} = 8.2$) were chosen. As dissolved electrolytes, the salts of substituted ammonium bases were used. The investigation was carried out according to the method of Drude (2nd method (1907) wave length $\lambda = 70$ cm. Temperature $t = 17$–$19°$). The results of the measurements are given in the following tables, in which the symbols have the following meaning:

p—Percentage of dissolved substance (in 100 g. of solution).

$\mathbf{K}_1$ and d_1—Dielectric constant and density of the substance.

$\mathbf{K}_2$ and d_2—Dielectric constant and density of solvent.

$\mathbf{K}$ and d—Dielectric constant of the solution.

To calculate the dielec. const. $\mathbf{K}_1$ of the dissolved salt from the directly determined values $\mathbf{K}_2$ and $\mathbf{K}$, the following equations were used:

$$\frac{\sqrt{\mathbf{K}_1} - 1}{d_1} = \frac{100(\sqrt{\mathbf{K}} - 1)}{pd/c} - \frac{(100 - p)}{d_2 p}(\sqrt{\mathbf{K}_2} - 1)^{[1]}$$

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[1] Philip, *Z. physik. Chem.*, **24**, 28 (1897).

or

$$\mathbf{K}_1 = \mathbf{K}_2 + (\mathbf{K} - \mathbf{K}_2)\frac{100}{p}{}^{1}$$

or

$$\frac{\mathbf{K}_1}{d_1} = \frac{\mathbf{K}_2}{d_2} + \left(\frac{\mathbf{K}}{d} - \frac{\mathbf{K}_2}{d_2}\right)\frac{100}{p}.{}^{2}$$

Each equation yields different results for $\mathbf{K}_1$. The constitutive character of this derived dielectric constant, $\mathbf{K}_1$ is most clearly seen when using the method of calculation of Philip. See Table I.

The following deductions may be drawn from this table:

1. The dielec. const. of a weakly ionizing solvent (chloroform) is undoubtedly increased by solution of certain binary salts.
2. This increase of dielectric constant of the solvent is apparently dependent upon the constitution of the salt.
3. The binary salts chosen may be separated into weak and strong on the basis of their specific influence.
4. Strong salts, *e. g.*, tetra-alkylated ammonium salts, which are characterized by a great dissociation tendency, at the same time possess a very large dielectric constant. For weak salts the reverse is true.
5. The electrolytic dissociation of a salt in a solvent is induced by the superposition of two effects; the ionizing tendency of the dissolved salt is added to the ion-forming tendency of the solution.
6. The highest degree of ionic dissociation is to be anticipated in the case of a solvent and dissolved salt each having a large dielectric constant.

A number of considerations may be added. It is to be remembered that, on the basis of the behavior of aqueous solutions, we are accustomed to consider the various binary salts as completely equivalent. Under the same conditions (equal temperature, equal concentration of the aqueous solution) practically identical degrees of electrolytic dissociation are actually exhibited by all binary salts of the alkali metals with mono-basic inorganic and organic acids; also by ammonium salts of the mono-, di-, tri- and tetra-alkyl substituted ammonium bases with hydrochloric, hydrobromic, hydriodic, nitric acids, etc. But the properties which the acids and the bases show as binary electrolytes in aqueous solutions are different. The degrees of ionization vary (in the same molecular concentrations) for the various acids, or bases, over the whole range of the available interval $\alpha > 0$ to $\alpha \leqslant 1$; and besides the weakest and weak acids or bases, we further distinguish between fairly strong, strong and strongest. Unfortunately these distinctions do not hold for all solvents, in fact, they are only admissible for water (and in part for other substances containing hydroxyl) as ionizing media. Thus, for example, we may

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[1] Bouty, *Compt. rend.*, 114, 1421 (1892).

[2] Silberstein, *Ann.*, 56, 661 (1895).

Table I.—Derived Values of Diel. Const. **K**$_1$ in Chloroform Solutions.

