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A GENERAL RELATION BETWEEN THE CONCENTRATION AND THE CONDUCTANCE OF IONIZED SUBSTANCES IN VARIOUS SOLVENTS.

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I. Introduction.[1]

Some time previous to the appearance of the epoch-making publication of Arrhenius(1),[2] in which was laid the foundation of the ionic theory, Ostwald(2) discovered certain regularities in the conductance curves of solutions of the organic acids in water.   On the appearance of the ionic theory, Ostwald(3) applied the law of mass action to the solutions which he had been studying, and found that in practically all cases this law held true, and that the empirical relationships which he had previously discovered were readily interpreted in the light of this law.

Although Ostwald makes no mention of the behavior of the so-called "strong electrolytes" in his papers, it must have been clear to him at the

[2] References to earlier investigations are numbered and will be found in the collected list of references at the end of this paper.

time that the mass-action law fails when applied to solutions of the mineral acids and bases and the neutral salts, for these electrolytes do not obey the empirical relationships which he found to hold for the organic acids, and which relationships he later found to be the direct consequences of the law of mass action. In the second edition of his "Lehrbuch der allgemeinen Chemie," however, he discussed this discrepancy. As a possible explanation, he suggested that the degree of ionization as measured by the conductance method is in some way at fault.[1] Many subsequent investigations have adopted the same view.

Some time later Rudolphi(4), on a purely empirical basis, suggested a modified dilution law, which is expressed by the equation:

$$\frac{(c\gamma)^2}{c^{1/2}(1-\gamma)} = \text{constant}, \qquad (Ia)$$

in which c is the total salt concentration, and γ the degree of ionization as determined from conductance measurements. Shortly afterward, van't Hoff(5) modified Rudolphi's equation so as to read:

$$\frac{(c\gamma)^{3/2}}{c(1-\gamma)} = \text{constant}. \qquad (Ib)$$

This equation accounted for the experimental data somewhat better than did that of Rudolphi. Storch(6) modified this equation still further to read:

$$\frac{(c\gamma)^n}{c(1-\gamma)} = D, \qquad (Ic)$$

where D is a constant and n is an exponent differing not greatly from the value $3/2$, but yet varying somewhat with different salts. Arrhenius(7) finally wrote the equation of Storch in the more general form:

$$\frac{(c\gamma)^2}{c(1-\gamma)} = D(\Sigma c\gamma)^m, \qquad (Id)$$

where $m = 2 - n$ and $\Sigma c\gamma$ is the sum of the ion-concentrations due to all the electrolytes in the solution. As may be seen, in this form the equation implies that the right-hand member, corresponding to the mass-action constant, is a function of the total ion-concentration $\Sigma c\gamma$. Arrhenius carried out numerous experiments to show that this equation holds for mixtures of electrolytes as well as for solutions of a single salt. It is evident that if the equations of Storch and Arrhenius are accepted, the mass-action law in its application to electrolytic solutions must be discarded, for at high dilutions the right-hand member, which corresponds to the mass-action constant, approaches the value zero. This procedure is fraught with grave consequences for the ionic theory, for, if the dilution be made sufficiently great, any forces acting between the molecules of the solute must vanish, and the mass-action law is a necessary theoretical

[1] Ostwald, *Lehrbuch der allgemeinen Chemie*, **2**, [1] 695 (1893).

consequence of the ionic theory (that there is an equilibrium between the ions and the un-ionized substance). Many attempts have been made to reconcile these discordant elements, but it cannot be said that any one of them has been successful either in correlating known facts or in suggesting new experiments which would serve to establish the truth or falsity of the fundamental assumptions.

Investigations were made at an early date to supplement the results obtained in aqueous solutions by experimental data in other solvents than water. The earliest of these is that of Kablukoff(8), who investigated the conductance of hydrochloric acid in ether and the alcohols. Among other things, he found that the equivalent conductance of hydrochloric acid in ether and in amylalcohol increases with increasing concentration. Later, numerous investigations were carried out in non-aqueous solvents, chiefly in the alcohols(9, 10, 11), but also in formic acid(12) and acetone(13). The results of these investigations could not be interpreted at the time. Not only did the mass-action law not hold, but the empirical dilution laws, which accounted fairly well for the results in aqueous solutions, failed in these non-aqueous solvents. The earliest data confirmatory of the mass-action law in non-aqueous solutions are due to Franklin and Kraus(14), who found fairly satisfactory agreement with that law in the case of a number of typical salts dissolved in liquid ammonia, provided the dilutions were sufficiently great. Later, Dutoit and his associates,[1] working at the University of Lausanne, found that in a considerable number of solvents typical salts yield solutions which conform to the mass-action law at high dilutions. The importance of these investigations seems not to have been recognized either by commentators or by those investigators who have been active in advancing the theory of solutions. This has been due, in a measure, to the fact that during the past fifteen years an enormous number of observations have been recorded in connection with the study of non-aqueous solutions. Many of these observations have been only roughly quantitative or otherwise fragmentary.[2] As a result, the whole field of non-aqueous solutions has been ignored as to its theoretical importance.

The present paper is the result of a detailed comparative study of the electrical conductance of electrolytic solutions in non-aqueous solvents as well as in water. Practically all available data, both for dilute and

[1] Reference numbers (15–23).

[2] No one can fully appreciate the hopeless inconsistency and inaccuracy of the major portion of the work done on solutions, particularly by the conductivity method, unless he has had occasion to attempt to utilize the results in a quantitative way. Conductance measurements constitute a most convenient method of accurately studying electrolytic solutions; and, while results of a semi-quantitative nature are sometimes permissible in surveying a new field of science, the continued accumulation of inexact conductivity data is well nigh valueless.

concentrated solutions, have been carefully sifted and the results have been studied in such manner as to bring out any relationships that may hold true over a wide range of concentration and for a large number of solvents. Our purpose has been to ascertain whether there are any common underlying laws applicable to all electrolytic solutions, irrespective of the nature of the solvent, or whether it is necessary to divide the various solvents into distinct classes depending upon their chemical constitution, physical properties, etc.

We have treated the subject from an empirical standpoint, and we have endeavored to maintain an unbiased attitude regarding the theoretical interpretation of the experimental results in order that it might appear wherein the prevailing conceptions are correct and wherein false. It has been our aim to discover the lines along which theoretical consideration might reasonably be expected to yield profitable results, and to suggest new lines of experiment which should prove of value in further developing theoretical conceptions.

This paper is restricted to a consideration of conductance data, not because the results obtained by the conductance method are *a priori* of greater significance than those obtained by other methods, but because it is the only method whose precision is such as to make possible a study of very dilute solutions. Both the freezing point and the electromotive-force methods may be utilized in studying equilibria in solutions, but sufficient data are not available in non-aqueous solutions to make it possible to draw convincing conclusions as to the equilibria in question. The freezing point method, in particular, is unreliable in the case of non-aqueous solutions, since the ionization of the solute is in most cases much smaller[1] than it is in water. The uncertainties attending the freezing point, boiling point, and vapor pressure methods have been pointed out by previous investigators,[2] and need not be further considered here.

Electromotive force measurements in non-aqueous solutions are much needed, although they can prove of value only when carried out with a high degree of precision. The difficulty of obtaining equilibrium conditions in water is very great; and it is to be expected that in a majority of instances the difficulties will be even greater in the case of non-aqueous solutions.

Transference measurements are in a few cases considered in this paper. Aside from aqueous solutions, only in the case of liquid ammonia solutions do we have anything approaching complete data regarding transference numbers, thanks to the admirable investigation of Franklin and Cady(25). In other solvents measurements have been made in isolated

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[1] Some investigators have lost sight of this important fact in interpreting their results, and in consequence needless controversy has arisen.

[2] Compare, for example, Washburn and MacInnes(24).

cases, but it is seldom that an estimate can be made of the probable accuracy of the results.

