

(b) the results on large and on small amounts of copper in the same or in different volumes are strictly comparable.

(6) It has been shown that absorption of iodine by precipitated cuprous iodide as a perceptible source of error does not occur in the iodide method as here performed. Hence this explanation of the discrepancy between the iodide and the copper standardizations of thiosulfate solutions is untenable.

(7) The ease with which the results of the iodide method are affected by a variety of conditions has been shown. Procedures have been described for testing the presence of these influences and for adjusting the conditions or quantitatively compensating them. These procedures have a general application, so that even for a high degree of accuracy the iodide method need not be limited to the special conditions of the original test analyses. The iodide method, only under control of conditions it must be emphasized, has the decided advantages of exceeding accuracy combined with rapidity.

I am under much obligation to Professor F. G. Benedict for advice and valuable criticism throughout this work. I was also ably assisted in obtaining the experimental data and in their re-examination by Mr. Richard I. Carney and Mr. Wm. F. O'Hara, of the staff of this laboratory.

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THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY. III. ELECTRICAL CONDUCTANCE.

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II. Theoretical Considerations.

This article is devoted to the consideration of the electrical conductance of solutions of single salts.

The conductance of a solution may be explicitly defined in terms of the ordinary units as the number of coulombs of electricity that pass through it per second when a potential-difference of one volt exists at the electrodes. The specific conductance (L) of a solution is the conductance of one centimeter cube of it between electrodes one centimeter apart.

The conductance of aqueous solutions of salts, acids and bases (hereafter referred to by the single word "salt") seems to be almost wholly

due to the salt, since pure water is known to have only an extremely small conductance; and it is conveniently expressed in the case of solutions containing only a single salt by the concept of equivalent conductance, which is defined as follows: The equivalent conductance (Λ) of a dissolved salt is the conductance between electrodes one centimeter apart of that volume of its solution which contains one equivalent of the salt. Hence $L = C\Lambda$, where C represents the concentration of the salt in equivalents per cubic centimeter of solution.

Since, in accordance with Faraday's law and the laws of transference, flow of electricity in an electrolyte is attended by a corresponding movement of the ion-constituents, the specific conductance of a solution must be equal to the number of equivalents of the ion-constituents that pass per second through a cross section of the solution of one square centimeter area when the potential gradient is one volt per centimeter, multiplied by the charge (F coulombs) carried by one equivalent. Moreover, the number of equivalents of any ion-constituent so passing must obviously equal the product of its mobility U^1 by its concentration C (expressed in equivalents per cubic centimeter). Hence the general expression for the specific conductance of a solution containing any number of positive or negative ion-constituents A, B, \dots is

$$L = F(C_A U_A + C_B U_B + \dots)^2 \quad (23)$$

Certain factors upon which the value of the mobility U_A of any ion-constituent A must depend will now be considered. In the case in which the constituent is contained as only a single kind of ion (as would be true, for example, of either constituent of potassium sulfate, if it be assumed that the salt is dissociated only into the ions K^+ and $SO_4^{=}$), this value must evidently be determined: (1) by the fraction γ_A of the constituent which exists in the state of ion, and (2) by the mobility $U_{A\pm}$ of the ion itself; for it is only the free ions that actually move under the influence of the electrical potential gradient. That is,

$$U_A = \gamma_A U_{A\pm}. \quad (24)$$

For the case that there is present in the solution only a single salt which gives rise to only one positive ion B^+ and one negative ion A^- , a combination of equations (10) and (11) yields the important relation:

$$\Lambda = L/C = \gamma(U_{B^+} + U_{A^-})F. \quad (25)$$

In this equation C represents the concentration of the salt in equivalents per cc., Λ its equivalent conductance, and γ its ionization (that is, the fraction of it existing as free ions). This equation results from (23)

¹ The velocity under a potential-gradient of one volt per centimeter is designated the *mobility*.

² Since conductance, unlike transference, is not essentially a directive quantity, mobilities will, throughout this paper, be considered positive whether the ion moves toward the cathode or anode.

and (24), since in the special case considered $C_A = C_B = C$, and $\gamma_A = \gamma_B = \gamma$.

Equation (25) may be written in the still simpler form

$$\Lambda = \gamma(\Lambda_{B+} + \Lambda_{A-}) \quad (26)$$

by replacing FU_{B+} and FU_{A-} by the quantities Λ_{B+} and Λ_{A-} . The quantity Λ_{B+} or Λ_{A-} may be called the equivalent conductance of the ion B^+ or A^- , since it represents the conductance of that volume of the solution of any concentration which contains one equivalent weight of the (free) ion B^+ or A^- , when placed between electrodes one centimeter apart.

As the concentration of the salt approaches zero, the value of Λ is found to approach a constant maximum value Λ_0 , obviously in consequence of the facts that γ approaches unity and that Λ_{B+} and Λ_{A-} approach a constant value. Hence, for $C = 0$,

$$\Lambda_{B+} + \Lambda_{A-} = \Lambda_0. \quad (27)$$

The separate values of the mobilities or conductances of the two ions which are involved in equations (25), (26), and (27) cannot be derived from conductance values alone, since these always involve the sum of the two quantities. They can, however, be obtained by multiplying the conductance by the transference number T of the ion-constituent in question; namely:

$$\Lambda T_B = \gamma F U_{B+} = \gamma \Lambda_{B+}, \text{ and } \Lambda_0 T_B = \Lambda_{B+}. \quad (28)$$

This last equation is of much importance, as it enables values of the equivalent conductance of the separate ions to be calculated.

A consideration most important to the quantitative development of the Ionic Theory is the question of the upper limit of concentration at which equation (27) can still be regarded as substantially accurate. It is commonly assumed that it can be so regarded so long as the solution, considered as a viscous medium which offers a certain mechanical resistance to the motion of the ions through it, does not differ appreciably from pure water. And accordingly, the ionization of salts up to moderate concentrations is commonly calculated by the equation

$$\gamma = \Lambda/\Lambda_0. \quad (29)$$

This equation, unlike the preceding ones, involves a distinctly hypothetical element. While the inherent probability that this relation holds true so long as the viscosity of the solution does not differ substantially from that of pure water should not be underestimated, yet the possibility that it may become invalid at much smaller concentrations should be recognized, especially in view of possible effects caused by the electric charges on the ions, such as have been suggested by Sutherland.¹ The calculation of the ionization of salts in dilute solution from the conductance ratio Λ/Λ_0 should therefore be considered to be based upon a

¹ *Phil. Mag.*, [6], 14, 3-7 (1907).

hypothesis which has a high degree of *a priori* probability, but which must be confirmed by testing its conformity with other related phenomena. It is to be noted, moreover, that even if the ratio does not have the significance of a degree of ionization, it is a convenient empirical expression of the change of conductance with the concentration, without reference to the ionization.

Another uncertainty of a different character involved in the calculation of ionization from the conductance ratio arises from the facts that the maximum value of Λ is not fully attained even at the smallest concentrations at which accurate measurements have thus far been made, and that, therefore, Λ_0 must be obtained by extrapolation from the Λ values at higher concentrations. The best that can be done is to base this extrapolation on the assumption that the functional relation between equivalent conductance and concentration which is found empirically to hold at higher concentrations continues to hold down to zero concentration. Besides the possibility of inaccuracy in this assumption, there is the possibility of considerable error in the practical application of it to the available data, especially in the case of salts of the higher valence types where the extrapolation is a fairly long one. This practical side of the question will be discussed in a later section of this article.

At concentrations so great that the viscosity (η) of the solution differs appreciably from the viscosity (η_0) of pure water, it is to be expected, as was suggested by Arrhenius,¹ early in the history of the Ionic Theory, that the mobility and conductance of the ions will decrease, at least approximately, in the same proportion in which the viscosity increases; and therefore that the ionization is given by the following relation:

$$\gamma = \Lambda\eta/\Lambda_0\eta_0 \quad (30)$$

Although this correction for the effect of the viscosity of the solution on the mobility of the ions can not be an exact one, there is little doubt that the ratio $\Lambda\eta/\Lambda_0\eta_0$ gives a much more nearly correct measure of ionization at moderately high concentrations than does the simple conductance ratio Λ/Λ_0 .

In justification of this viscosity correction the following considerations may be presented. In the first place, the theoretical relationship of the two properties is a close one, viscosity being essentially the frictional resistance encountered by molecules of the solution in moving over one another, and ion-mobility being determined by the frictional resistance encountered by ions in moving over the molecules of the solution. Aside from this, moreover, there is much direct experimental evidence that conditions which affect the viscosity of the medium affect in an approximately inverse proportion. This is most clearly shown in the case of temperature, the effects of which on the viscosity of water and on the

¹ *Z. physik. Chem.*, 9, 495 (1892).

mobility of ions in dilute aqueous solution are approximately the same.¹ Thus multiplying the viscosities of water at 0° and 18° by the respective means of the conductance values² for the univalent ions K⁺, Na⁺, Ag⁺, Cl⁻, NO₃⁻, ClO₃⁻, the following results are obtained:

$$\text{At } 0^\circ: \eta_0 \Lambda_0 = 0.01793 \times 35.17 = 0.630.$$

$$\text{At } 18^\circ: \eta_0 \Lambda_0 = 0.01052 \times 57.18 = 0.604.$$

Furthermore, it has been shown³ that for five uni-univalent salts investigated at 18°, 100°, and 156° the values of $\eta_0 \Lambda_0$ are:

$$\text{At } 18^\circ: \eta_0 \Lambda_0 = 0.01052 \times 113 = 1.19.$$

$$\text{At } 100^\circ: \eta_0 \Lambda_0 = 0.00283 \times 369 = 1.04.$$

$$\text{At } 156^\circ: \eta_0 \Lambda_0 = 0.00179 \times 566 = 1.01.$$

The form of the viscosity correction has recently been discussed in detail by Washburn.⁴ Upon the basis of the relation between the changes in ion-mobility and viscosity produced (1) by change of temperature (as calculated by Johnston⁵), (2) by the addition of non-electrolyte (as shown by the experiments of Green⁶), and (3) by dissolving the same salt in separate solvents (as shown by the experiments of Dutoit and Duperthuis⁷), Washburn suggests for calculating ionization the equation

$$\gamma = \frac{\Lambda}{\Lambda_0} \left(\frac{\eta}{\eta_0} \right)^m. \quad (31)$$

He shows that the value of m never differs from unity by more than 0.2, and that the ionization values up to 0.5 normal calculated by equations (30) and (31) differ in the cases cited by him by only 2%, while those calculated by (29) and (30) differ by nearly 9% of their values.

The existing evidence may therefore be said to lead to the conclusion that, so far as the viscosity correction is concerned, the ratio $\Lambda\eta/\Lambda_0\eta_0$ furnishes a much closer approximation to the true ionization values than the ratio Λ/Λ_0 and one sufficiently close for most salts up to moderate concentrations, such as 0.5 normal; but that equation (31) gives a still closer approximation.

Throughout this article the ratio $\Lambda\eta/\Lambda_0\eta_0$ will be employed as a measure of ionization, because of its greater simplicity and because at the higher concentrations, where equation (31) would give an appreciably different result, other factors doubtless influence the ionization values to a far greater extent.

Entirely aside from physical effects which may cause the mobility of

¹ Cf. Kohlrausch, *Proc. Roy. Soc.*, 71, 383 (1903).

² For the ion-conductances at 18° see Table XIII of this article; for those at 0° see Johnston, *THIS JOURNAL*, 31, 1015 (1909).

³ *THIS JOURNAL*, 30, 342 (1908).

⁴ *Ibid.*, 33, 1464-1474 (1911).