Compound.	Dilution V in liters.	Concentration $c = pd_1$.	**K** values read directly.	$\frac{\sqrt{K_1-1}}{d_1}$.	**K**$_1$ calc. acc. to Philip.	**K**$_1$ calc. acc. to Bouty.	**K**$_1$ calc. acc. to Silberstein.
Pure chloroform	...	....	4.95	0.832	(4.95)	(4.95)	(4.95)
I. $N(C_2H_5)_4Cl$	10	1.655	7.05	26.8	900	192	140
	15	1.103	6.40	27.9	970	199	146
II. $N(C_2H_5)_4Br$	10	2.10	6.77	19.1	756	139	130
	20	1.05	5.95	21.2	924	146	137
III. $N(C_2H_5)_4NO_3$	10	1.92	7.05	23.2	784	166	131
	15	1.28	6.40	24.8	889	172	136
IV. $N(C_3H_7)_4I$	10	3.13	7.2	15.46	454	111	99
	15	2.09	6.40	15.53	458	108	96
V. $N(C_3H_7)_4NO_3$	10	2.48	6.8	16.3	330	115	82
	20	1.24	5.95	18.1	400	124	89
VI. $C_6H_5N(CH_3)_2HBr$	10	2.02	5.95	11.4	256	78	69
VII. $C_6H_5N(CH_3)HHBr$	2.5	7.52	5.55	2.57	17	17	14
	5–15	3.76–1.25	4.95	(0.832)	(4.95	(4.95)	(4.95)
VIII. $N(C_2H_5)_3HCl$	10	1.38	6.2	20.0	500	138	100
IX. $HN(C_2H_5)_2HCl$	2.5	4.38	5.60	4.07	27.7	37	19
	10	1.10	5.10	3.83	25	25	18
X. $HN(C_2H_5)_2HNO_3$	2.5	5.44	6.0	4.97	46	33	26
	5	2.72	5.4	4.47	38	29	23
XI. $HN(C_5H_{11})_2Cl$	5	3.87	5.1	1.69	7	10.5	7
	10	1.94	4.95	(0.832)	(4.95)	(4.95)	(4.95)
XII. $H_2N(C_5H_{11})HCl$	5	2.47	5.0	1.28	5.2	8	5.4

convert tribromoacetic acid or picric acid, which are counted among the strongest acids in aqueous solutions, into exceedingly weak acids if we examin them in acetonitrile, nitromethane or acetone as ionizing medium. A similar conversion, and, at the same time, a differentiation, may be made in the case of the above named binary salts, in spite of the fact that in aqueous solutions they act as equally strong electrolytes. As early as 1900 the author[1] has repeatedly directed attention to the fact that the nature of the salt deserves greater notice than it has been customary to give to it. It was possible to show, in the case of liquid sulfur dioxide,[2] that the relation between the "strength" of the mono-, di-, tri- and tetra-ethyl substituted salts of ammonium chloride, at the same dilution (*a*) in sulfur dioxide (*b*) in water, could be reproduced by the following numerical values for the degrees of ionization.

	SO_2.	H_2O.	**K** (CH_3Cl).
$(C_2H_5)NH_2.HCl$ (v = 32) α = approx......	0.03	0.88	5
$(C_2H_5)_2NH_2.HCl$ (v = 32) α = approx......	0.08	0.86	25
$(C_2H_5)_3N.HCl$ (v = 32) α = approx.........	0.12	0.86	500
$(C_2H_5)_4N.Cl$ (v = 32) α = approx..........	0.58	0.86	940

While the four salts must be designated as equal and strong electrolytes, on the basis of their behavior in aqueous solutions, they appear as electrolytes of different ionization tendency in sulfur dioxide, that is, they are differentiated into weak and strong salts. From the tabulated values of the dielectric constants of the various salts, we now perceive that the tetra-alkylated ammonium salts have the highest dielectric constants, while the lowest value is to be ascribed to the mono-alkylated salts. Furthermore, the ionizing tendency in the relatively weak medium, sulfur dioxide, runs parallel with this.

In general, therefore, we may speak of a *parallelism between the readiness with which these electrolytes ionize and their dielectric constant* (in $CHCl_3$ solution). The salts with the highest dielectric constants are at the same time the best electrolytes (with a greater tendency to ionize). According to Thomson and Nernst, the rule holds for solvents that the electrolytic dissociation of a dissolved electrolyte increases as the dielectric constant of a solvent increases. The final result, that is, the degree of electrolytic dissociation, is therefore produced by the superposition of two effects, which intensify each other and are dependent, in the same manner, upon all components of the solution (dissolved substance and ions, solvent and their mutual association products) and which may be evaluated physically from the dielectric constants of the solvent and of the dissolved electrolyte.

In addition to chloroform as solvent, other substances have been taken into consideration, namely methylene chloride, CH_2Cl_2 and ethylformate.

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[1] *Z. anorg. Chem.*, **25**, 224 (1900); **54**, 142, 147, 169, 170, 181 (1905).

[2] P. Walden and M. Centnerszwer, *Ibid.*, **39**, 528 (1902).

Table II.—Derived Values of Diel. Const. $\mathbf{K}_1$ in Methylene Chloride Solution.