From the foregoing it is clear that any investigation into the nature of the equilibrium of electrolytes in non-aqueous solutions at the present time must be made on the basis of the available conductance data. As is well known, the mass-action law for a binary dissociation may be written:

$$\frac{(c\gamma)^2}{c(1-\gamma)} = K, \tag{I}$$

where c is the total salt concentration, γ is the degree of dissociation, and K is a constant. In the case of electrolytic solutions, this law, as was above stated, may be tested by means of conductance data. In this case the assumption is made that the degree of ionization is equal to the ratio Λ/Λ_0 of the equivalent conductance Λ, at any dilution, to the limiting value Λ_0 which the equivalent conductance approaches as the dilution increases. This involves the fundamental assumption that the speed of the ions is sensibly independent of the concentration of the solution. As already stated, Ostwald inclined to the view that the conductance measurements do not give the correct value of γ, which means, of course, that the mobility of the ions changes with the concentration. To make the mass-action law hold it would have to be assumed that the mobility increases with concentration.[1] There has been much controversy with regard to the relative merits of these two views in accounting for the discrepancy between the observed conductance values and the values predicted on the basis of the law of mass action; and up to the present time no definit advantage has been apparent to either side. Our examination of the conductance of solutions was undertaken from an empirical standpoint and the results are for the most part independent of the particular interpretation that may be placed upon them. This subject will be discussed in Section XII, but it may be stated in this place that, so far as our results bear on the question of the correctness of the conductance method as a measure of the degree of ionization of electrolytes, the balance of the evidence is strongly in favor of this method. In presenting the results we shall speak of γ as the degree of ionization, defining it as equal to the conductance ratio Λ/Λ_0. The correctness of the equations connecting the conductance and the concentration of electrolytic solutions will be in no wise affected should this conductance ratio be interpreted differently.

II. A General Dilution Law.

For strong binary electrolytes in aqueous solutions the experimental results are well accounted for by the empirical equation of Storch, which may be expressed in the form suggested by Arrhenius, as follows, D and m being empirical constants:

[1] Cf. a recent article by Gilbert N. Lewis(66).

$$\frac{(c\gamma)^2}{c(1-\gamma)} = D(c\gamma)^m. \tag{II}$$

It is obvious that, since the right-hand member approaches zero at infinit dilution, the equation is not transformable into a form which is in agreement with the mass-action law. This relation, however, is so generally applicable to aqueous solutions that it is probable that a large element of truth is contained in it. In examining the experimental data relating to non-aqueous solvents, it seemed desirable to bring them into harmony with the mass-action law (Equation I) in dilute, and with Equation II in concentrated solutions. Combined in the simplest possible manner, these equations yield the expression:

$$\frac{(c\gamma)^2}{c(1-\gamma)} = K + D(c\gamma)^m, \tag{III}$$

where c, γ, m and D have the same significance as in II, and K is the true mass-action constant.

It is evident that, at high dilutions, this equation approaches the mass-action law as a limit, while in concentrated solutions the mass-action constant K tends to disappear in comparison with the term involving $(c\gamma)^m$. The form of this term implies that the deviations from the mass-action law are a function of the ion-concentration $c\gamma$, and not of the concentration of the total salt or of the un-ionized fraction.

A study of Equation III[1] in connection with a large variety of experimental data has shown that it is applicable to practically all binary electrolytes thus far investigated in aqueous and non-aqueous solutions.[2]

At first glance it may appear that the proposed equation is a purely arbitrary one, involving four constants, Λ_0, D, K, and m (Λ_0 being involved in the determination of γ). The constants, however, are not arbitrarily determined in all respects. The constants K and Λ_0 are, of course, interdependent, but they may in most cases be determined inde-

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[1] This general equation was first proposed by Kraus in 1908, *Proc. Am. Chem. Soc.,* 1909, p. 15, as a result of the preliminary investigation of the available conductance data in various solvents. During the past academic year (1911–12) the work was again taken up, earlier calculations being verified and extended by the authors; and the results were presented by Bray before the American Chemical Society at Washington (*Science,* **35,** 433, (1912)), and the American Electrochemical Society at Boston (*Transactions,* **21,** 1912). The same equation has recently been applied independently to aqueous solutions by MacDougall, THIS JOURNAL, **34,** 855 (1912).

The analysis of the experimental data considered in the present paper was completed in Oct., 1912, and later material has not been discussed in detail. In a few instances, however, brief references to recent articles have been inserted.

[2] There is no reason for believing that this equation will fail in the case of electrolytes of higher valence types. With the exception of aqueous solutions, the available material is very meager, while, at the same time, the problem is complicated, owing to the possible formation of intermediate ions. We shall later adduce evidence tending to show that intermediate ions are present in non-aqueous solutions (Section X).

pendently of D and m. On the other hand, in many cases m may be determined independently of the three remaining constants. The fact that the constants may be thus independently determined, and thereafter be employed to represent the experimental results from the highest dilutions to concentrations in some cases greater than normal, gives to the equation a significance which otherwise it would not possess.

The general form of the conductance-concentration curve is largely determined by the value of m. The smaller the value of m, the more nearly does the solution conform to the mass-action law, other factors remaining equal. For values of $m < 1$, the equivalent conductance of the solution decreases with increasing concentration, however far the concentration may be carried. On the other hand, for $m > 1$, the equivalent conductance of the solution passes through a minimum, after which it continues to increase with increasing concentration.

Before taking up the general consideration of the experimental data, we shall examin the conductance curves for a typical electrolyte in liquid ammonia, in order to illustrate the manner in which the various constants of the equation may best be determined from the experimental data. Potassamide, KNH_2, has been chosen as the illustrative example because the measurements were made by one investigator [Franklin(26)] over a very large range of concentrations, 0.0001 to 8-normal. The experimental results (at $-33.5°$) are given in Table I, together with the calculated quantities used in constructing Figures 1 to 4.

The Roman numerals in the first column of the table refer to the series of measurements of which six were described in the original paper. The experiments in each series are arranged in order from dilute to concentrated solutions, but it is to be noted that the measurements were made in the reverse order. The method of successive dilutions was employed and it is therefore evident that the results for the most dilute solutions in each series are most likely to be in error. A single series may properly be rejected when the results do not agree with those of the other series.[1]

The experimental results given in the original paper are reproduced in the second and fourth columns of the table: v is the volume (in liters) of the solution containing one gram molecule of solute, and Λ is the molecular conductance, equal to $1000 \, L/c$, where L is the specific conductance in reciprocal ohms and c is the concentration in mols per liter. (In general, Λ is identical with the equivalent conductance, since we are dealing only with binary electrolytes.) The significance of the remaining quantities given in the table requires no explanation. The values of these quantities at infinit dilution are shown in the first line of Table I A; and the values of the constants are given at the head of the table.

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[1] Thus the results of Series V, between $v = 155.2$ and $v = 10.2$, were rejected because the values of Λ were uniformly lower than those at the same concentrations derived from Series II, IV, and VI.

TABLE I.—SOLUTIONS OF POTASSAMIDE IN AMMONIA.

$\Lambda_0 = 301$, $K = 1.20 \times 10^{-4}$, $D = 0.095$, $m = 1.18$.