⁵ *Ibid.*, 31, 1010 (1909).

⁶ *J. Chem. Soc.*, 93, 2049 (1908).

⁷ *J. chim. phys.*, 6, 726 (1908).

the ions to vary with increasing concentration, the calculation of ionization from the conductance ratio or the conductance-viscosity ratio may lose its significance owing to changes in the chemical composition of the ions.

Of such possible changes the simplest is a decrease in the hydration of the ions with increasing concentration, whereby their mobility would presumably be increased. Such a change doubtless takes place in many cases at high concentration, but probably to an important extent only after the chemical activity of the water in the solution has become substantially different from that of pure water. Now the vapor pressure is a measure of the active mass¹ or activity² of the solvent; and Raoult's law gives for the ratio of the vapor pressure of solution and pure solvent the expression $p/p_0 = N_0/(N_0 + iN)$, where N_0 and N are the numbers of mols of solvent and solute, respectively, and i is the mol-number of the solute. Using the mean values of i given for the uni-univalent salts in the first paper of this series,³ the values p/p_0 at concentrations between 0.05 and 0.5 normal are found to be as follows:

Concentration.....	0.05	0.1	0.2	0.5
p/p_0	0.998	0.997	0.993	0.984

It will be seen that the change in activity of the water begins to be considerable at 0.1 normal, and that it becomes much larger at the higher concentrations. In the case of ions which form relatively unstable hydrates (that is, such as are in a state of partial dissociation), it may therefore be expected that the mobility will increase fairly rapidly above 0.1 normal.

A second important chemical change, also involving the solvent, is hydrolysis, which takes place especially in the case of salts of weak acids or bases. This, even when relatively small, is likely to influence seriously the determination of the Λ_0 value. It is therefore desirable to note the relation between hydrolysis at different concentrations and the ionization constant K_A or K_B of the weak acid or base which may be involved. The following table shows the percentage hydrolysis ($100h$) calculated by the approximate mass-action equation $\frac{h^2}{1-h} = \frac{K_w}{C K_A \text{ or } B}$ for salts of a slightly ionized acid (or base) and a nearly completely ionized base (or acid) at 25° (where the ionization constant of water K_w is 10^{-14}).

K_A or K_B .	10^{-4} .	10^{-5} .	10^{-6} .	10^{-7} .	10^{-8} .
0.1 N	0.0032	0.0100	0.0316	0.100	0.316
0.01 N	0.0100	0.0316	0.100	0.316	0.995
0.001 N	0.0316	0.100	0.316	0.995	3.11
0.0001 N	0.100	0.316	0.995	3.11	9.51

¹ See Nernst, "Theoretische Chemie," 4th Ed., pp. 457, 633 (1903).

² Lewis, *Proc. Amer. Acad.*, 43, 279 (1907).

³ THIS JOURNAL, 32, 1027 (1910).

In the case of salts of the uni-bivalent type or of a higher valence type, if, as seems *a priori* probable, the intermediate ion is present in considerable proportion, the conductance ratio or conductance-viscosity ratio must lose its significance as an exact measure of ionization, even at fairly small concentrations. Thus if a salt B_2A is ionized to an extent γ_1 into B^+ and BA^- , and to an extent γ_2 into $2B^+$ and $A^{=}$, we have

$$\frac{\Lambda}{\Lambda_0} = \frac{\gamma_2(\Lambda_{B^+} + \Lambda_{A^{=}}) + \frac{1}{2}\gamma_1(\Lambda_{B^+} + \Lambda_{BA^-})}{\Lambda_{B^+} + \Lambda_{A^{=}}}; \quad (32)$$

or

$$\gamma = \gamma_2 + \frac{1}{2}\gamma_1 \frac{\Lambda_{B^+} + \Lambda_{BA^-}}{\Lambda_{B^+} + \Lambda_{A^{=}}}. \quad (33)$$

The factor in the last term by which $\frac{1}{2}\gamma_1$ is multiplied is probably always considerably less than unity, since BA^- is an ion of smaller valence and of greater complexity than $A^{=}$. Therefore, since the equivalent concentrations (C_{B^+} and $C_{A^{=}}$) of the ions B^+ and $A^{=}$ are really equal to the equivalent concentration C of the salt multiplied by $\gamma_2 + \frac{1}{2}\gamma_1$, and by γ_2 , respectively, C_{B^+} will evidently be found somewhat too small and $C_{A^{=}}$ somewhat too large if calculated in the usual way by multiplying C by Λ/Λ_0 .

Throughout this article, however, the ratio Λ/Λ_0 , or at the higher concentrations the ratio $\Lambda\eta/\Lambda_0\eta_0$, will be called the *ionization*, it being understood that it has the theoretical significance which this word properly denotes only when none of the complicating factors which have been discussed in the preceding paragraphs come into consideration.

12. The Conductance and Viscosity Data.

In the preceding papers on freezing point and transference, the attempt was made to summarize all the existing data that seemed to be fairly accurate. The experimental material relating to conductance is, however, so extensive that a complete presentation of it seems superfluous. From the available data a selection has therefore been made with the view only of bringing together enough of the best results thus far attained to furnish adequate material for the discussion of the theoretical relations, which forms the main purpose of this series of articles. At 18° all the data published since 1898 by Kohlrausch and his associates have been reproduced, as well as those obtained by the workers in this laboratory; in addition, the results of Wershoven on the cadmium salts, and a few other results of special interest, have been included. At 25° only such data have been used as seem most suitable for determining the equivalent conductances of the separate ions at that temperature. At 0° the data have been selected with the ideas of furnishing the material for calculating the change of ionization between 0° and 18° and the ionization at 0° of those salts whose freezing points have been determined.

The following tables contain the experimental values of the equivalent conductance, expressed in reciprocal ohms per equivalent per cubic centimeter, Kohlrausch's values being corrected so as to conform to the international atomic weights for 1911. Tables VIII and X have been divided for convenience into two parts: the first part includes the data for the concentrations from 0 to 5 millinormal, up to which the viscosity of the solution is, with the few exceptions noted, identical with that of water within 0.1%; the second part includes the data for the higher concentrations, the equivalent conductance Λ being always given for each salt in the first row, the viscosity ratio η/η_0 (represented in the tables by η) being given in the second row, and the product of the conductance by the viscosity ratio $\Lambda\eta/\eta_0$ being given in the third row. The figures within parentheses following the formula of the salt refer to the notes at the end of the tables, which show the source from which the data in the same row were obtained.

TABLE VIIIa.—VALUES OF THE EQUIVALENT CONDUCTANCE AT 18° AT CONCENTRATIONS 0 TO 5 MILLI-EQUIVALENTS PER LITER.

Concentration.....	0.	0.1.	0.2.	0.5.	1.	2.	5.
NaCl (1)...	108.9	108.03	107.75	107.11	106.42	105.48	103.71
KCl (1)...	130.0	129.00	128.70	128.04	127.27	126.24	124.34
LiCl (1)...	98.8	97.96	97.67	97.01	96.34	95.44	93.75
RbCl (3)...	133.0	132.3	130.3
CsCl (3)...	133.5	132.2	131.9	131.24	130.54	129.38	127.33
TlCl (3)...	131.4	130.33	130.00	129.18	128.23	126.81	123.73
NH ₄ Cl (7a)...	130.2	126.5
KBr (3)...	132.2	131.05	130.76	130.05	129.28	128.22	126.31
KI (3)...	131.1	129.76	129.50	128.97	128.25	127.21	125.33
KSCN (3)...	121.2	120.13	119.93	119.29	118.55	117.57	115.73
KF (3)...	111.2	110.37	110.13	109.48	108.80	107.82	106.07
NaF (3)...	90.1	89.24	88.95	88.39	87.76	86.89	85.17
TlF (3)...	112.6	114.38	114.64	114.45	113.25	111.29	108.18
NaNO ₃ (1)...	105.2	104.45	104.09	103.53	102.75	101.80	99.97
KNO ₃ (1)...	126.3	125.40	125.08	124.34	123.55	122.50	120.38
LiNO ₃ (1)...	95.1	94.30	93.99	93.36	92.71	91.81	{90.18 90.3*
TlNO ₃ (3)...	127.7	126.63	126.30	125.61	124.70	123.48	121.11
AgNO ₃ (3)...	115.8	115.01	114.56	113.88	113.14	112.07	110.03
KClO ₃ (3)...	119.6	118.63	118.35	117.68	116.92	115.84	113.84
KBrO ₃ (5)...	112.1	109.9	108.7	106.9
NaIO ₃ (2)...	77.4	76.69	76.44	75.83	75.19	74.30	72.62
KIO ₃ (2)...	98.5	97.64	97.34	96.72	96.04	95.04	93.2
LiIO ₃ (2)...	67.3	66.66	66.43	65.87	65.27	{64.43 64.5*	{62.89 63.0*
HCl (6)...	380.0	378.1	377.8	377.0	375.9	375.3	372.6
HNO ₃ (6)...	376.5	373.9	372.9	371.4
BaCl ₂ (4)...	120.9	117.01	115.60
CaCl ₂ (4)...	117.4	115.17	114.55	113.34	111.96	110.07	{106.70 106.8*

* Corrected for viscosity.

TABLE VIIIa (continued).

Concentration.....	0.	0.1.	0.2.	0.5.	1.	2.	5.
MgCl ₂ (4)...	111.4	109.43	108.87	107.68	106.35	{ 104.52 104.6*	{ 101.30 101.4*
PbCl ₂ (5)...	126.3	119.15	115.8	109.2
CdCl ₂ (8)...	111.9	104.2	99.7	89.9
CdBr ₂ (8)...	114.1	102.3	97.9	85.5
CdI ₂ (8)...	113.0	97.5	91.4	76.3
Ba(NO ₃) ₂ (4)...	117.2	115.32	114.65	113.30	111.72	109.50	105.29
Sr(NO ₃) ₂ (4)...	113.7	111.74	111.07	109.76	108.31	106.35	102.74
Ca(NO ₃) ₂ (4)...	113.7	111.91	111.19	109.93	108.49	106.54	103.07
Mg(NO ₃) ₂ (5)...	107.7	102.6	100.8	97.7
Cd(NO ₃) ₂ (8)...	108.2	107.8	105.4	99.2
Pb(NO ₃) ₂ (4)...	122.6	120.73	119.94	118.08	116.13	113.54	108.68
Ba(BrO ₃) ₂ (5)...	103.0	97.5	95.5	91.9
K ₂ SO ₄ (4)...	133.0	130.7	130.0	128.5	126.9	124.6	120.3
Na ₂ SO ₄ (9)...	111.9	109.3	108.3	106.7	105.1	103.5	99.8
Li ₂ SO ₄ (4)...	101.8	97.71	96.27
Tl ₂ SO ₄ (5)...	134.4	127.35	124.2	118.4
Ag ₂ SO ₄ (5)...	122.5	116.3	113.6	108.4
K ₂ C ₂ O ₄ (4)...	127.5	125.09	124.83	123.82	122.43	120.46	116.73
MgSO ₄ (4)...	114.4	109.90	108.07	104.21	99.89	{ 94.14 94.2*	{ 84.53 84.7*
ZnSO ₄ (4)...	115.5	109.7	107.7	103.5	98.6	{ 92.2 92.3*	{ 81.9 82.0*
CdSO ₄ (4)...	114.9	109.84	107.60	102.93	97.72	90.92	79.70
CuSO ₄ (4)...	114.4	109.95	107.95	103.56	98.56	{ 91.94 92.0*	{ 80.98 81.1*
MgC ₂ O ₄ (4)...	109.0	94.5	87.0	74.5	63.4	51.4	38.2
K ₄ Fe(CN) ₆ (II)...	159.5	137.0
Ca ₂ Fe(CN) ₆ (II)...	147.0	75.5
La(NO ₃) ₃ (II)...	122.8	110.8
La ₂ (SO ₄) ₃ (II)...	129.5	60.1
K ₃ C ₆ H ₅ O ₇ (II)...	124.6	120.1	115.4	109.9

The Λ_o values at 18°, given in the tables, were obtained as follows: For the uni-univalent salts for which Kohlrausch gives accurate results, the values of Λ_o given by him¹ have been adopted (after correcting them for the change in atomic weights). For the remaining uni-univalent substances and for the salts belonging to higher types, the Λ_o values were found by the graphical method commonly employed in this laboratory, which consists in plotting the values of ι/Λ for concentrations up to 0.02 normal as abscissas against those of $(CA)^{n-1}$ as ordinates, the values of $(n-1)$ being varied until a straight line is obtained (or as nearly a straight line as possible); and reading from this plot by extrapolation to $CA = 0$, the value of ι/Λ_o .