Compound.	Dilution V in liters.	Concentration $c = pd_1$.	$\mathbf{K}$ values read directly.	$\frac{\sqrt{\mathbf{K}_1 - 1}}{d_1}$.	$\mathbf{K}_1$ calc. acc. to Philip.	$\mathbf{K}_1$ calc. acc. to Bouty.	$\mathbf{K}_1$ calc. acc. to Silberstein.
CH_2Cl_2 as solvent	..	...	8.3	1.414	(8.3)	(8.3)	(8.3)
$N(C_2H_5)_4Cl$	20	0.827	10.15	38.2	1790	310	248
	40	0.414	9.3	42.2	2170	330	268
$N(C_2H_5)_4Br$	20	1.05	9.9	26.7	1450	210	220
	50	0.42	9.0	29.7	1780	230	240
$N(C_2H_5)_4I$	50	0.514	9.35	35.8	3250	280	330
$N(C_2H_5)_4NO_3$	20	0.96	9.9	29.0	1200	230	200
	30	0.64	9.5	32.8	1530	260	225
$N(C_3H_7)_4NO_3$	20	1.24	10.5	30.4	1100	240	190
	40	0.62	9.5	33.8	1350	270	210
$HN(C_2H_5)_2HCl$	5	2.19	9.2	8.3	94	63	49
	10	1.095	8.7	7.7	82	57	45
$N(C_2H_5)_3HCl$	5	2.75	10.9	16.7	355	134	108
	10	1.375	9.5	18.3	423	143	116
$HN(C_2H_5)_2HNO_3$	5	2.72	9.1	6.4	71	47	41
$C_5H_{11}N.C_6H_2(NO_2)_3OH$	10	3.14	9.5	7.8	77	59	45
	20	1.57	8.9	7.9	79	59	45
$N(C_2H_5)_3HNO_3$	10	1.64	10.0	18.0	425	146	125
$HN(C_2H_5)_2HBr$	5	3.08	8.7	..	...	25.5	...
$N(C_2H_5)_3HBr$	10	1.82	10.3	..	...	154	...
$HN(C_2H_5)_2.HI$	5	4.02	9.0	..	...	32	...
$HN(C_6H_5).CH_3.HBr$	5	3.76	8.8	..	...	26	...
$C_6H_5N(CH_3)_2.HBr$	10	2.02	10.1	..	...	128	...

In this way the role of the solvent in connection with the value of the dielectric constants of the dissolved substance was to be investigated. See Table II.

The next solvent is ethylformate, which is a representative of another type, namely of a substance containing oxygen. A further advantage of this substance was its solvent action on inorganic salts. For comparison with the substituted ammonium salts, sodium iodide, lithium bromide, potassium iodide and mercuric chloride were chosen. See Table III.

TABLE III.—DERIVED VALUES OF DIEL. CONST. K_1 IN ETHYLFORMATE SOLUTIONS.

Compound.	Dilution V in liters.	Concentration $c = pd_1$.	K values read directly.	$\frac{\sqrt{K_1}-1}{d_1}$	K_1 calc. acc. to Philip.	K_1 calc. acc. to Bouty.	K_1 calc. acc. to Silberstein.
$HCOOC_2H_5$ as solvent	..	...	8.2	2.048	(8.2)	(8.2)	...
$N(C_2H_5)_4Br$	20	1.05	9.9	29.0	1700	156	237
$HN(C_2H_5)_2HNO_3$	7.5	1.813	8.7	6.8	79	33	42
$N(C_2H_5)_3HNO_3$	10	1.64	9.7	17.3	395	92	109
NaI	10	1.50	9.9	20.8	5595	110	434
	15	1.00	9.45	23.0	6820	120	476
LiBr	10	0.87	9.1	19.6	4760	100	390
	15	0.58	8.9	20.7	5300	118	450
CaI_2	10	2.94	9.2	7.8	1540	40	210
$HgCl_2$	10	2.71	8.5	3.9	490	19	108

The dissolved salts give very nearly the same values of the dielectric constant for the two solvents, CH_2Cl_2 and $HCOOC_2H_5$ (which have nearly equal dielectric constants but entirely different chemical character). This is of importance in connection with the dielectric constants of those inorganic salts which could be measured in ethyl formate only. As far as these salts are concerned in particular, they are also characterized by different values of the dielectric constants in accordance with their nature. The two alkali salts, sodium iodide and lithium bromide, give values which are very nearly in the order of magnitude of that of tetra-ethylammonium iodide. As a matter of fact, both salts are very good electrolytes in organic solvents, too. On the other hand, mercuric chloride is found to be a weak electrolyte, while calcium iodide occupies an intermediate position.

It may be seen from the average values of **K** (Table IV), in the solvents chloroform, methylene chloride and ethyl formate, that for any particular salt **K** increases, in general, in the order CH_2Cl_2, $HCOOC_2H_5$. Now chloroform is a relatively weak ionizing medium ($\mathbf{K} = 4.95$), while methylene chloride and ethyl formate cause a greater degree of ionization and have values $\mathbf{K} = 8.3$ and 8.2.