A. Dilute Solutions.

No.		$v.$	$\log c.$	$\Lambda.$	$100\,\gamma$	$10^4 c\gamma$	$10^4 c\gamma^2/1-\gamma$	$10^4(c\gamma)^{1.18}$	$100c\,\Lambda.$	$1000/\Lambda.$
		∞	$-\infty$	301	100	0	1.20	0	0	3.322
VI.	1	15050.0	$\bar{5}.8225$	209.2	69.50	0.462	1.053	0.077	1.358	4.780[1]
	2	7620.0	$\bar{4}.1180$	183.0	60.80	0.798	1.246	0.146	2.402	5.464
	3	3859.0	$\bar{4}.4135$	148.2	49.24	1.276	1.238	0.254	3.841	6.747
	4	1954.0	$\bar{4}.7091$	116.6	38.73	1.982	1.253	0.427	5.969	8.574
	5	989.0	$\bar{3}.0048$	89.5	29.73	3.006	1.272	0.682	9.048	11.17
	6	500.9	$\bar{3}.3002$	68.22	22.66	4.524	1.326	1.131	13.61	14.66
	7	253.6	$\bar{3}.5958$	51.55	17.12	6.751	1.395	1.814	20.32	19.40
	8	128.4	$\bar{3}.8914$	38.88	12.92	10.06	1.492	2.904	30.28	25.72
IV.	14	2301.0	$\bar{4}.6381$	112.2	37.27	1.620	0.963	0.336	4.876	8.913[1]
	15	1165.0	$\bar{4}.9337$	95.5	31.72	2.723	1.266	0.621	8.198	10.47
	16	589.7	$\bar{3}.2294$	72.18	23.98	4.066	1.283	0.997	12.23	13.86
	17	298.7	$\bar{3}.5248$	54.36	18.06	6.047	1.333	1.594	18.20	18.40
	18	151.2	$\bar{3}.8204$	45.98	15.28	10.10	1.821	2.919	30.41	21.75[2]

B. Remaining Solutions.

No.		$v.$	$\log c.$	$\Lambda.$	$100\,\gamma.$	$10^4 c\gamma.$	$10^4 c\gamma^2/(1-\gamma).$	$10^4(c\gamma)^{1.18}.$	$\log c\gamma.$	$\log\left(\dfrac{c\gamma^2}{1-\gamma}-K\right)$
VI.	9	65.00	$\bar{2}.1871$	29.67	8.57	15.16	1.635	4.71	$\bar{3}.1808$	$\bar{5}.6385$
	10	32.91	$\bar{2}.4827$	23.27	7.73	23.49	1.968	7.90	$\bar{3}.3709$	$\bar{5}.8854$
	11	16.66	$\bar{2}.7783$	18.91	6.28	37.71	2.528	13.80	$\bar{3}.5764$	$\bar{4}.1232$
	12	10.98	$\bar{2}.9394$	17.11	5.69	51.77	3.120	20.07	$\bar{3}.7141$	$\bar{4}.2833$
	13	8.44	$\bar{1}.0737$	16.24	5.40	63.93	3.646	25.75	$\bar{3}.8057$	$\bar{4}.3885$
IV.	19	76.50	$\bar{2}.1163$	31.12	10.34	13.51	1.598	4.11	$\bar{3}.1307$	$\bar{5}.5999$
	20	38.75	$\bar{2}.4117$	24.05	7.99	20.62	1.790	6.77	$\bar{3}.3142$	$\bar{5}.7709$
II.	21	17.83	$\bar{2}.7488$	20.23	6.720	37.69	2.715	13.80	$\bar{3}.5762$	$\bar{4}.1804^2$
	22	9.390	$\bar{1}.0273$	16.97	5.025	60.03	3.564	23.90	$\bar{3}.7784$	$\bar{4}.3737$
	23	4.686	$\bar{1}.3292$	15.14	5.030	107.3	5.683	47.44	$\bar{2}.0307$	$\bar{4}.6516^3$
	24	3.498	$\bar{1}.4562$	15.32	5.090	145.5	7.804	67.95	$\bar{2}.1629$	$\bar{4}.8198$
	25	2.238	$\bar{1}.6312$	15.38	5.110	218.6	11.77	83.7	$\bar{2}.3396$	$\bar{3}.0241$
	26	1.745	$\bar{1}.7582$	15.71	5.220	299.1	16.47	159.0	$\bar{2}.4758$	$\bar{3}.1838$
	27	1.165	$\bar{1}.9337$	16.30	5.415	464.8	26.61	267.5	$\bar{2}.6673$	$\bar{3}.4050$
I.	28	3.270	$\bar{1}.4854$	15.34	5.096	155.8	8.366	....	$\bar{2}.1926$	$\bar{4}.8553$
	29	1.631	$\bar{1}.7924$	15.72	5.223	323.8	17.84	....	$\bar{2}.5103$	$\bar{3}.2212$
	30	0.831	0.0899	17.20	5.710	702.8	42.58	....	$\bar{2}.8468$	$\bar{3}.6168$
	31	0.5145	0.2886	18.30	6.080	1182.0	78.27	....	$\bar{1}.0725$	$\bar{3}.8869$
	32	0.4057	0.3918	18.99	6.308	1555.0	104.7	....	$\bar{1}.1917$	$\bar{2}.0149$
III.	33	0.6688	0.1747	18.10	6.013	899.0	57.58	....	$\bar{2}.9538$	$\bar{3}.7511$
	34	0.5830	0.2343	18.38	6.107	1047.0	68.12	....	$\bar{1}.0201$	$\bar{3}.8256$
	35	0.4991	0.3018	18.82	6.252	1253.0	83.52	....	$\bar{1}.0978$	$\bar{3}.9155$
	36	0.4230	0.3737	19.16	6.365	1505.0	102.3	....	$\bar{1}.1775$	$\bar{2}.0048$
	37	0.3335	0.4769	19.27	6.401	1920.0	131.3	....	$\bar{1}.2832$	$\bar{2}.1143^4$
	38	0.2908	0.5364	19.31	6.415	2206.0	151.2	....	$\bar{1}.3436$	$\bar{2}.1761^4$
	39	0.2490	0.6038	19.06	6.331	2543.0	171.9	....	$\bar{1}.4053$	$\bar{2}.2322^4$
	40	0.2110	0.6757	18.51	6.149	2914.0	191.0	....	$\bar{1}.4645$	$\bar{2}.2783^4$
	41	0.1610	0.7932	16.56	5.502	3417.0	199.0	....	$\bar{1}.5337$	$\bar{2}.2962^4$
	42	0.1404	0.8523	15.23	5.060	3601.0	191.8	....	$\bar{1}.5564$	$\bar{2}.2801^4$
	43	0.1202	0.9201	13.33	4.430	3684.0	170.7	....	$\bar{1}.5663$	$\bar{2}.2292^4$

[1] Λ too low.   [2] Λ too high.   [3] Minimum Λ.   [4] The law ceases to hold at these high concentrations.

The variation of the conductance of KNH_2 with the concentration is shown in Fig. 1. Here values of Λ are plotted as ordinates, and
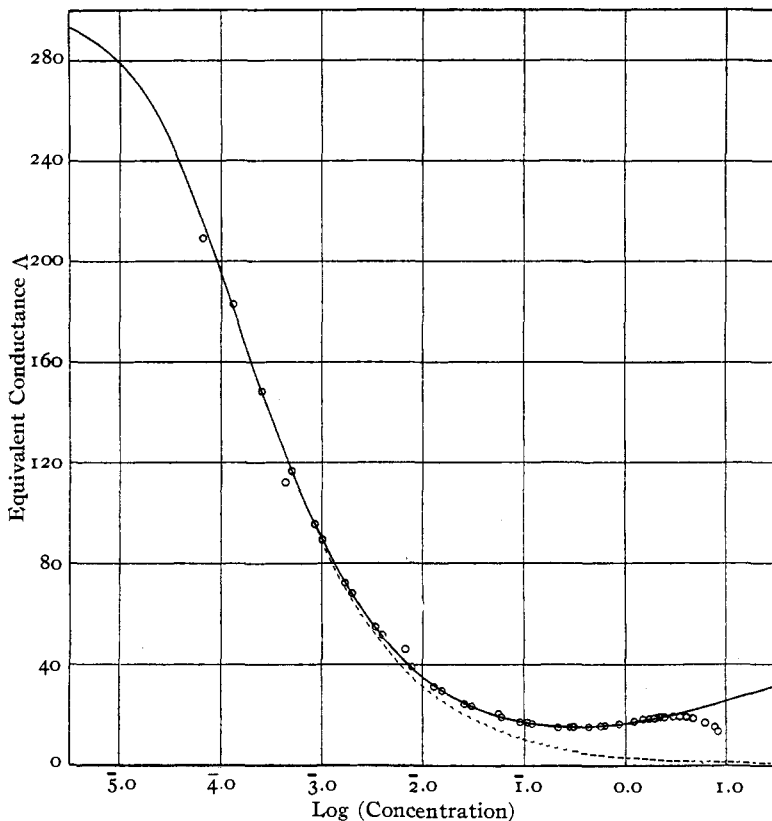