The Λ_o values at 0° were also obtained by the same extrapolation

* Corrected for viscosity.

¹ See Landolt-Börnstein-Meyerhoffer's Tabellen, p. 744.

TABLE VIIIb.—VALUES OF THE CONDUCTANCE, VISCOSITY, AND THE CONDUCTANCE-VISCOSITY PRODUCT AT 18° AT CONCENTRATIONS 10 TO 1000 MILLI-EQUIVALENTS PER LITER.

Concentration.....		10.	20.	50.	100.	200.	500.	1000.
NaCl	<i>A</i> (1).....	101.88	99.55	95.66	91.96	87.67	80.89	74.31
"	η (23).....	(1.0009)	(1.0018)	1.0046	1.0086	1.0167	1.041	1.086
"	$\Delta\eta$	101.97	99.73	96.10	92.75	89.13	84.21	80.70
KCl	<i>A</i> (1).....	122.37	119.90	115.69	111.97	107.90	102.36	98.22
"	η (23).....	(0.9996)	(0.9991)	0.9982	0.9959	0.9898	0.982
"	$\Delta\eta$	122.37	119.9	115.6	111.8	107.5	101.3	96.5
LiCl	<i>A</i> (1).....	91.97	89.75	85.97	82.28	77.80	70.60	63.27
"	η (23).....	(1.0016)	(1.0032)	(1.0080)	1.0161	1.031	1.072	1.150
"	$\Delta\eta$	92.1	90.0	86.7	83.6	80.2	75.7	72.8
RbCl	<i>A</i> (3).....	125.3	113.9	101.9
"	η (21).....	(0.998)	(0.976)
"	$\Delta\eta$	125.3	113.7	99.5
CsCl	<i>A</i> (3).....	125.07	113.44
"	η (21).....	(0.997)
"	$\Delta\eta$	125.07	113.1
TlCl	<i>A</i> (3).....	120.21
NH ₄ Cl	<i>A</i> (7a).....	122.5	118.1 ¹
KBr	<i>A</i> (3).....	124.31	121.78	117.69	114.14	110.32	105.30
"	η (20).....	(0.9995)	(0.9989)	(0.9973)	(0.9946)	(0.9893)	(0.9623)
"	$\Delta\eta$	124.3	121.7	117.4	113.5	109.1	101.3
KI	<i>A</i> (3).....	123.44	121.10	117.26	113.98	106.2	103.60
"	η (23).....	(0.9992)	(0.9983)	(0.9955)	0.9908	0.9551	0.920
"	$\Delta\eta$	123.3	120.9	116.7	112.9	101.4	95.3
KSCN	<i>A</i> (3).....	113.87	111.51	107.67	104.21	95.63	91.55
KF	<i>A</i> (3).....	104.19	101.78	97.65	93.94	82.0	75.95

¹ At 30 millinormal.

TABLE VIIIb (continued).

Concentration.....		10.	20.	50.	100.	200.	500.	1000.
NaF	<i>A</i> (3).....	83.38	81.0	76.94	73.06	67.9	59.9	51.9
TlF	<i>A</i> (3).....	105.44	102.22	97.38	92.61	78.78	71.54
NaNO ₂	<i>A</i> (1).....	98.07	95.57	91.35	87.16	82.21	73.99	65.81
"	<i>η</i> (23).....	(1.0005)	(1.0009)	1.0023	1.0044	1.0082	1.0219	1.054
"	<i>Δη</i>	98.1	95.7	91.6	87.5	82.9	75.6	69.4
KNO ₃	<i>A</i> (1).....	118.10	115.12	109.78	104.71	98.67	89.18	80.41
"	<i>η</i> (23).....	(0.9995)	(0.9989)	0.9972	0.9941	0.9883	0.9745	0.962
"	<i>Δη</i>	118.1	115.0	109.5	104.1	97.5	86.9	77.4
LiNO ₃	<i>A</i> (1).....	88.46	86.27	82.58	79.06	74.89	67.88	60.69
"	<i>η</i> (23).....	(1.0017)	(1.0033)	1.0062	1.0112	1.020	1.0503	1.102
"	<i>Δη</i>	88.6	86.6	83.1	79.9	76.4	71.3	66.9
TlNO ₃	<i>A</i> (3).....	118.38	107.93	101.19
"	<i>η</i>	(0.9995) ¹	(0.997) ¹	(0.994) ¹
"	<i>Δη</i>	118.3	107.6	100.6
AgNO ₃	<i>A</i> (3).....	107.80	105.1	99.50	94.33	77.5	67.6
"	<i>η</i> (21).....	1.020	1.057
"	<i>Δη</i>	107.80	105.1	99.50	94.33	79.1	71.5
KClO ₃	<i>A</i> (3).....	111.64	108.81	103.74	99.19	93.73	85.28
"	<i>η</i> (22).....	(0.999)	(0.997)	(0.995)	(0.986)
"	<i>Δη</i>	111.64	108.81	103.6	98.9	93.3	84.1
KBrO ₃	<i>A</i> (5).....	104.7	102.0	97.3	93.0	87.8
NaIO ₃	<i>A</i> (2).....	70.86	68.56	64.43	60.46	55.45
"	<i>η</i> (23).....	(1.002)	(1.005)	(1.012)	(1.025)	1.050
"	<i>Δη</i>	71.0	68.9	65.2	62.0	58.2
KIO ₃	<i>A</i> (2).....	91.24	88.64	84.06	79.67	74.34
"	<i>η</i> (23).....	(1.0014)	(1.0027)	(1.0067)	(1.0134)	1.0270
"	<i>Δη</i>	91.4	88.9	84.7	80.7	76.3

LiIO ₃	<i>A</i>	(2).....	61.23	59.05	55.26	51.50	46.88	38.98	31.21
"	η	(23).....	(1.003)	(1.006)	(1.016)	1.031	1.062	(1.178)	1.388
"	<i>A</i> η	61.4	59.4	56.1	53.1	49.8	45.9	43.3
HCl	<i>A</i>	(6).....	369.3	365.5	358.4	351.4
HNO ₃	<i>A</i>	(7).....	365.0	353.7	346.4
BaCl ₂	<i>A</i>	(4).....	106.67	102.53	96.04	90.78	85.18	77.29	70.14
"	η	(18).....	(1.001)	(1.002)	(1.005)	(1.011)	(1.021)	(1.052)	1.107
"	<i>A</i> η	106.8	102.7	96.5	91.8	87.0	81.3	77.6
CaCl ₂	<i>A</i>	(4).....	103.37	99.38	93.29	88.19	82.79	74.92	67.54
"	η	(23).....	(1.0017)	(1.0033)	(1.0083)	1.0167	(1.0306)	1.0751	1.1501
"	<i>A</i> η	103.6	99.7	94.1	89.7	85.3	80.5	77.7
MgCl ₂	<i>A</i>	(4).....	98.14	94.33	88.47	83.42	77.84	69.50	61.45
"	η	(23).....	(1.0023)	(1.0051)	(1.0116)	(1.0209)	1.0423	(1.101)	1.213
"	<i>A</i> η	98.4	94.8	89.5	85.2	81.1	76.5	74.5
PbCl ₂	<i>A</i>	(5).....	102.1	93.2	79.2
CdCl ₂	<i>A</i>	(8).....	82.2	74.2	62.1	50.1	41.0	30.4	21.4
"	η	(21).....	(1.002)	(1.006)	(1.012)	(1.025)	(1.063)	(1.134)
"	<i>A</i> η	82.2	74.3	62.5	50.7	42.0	32.3	24.3
CdBr ₂	<i>A</i>	(8).....	75.4	65.4	51.7	43.0	34.8	24.9	17.9
CdI ₂	<i>A</i>	(8).....	64.8	53.0	39.0	29.5	23.3	18.1	15.1
Ba(NO ₃) ₂	<i>A</i>	(4).....	100.96	95.66	86.81	78.94	70.18	56.60
"	η	(21).....	1.002	1.004	1.008	1.017	1.044
"	<i>A</i> η	100.96	95.9	87.2	79.6	71.4	59.1
Sr(NO ₃) ₂	<i>A</i>	(4).....	99.04	94.52	87.30	80.93	73.80	62.72	52.07
"	η	(21).....	1.002	1.004	1.009	1.019	1.049	1.115
"	<i>A</i> η	99.04	94.7	87.6	81.7	75.2	65.8	58.1
Ca(NO ₃) ₂	<i>A</i>	(4).....	99.53	95.18	88.41	82.48	75.94	65.70	55.86
"	η	(21).....	1.001	1.002	1.004	1.008	1.017	1.053	1.117
"	<i>A</i> η	99.6	95.3	88.8	83.1	77.2	69.2	62.4

¹ Assumed to be identical with the values for KNO₃.

TABLE VIIIb (continued).

Concentration.....		10.	20.	50.	100.	200.	500.	1000.
Mg(NO ₃) ₂	A (5).....	94.65	90.9	85.3	80.5	75.3
"	η (21).....	1.002	1.003	1.008	1.016	1.032
"	Aη.....	94.8	91.2	86.0	81.8	77.7
Cd(NO ₃) ₂	A (8).....	94.1	91.4	85.1	77.9	71.8	63.2	53.6
"	η (21).....	1.001	1.003	1.007	1.015	1.031	1.074	1.165
"	Aη.....	94.2	91.7	85.7	79.1	74.0	67.9	62.4
Pb(NO ₃) ₂	A (4).....	103.55	97.01	86.38	77.27	67.36	53.21	42.02
"	η (23).....	(1.0009)	(1.0017)	(1.0043)	1.0087	1.0166	1.044	1.100
"	Aη.....	103.6	97.2	86.8	77.9	68.5	55.6	46.2
Ba(BrO ₃) ₂	A (5).....	88.2	83.6
K ₂ SO ₄	A (4).....	115.8	110.3	101.9	94.9	87.7	78.4	71.6
"	η (23).....	(1.0014)	(1.0033)	(1.0060)	1.0111	(1.021)	(1.049)	1.101
"	Aη.....	116.0	110.7	102.5	96.0	89.5	82.2	78.8
Na ₂ SO ₄	A (9)(10).....	95.7	83.64	77.07	69.95
"	η (18).....	(1.002)	(1.011)	(1.022)	(1.044)
"	Aη.....	95.9	84.6	78.8	73.0
Li ₂ SO ₄	A (4).....	86.73	82.06	74.59	68.07	60.97	50.45	41.31
"	η (23).....	(1.0032)	(1.0065)	1.015	1.029	1.057	1.143	1.303
"	Aη.....	86.9	82.6	75.7	70.0	64.4	57.7	53.8
Tl ₂ SO ₄	A (5).....	112.3	104.55	92.7	83.1	73.8
"	η.....	1.0014 ¹	1.0033 ¹	1.0060 ¹	1.0111 ¹	1.021 ¹
"	Aη.....	112.5	104.9	93.3	84.0	75.4
Ag ₂ SO ₄	A (5).....	102.9	96.1
K ₂ C ₂ O ₄	A (4).....	112.83	108.07	100.77	94.79	88.57	73.63
"	η (23).....	(1.0013)	(1.0025)	(1.0063)	1.0127	1.0236	1.113
"	Aη.....	113.0	108.3	101.4	96.0	90.7	82.0
H ₂ SO ₄	A (7).....	309.0	253.5	233.3