It was, therefore, a reasonable assumption that this increase of dielectric constant depends not so much upon the different constitution of the

TABLE IV.—COMPARISON OF THE AV. VALUES OF **K** FOR SALTS IN DIFFERENT SOLVENTS.

	From chloroform soln. Diel. const. acc. to			From CH_2Cl_2 soln. Diel. const. acc. to			From $HCOOC_2H_5$ soln. Diel. const. acc. to		
Compound.	Philip.	Bouty.	Silberstein.	Philip.	Bouty.	Silberstein.	Philip.	Bouty.	Silberstein.
$N(C_2H_5)_4Cl$	935	195	143	1980	320	258	..	...	...
$N(C_2H_5)_4Br$	840	142	133	1600	220	230	1700	156	237
$N(C_2H_5)_4NO_3$	836	169	133	1370	245	213	..	...	...
$N(C_2H_5)_4I$	...	...	...	3250	280	330	..	...	...
$N(C_3H_7)_4NO_3$	365	120	84	1225	255	200	..	...	...
$N(C_3H_7)_4I$	456	110	97	..	...	...	..	...	...
$N(C_2H_5)_3HCl$	500	138	100	390	139	112	..	...	...
$N(C_2H_5)_3HNO_3$	...	...	...	425	146	125	395	92	110
$C_6H_5N(CH_3)_2HBr$	256	78	69	..	126	...	..	...	...
$HN(C_2H_5)_2HCl$	26	26	19	88	60	47	..	...	...
$HN(C_2H_5)_2HNO_3$	42	31	25	71	47	41	79	33	42
$HN(C_6H_5)CH_3.HBr$	17	17	14	..	26	...	..	...	...
$HN(C_5H_{11})_2HCl$	ca 8	ca 11	ca 7	..	...	...	..	...	...
$H_2N(C_5H_{11}).HCl$	ca 5	ca 8	ca 5	..	...	...	..	...	...
Piperidine Picrate	...	...	...	78	79	45	..	...	...
$HgCl_2$	...	...	...	..	...	...	490	19	108
CaI_2	...	...	...	..	...	...	1540	40	210
LiBr	...	...	...	..	...	...	5000	110	420
NaI	...	...	...	..	...	...	6200	115	455

solvent (the **K** values being nearly equal in CH_2Cl_2 and $HCOOC_2H_5$) as upon the presence of ions. In accordance with this, solvents causing still greater ionization, and consequently having greater ion concentrations, should give still higher values for the dielectric constants. This actually appears to be what occurs:

	Chloroform.		Methylenechloride.		Acetone.	
Salts.	V.	$\mathbf{K}_1$ calc.	V.	$\mathbf{K}_1$ calc.	V.	$\mathbf{K}_1$ calc.
Diethylammonium chloride	...	...	5	26	40	204
Phenylmethylammonium bromide	2.5	17.0	5	26.0	20	114.0
Dielectric constants of the solvents	...	4.95	..	8.3	..	20.4

It is apparent at once, in the case of both salts, that the higher the dielectric constant of the solvent, the higher does the calculated value of **K** become for both salts. Conversely too, the degree of ionization of the dissolved salt is greater, the greater the dielectric constant of the solvent is. It is reasonable, therefore, to think of the ionization as affecting (increasing) the dielectric constant to be calculated for the salt.

Other solvents, belonging to the strongly ionizing ones, were included in order to test further whether such a parallelism actually exists. Our "normal salt," $N(C_2H_5)_4I$, was used as the salt.

The values for aqueous solutions have been calculated by myself from the measurements of Smale[1] and Nernst.[2] For the sake of simplicity the equation of Bouty has been employed.

Solvent.	Diel. const. K_2.	Solutions. Dilution V.	Solutions. Observed diel. const. K.	Degree of ionization. α.	Salt. K_1 calc. acc. to Bouty.	
Chloroform	4.95	10	7.20	Very small	110	$[N(C_3H_7)_4I]$
Methylene chloride	8.3	50	9.35	Small	280	$[N(C_2H_5)_4I]$
Acetyl acetone	26.0	100	27.2	0.70	480	
Propionitril	26.5	200	27.3	0.72	510	
Acetonitril	36.3	200	37.5	0.82	770	
Water	81.7	100	90.9	0.94	12400	KCl
		200	84.5	0.96	7600	
		1000	82.8	0.98	14000	

It is readily seen that *the formation of ions increases the calculated dielectric constant* K_1 *for electrolytically equivalent salts.* As a result of this, retroactively, the tendency of the salt to ionize, or the dissociating capacity of the solvent, is increased.[3]

The enormous increase of the dielectric constant upon ionization can be illustrated by the following data:

	Solid K det.	Aqueous solution. K calc.
Potassium chloride	4.9 (Schmidt)	10,000 (approx.)
Copper sulfate	5.5 (Thwing)	3,000
Hydrogen chloride (liquid)	4.6 (Schlundt)	30,000

The values for aqueous solutions have been calculated from Smale's measurements.