Fig. 1.—KNH_2. Conductance-Concentration Plot.

those of $\log c$ as abscissas. The experimental points are indicated by circles, while the continuous curve corresponds to the equation:

$$c\gamma^2/(1 - \gamma) = 1.20 \times 10^{-4} + 0.095(c\gamma)^{1.18}.$$

It is evident that the calculated curve is in excellent agreement with the results up to a concentration of about 2.5 normal, except in the case of points Nos. 1, 14, 18 and 21. Of these, Nos. 1, 14, and 21 are the last measurements in Series VI, IV, and II, respectively.

The dotted curve in Fig. 1 corresponds to the mass-action law relation:

$$c\gamma^2/(1 - \gamma) = 1.20 \times 10^{-4}.$$

It is sensibly coincident with the continuous curve in very dilute solutions, and lies below it at higher concentrations. Thus at 0.2 normal the meas-

ured value of Λ is about twice as large as that predicted by the law of mass action.

In determining the constants, graphical methods have been employed throughout, the variables chosen in plotting being such that a straight line results in case the experimental data conform to Equation III. This method has proved invaluable in studying the experimental data, since a large number of determinations had to be taken into account, any one of which was liable to be affected by an accidental error of considerable magnitude. In this connection, it should be pointed out that it is not permissible to smooth out the experimental values (as is often done) on the original conductance curve. In a complex curve, such as the conductance curve of potassamide (Fig. 1), for example, great errors may thus be introduced. By examining all the data with reference to a straight line plot, however, the separate points may be properly and quickly weighted and a result obtained with an accuracy otherwise obtainable only after making laborious calculations.

The experimental results in very dilute solutions were used in determining the values of Λ_0 and K. By substituting Λ/Λ_0 for γ, the mass-action equation may be transformed into a linear relation between $c\Lambda$ and $1/\Lambda$, namely:

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{1}{K\Lambda_0{}^2} (c\Lambda), \tag{IV}$$

a function which renders it possible to test the mass-action law without assuming a definit value of Λ_0.

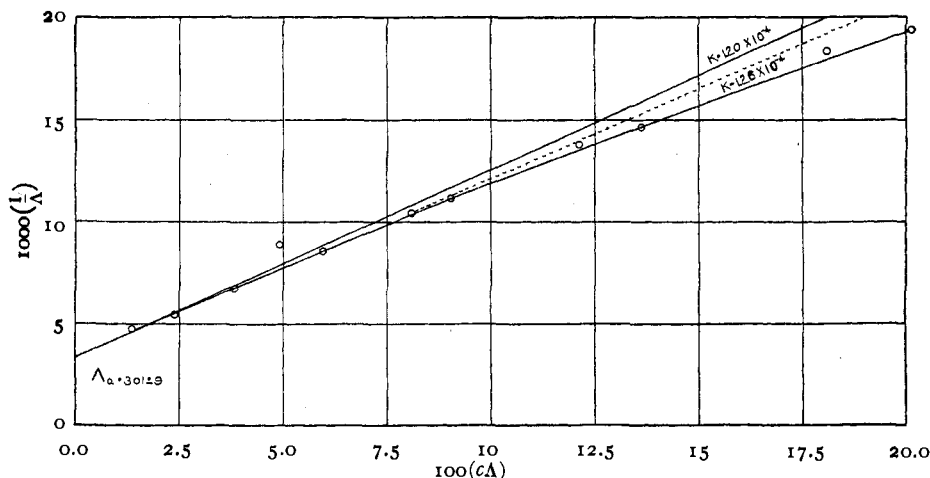In Fig. 2,[1] values of $c\Lambda$ and $1/\Lambda$ are plotted as abscissas and ordinates,

Fig. 2.—KNH$_2$. Λ_0-K Plot.

[1] For the sake of brevity and clearness, each plot is designated by the names of the constants which are determined from it, thus: Figure 2 is a "Λ_0-K plot."

respectively, for solutions of KNH_2 in ammonia. The smooth curve (the lowest line) is drawn through the points corresponding to experiments 2 to 7 in Series VI. The points corresponding to experiments 15 to 17 in Series IV and experiment 1 in Series VI lie very close to this curve, but a little above it. Experiment 14 was rejected since the corresponding point lies considerably above the curve. The fact that this is a curve and not a straight line shows that the mass-action law cannot hold above 0.001 normal; but, since the curve appears to be approaching a straight line in more dilute solutions, it is evident that at higher dilutions the ionization curve is approaching a limit corresponding to that law.[1] Two possible straight lines are shown in the figure. The intercept on the axis of ordinate gives the value of $1/\Lambda_0$, from which Λ_0 may be calculated to be 301, with a possible error of about 9; and the slopes of the lines give values of $1/K\Lambda_0^2$, from which the values of K may be calculated to be 1.26×10^{-4} for the dotted line and 1.20×10^{-4} for the heavy line. The dotted line was drawn to pass through as many points as possible, but it will be shown later (in the discussion of Fig. 4) that the steeper line gives for K the more probable value of 1.20×10^{-4}. In connection with this plot it may be noted that approximate values of the degree of ionization γ, corresponding to any point on the curve, may be quickly determined from the plot by comparing the corresponding value of the ordinate $1/\Lambda$ and $1/\Lambda_0$.

From the value of Λ_0 obtained in the Λ_0-K plot, exact values of the conductance ratio, $\Lambda/\Lambda_0 = \gamma$, were next calculated for each salt. In the present example, KNH_2, the possible error in the value of Λ_0 obtained by extrapolation is fairly large, namely, about 3 per cent. This is directly related to the fact that this salt is ionized to a relatively small extent. As will be seen later, nearly all common salts are much more highly ionized in liquid ammonia, and the possible percentage error in Λ_0 is much smaller than with KNH_2; in fact, it is usually less than 1 per cent.

The values of the constants m and D were determined by plotting the values of $\log (c\gamma)$ as abscissas against those of $\log \left(\dfrac{c\gamma^2}{1-\gamma} - K \right)$ as ordinates. Equation III may be written in the form:

$$\log \left(\frac{c\gamma^2}{1-\gamma} - K \right) = m \log (c\gamma) + \log D, \qquad (V)$$

and it is evident that a linear plot will result when this relation holds true. The intercept on the axis of ordinates at $\log (c\gamma) = 0$ gives the value of $\log D$, and the slope of the line gives the value of m. Since $c\gamma^2/(1-\gamma)$ approaches K in dilute solutions, it follows that any un-

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[1] Much more conclusive evidence that the mass-action law is obeyed in dilute solutions in liquid ammonia is furnished by the data for other salts as shown in the Λ_0-K plots, Figs. 6, 9, 12, 13, and 16.

certainty in the value of K and any experimental error in the value of Λ will make the points for dilute solutions very unreliable. The values of m and D were accordingly determined from the results for the more concentrated solutions, and they are in many cases practically independent of the value of K chosen.