MgSO ₄	<i>A</i>	(4).....	76.21	67.68	56.92	49.68	43.19	28.91
"	<i>η</i>	(23).....	(1.0039)	1.0077	1.0181	1.034	1.068	1.381
"	<i>Δη</i>	76.5	68.2	57.9	51.4	46.1	39.9
ZnSO ₄	<i>A</i>	(4).....	72.9	63.8	52.8	45.4	39.1	26.2
"	<i>η</i>	(18).....	(1.003)	(1.006)	(1.016)	(1.031)	(1.064)	1.362
"	<i>Δη</i>	73.1	64.2	53.6	46.8	41.6	35.7
CdSO ₄	<i>A</i>	(4).....	70.34	60.95	49.60	42.21	35.89	28.74	23.58
"	<i>η</i>	(21).....	1.002	1.005	1.013	1.026	1.061	1.157	1.347
"	<i>Δη</i>	70.5	61.3	50.2	43.3	38.1	33.3	31.8
CuSO ₄	<i>A</i>	(4).....	71.74	62.40	51.16	43.85	37.66	25.77
"	<i>η</i>	(18).....	(1.004)	(1.008)	(1.016)	(1.032)	(1.064)	1.371
"	<i>Δη</i>	72.0	62.9	52.0	45.3	40.1	35.3
MgC ₂ O ₄	<i>A</i>	(4).....	29.6	23.0	16.4	12.7	10.0
C = 12.5									
K ₄ Fe(CN) ₆	<i>A</i>	(11).....	113.4	93.7	84.9	77.8
"	<i>η</i>	(20).....	(1.001)	(1.005)	(1.011)	(1.021)
"	<i>Δη</i>	113.5	94.2	85.8	79.4
Ca ₂ Fe(CN) ₆	<i>A</i>	(11).....	49.9	38.5	35.1	32.9
La(NO ₃) ₃	<i>A</i>	(11).....	98.5	86.1	79.4	72.1
La ₂ (SO ₄) ₃	<i>A</i>	(11).....	37.4	25.7	21.4	17.8
K ₂ C ₆ H ₄ O ₇	<i>A</i>	(11).....	101.8	87.8	80.8

¹ Assumed to be identical with the values for K₂SO₄.

TABLE IXa.—VALUES OF THE EQUIVALENT CONDUCTANCE AT 0° AT CONCENTRATIONS
0 TO 12.5 MILLI-EQUIVALENTS PER LITER.

Concentration.....	0.	0.5.	1.	2.	5.	10.	12.5.
KCl (17).....	82.0	80.3	77.6
" (13).....	82.0	80.9	80.4	79.7	78.6	77.4
" (12) ¹	81.4	80.3	80.0	79.6	78.7	77.6
" (24).....	81.0
NaCl (17).....	67.6	65.9	63.3
" (13).....	67.2	65.5	63.3	61.7
LiCl (24).....	60.3
KI (17).....	83.5	81.8
NaNO ₃ (17).....	66.1	64.7	61.7
" (13).....	65.1	64.4	63.4	61.9	60.4
KNO ₃ (17).....	81.1	79.3	75.7
" (13).....	80.8	77.8	77.1	76.1	74.6	73.1
" (11).....	78.6	75.3
CsNO ₃ (24).....	84.0
AgNO ₃ (17).....	73.3	71.6	68.3
" (13).....	(71.8)	70.7	70.2	69.6	68.4	67.1
KClO ₃ (13).....	(74.2)	72.5	71.9	71.2	70.0	68.8
BaCl ₂ (17).....	75.2	71.9	66.3
" (12) ²	75.5	73.1	72.3	71.1	69.0	66.9
" (13).....	72.8	68.7	65.3
Ba(NO ₃) ₂ (17).....	73.6	70.3	63.3
" (13).....	(71.0)	68.8	67.8	66.4	64.0	61.6
Sr(NO ₃) ₂ (13).....	69.1	67.0	66.0	64.6	62.3	60.2
Ca(NO ₃) ₂ (11).....	66.5	61.6
K ₂ SO ₄ (13).....	78.2	77.0	75.6	73.2	70.8
" (17).....	83.2	79.0	72.4
Na ₂ SO ₄ (17).....	68.5	64.2	58.5
K ₂ C ₂ O ₄ (11).....	74.9	69.3
MgSO ₄ (17).....	68.9	60.5	46.6
" (12) ³	70.7	63.9	61.4	(57.9)	51.2	46.8
" (13) ⁴	(69.0)	63.3	60.3	56.6	50.9	46.3
CuSO ₄ (12) ⁵	70.7	63.3	60.2	56.3	50.0	44.5
" (13) ⁶	(70.7)	63.0	60.0	56.3	50.1	44.8
ZnSO ₄ (13).....	(70.0)	63.6	60.3	56.4	50.4	45.4
CdSO ₄ (13).....	(69.0)	61.6	58.7	55.1	49.0	43.7
La(NO ₃) ₃ (11).....	68.9	61.4
K ₃ C ₆ H ₅ O ₇ (11).....	71.0	67.6	62.9

¹ 80.6 for C = 0.2 and 0.1.² 73.9 for C = 0.2; 74.2 for C = 0.1.³ 66.3 for C = 0.2; 67.6 for C = 0.1. The result for C = 2 is incorrect, as shown by the plot.⁴ 66.6 for C = 0.2; 68.6 for C = 0.1.⁵ 66.0 for C = 0.2; 67.4 for C = 0.1.⁶ 65.9 for C = 0.2; 67.6 for C = 0.1.

TABLE IXa (continued).

Concentration.....	0.	0.5.	1.	2.	5.	10.	12.5.
$K_4Fe(CN)_6$ (11).....	98.4	91.6	84.8	71.0
$La_2(SO_4)_3$ (11).....	39.8	24.9
$Ca_2Fe(CN)_6$ (11).....	47.1	31.2
" (14).....	60.0	52.6	45.3	37.1	31.8
$Sr_2Fe(CN)_6$ (14).....	60.3	52.5	44.9	36.8	31.9
$KMnO_4$ (12) ¹	75.9	75.5	75.1	74.6	73.5	72.2
$K_3Fe(CN)_6$ (12) ²	97.4	92.8	91.1	88.7	84.6	80.5

TABLE IXb.—VALUES OF THE EQUIVALENT CONDUCTANCE AT 0° AT CONCENTRATIONS 20 TO 1000 MILLI-EQUIVALENTS PER LITER.

Concentration.....	20.	50.	100.	200.	500.	1000.
KCl (17).....	73.7
" (13).....	76.0	73.7	71.7	69.7	67.2	65.6
" (12).....	76.1	74.0
" (24).....	73.9	71.5	69.1	66.6
NaCl (17).....	59.6
" (13).....	60.2	58.2	56.3	54.0	50.8	47.4
LiCl (24).....	53.0	51.1	48.4	44.0
KI (17).....	75.3
$NaNO_3$ (17).....	57.8
" (13).....	58.7	55.9	53.4	51.1	48.0	46.5
KNO_3 (17).....	70.5
" (13).....	71.1	68.0	65.1	61.7	56.5	52.1
" (11).....	70.7	67.2
$CsNO_3$ (24).....	72.9	69.3	65.2	59.3
$AgNO_3$ (17).....	63.1
" (13).....	65.4	61.8	57.6	53.1	47.9	44.5
$KClO_3$ (13).....	67.2	64.2	61.1	56.9
$BaCl_2$ (17).....	60.0
" (12).....	64.5	60.7
" (13).....	61.9	57.9	54.8	51.6	47.0	44.0
$Ba(NO_3)_2$ (17).....	54.2
" (13).....	58.4	52.2	47.0	42.8
$Sr(NO_3)_2$ (13).....	57.4	53.0	49.1	44.6	38.4	32.1
$Ca(NO_3)_2$ (11).....	55.6	51.9	48.3
K_2SO_4 (17).....	63.7
" (13).....	67.7	62.7	58.5	52.0	48.4
Na_2SO_4 (17).....	51.2

¹ These results are given in arbitrary conductance units. Additional values are 75.5 for C = 0.2; 75.6 for C = 0.1.

² These results are given in arbitrary conductance units. Additional values are 94.3 for C = 0.2; 95.1 for C = 0.1.

TABLE IXb (continued).

Concentration.....	20.	50.	100.	200.	500.	1000.
K ₂ C ₂ O ₄ (11).....	63.0	59.3	55.8
MgSO ₄ (17).....	35.0
" (12).....	41.7	35.3	30.9	27.0	22.3
" (13).....	41.6	35.2	30.8	26.5	21.2	17.6
CuSO ₄ (12).....	38.8	32.6	28.2	24.3	19.1	15.9
" (13).....	39.1	32.3	27.7	23.6	19.0	15.9
ZnSO ₄ (13).....	40.1	33.7	29.6	25.7	21.7	16.3
CdSO ₄ (13).....	38.1	31.1	26.2	22.4	18.3	15.0
La(NO ₃) ₃ (11).....	54.0	49.9	46.0
K ₃ C ₆ H ₅ O ₇ (11).....	54.4	50.2	43.5
K ₄ Fe(CN) ₆ (11).....	58.2	53.0	48.8
La ₂ (SO ₄) ₃ (11).....	17.2	14.4	12.1
Ca ₂ Fe(CN) ₆ (11).....	24.1	21.9	20.6
" (14).....	27.4	23.3	21.2	20.0	19.0	18.4
Sr ₂ Fe(CN) ₆ (14).....	28.0	24.1	21.6	20.0	18.4	17.2
KMnO ₄ (12).....	70.6

TABLE Xc.—VALUES OF THE EQUIVALENT CONDUCTANCE AT 25° AT CONCENTRATIONS
O TO 5 MILLI-EQUIVALENTS PER LITER.

Concentration.....	0.	0.2	0.5	1.	2.	5.
NaCl (15)(5).....	127.0	124.1	123.05	121.0
KCl (15).....	150.6	146.55	143.95
KI (16).....	151.3	147.9	146.7	144.5
KNO ₃ (11).....	145.4	140.7	...
KBrO ₃ (5).....	129.6	126.9	125.6	123.4
HCl (5).....	426.0	420.4	418.6	415.3
HNO ₃ (7).....	420.0	...	417.0	...	413.7	...
PbCl ₂ (5).....	147.0	138.7	134.5	126.8
Mg(NO ₃) ₂ (5).....	125.6	119.5	117.4	{ 113.7 113.8*
Ca(NO ₃) ₂ (11).....	130.6	123.7	...
Ba(BrO ₃) ₂ (5).....	120.0	113.6	111.2	106.95
K ₂ SO ₄ (15).....	154.8	144.8	139.8
Na ₂ SO ₄ (15).....	131.2	122.3	{ 117.45 117.6*
Tl ₂ SO ₄ (5).....	156.0	147.8	144.2	137.3
Ag ₂ SO ₄ (5).....	143.4	135.7	132.6	126.3
K ₂ C ₂ O ₄ (11).....	147.5	139.2	...
K ₄ Fe(CN) ₆ (15).....	185.0	...	173.1	...	160.1	146.9
Na ₄ Fe(CN) ₆ (15).....	162.0	...	150.7	...	140.5	129.6
Ca ₂ Fe(CN) ₆ (11).....	171.0	86.2	...
La(NO ₃) ₃ (11).....	142.6	128.9	...
La ₂ (SO ₄) ₃ (11).....	152.0	67.9	...
K ₃ C ₆ H ₅ O ₇ (11).....	144.5	...	139.4	...	134.5	128.2

* Corrected for viscosity

TABLE Xb.—VALUES OF THE EQUIVALENT CONDUCTANCE, VISCOSITY, AND CONDUCTANCE-VISCOSITY PRODUCT AT 25° AT THE CONCENTRATIONS 10 TO 1000 MILLI-EQUIVALENTS PER LITER.