The general result of these determinations is as follows: *The dielectric constant of the solution, and hence the ionizing power, as well as the ionic dissociation, rises upon solution of strong electrolytes (especially of binary salts of the alkali metals and the tetraethylammionium bases) in it; this rise increases proportionally to the increase of the salt concentration in very weak ionizing media, while in good ionizing media the presence of ions also produces a rise in the value of the dielectric constant.* As a result of this, it becomes possible to examin a number of questions not cleared up heretofore, from a new point of view. First of all, I would like to direct attention to the large question of the *action neutral salts* and the problem of the *deviation of strong electrolytes, particularly salts, from Ostwald's dilution law.* The work of W. Ostwald (1883), Spohr (1888), and S. Arrhenius (since 1889), which showed the accelerating action of neutral salts on the

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[1] *Wied. Ann.*, 60, 627 (1907).

[2] *Ibid.*, 612.

[3] The dielectric constant of the solvent has been assumed constant. This assumption appeared to be the simplest one to make, otherwise, for example, in a comparison of the salt in chloroform and water, assuming a constant K_1 value for the salt, the dielectric constant of the solvent would apparently be increased to such an extent that it should also become an electrolyte.

catalytic action (saponification) of acids on esters and on cane sugar (inversion) is well known. Arrhenius proved (1899) that the ionization constant of a weak acid was increased by the addition of salts. In the same way, the reaction velocity of water itself is increased by dissolving neutral salts in it (Smith, 1898; Euler, 1900–1). Decomposition of the salts of organic halogen acids is also hastened by addition of neutral salts (Senter, 1907, Holmberg, 1912; Johansson, 1912). Even Euler (*l. c.*) sought for an explanation of this accelerating action. This action consists in an increase of the degree of ionization of the reaction components, that is of the acids and of the water, by the ions. As far as the deviation of strong electrolytes, consequently binary salts also, from the dilution law is concerned, Arrhenius gave expression to the following opinion as early as 1901; "Perhaps the explanation of this peculiar deviation from the mass-action law is to be found in the fact, that the addition of ions of the strong electrolyte causes a considerable increase in the dissociating power of water. Partington[1] (1910) formulated a modified equation for the dilution law on the basis of these considerations and showed its applicability. More recently McDougall[2], from a consideration of the action of the electrical charges of the ions on the dissociation of the salt molecules, obtained a more accurate expression for the dilution law. Bray and Kraus[3] developed the same equation independently.

Returning to our general conclusion, we recall that solution of strong electrolytes increases the dielectric constant of the solvent, and that parallel with it the ionizing power is increased. Naturally then, the degree of ionization, of the dissolved acid for instance, and with it the *concentration* of the hydrogen ion, must increase. Hence the reaction velocity of this acid must be accelerated. In the same manner as the electrons condense water vapor upon their surface, it is plausible to assume that in solution, too, the ions solvate or surround themselves with an envelope of the solvent, and it is conceivable that in aqueous solution, for instance, the water molecules grouped about the ion as nucleus themselves suffer a partial dissociation or auto-ionization. It will be remembered that, at the present time, a very extended hydration of the ions is assumed to take place. The "auto-ionization" of water, however, also tends toward an increase of the H ions, that is, solution of neutral salt in water may, of itself, cause an increase of the reactivity of the water.

The deviation of strong electrolytes (binary alkali salts) from the Ostwald dilution law $k = \alpha^2/(1 - \alpha)v$ expresses itself, as will be remembered, in the fact that, starting from higher concentrations, k gradually dimin-

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[1] Partington, *J. Chem. Soc.*, **97**, 1158 (1910); Arrhenius, "Theory of Solutions," **1912**, 180.

[2] THIS JOURNAL, **34**, 855 (1912).

[3] Bray and Kraus, *Science*, **35**, 433 (1912). See also THIS JOURNAL, **35**, 1315.