The nature of this "m-D plot" is well illustrated by Fig. 3, which shows the results for KNH_2 at dilutions less than 65 liters. The straight
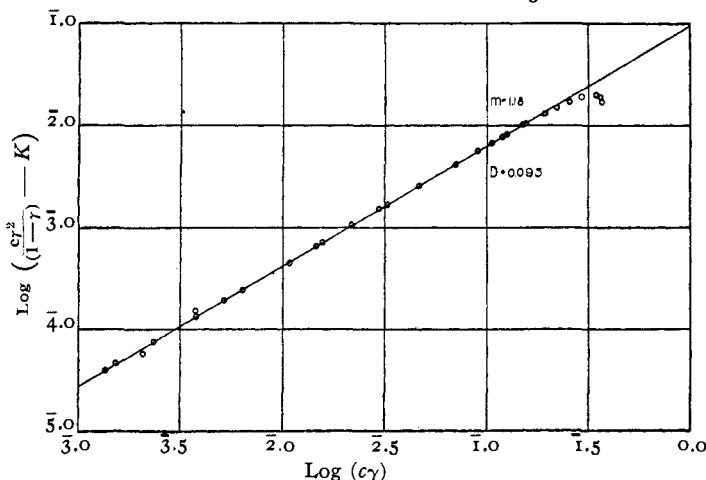

Fig. 3.—KNH_2. m-D Plot.

line lies very close to all the points (except No. 21, which lies above the line) up to a concentration of about 2.5 normal. The values of the constants were found to be

$$m = 1.18 \quad \text{and} \quad D = 0.095.$$

At higher concentrations the straight line lies above the points, and a curve through them would pass through a maximum. This regular deviation corresponds to the result shown in Fig. 1, that the measured values of Λ in the concentrated solutions are lower than those calculated. A probable explanation is that suggested by Franklin and Gibbs(27)[1], namely, that the decreasing values of Λ are mainly due to the rapidly increasing viscosity of these concentrated solutions. This question will be discussed later; but it may be mentioned now that the phenomenon is a general one, since it recurs in all other cases in which measurements have been carried to sufficiently high concentrations.

It is to be noted that the value of m for KNH_2 is greater than unity. In such cases, as was pointed out above, the general relation (Equation III) predicts that the equivalent conductance shall pass through a minimum. This minimum is shown in Fig. 1 at a concentration of about 0.3 normal.

[1] See also Franklin(28).

Another plot which has been used in presenting the results is the "K-D plot," in which values of $c\gamma^2/(1 - \gamma)$ are plotted as ordinates against values of $(c\gamma)^m$ as abscissas. Here again a straight line should be obtained if Equation III represents the data satisfactorily. The intercept on the ordinate axis gives the value of K, and the slope of the line the value of D. This plot deals with the data in the range of concentration between the very dilute solutions shown in the Λ_0-K plot and the concentrated solutions shown in the m-D plot, and it is especially valuable in that it makes it possible to determin K more accurately than from the Λ_0-K plot above.[1]

Fig. 4 is the K-D plot for KNH_2, and shows the results from the most dilute solutions up to about 0.1 normal concentration. All the experiments are concordant, except Nos. 18 and 21, where Λ, and therefore
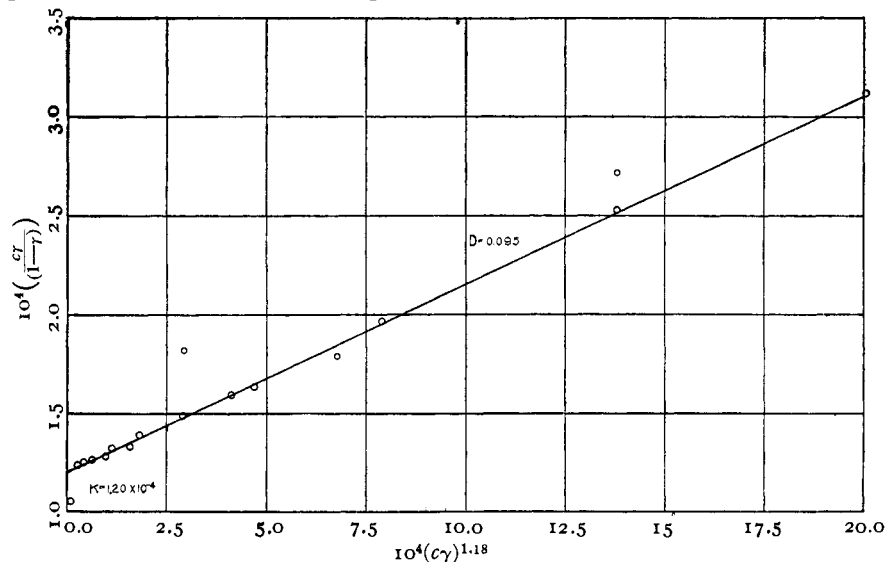

Fig. 4.—KNH_2. K-D Plot.

$c\gamma^2/(1 - \gamma)$, appears to be too high, and Nos. 1 and 14, where Λ is too low. The last point is so low that it does not appear on the plot. The remaining points lie very close to a straight line. From the position of this line the values of the constants were determined to be:

$$K = 1.20 \times 10^{-4} \quad \text{and} \quad D = 0.095.$$

[1] A straight line will not result in dilute solutions if the value of Λ_0 is in error. Even a small error causes a large deviation in dilute solutions, since $1 - \gamma$ is small under these conditions. As will be seen, no change was ever found necessary in the initial values obtained for Λ_0 in ammonia solutions from the $\Lambda°$-K plot. In water and sulfur dioxide, however, the K-D plot has led us to reduce the accepted Λ_0 values; (see Sections V and IX). In such cases it is preferable to modify the plot so as to make it independent of Λ_0 (see second foot-note, Section V).

This value of D (based on dilute solutions) agrees exactly with that obtained from concentrated solutions in the m-D plot, Fig. 3. It follows, therefore, that Equation III represents the experimental results from very dilute solutions up to a concentration of about 2.5 normal.

The above procedure has been described at length for the reason that it constitutes a most convenient method of obtaining the constants. Indeed, the present investigation would have been practically impossible without this convenient graphical method of studying the experimental data.

The general method of procedure may be summarized as follows: Λ_0 is determined from the Λ_0-K plot or by comparison with other salts with common ions; and values of γ, $c\gamma^2/(1 - \gamma)$, etc., are calculated. A preliminary value of K is determined from the Λ_0-K plot, and then a preliminary value of m from the m-D plot, by means of the points corresponding to the more concentrated solutions. Using this value of m, a new value of K is determined from the K-D plot. This is the final value of K, since it is independent of any moderate changes of m which may later be made. If this value of K differs from the preliminary one, the necessary alterations are made in the m-D plot, the final value of m is chosen, and the K-D plot reconstructed. The value of D for concentrated solutions is determined from the m-D plot, and that for more dilute solutions from the K-D plot. The two values of D so determined should coincide and they do so when the data are reliable.

It often happens that the electrolyte in question is only slightly dissociated in concentrated solutions. In such cases the variation of $\Lambda_0 - \Lambda$ may be neglected in comparison with that of Λ. This leads to the following simple equation:

$$c\Lambda^2 = P(c\Lambda)^m + K\Lambda_0(\Lambda_0 - \Lambda), \qquad \text{(VI)}$$

where

$$P = D\Lambda_0{}^{1-m}(\Lambda_0 - \Lambda). \qquad \text{(VII)}$$

In many cases the K-term is negligible in comparison with $P(c\Lambda)^m$, and Equation VI becomes

$$c\Lambda^2 = P(c\Lambda)^m. \qquad \text{(VI}a\text{)}$$

Under these conditions m may be determined from a plot of $\log(c\Lambda^2)$ against $\log(c\Lambda)$ ("m-P plot"), m being determined by the slope of the straight line and P by the intercept on the axis of $\log(c\Lambda^2)$. It is clear that in this determination of m no other constant is involved.