Concentration.....		10.	20.	50.	100.	200.	500.	1000.
NaCl	<i>A</i> (15)(5).....	118.7	115.9	111.2	106.8	101.7	93.45
"	η (19).....	(1.001)	(1.002)	(1.005)	(1.010)	(1.0191)	1.0471
"	<i>A</i> η	118.8	116.1	111.8	107.9	103.6	97.9
KCl	<i>A</i> (15).....	141.4	138.65	133.65	129.0	124.2	118.8	117.4
"	η (21).....	(0.9994)	(0.9988)	(0.9971)	(0.9942)	(0.9922)	0.9874	0.9872
"	<i>A</i> η	141.4	138.5	133.3	128.3	123.2	117.3	115.9
KI	<i>A</i> (16).....	142.3	139.4	134.7	130.8
"	η (22).....	(0.9994)	(0.9987)	(0.9967)	(0.9934)
"	<i>A</i> η	142.2	139.2	134.3	129.9
	C =	12.5
KNO ₃	<i>A</i> (11).....	134.9	126.3	120.3
"	η (21).....	(0.9992)	(0.9968)	(0.9937)
"	<i>A</i> η	134.8	125.9	119.5
	C =	10
KBrO ₃	<i>A</i> (5).....	121.0	117.8	112.4	107.2	101.1
HCl	<i>A</i> (5).....	411.6	406.7	398.4	390.4	380.2
"	η (19).....	(1.001)	(1.002)	(1.004)	(1.008)	(1.0134)	1.0338	1.0671
"	<i>A</i> η	412.0	407.5	400.0	394.4	385.3
HNO ₃	<i>A</i> (7).....	406.0	393.3	385.0
"	η (19).....	(1.0011)	(1.0021)
"	<i>A</i> η	406.0	393.7	385.8
PbCl ₂	<i>A</i> (5).....	118.2	107.6	91.3
Mg(NO ₃) ₂	<i>A</i> (5).....	110.05	105.7	99.0	93.4	87.2
"	η (21).....	(1.002)	(1.003)	(1.008)	(1.016)	(1.032)
"	<i>A</i> η	110.3	106.0	99.8	94.9	90.0

TABLE Xb (continued).

Concentration.....		10.	20.	50.	100.	200.	500.	1000.
		C = 12.5						
Ca(NO ₃) ₂	A (11).....	114.5	102.6	95.8	88.8
"	η (27).....	1.001	(1.004)	(1.008)	(1.017)
"	Aη	114.6	103.0	96.5	90.3
		C = 10						
Ba(BrO ₃) ₂	A (5).....	102.7	97.3
K ₂ SO ₄	A (15).....	134.4	128.1	118.15	109.9	101.4	90.4
"	η (21).....	(1.0006)	(1.0013)	(1.0031)	(1.0062)	(1.0165)	1.0486
"	Aη	134.5	128.3	118.5	110.6	103.1	94.8
Na ₂ SO ₄	A (15).....	112.55	106.95	97.9	90.1	81.65
"	η (21).....	(1.002)	(1.004)	(1.009)	(1.019)	(1.042)
"	Aη	112.8	107.4	98.8	91.8	85.1
Tl ₂ SO ₄	A (5).....	130.0	120.9	107.1	96.0	85.0
"	η ¹	(1.0006)	(1.0013)	(1.0031)	(1.0062)	(1.0165)
"	Aη	130.1	121.1	107.4	96.6	86.4
Ag ₂ SO ₄	A (5).....	119.9	111.7
		C = 12.5						
K ₂ C ₂ O ₄	A (11).....	129.2	116.5	109.5	102.3
		C = 10						
K ₄ Fe(CN) ₆	A (15).....	135.35	123.3	108.3	98.2	89.75
"	η (21).....	(1.001)	(1.002)	(1.005)	(1.009)	(1.018)
"	Aη	135.5	123.5	108.8	99.1	91.4
Na ₄ Fe(CN) ₆	A (15).....	120.0	110.0	97.0	88.15	80.2
		C = 12.5						
Ca ₂ Fe(CN) ₆	A (11).....	57.4	44.4	40.2	37.8
La(NO ₃) ₃	A (11).....	114.4	99.7	91.8	83.5
La ₂ (SO ₄) ₃	A (11).....	42.0	28.7	23.9	19.8
K ₃ C ₆ H ₆ O ₇	A (11).....	118.7	102.1	93.9

¹ Assumed to be identical with K₂SO₄.

References to Conductance Data:

- (1) Kohlrausch and Maltby, *Sitz. ber. königl. Preuss. Akad.*, 1899, 665.
- (2) Kohlrausch, *Ibid.*, 1900, 1002.
- (3) Kohlrausch and Steinwehr, *Ibid.*, 1902, 581.
- (4) Kohlrausch and Grüneisen, *Ibid.*, 1904, 1215.

All the values obtained in these four investigations have been corrected so as to conform to the international atomic weights for 1911 in the way suggested by Kohlrausch (*Z. physik. Chem.*, 72, 43 (1909)), assuming when not definitely stated that the official atomic weights for the year in which the article was published were used.

- (5) Hunt, *THIS JOURNAL*, 33, 795 (1911).
- (6) Goodwin and Haskell, *Phys. Review*, 19, 386 (1904).
- (7) Noyes and Eastman, *Carnegie Publ.*, 63, 262. *THIS JOURNAL*, 30, 335 (1908).
- (7a) Sosman, *Carnegie Publ.*, 63, 225 (1908).
- (8) Wershoven, *Z. physik. Chem.*, 5, 481 (1890).

The results on some of the cadmium salts given in this paper were used. The ratio between the units used by Wershoven and those used by Kohlrausch and Steinwehr was obtained by a comparison of their results with potassium iodide, and was found to be 1.064. This ratio gave a satisfactory agreement between the measurements of Wershoven and of Kohlrausch and Grüneisen for cadmium sulfate between $C = 1000$ and $C = 10$ but showed deviations amounting to 1% between $C = 10$ and $C = 2$.

- (9) Archibald, *Proc. N. S. Inst.*, 10, 49, 129.

The results for sodium sulfate at 18° were taken. The correction factor, 1.055, was found to give satisfactory results for potassium sulfate compared with the results of Kohlrausch and Grüneisen.

- (10) Sherrill, *THIS JOURNAL*, 32, 744 (1910).
- (11) Noyes and Johnston, *Ibid.*, 31, 987 (1909).
- (12) Whetham, *Proc. Roy. Soc.*, 71, 332 (1903).
- (13) Kahlenberg, *J. Phys. Chem.*, 5, 339 (1901).

The results at 0° were used. The values of Λ and C as given were plotted as ordinates and abscissas, and the results for the concentrations desired taken from the curve. No satisfactory curve was obtained for potassium iodide, so it is omitted. The results for FeSO_4 , NiSO_4 , CoSO_4 , and MnSO_4 are also omitted.

- (14) Earl of Berkeley, Hartley and Stephenson, *Trans. Roy. Soc.*, (A) 209, 319 (1909).
- (15) Results obtained by A. C. Melcher in this laboratory not yet published.
- (16) Bray and Mackay, *THIS JOURNAL*, 32, 914 (1910).
- (17) Déguisne, Landolt-Börnstein-Meyerhoffer, Tabellen, p. 755 (1905).
- (24) Washburn, *THIS JOURNAL*, 33, 1473 (1911).

References to Viscosity Data:

- (18) Arrhenius, *Z. physik. Chem.*, 1, 284 (1887).
- (19) Reyher, *Ibid.*, 2, 744 (1888).
- (20) Abegg, *Ibid.*, 11, 251 (1893).
- (21) Wagner, *Ibid.*, 5, 31 (1890).
- (22) Sprung, *Pogg. Ann.*, 159, 1 (1876).
- (23) Grüneisen, *Wiss. Abh. der Phys. Tech. Reichsanstalt*, 4, 239 (1905).
- (24) Washburn, *THIS JOURNAL*, 33, 1473 (1911).

method that was used at 18° for those substances for which an apparently accurate series of data was available. Another procedure for obtaining the Λ_0 values at 0° was also employed. This consisted in using the quadratic equations which Kohlrausch¹ derived from the conduc-

¹ *Sitzungsber. königl. Preuss. Akad.*, 1901, 1026.

tance measurements of Déguisne at 2°, 10°, 18°, 16°, and 34°, and which express the Λ_0 values for the salts at various temperatures in terms of the Λ_0 values at 18° and specific temperature coefficients. From them the Λ_0 values given in Table IX opposite the reference number (17) were calculated.

The Λ_0 values for the substances shown in Table X at 25° were obtained in collaboration with Dr. W. C. Bray by plotting the values of i/Λ and $(\Lambda)^{n-1}$ and extrapolating as already indicated, and also by taking into account the fact that ionizations calculated with them for 25° should not differ materially from ionizations calculated for 18°, for which temperature a reliable series of Λ_0 values is known.

The viscosity data given within parentheses in the tables were derived from the nearest measured value with the aid of the exponential function, $\eta/\eta_0 = k_1C$ or $\log(\eta/\eta_0) = k_2C$, where C is the concentration and k_1 or k_2 is a constant calculated from the measured value. The values given in Table VIIIb were based on measurements at or near 18°, except those of Wagner (reference (21)) which were made at 25°. These values were assumed to be the same at 18° and were used in correcting the conductance values at 18°, except in the case of cesium and rubidium chlorides, whose viscosities were corrected to 18° by means of the same temperature coefficient which potassium and ammonium chlorides have been found to have:

13. Ionization Values at 18°.

TABLE XI.—VALUES OF THE PERCENTAGE IONIZATION ($100 \Lambda/\Lambda_0\eta_0$) AT 18°.