ishes with dilution, tending finally toward a constant limit. That is, in the beginning the degree of dissociation is greater than corresponds to the requirements of the mass law. According to our measurements, it *must* at the higher concentrations appear greater than corresponds to the ionizing power of the pure solvent, since the dielectric constant and hence the dissociating power has been increased to no small degree. At higher dilutions the action of the ions (the concentration of the molecules having become small) prevails. Still another cause may be taken into consideration, namely the auto-ionization of the solvent water, or similar media. This possibility has been mentioned before and it would cause an increased conductivity as a consequence of the great mobility of the H and OH ions, hence an increased degree of ionization. Finally a third factor may be thought of, namely, an increase of the ionic mobility with an increase of the dielectric constant, or in general, a change of ionic velocity with changes on the concentration of the salt and of the ions. The oppositly charged ions exert an attraction one upon the other, which is weakened by the dielectric between them. If now the dielectric constant of the solution changes upon dilution, the attraction between the ions will also change and they will move by each other with greater or less ease, dependent upon the increase or decrease of the dielectric constant of the solution. When both the presence of the neutral salt, as well as that of the ions and their envelope of solvent, alter the dielectric constant, then the ionic velocity of one and the same salt changes in one and the same solvent. The fact that G. N. Lewis[1] has recently considered the deviations of the strong electrolytes from the mass law to be a result of the increase in ionic mobility with the total ion concentration, is an interesting circumstance. According to Clausius-Mosotti we have

$$x = \mathbf{K} - 1/\mathbf{K} + 2 \quad \text{or} \quad x/d = \mathbf{K} - 1/(\mathbf{K} + 2)d.$$

Where x is the fraction of the total volume actually occupied by the molecules; x/d is therefore the true sp. vol., and $Mx/d = (\mathbf{K} - 1)M/(\mathbf{K} - 2)d$ represents the true molecular volume, that is, that *fraction* of the apparent molecular volume, $V_m = M/d$, which is actually taken up by the molecules.

In what way are the salts, as strong electrolytes, to be distinguished from the non-electrolytes when compared as to this "true volume" measured dielectrically? A few examples may illustrate this.

It is at once evident that in the formation of the tabulated ammonium salts from the components a far-reaching contraction takes place. The fraction x becomes practically equal to one, the apparent molecular volume coincides with the true volume, determined dielectrically, and *the total volume is therefore actually occupied completely by the molecules.*

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[1] THIS JOURNAL, 34, 1644 (1912).

	K.	Density, *d*.	$Vm = M/d$.	$x = \frac{\mathbf{K}-1}{\mathbf{K}+2}$.	xM/d.
Ethyliodide, $C_2H_5I^1$	7.4	1.938 (18°)	80.5	0.681	54.9
Ethyl bromide, $C_2H_5Br^2$	9.4	1.439	75.8	0.737	55.5
Ethyl chloride, $C_2H_5Cl^3$	28 (approx.)	0.900	71.6	0.900	64.4
Methylamine, $N(C_2H_5)_3{}^4$	3.2	0.729	138.5	0.423	58.6
Electrolytes, composed of the above non-electrolytes.	*x*.				
N.(CH)Br	1615	1.388	151.3	0.998	151.1
N(CH)I	3250	1.566	164.0	0.999	164.0
N(CH)	1980	1.080	153.2	0.999	153.2
NaI	6200	3.55	42.3	1.000	42.3

The chlorides, bromides, iodides, thiocyanates, nitrates and similar salts of the alkali-metals are, as is well known, strong binary electrolytes. The corresponding salts of ammonium and of the tetra-allyl substituted ammonium bases are, however, to be classed with them. On the other hand, these salts have the common characteristic that their molecules are polymerized to a considerable extent. This polymerization of the salt molecules has, for instance, been proven, 1st for the fused salts, results being in agreement according to various methods;[5] 2nd, for the same salts in solution; since the binary salts of the substituted ammonium bases are soluble in solvents[6] with exceedingly small ionizing power, even in benzene, chloroform and methylene chloride. It has been possible to determin the molecular weight of such salts by osmotic methods, the electrolytic dissociation being practically equal to zero. A further characteristic property of these salts, or strong binary electrolytes, was the *exceptionally high dielectric constant* which could be established in solutions, as shown above. Empirically it has therefore been shown that with the binary salts mentioned[7] we have parallel with each other, a strong electrolytic character (that is, great dissociation even in non-aqueous solutions), a high degree of polymerization of the molecules and a high dielectric constant of the latter.

It seems reasonable to bring these prominent characteristics into causal connection with the readiness with which ions are formed.

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[1] Drude.

[2] Walden.

[3] Eversh.

[4] Walden.

[5] P. Walden, *Z. Electrochem.*, **14**, 723 (1908); R. Lorenz and Kaufler, *Ber.*, **41**, 3727 (1908).

[6] Turner, *J. Chem. Soc.*, **99**, 880 (1911); Hantsch, *Ber.*, **44**, 1776 (1911); Walden, *Z. physik. Chem.*, **55**, 689 (1906) and unpublished results.

[7] That the strong inorganic acids form polymerized molecules is proven by the examples of sulfuric and phosphoric acids; in solution, also for hydrogen chloride (in formic acid and in nitrobenzene).