Should the K-term not be negligible, the value of m may still be determined independently of the other constants by plotting the functions $c\Lambda^2$ and $(c\Lambda)^m$ for different values of m ("m plot"), the correct value of m giving a straight line. The slope of the line gives the value of P and the intercept on the axis of $c\Lambda^2$ the value of $K\Lambda_0(\Lambda_0 - \Lambda)$. It is under-

stood that the variation of $\Lambda_0 - \Lambda$ is negligible in comparison with that of Λ. This method of determining m is illustrated in Fig. 5 for the case of KNH_2. Here $(c\Lambda^2)$ and $(c\Lambda)^m$ are plotted as abscissas and ordi-
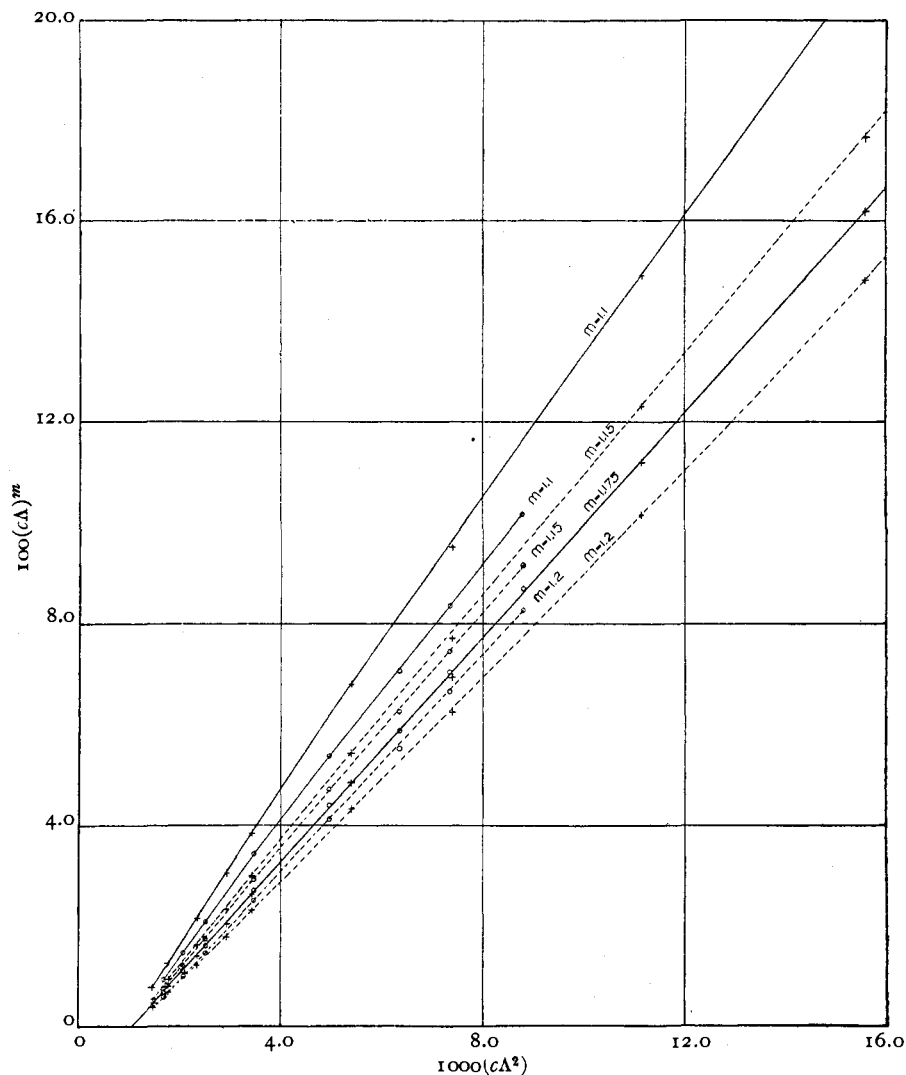

Fig. 5.—m Plot for KNH_2.

nates, respectively. The scale shown on the figure applies to the points indicated by crosses. The points indicated by circles refer to more concentrated solutions for which the scale was reduced tenfold.

It is evident that Equation VI represents a family of curves passing through common points at $(c\Lambda)^m = 0$ and $(c\Lambda)^m = 1$. The value of

m which corresponds to Equations III and VI will give a straight line plot. It will be seen from Fig. 5 that, for $m = 1.175$, a straight line results. The straight line obtained from the more dilute solutions coincides with that obtained from the more concentrated solutions. This is not true for other values of the exponent m. The value of m obtained from the m-D plot (Fig. 3) is 1.18, which is in excellent agreement with the present value, 1.175. It is seen, therefore, that for salts which are not too highly ionized the value of m may be obtained without reference to any of the other constants involved in Equation III. Both the m plot and the m-P plot are often used of necessity, since there are many cases in which the values of Λ_o and K are not obtainable by direct experiment.

If $m > 1$, in which case the conductance-concentration curve possesses a minimum, a new relation may be introduced involving the concentration c' and ionization γ' at the minimum point. One of the four constants may therefore be eliminated in Equation III, in terms of c' and γ'. At the minimum point $d\gamma/dc = 0$.[1] Differentiating Equation III, solving for $d\gamma/dc$, and equating to zero, we obtain:

$$mD(c'\gamma')^{m-1} = \frac{\gamma'}{1-\gamma'}. \qquad \text{(VIII)}$$

We may eliminate $\gamma'/(1 - \gamma')$ by means of Equation III, which gives:

$$(c'\gamma')^m = \frac{K}{D(m-1)}. \qquad \text{(IX)}$$

For a given value of m, the ion-concentration at the minimum point will be the smaller, the smaller the ratio K/D. As a rule, K and m are subject to much greater variation than D with temperature change, which results in considerable variation of the minimum point with changing temperatures. In the case of solvents which, like ammonia, have a value of m near to unity, the conductivity curve varies greatly for different electrolytes since the curve is very sensitive to a variation of m in the neighborhood of this value.

From the value of the constants given above for KNH_2, the concentration and ionization at the point of minimum molecular conductance may be calculated. The values found are: $c' = 0.2992$, and $\gamma' = 0.04996$.

III. Solutions in Liquid Ammonia.

The conductance data examined in this section are taken from two papers by Franklin and Kraus (14, 29) and one by Franklin(26). The abbreviations F-K_I, F-K_{II} and F are used for these papers in the tables below, and the points in the figures are marked by circle, cross, and combined cross and circle, respectively.

[1] Actually, it is simpler to assume $c\gamma$ and $\gamma/1 - \gamma$ to be the variables. The result (Equation VIII) will be the same as though γ and c were chosen as variables.