Concentration..	1.	2.	5.	10.	20.	50.	100.	200.	500.	1000.
NaCl.....	97.7	96.9	95.3	93.6	91.6	88.2	85.2	81.8	77.3	74.1
KCl.....	97.9	97.1	95.6	94.1	92.2	88.9	86.0	82.7	77.9	74.2
LiCl.....	97.5	96.6	94.9	93.2	91.1	87.8	84.6	81.2	76.6	73.7
RbCl.....	98.0	94.2	85.5	74.8
CsCl.....	97.8	96.9	95.4	93.7	84.7
TlCl.....	97.6	96.5	94.2	91.5
KBr.....	97.8	97.0	95.5	94.0	92.1	88.8	85.9	82.5	76.6
KI.....	97.8	97.0	95.6	94.1	92.2	89.0	86.9	77.3	72.7
KSCN.....	97.8	97.0	95.5	94.0	92.0	88.8	86.0
KF.....	97.8	97.0	95.4	93.7	91.5	87.8
NaF.....	97.4	96.4	94.5	92.5	89.9	85.4
TlF.....	96.1	93.6	90.8	86.5
NaNO ₃	97.7	96.8	95.0	93.2	91.0	87.1	83.2	78.8	71.9	66.0
KNO ₃	97.8	97.0	95.3	93.5	91.1	86.7	82.4	77.2	68.8	61.3
LiNO ₃	97.5	96.5	95.0	93.2	91.1	87.4	84.0	80.3	75.0	70.3
TlNO ₃	97.7	96.7	94.8	92.6	84.3	78.8
AgNO ₃	97.7	96.8	95.0	93.1	90.8	85.9	81.4	68.3	61.7
KBrO ₃	98.0	97.0	95.4	93.4	91.0	86.8	83.0
KClO ₃	97.8	96.9	95.2	93.3	91.0	86.6	82.7	78.0	70.3
NaIO ₃	97.1	96.0	93.9	91.7	89.0	84.2	80.1	75.2
KIO ₃	97.5	96.5	94.6	92.8	90.3	86.0	81.9	77.5
LiIO ₃	97.0	95.8	93.6	91.2	88.3	83.4	78.9	74.0	68.2	64.3

TABLE XI (continued).

Concentration..	1.	2.	5.	10.	20.	50.	100.	200.	500.	1000.
HCl.....	99.0	98.8	98.1	97.2	96.2	94.4	92.5
HNO ₃	99.2	98.7	97.0	94.0	92.1
BaCl ₂	95.6	88.3	85.0	79.8	75.9	72.0	67.2	64.2
CaCl ₂	95.4	93.8	91.0	88.2	84.9	80.2	76.4	72.7	68.6	66.2
MgCl ₂	95.5	93.9	91.0	88.3	85.1	80.3	76.5	72.8	68.7	66.9
PbCl ₂	94.3	91.7	86.5	80.8	73.8	62.7
CdCl ₂	93.1	89.1	80.3	73.5	66.4	55.9	45.3	37.5	28.9	21.7
CdBr ₂	89.7	85.8	74.9	66.1	57.3
CdI ₂	87.0	80.9	67.5	57.3	46.9
Ba(NO ₃) ₂	95.3	93.4	89.8	86.1	81.8	74.4	67.9	60.9	50.4
Sr(NO ₃) ₂	95.3	93.5	90.4	87.1	83.3	77.0	71.9	66.1	57.9	51.1
Ca(NO ₃) ₂	95.4	93.7	90.7	87.6	83.8	78.1	73.1	67.9	60.9	54.9
Mg(NO ₃) ₂	95.3	93.6	90.7	88.0	84.7	79.9	76.0	72.1
Pb(NO ₃) ₂	94.7	92.6	88.6	84.5	79.3	70.8	63.5	55.9	45.4	37.7
Cd(NO ₃) ₂	99.6	97.4	91.7	87.1	84.8	79.2	73.1	68.4	62.8	57.7
Ba(BrO ₃) ₂	94.7	92.7	89.2	85.6	81.2
K ₂ SO ₄	95.4	93.7	90.5	87.2	83.2	77.1	72.2	67.3	61.8	59.2
Na ₂ SO ₄	93.9	92.5	89.3	85.7	75.6	70.4	65.2
Li ₂ SO ₄	94.6	85.4	81.1	74.4	68.8	63.3	56.7	52.8
Tl ₂ SO ₄	94.8	92.4	88.2	83.7	78.0	69.4	62.5	56.1
Ag ₂ SO ₄	94.9	92.7	88.5	84.0	78.4
K ₂ C ₂ O ₄	96.0	94.5	91.6	88.6	84.9	79.5	75.3	71.1	64.3
MgSO ₄	87.3	82.3	74.0	66.9	59.6	50.6	44.9	40.3	34.9
ZnSO ₄	85.4	79.9	71.0	63.3	55.6	46.4	40.5	36.0	30.9
CdSO ₄	85.0	79.1	69.4	61.4	53.4	43.7	37.7	33.2	29.0	27.7
CuSO ₄	86.2	80.4	70.9	62.9	55.0	45.5	39.6	35.1	30.9
MgC ₂ O ₄	58.2	47.2	35.0	27.3
C =				12.5						
K ₄ Fe(CN) ₆	85.9	71.2	59.1	53.8	49.8
La(NO ₃) ₃	90.2	80.2	70.1
K ₃ C ₆ H ₅ O ₇	92.6	88.2	81.7	70.5
La ₂ (SO ₄) ₃	46.4	28.9	19.8
Ca ₃ Fe(CN) ₆	51.4	33.9	26.2

14. Discussion of the Ionization Values at 18°.

A study of the data of Table XI leads to the following conclusions in regard to the relations between the degree of ionization and the chemical composition and valence type of the salts.

1. All the chlorides, bromides, and iodides of all of the alkali elements have, even up to normal concentration, ionization values which are approximately identical, the variations from the average value scarcely ever exceeding 1.5% of that value.

2. The nitrates of the alkali elements and potassium chlorate and bromate form another group for which up to 0.1 normal the ionization values are almost identical (the variations not exceeding 1%).

3. The chlorides of magnesium, calcium, and barium form a third group whose members have within 1% the same ionization up to 0.2 normal.

4. The two acids, hydrochloric and nitric, have also substantially the same ionization values at all concentrations. These are much larger than those for the uni-univalent salts.

5. The average values for these four groups of substances at various equivalent concentrations are as follows:

Conc.	1.	2.	5.	10.	20.	50.	100.	200.	500.	1000.
I. M^+X^-	97.8	96.9	95.4	93.8	91.8	88.5	85.5	82.1	77.1	73.9
II. $M^+YO_4^-$	97.8	96.8	95.2	93.3	91.0	86.9	83.1
III. $M^{++}Cl_2^-$	95.5	93.9	91.0	88.3	85.0	80.1	76.3	72.5
IV. H^+A^-	99.1	98.8	98.1	97.1	96.2	94.2	92.3

6. Of the other uni-univalent salts, potassium sulfocyanate up to 0.1 normal has values conforming to those of Group I; and those for silver nitrate coincide with those of Group II up to 0.02 normal, but become considerably smaller at higher concentrations. Thallous chloride and thallous nitrate have much lower values than the corresponding salts of the alkali elements; thus thallous chloride has a 2.5% lower value at 0.01 normal, and thallous nitrate a 5.5% lower value at 0.1 normal.

7. The nitrates of the univalent elements, and still more markedly, those of the bivalent elements, exhibit a steady decrease in their ionization values, as the atomic weight of the metal increases. Thus at 0.1 normal the values are:

H.	Li.	Na.	K.	Ag.	Cs.	Tl.
92.1	84.0	83.2	82.4	81.4	80.8*	78.8
		Mg.	Ca.	Sr.	Ba.	Pb.
		76.0	73.1	71.9	67.9	63.5

8. In the case of the sulfates the order of decreasing ionization is reversed for the alkali elements, but these have values which are much larger than those for silver and thallium sulfates. Thus at 0.1 and 0.02 normal the values are:

Conc.	K.	Na.	Li.	Ag.	Tl.
0.1	72.2	70.4	68.8	62.5
0.02	83.2	81.7	81.1	78.4	78.0

9. The chlorides and iodates of these univalent metallic elements exhibit differences in the same direction as the sulfates, but of much smaller magnitude.

10. The sulfates of the periodic group embracing magnesium, zinc, and cadmium show decreasing ionization in the order named. Copper sulfate has nearly the same value as zinc sulfate.

11. The ionization values for the salts of the alkali and alkaline earth elements are related to the nature of the anion as shown by the following

* Value at 0°.

grouping—the anions in the same horizontal row having substantially the same influence, and those in any row giving rise to larger ionization than those in the row beneath:

Cl.	Br.	I.	SCN.
NO ₂	ClO ₂	BrO ₂
IO ₂

12. A consideration of all these results shows, however, that in general ionization is not an additive property with respect to the ion-constituents; also that its value is not related to those of the mobilities of the ions.

13. The relation of the ionization value to the valence type of the salt is illustrated by the following figures, which represent the average and limiting values at 18° of the ionization at 0.05 normal and 0.05 formal¹ of the uni-univalent and uni-bivalent salts of the alkali and alkaline earth elements (including magnesium) and of a variety of salts of still higher types.

Valence product.	Ionization at 0.05 normal.			Ionization at 0.05 formal.		
	Average.	Maximum.	Minimum.	Average.	Maximum.	Minimum.
1 × 1	87.0	89.0	83.4	87.0	89.0	83.4
2 × 1	77.8	80.3	74.4 ²	73.1	76.5	67.9
3 × 1	70.3 ³	70.5	70.1	61.0 ³
4 × 1	58.4 ⁴	59.0	57.7	48.8 ⁴	49.8	47.8
5 × 1	40.6 ⁵
2 × 2	46.6 ⁶	50.6	43.7	40.7 ⁶	44.9	37.7

14. The average percentages unionized at 0.05 formal for the different types and the ratio of these to the valence products (v_1v_2) are as follows:

v_1v_2 .	1 × 1.	2 × 1.	3 × 1.	4 × 1.	5 × 1.	2 × 2.
1— γ	13.0	26.9	39.0	51.2	59.4	59.3
(1— γ)/ v_1v_2	13.0	13.5	13.0	12.8	11.9	14.8

15. Comparison of the Ionization Values at 0° and 18°.

Table XII contains the values of the ratio $100\Lambda/\Lambda_0$ at 18° and 0°. Since its purpose is to show the relative values of the ionization at these two temperatures, and since few viscosity data at 0° are available, the viscosity correction has not been applied at either temperature. This cor-

¹ By 0.05 *formal* is meant a solution containing 0.05 formula-weights of salt per liter of solution.

² Thallous sulfate, lead nitrate and lead chloride have at 0.05 normal the much lower values 69.4, 70.8 and 62.7, respectively.

³ Average for K₂C₆H₅O₇ (potassium citrate) and La(NO₃)₃, uncorrected for viscosity.

⁴ Value for K₄Fe(CN)₆ and for Na₄C₁₁H₂O₁₀ (tetrasodium benzenepentacarboxylate), interpolated from the values of Noyes and Lombard (THIS JOURNAL, 33, 1433 (1911)).

⁵ Value of Na₅C₁₁HO₁₀, pentasodium benzenepentacarboxylate (Noyes and Lombard, *Loc. cit.*).

⁶ Average for MgSO₄, ZnSO₄, CdSO₄, CuSO₄.

TABLE XII.—IONIZATION VALUES AT 0° AND 18° (UNCORRECTED FOR VISCOSITY).

Concentration.	10.	50.	100.	200.	500.
KCl 18°	94.1	89.0	86.1	83.0	78.7
" 0° ¹	94.4	89.9	87.3	84.6	81.7
NaCl 18°	93.6	87.8
" 0° ²	93.6	88.2
LiCl 18°	93.1	87.0	83.3	78.7	71.5
" 0°	87.8	84.7	80.2	73.0
KI 18°	89.4
" 0°	90.2
NaNO ₃ 18°	93.2	86.8
" 0° ³	93.3	87.4
KNO ₃ 18°	93.5	86.9	82.9
" 0° ⁴	93.3	87.2	82.9
AgNO ₃ 18°	93.1	85.9	81.4	66.9
" 0° ⁵	93.5	86.1	80.2	74.0	66.7
	93.2	86.1
KClO ₃ 18°	93.4	86.7	82.9	78.9
" 0°	92.7	86.5	82.3	76.7
BaCl ₂ 18°	88.2	79.4
" 0° ⁶	88.6	80.4
Ba(NO ₃) ₂ 18°	85.4	74.1	67.4	59.9
" 0°	86.8	73.5	66.2	60.3
	86.0	73.6
Sr(NO ₃) ₂ 18°	87.1	76.8	71.9	66.1	57.9
" 0°	87.1	76.7	71.1	64.5	55.6
K ₂ SO ₄ 18°	87.1	76.6
" 0° ⁴	87.0	76.6
Na ₂ SO ₄ 18°	85.5	74.7
" 0°	85.4	74.7
MgSO ₄ 18°	66.6	49.8	43.4	37.8
" 0° ⁷	67.1	51.0	44.6	38.4
CuSO ₄ 18°	62.7	44.7	38.3	32.9
" 0° ⁸	63.2	45.9	39.5	33.9
	C = 12.5				
K ₄ Fe(CN) ₆ 18°	71.1	58.7	53.2	48.8
" 0°	72.2	59.1	53.9	49.6

¹ Average values of λ were used with $\lambda_0 = 82.0$.