Let us recall all the significant circumstances again. We have a solid binary salt, which we are justified in considering as stable ingeneral. We dissolve it in a suitable solvent and obtain, according to Arrhenius, a decomposition into ions which is attained momentarily, and readily reaches 80 to 90%. These ions are now provided with electric charges, or combined with electrons, while electrostatic repulsion exists between ions of like charge and electrostatic attraction exists between the oppositly charged positive and negative ions. These forces tend to produce a recombination of the oppositly charged ions to neutral molecules. The greater, however, the dielectric constant of the interposed solvent, the less is the electrostatic attractive force 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. Such an authority as W. Nernst remarks only that if, in spite of electrostatic forces tending toward recombination of the ions to neutral molecules, so far reaching dissociation into ions nevertheless takes place "other agencies," of which the nature is still unknown to us (perhaps the kinetic energy of the components of the molecule) must tend toward separation, and that the dissociation equilibrium arises from the competition of these two oppositly directed causes."[1]

At this point I desire to return to the connection established above between ionic cleavage, polymerism and dielectric constant, and to express the view that *the process of disaggregation of the polymerized salt molecules also causes and induces the process of ionic cleavage.*

Let us consider the binary salt Me X, which is polymerized or associated to the extent of x; $(\mathrm{Me\ X})_x$ then represents the unit molecule of salt. Further, let $\oplus$ and $\ominus$ represent a positive and a negative electron; hence $\oplus\ominus$ a neutral electron (neutron), Me $\oplus$ a cation, X $\ominus$ an anion. We then assume the following processes:

$$(\mathrm{Me\ X})_x \rightleftarrows (\mathrm{MeX})_{x-1} + \mathrm{Me\ X} + \oplus\ominus \qquad \text{I. Depolymerization.}$$

$$\mathrm{Me\ X} + \oplus\ominus \longrightarrow \mathrm{Me}\oplus + \mathrm{X}\ominus \qquad \text{II. Ionization.}$$

$$(\text{or } \mathrm{Me\ X}\oplus + \bigcirc \longrightarrow \mathrm{Me}\oplus + \mathrm{X}\ominus)$$

Both reactions may naturally occur in steps. We have shown above, how, for instance, in the case of tetra-alkylated ammonium salts the apparent molecular volume $V_m = \mathrm{M}/d$ practically agrees with the dielectrically determined, that is the actually occupied volume $(\mathbf{K} - 1)\mathrm{M}/(\mathbf{K} + 2)d$. In these salts the total volume is therefore filled completely by the mole-

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[1] W. Nernst, *Theoretische Chemie*, **1907**, 374.

cules; unit space consequently contains the *maximum* of molecular accumulation and, hence, probably a *minimum* of the vibration spaces for the atoms and electrons. Such a molecule obviously is in a condition of constraint or tension, as a result of which the tendency to cleavage, toward depolymerization, and to the emission of electrons is developed. (Equation I.)

That such an enormous contraction, or mass accumulation, in a molecule leads to more or less ready disruption is shown by highly complex chemical individuals (on heating). That such disruption may even proceed spontaneously or with the emission of electrons is manifested by elements like uranium, thorium, radium, etc.

The atoms of sodium and potassium, for instance, and probably also the analogous organic ammonium radicals, are known to give up negative electrons with comparative ease or to take up positive electrons, as a result of which, in the above case, the simultaneous production of *cations* and *anions* occurs in the solution. That these do not recombine to neutral molecules, in spite of their opposit charges, is a consequence of the dielectric media interposed between the ions or enveloping them. The greater the dielectric constant of this intermediate layer and ionic envelope, the more will the electrostatic attractions between anions and cation be weakened. Now, we saw above that (1) not only does the *solvent* represent such a dielectric, but also (2nd) that the dissolved salt molecules themselves are dielectrics with very large constants, and (3rd) that the presence of the ions causes a further increase of the dielectric constant of the whole system. (Equation II.)

In a previous page it was mentioned that the process of disaggregation, or depolymerization, of the highly associated molecules of the salt is the cause of and induces the dissociation into ions. The method and the degree of both processes may vary greatly. The depolymerization may proceed either in separate steps or directly down to the simplest products; this may further involve only a few molecules or 80 or more per cent. of them (for instance in water). This depends upon; (1st) the nature of the electrolyte; (2nd) the peculiarity of the solvent. The maximum of degradation of polymeric molecules into simple ions will occur when we dissolve a binary alkali salt (with high dielectric constant) in water (also with high dielectric constant). The minimum degradation will result, on the other hand, when we dissolve a binary (monoalkylated) ammonium chloride (with low dielectric constant) in a solvent, for instance in CH_3Cl, with low dielectric constant. In the latter case the solution will contain an extremely small number of ions only, but an exceedingly great number of associated salt molecules. If we examin such a solution for its electrical conductivity, it shows a weak molecular conductivity, as a rule, *which will decrease with dilution.* This phenomenon seems, in general, to be peculiar to electrolytes in weakly ionizing media (having a dielectric constant between 2 and 10). The limited ionizing effect of such solvents is increased appreciably by dissolving salts in them. The extent to which this happens at greater concentrations may be shown by an example. Let us take the very feeble ionizing medium chloroform (**K** = 4.95) and dissolve in it the salt $N(C_2H_5)_4Cl$. Then we will obtain at the various dilutions V (—liters to one molecule of salt) the following approximate dielectric constants **K.**