The experimental results have been examined as described in the preceding section for KNH_2, except that in some cases, where data in concentrated solutions are lacking, only the Λ_0-K plots were constructed.
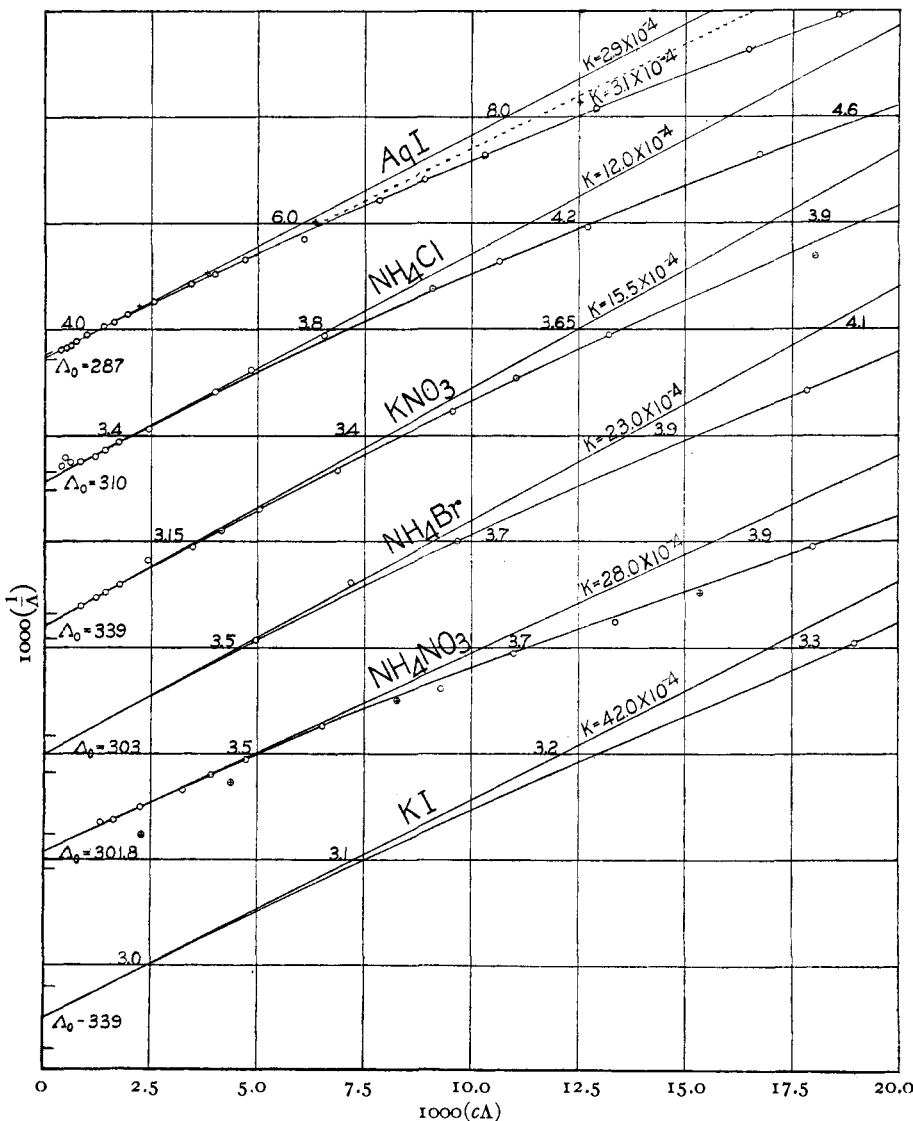
Fig. 6.—Λ_0-K Plot.

The nature of the agreement of the experimental results among themselves as well as with Equation III is shown by the plots and the brief descriptive notes. Since the above-mentioned papers are easily accessible, it is

unnecessary to publish the lengthy tables (corresponding to Table I) containing the original experimental data and the various quantities used in constructing the plots.

The division of the results into inorganic and organic electrolytes, which has been adopted in this paper, is a purely arbitrary one, made for the sake of convenience in presenting the subject and not because of any
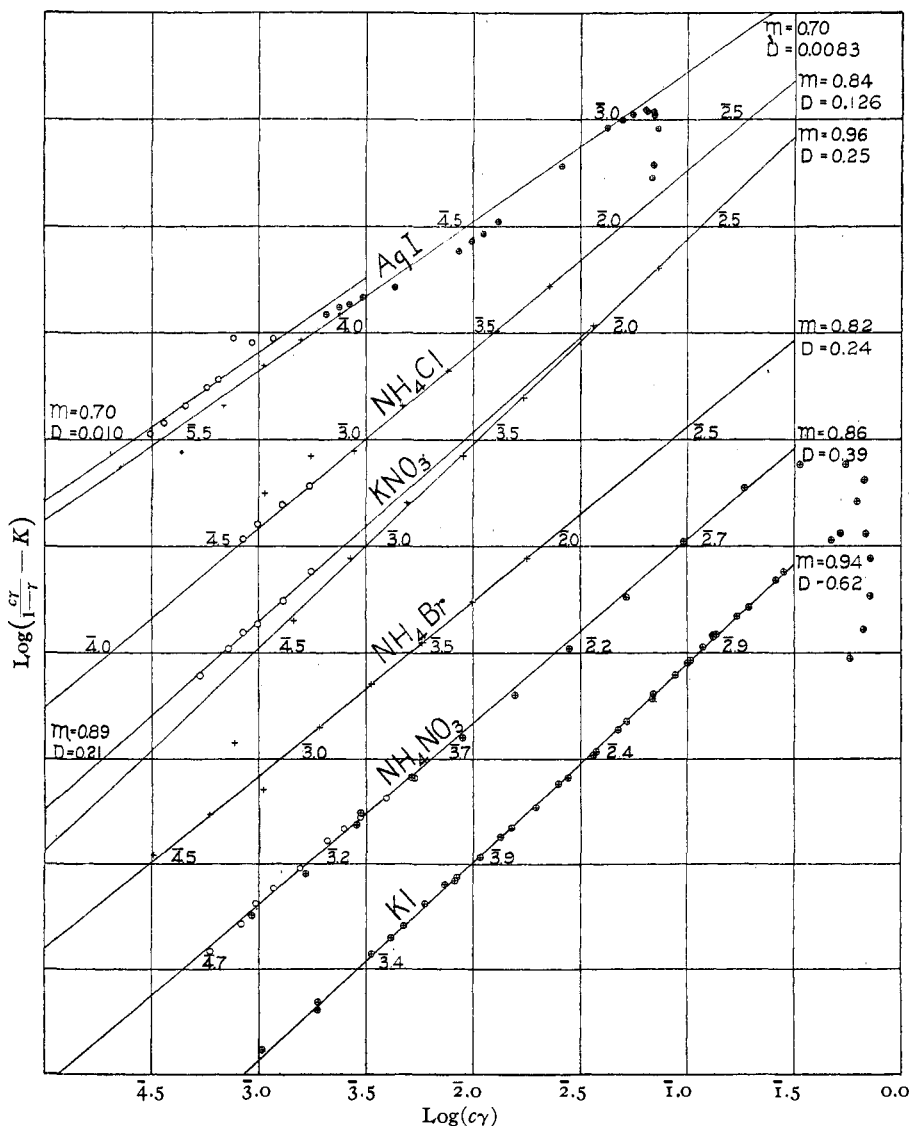
Fig. 7.—m-D Plot.

essential difference between these two classes of electrolytes. All measurements were made at $-33.5°$, the boiling point of liquid ammonia.