² Déguisne's results. A satisfactory λ_0 could not be obtained from Kahlenberg's results.

³ Déguisne's results.

⁴ Results of Déguisne and of Noyes and Johnston. Since Noyes and Johnston's values at 25° agree with those calculated for 25° by Déguisne's equation, the results of Kahlenberg appear to be influenced by some constant error.

⁵ Both series of results were used, each with the λ_0 value obtained from its own set of measurements. Déguisne's values are in the lower row.

⁶ Whetham's results.

⁷ Kahlenberg's results were used, since these agree better with Déguisne's results for the dilute solutions than do Whetham's.

⁸ Average of Whetham's and Kahlenberg's results.

rection, up to moderate concentrations, cannot, however, be much different at the two temperatures.¹

In studying the change of ionization between 18° and 0°, it has seemed best to eliminate the irregularities arising from experimental errors by finding the average values at 18° and 0° for all of the salts of each valence type given in the table. These averages are as follows:

Equiv. conc.	10.	50.	100.
Uni-univalent 18°	93.4	87.4	83.3
" 0°	93.4	87.9	83.5
Uni-bivalent 18°	86.7	76.3	69.7
" 0°	86.9	76.4	68.7
Bi-bivalent 18°	64.7	47.3	40.9
" 0°	65.2	48.5	42.1

The differences in the values at 18° and 0° are so small that they do not exceed the probable error. This result shows that ionization values derived from the conductance at 18° may be employed at 0° (for example, in comparisons with those from the freezing-point lowering) without incurring an error greater than that in the determinations at 0°.

16. Equivalent Conductance of the Separate Ions.

Table XIII contains the equivalent conductances of the separate ions at 18° and 25°. The value for the univalent ions at 18° are primarily based on those of Kohlrausch.² The small modifications are due to the use of 0.496, instead of 0.497, for the cation-transference number of potassium chloride and to the change to the 1911 atomic weights. The values for the univalent ions at 25° were obtained from the Λ_0 values of Table Xa, taking 0.497 as the transference number of potassium chloride, and equalizing the different values for each ion. The value

TABLE XIII.—EQUIVALENT CONDUCTANCES OF THE SEPARATE IONS.
Values at 18°. Values at 25°.

Values at 18°.			Values at 25°.		
Cs... 68.0	Pb... 60.8	Br..... 67.7	Tl... 76.0	I..... 76.5	
Rb... 67.5	Ba... 55.4	I..... 66.6	K... 74.8	Cl..... 75.8	
Tl... 65.9	Ca... 51.9	Cl..... 65.5	Ag... 63.4	NO ₃ ... 70.6	
NH ₄ ... 64.7	Sr... 51.9	NO ₃ ... 61.8	Na... 51.2	BrO ₃ ... 54.8	
K... 64.5	Zn... 47.0	SCN..... 56.7	H... 35.0
Ag... 54.0	Cd... 46.4	ClO ₃ ... 55.1	Pb... 71.0	SO ₄ ... 80.0	
Na... 43.4	Mg... 45.9	BrO ₃ ... 47.6	Ba... 65.2	C ₂ O ₄ ... 72.7	
Li... 33.3	Cu... 45.9	F..... 46.7	Ca... 60.0
H... 314.5	La... 61	IO ₃ ... 34.0	Mg... 55.0
		SO ₄ ... 68.5	La... 72	Fe(CN) ₆ * 110.5	
		C ₂ O ₄ ... 63.0			
		Fe(CN) ₆ * 95			

¹ See for example the results of Noyes and Lombard (THIS JOURNAL, 33, 1432-3 (1911)) with two salts of exceptionally high viscosity.

² Z. Elektrochem., 13, 333 (1907).

* Ferrocyanide ion.

for the bivalent ions at both temperatures were obtained by subtracting those for the univalent ions from Λ_0 values for the uni-bivalent salts given in Table VIIIa, and equalizing the divergencies. These new values of the ionic conductances are due in large measure to Dr. W. C. Bray, for whose coöperation we are greatly indebted.

17. Change of the Equivalent Conductance with the Concentration.

A variety of functions have been proposed for expressing the change of the equivalent conductance with the concentration.¹ Of these, the exponential function $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$, corresponding to the ionization function $(C\gamma)^n/C(1-\gamma) = K$, may be first considered. Previous investigations have shown that the value of the exponent n varies with the nature of the salt, but usually only within the comparatively narrow limits of 1.40 to 1.60 in dilute solution, even with salts of different valence types. The function does not, however, fully express the results through the whole range of concentration from 0.0001 to 0.2 normal,² as is shown by the fact that different values of n are derived for different concentration intervals.³

This function has, however, been previously tested only with conductance or ionization values uncorrected for viscosity. Table XIV gives the values of the exponent n obtained from the corrected ionization values at 18° of Table XI, for the two concentration intervals 0.1-20 and 10-200 millinormal, by the graphical method describing in the paragraphs preceding Table VIII.

TABLE XIV.—VALUES OF n IN THE FUNCTION $C(1-\gamma) = K(C\gamma)^n$.

Milli-equiv. per liter.			Milli-equiv. per liter.			Milli-equiv. per liter.		
Salt.	0.1-20.	10-200.	Salt.	0.1-20.	10-200.	Salt.	0.1-20.	10-200.
LiCl.....	1.48	1.33	MgCl ₂	1.48	1.20	MgSO ₄	1.60	1.18
NaCl.....	1.50	1.33	CaCl ₂	1.45	1.20	ZnSO ₄	1.60	1.25
KCl.....	1.48	1.33	BaCl ₂	1.47	1.20	CuSO ₄	1.62	1.20
KBr.....	1.45	1.33	Mg(NO ₃) ₂ ...	1.47	1.20	CdSO ₄	1.62	1.20
KI.....	1.45	1.37	Ca(NO ₃) ₂ ...	1.50	1.33			
LiNO ₃	1.48	1.37	Sr(NO ₃) ₂ ...	1.52	1.44			
NaNO ₂	1.50	1.40	Ba(NO ₃) ₂ ...	1.55	1.54			
KNO ₃	1.53	1.55	Pb(NO ₃) ₂ ...	1.58	1.58			
AgNO ₃	1.53	1.55	Li ₂ SO ₄	1.52	1.33			
KClO ₃	1.50	1.45	Na ₂ SO ₄	1.33			
LiIO ₃	1.52	1.40	K ₂ SO ₄	1.50	1.33			
NaIO ₃	1.50	1.40	Tl ₂ SO ₄	1.58	1.40			
KIO ₃	1.50	1.40	K ₂ C ₂ O ₄	1.50	1.22			

It will be seen from the table that the two values of n for the two con-

¹ For reference to some of the many articles on this subject see Noyes, *Carnegie Inst. Publ.*, 63, 48 (1907).

² Cf. Johnston, *THIS JOURNAL*, 31, 1010-11 (1909).

³ Abbott and Bray, *THIS JOURNAL*, 31, 746 (1909). Bray and MacKay, *Ibid.*, 32, 920 (1910). Hunt, *Ibid.*, 33, 800 (1911).

centration intervals as a rule differ considerably, showing that the function $(C\Lambda)^n = KC(\Lambda_0 - \Lambda)$ or its equivalent $(C\gamma)^n = KC(1 - \gamma)$ with a single value of the exponent does not express the change of conductance satisfactorily through the range of concentration from 0.0001 to 0.2 normal.

It is especially noteworthy, however, that for the lower concentration interval the values become nearly identical and equal to about 1.50 for all the salts of both these types (the limits being 1.45 and 1.58). This shows that, at fairly small concentrations, at any rate, the functional relation between ionization and concentration is independent of the number of ions into which the salt dissociates—a result that is in complete disagreement with the requirements of the mass-action law.

The values of n for the higher concentration interval, on the other hand, vary greatly with different salts; thus, between 1.33 and 1.55 for the uni-univalent salts, and between 1.20 and 1.58 for the uni-bivalent salts; but again there is no systematic difference between the values for the two types of salt.

With reference to the specific substances, it may be pointed out that there is a progressive increase in the value of n with increasing atomic weight in the case of the nitrates, just as there is a progressive decrease in their ionization values; but this is not true in the case of the chlorides and sulfates. The four bi-bivalent sulfates have almost identical ionization relations. The difference in the n values for the two concentration intervals is larger than for any of the other substances.

It seemed also desirable to test with the values corrected for viscosity the simple function $\Lambda\eta/\eta_0 = B - KC^{\frac{1}{3}}$, corresponding to the expression $\Lambda = B - KC^{\frac{1}{3}}$, which Kohlrausch found to hold closely for many uni-univalent salts between the concentrations 0.001 and 0.1 normal. The experimental values of $\Lambda\eta/\eta_0$ given in Tables VIIIa and VIIIb were plotted against the corresponding values of $C^{\frac{1}{3}}$; the straight line best representing the points between 1 and 100 millinormal was drawn; and the deviations of the separate points from the line were read off. The corresponding differences (multiplied by ten) between the observed and calculated values of $\Lambda\eta/\eta_0$ are given in Table XV, together with the constants B and K of the cube-root equation corresponding to the calculated values.

An examination of Table XV shows that the deviations of the values $\Lambda\eta/\eta_0$ from those required by the cube-root equation do not exceed 0.4 unit in the case of the uni-univalent salts between the concentrations of 1 and 200 millinormal (except in the single instance of 200 millinormal KCl); but that in the case of the uni-bivalent salts deviations as large as 0.9 to 1.2 units are common even between 1 and 100 millinormal, and frequently amount to 2.5 to 4.0 units at 200 millinormal. Cadmium chloride

TABLE XV.—DEVIATIONS $\times 10$ OF THE VALUES OF $\Lambda\eta/\eta_0$ FROM THOSE REQUIRED BY THE EQUATION $\Lambda\eta/\eta_0 = B - KC^{\frac{1}{2}}$.