V................	1	2	5	10	15	40	..
K................	26.8	15.9	9.3	7.05	6.4	5.5	4.95

It is obvious from this, that we can obtain enormous increases, about 500%, in the dielectric constants and consequently in the dissociating power of the medium if, for instance, we start out from normal solutions. With *progressive dilution the dielectric constant falls rapidly,* soon reaching a value differing but little from the value of the pure solvent. Connected with this a *rapid decrease* of the dissociating power takes place, that is, a *decrease in the molecular conductivity* also; which corresponds to the facts. If the dissociating power of the solvent is sufficient to cause the formation of a certain number of ions from the salt molecules, a gradual *increase* of the dielectric constant takes place as a consequence. The resultant of both actions (decrease of the dissociating power in consequence of the diminution of the salt concentration and increase in consequence of ion formation) causes the molecular conductivity to pass through a *minimum* with a subsequent gradual increase. This phenomenon also corresponds with the results.[1]

Mention may further be made of the fact that in concentrated solutions of such weakly ionizing media polymeric molecules exist which may give polymeric ions of low velocity. At greater dilutions these complex ions will break up into simpler ones and will thereby lead to an increase of the conductivity.

Molten salts also represent a solution. Besides the molecules of the salt, for instance $(KNO_3)_x$, we have molecules depolymerized and broken up into ions in the melt. Since these molecules (NaI, LiBr in solution) possess a very high dielectric constant, the decomposition into ions is greatly favored and the recombination of the ions will be very greatly hindered. In other words, *salts of the type of the alkali iododes, bromides, chlorides or nitrates will show a far reaching dissociation in the liquid (melted) state,* since in this case *both* factors—high dielectric constant both of the solvent and of the salt molecules tending to dissociate—are active. As a

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[1] With my own determinations and especially the investigations of E. C. Franklin, Gibbs, Fitzgerald, Sachanov and others. That other factors are also contributory (viscosity, auto-ionization, association) has been laid stress on in particular by Franklin, Steele and McIntosh, and Sachanov.

matter of fact, the preëminent investigations of Arndt (and Gessler) Goodwin and Mailey, J. van Laar, R. Lorenz (and Kauffler) Sackur and others have proven this fact experimentally.

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IN COMMEMORATION OF THE CENTENNIAL OF THE PUBLICATION OF THE BERZELIAN SYSTEM OF SYMBOLS.

BY HENRY LEFFMANN.

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Systems for the brief and concise expression of ideas are probably as old as the intellectual activity of the human race. The ancients had systems of shorthand, and Berthelot has shown, in his elaborate edition of the work of the Greek alchemists, that they used a rude system for expressing the composition of substances. Of course, their system has only historic interest, because their knowledge of the composition of most substances was imperfect or entirely wanting. Thus, for a long while, a native alloy of gold and silver was believed to be a distinct metal. Berthelot gives many examples of this early symbolism. A combination of the signs for gold and silver, respectively, that is, the signs for the sun and moon, would indicate an alloy of these metals. In some representations he gives of symbols, from a MS in the celebrated St. Mark's library, gold is represented not by the present day sign of the sun, a circle with a central dot, but by a circle with two lines meeting in a point, resembling very much the conventional fool's cap, but evidently a rude picture of the sun and its rays. Silver is represented by the crescent moon.

Dalton used several signs, derived practically from the circle, as a conventional representation of the atom.

All systems gave way early to that proposed by Berzelius, which was not only simple and self-explanatory, but had the advantage of easy indefinit expansion along the original lines. The vast advantage that this system has for chemists, even if we regard it only as a step towards an international language, seems to me to make worth while some special note on the occasion of the one hundredth anniversary of its publication.

The earliest formal publication of the system, is in Thomson's *Annals of Philosophy*, Volume 2, 1813, p. 443. The paper is a long one, extending through several numbers. It is entitled "*Essay on the Cause of Chemical Proportions, and Some Circumstances Relating to Them, Together with a Short and Easy Method of Expressing Them.*" *By Jacob Berzelius, M.D., F.R.S., Professor of Chemistry in Stockholm.*

The system is developed in the third section of the essay, and I think it will be of interest to transcribe the whole description, as copied by me from the original in the library of the Franklin Institute.