Salt.	K.	B.	0.	0.5.	1.	2.	5.	10.	20.	50.	100.	200.	500.
KCl.....	4.275	131.5	-15	-1	+1	+1	+1	+1	± 0	-1	-3	+10	+34
NaCl.....	3.556	109.6	-7	+3	+4	+4	+3	+1	-2	-4	-3	+2	+28
LiCl.....	3.300	99.2	-4	+4	+4	+4	+2	± 0	-2	-3	-3	+3	+47
KBr.....	4.172	133.1	-9	+3	+4	+4	+3	+2	-1	-3	-2	+4	+13
KI.....	4.224	132.4	-13	± 0	+2	+1	+1	± 0	± 0	-1	+1	...	+25
KNO ₃	5.386	129.3	-30	-7	-3	± 0	+3	+4	+3	± 0	-2	-3	+4
NaNO ₃	4.138	106.9	-17	-1	± 0	+1	+2	+1	± 0	-1	-2	+2	+15
LiNO ₃	3.369	95.8	-7	+3	+3	+2	+3	+1	-1	-3	-3	+3	+16
AgNO ₃	5.164	118.6	-28	-6	-3	± 0	+2	+3	+5	-1	-3	...	+15
KClO ₃	4.942	122.0	-24	-4	-2	± 0	+3	+2	+2	-2	-2	+2	+13
KBrO ₃ ¹	4.634	114.6	-25	-1	-1	+2	+1	± 0	-2	-1	+3
KIO ₃	4.121	100.1	-16	-1	± 0	+1	+1	+2	± 0	-2	-3	+3
NaIO ₃	3.505	78.4	-10	+2	+3	+3	+3	+2	± 0	-3	-1	+3
LiIO ₃	3.181	68.1	-8	+3	+4	+4	+3	+2	-3	-3	-2	+3	+30
MgCl ₂	5.711	111.1	+3	+11	+10	+7	+1	-4	-8	-6	+6	+34	+97
CaCl ₂	6.156	117.3	+1	-1	+9	+6	± 0	-4	-9	-5	+9	+40	+121
BaCl ₂	6.430	120.8	+1	+13	+12	-1	-6	-6	+8	+38	+115
CdCl ₂	13.20	114.4	+5	+60	+49	+11	-8	-13	-3	+6	+78
Mg(NO ₃) ₂	5.660	107.4	+3	+9	+5	± 0	-4	-8	-5	+7	+34
Ca(NO ₃) ₂	6.857	114.0	-3	+13	+14	+11	+8	+4	-1	+1	+9	+33	+96
Sr(NO ₃) ₂	7.284	114.9	-12	+7	+7	+7	+3	-2	-4	-5	+6	+29	+87
Ba(NO ₃) ₂	8.635	119.5	-23	+4	-2	+9	+6	+1	-2	-5	+2	+24	+81
Pb(NO ₃) ₂	9.918	124.8	-22	+12	+12	+12	+9	+2	-7	-15	-9	+17	+95
Cd(NO ₃) ₂	6.618	110.0	-18	+44	+37	+5	-15	-3	+1	-2	+27	+104
K ₂ SO ₄	8.38	134.0	-10	+12	+9	+12	+7	+1	-5	-6	+9	+35	+147
Na ₂ SO ₄	7.199	111.8	+1	+6	+5	+8	+4	-4	-7	+4	+33
Li ₂ SO ₄	6.070	99.2	+26	+33	+32	+8	-1	-11	-10	+7	+67
Tl ₂ SO ₄	11.90	138.6	-42	+7	+6	+2	-5	-14	-15	+6	+64
K ₂ C ₂ O ₄	7.216	128.9	-14	+6	+7	+7	+2	-4	-10	-9	+6	+40

¹ Conductance values not corrected for viscosity.

TABLE XVI.—DEVIATIONS $\times 10$ OF THE VALUES OF $\Delta\eta/\eta_0$ FROM THOSE REQUIRED BY THE EQUATION $\text{Log } \Delta\eta/\eta_0 = \text{Log } B' - K'c^{\frac{1}{2}}$.

Salt.	$10^3 K'$.	B' .	0.	0.5.	1.	2.	5.	10.	20.	50.	100.	200.	500.
KCl.....	15.39	132.0	-20	-30	-1	0	+1	+1	0	-2	-2	+2	+17
NaCl.....	15.97	110.3	-14	-1	0	+2	+1	+1	-1	-3	-2	+1	+18
LiCl.....	16.54	100.0	-12	0	0	+1	0	0	-2	-2	-2	+2	+18
KBr.....	15.25	133.8	-16	-1	+1	+2	+3	+2	0	-2	-2	+1	0
KI.....	15.22	132.9	-18	-2	0	0	+1	+1	+1	-1	0	+8
KNO ₃	22.23	131.8	-55	-23	-16	-11	-4	0	+3	+3	+1	-2	-9
NaNO ₃	19.29	107.8	-26	-6	-3	-1	+1	+2	+2	+1	-2	-2	-2
LiNO ₃	17.89	96.7	-16	-2	-1	0	+1	+1	+1	0	0	+4	-15
AgNO ₃	23.31	121.0	-52	-21	-16	-10	-4	0	+5	+2	0	+1
KClO ₃	20.04	122.8	-32	-7	-4	-1	+3	+4	+5	0	-2	-5	-10
KBrO ₃ ¹	20.40	115.7	-36	-6	-4	+1	+1	+1	-1	-1	-1
KIO ₃	20.69	100.9	-24	-5	-2	0	+2	+3	+2	0	-2	-1
NaIO ₃	23.29	79.7	-23	-5	-3	-1	0	0	0	-2	-1	0
LiIO ₃	25.34	69.6	-23	-5	-3	-2	0	0	0	0	-5	+3	+21
MgCl ₂	26.33	112.5	-11	+5	+6	+4	0	-3	-6	-4	+3	+22	+70
CaCl ₂	26.30	118.3	-9	+5	+6	+5	+1	-2	-7	-5	+4	+23	+73
BaCl ₂	27.00	122.0	-11	+9	+10	+1	-4	-5	+4	+22	+68
CdCl ₂	81.39	125.9	-140	-2	+3	-15	-21	-16	-6	-21	-1	+39
Mg(NO ₃) ₂	25.48	107.7	0	+11	+8	+3	-1	-6	-7	-2	+13
Ca(NO ₃) ₂	31.36	116.3	-26	0	+3	+3	+3	0	-3	-4	-1	+9	+36
Sr(NO ₃) ₂	32.66	116.4	-27	+1	+3	+5	+3	0	-2	-6	-4	+2	+17
Ba(NO ₃) ₂	40.44	123.1	-59	-10	-5	0	+3	+3	+3	-2	-3	0	+3
Pb(NO ₃) ₂	47.78	130.4	-78	-14	-7	-1	+6	+7	+4	-2	-4	0	+11
K ₂ SO ₄	33.65	136.9	-39	-2	+2	+4	+5	+1	-2	-4	+5	+24	+85
Na ₂ SO ₄	34.64	114.2	-23	-5	-4	+2	+2	-3	-6	-1	+13
Li ₂ SO ₄	38.35	105.2	-34	-4	0	-1	-2	-3	+2	+16	+55
Th ₂ SO ₄	50.25	143.6	-92	-5	+1	+7	+6	0	-5	+1	+24
K ₂ C ₂ O ₄	29.45	130.8	-33	-2	+1	+4	+3	0	-5	-5	+5	+26

¹ Conductance values not corrected for viscosity.

and nitrate show especially large deviations. It will also be observed that the values of the constant B for the uni-univalent salts are considerably greater, as shown by the deviations at zero concentration, than the values of Λ derived with the aid of the function $\Lambda_0 - \Lambda = K(C\Lambda)^n$. This is a consequence of the fact that the cube-root function does not satisfactorily express the observed results at the very small concentrations 0.1-1.0 millinormal.

In order to find a more satisfactory expression for the results with the uni-bivalent salts, the function $\log \Lambda\eta/\eta_0 = \log B' - K'C^{\frac{2}{3}}$ was tried. Table XVI shows the deviations, computed as in the previous case, between the observed and calculated values of $\Lambda\eta/\eta_0$. A comparison of these deviations with those of Table XV shows there is not much choice between the two functions in the case of the uni-univalent salts, but that the logarithmic one is as a rule considerably better for the uni-bivalent salts. Thus the deviations from this function between 1 and 100 millinormal seldom exceed 0.7 unit (except in the case of cadmium chloride).

The function $\Lambda\eta/\eta_0 = B'' - K''C^n$ (where n is a smaller power of the concentration than $\frac{1}{3}$) was also tried with a few of the uni-bivalent salts. The deviations are given in Table XVII:

TABLE XVII.—DEVIATIONS $\times 10$ OF THE VALUES OF $\Lambda\eta/\eta_0$ FROM THOSE REQUIRED BY THE EQUATION $\Lambda\eta/\eta_0 = B'' - K''C^n$.

Salt.	n .	B'' .	0.	1.	2.	5.	10.	20.	50.	100.	200.
CaCl ₂	0.15	136.8	-194	0	+4	+2	+6	+2	-3	-3	0
Pb(NO ₃) ₂	0.25	134.4	-118	-7	-1	+5	+2	+6	-9	-9	0
Mg(NO ₃) ₂	0.20	116.2	-85	-1	+3	+4	+3	-1	-3	-1	+8
K ₂ SO ₄	0.20	148.2	-152	-7	0	+5	+4	0	-6	-5	+5
Na ₂ SO ₄	0.20	123.4	-115	-8	+1	+5	+3	...	-5	-6	0

These results show that for all these uni-bivalent salts a close agreement with the observed values can be secured between the concentrations 2 and 200 millinormal by employing the exponent 0.20 (instead of 0.33).

It will be seen that none of these empirical functions, even though they contain three arbitrary constants, expresses the conductance through the whole range of concentration from 0.1 to 200 millinormal. Thus, if any of the functions is made to apply through the higher concentration interval, it shows considerable deviations at the lower concentrations, and *vice versa*.

By employing a function with four empirical constants a closer agreement with the observed values over a wider range can, of course, be obtained. Reference will be made here to only one such function—that recently employed by C. A. Kraus. This function has the form $\frac{(C\Lambda)^2}{C(\Lambda_0 - \Lambda)} =$

$K' + D'(C\Lambda)^m$ corresponding to $\frac{(C\gamma)^2}{C(1-\gamma)} = K + D(C\gamma)^m$. As will be

shown in a contribution from this laboratory soon to be published by C. A. Kraus and W. C. Bray, this function has, in the case of uni-univalent salts, an extraordinary range of applicability. Thus it expresses satisfactorily the results from very small concentrations up to fairly high concentrations (0.5 normal and beyond) not only for solutions in water, but in a variety of non-aqueous solvents. It has, moreover, an obvious theoretical interpretation in the sense that the term $D(C\gamma)^m$ expresses the fact that the mass-action expression $(C\gamma)^2/C(1-\gamma)$ increases with the ion concentration $C\gamma$ in the solution. The function requires, moreover, that when $C\gamma$ becomes sufficiently small, the mass-action law hold true for any solute in any solvent. In the case of aqueous solutions of salts, strong acids, and bases, the value of K is so small in comparison with $D(C\gamma)^m$, except at small concentrations, that as has been seen above, an equation which contains only the latter term expresses the actual conductance fairly well within a limited concentration interval. This function appears to furnish by far the most general and satisfactory expression thus far discovered of the relation between the conductance and concentration of the uni-univalent salts. Further discussion of it in this article is, however, inappropriate, as it will be fully treated in the future paper just referred to.

In the case of salts of the uni-bivalent and higher types, the relation between concentration and ionization is probably further complicated by the presence of the intermediate ion. The most probable assumptions which can be employed for estimating its concentration in solutions of uni-bivalent salts have been discussed by W. D. Harkins in a recent contribution from this laboratory.¹

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 81.]

THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY. IV. COMPARISON OF THE IONIZATION VALUES DERIVED FROM THE FREEZING POINT LOWERING AND FROM THE CONDUCTANCE RATIO.

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CONTENTS.—18. Tabulation of the Ionization Values Derived from Freezing Point Lowering and from the Conductance Ratio. 19. Discussion of the Ionization Values Derived by the Two Methods.

18. Tabulation of the Ionization Values Derived from Freezing Point Lowering and from the Conductance Ratio.

In Table XVIII are brought together the values of the percentage ionization (100 γ) corresponding to the mol-numbers derived from the

¹ THIS JOURNAL, 33, 1863 (1911).