A. Inorganic Electrolytes.

The Λ_o-K plot was first constructed for each salt and preliminary values of Λ_o and K were obtained. The preliminary Λ_o values are shown in Table II,[1] together with approximate estimates of the possible errors due to irregularities in the experimental results or to obvious errors in the
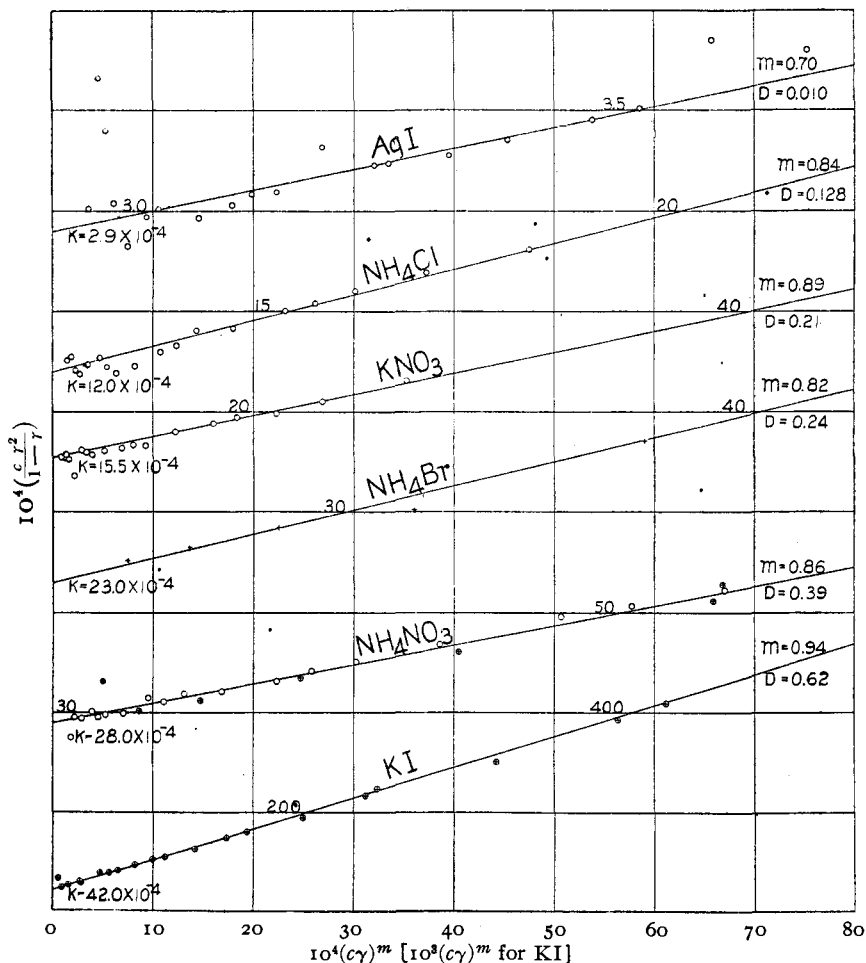
Fig. 8.—K-D Plot.

[1] The Λ-K plots are reproduced in Figs. 2, 6, 9, and 12. No salt examined in the preliminary investigation has been omitted except $TlNO_3$, $\Lambda_o = 323 \pm 3$. The Λ_o value of one other salt, $NaBrO_3$, Fig. 12, $\Lambda_o = 278 \pm 3$, has also not been included in Tables II and III. The corresponding ion-conductances for these two salts, however, are shown in Table IV, and approximate values of K are given in Table V.

very dilute solutions.   From these results alone were determined the final Λ_0 values, given in Table III, which are adjusted so as to be concordant among themselves.   As may be seen, no changes were made exceeding the probable error given in Table II.   The two values in parentheses (those for $NaNH_2$ and KI) were derived from the Λ_0 values of other salts and not from the conductance data in dilute solutions.   Accurate

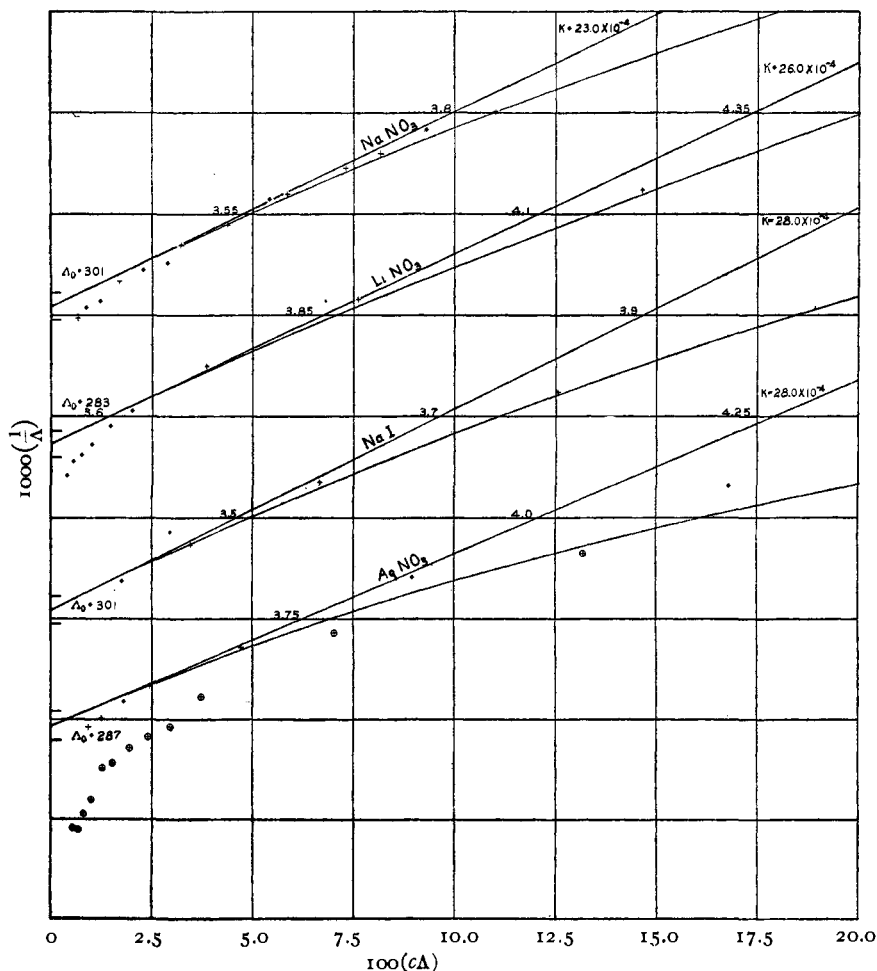Fig. 9.—Λ_0-K Plot.

data are lacking in the case of KI, while $NaNH_2$ is so little ionized that Λ_0 cannot be determined from conductance measurements of this salt alone.   Although it was later found necessary to decrease slightly the preliminary values of K, as a result of the investigation of the nature of the deviations from the mass-action law in the more concentrated solu-

tions, no alterations whatever were made in the values of Λ_0. It is therefore evident that the values of Λ_0 in liquid ammonia may be determined directly from the experimental results without reference to the values of the other constants.

TABLE II.—PRELIMINARY Λ_0 VALUES AT $-33.5°$.

	Li.	Ag.	Na.	NH₄.	K.
NH₂	......	......	......	......	301 ± 9
NO₃	283 ± 2	288 ± 10	301 ± 2	301 ± 1	338.5 ± 0.5
I	......	285 ± 2	302 ± 1	......	....
Br	......	......	302 ± 1	302 ± 3	342 ± 2
Cl	......	......	309 ± 1	310 ± 1	....

TABLE III.—FINAL Λ_0 VALUES (FIGS. 2, 6, 9, 12).

	Li.	Ag.	Na.	NH₄.	K.
NH₂	...	...	(263)	...	301
NO₃	283	287	301	302	339
I	...	287	301	302	(339)
Br	...	...	302	303	340
Cl	...	...	309	310	...

The agreement between the two sets of Λ_0 values given in Tables II and III furnishes a verification of the Kohlrausch law of the additivity of ionic conductances; or, if this law is accepted, the agreement is a striking proof of the accuracy of the experimental results. It is interesting to note that, with the exception of the chlorides, the values of Λ_0 chosen by Franklin and Kraus(29, p. 219) are in good agreement with those given in Tables II and III.

By means of the transference measurements of Franklin and Cady(25), which are discussed below, the conductances of the separate ions were calculated. The results are shown in Table IV:

TABLE IV.—ION-CONDUCTANCES.

Cation.	Ion-conductance.	Anion.	Ion-conductance.
Li⁺	112	NH₂⁻	133
Ag⁺	116	BrO₃⁻	148[1]
Na⁺	130	NO₃⁻	171
NH₄⁺	131	I⁻	171
Tl⁺	152[1]	Br⁻	172
K⁺	168	Cl⁻	179

The plots by means of which the constants Λ_0, K, m, and D for ten of the salts were determined are shown in Figs. 6–11. In Figs. 6, 7 and 8 are reproduced the Λ_0-K, m-D, and K-D plots, respectively, for six salts, and in Figs. 9, 10 and 11 are reproduced the corresponding plots for the remaining four. The salts in each group are arranged in the same order in the three figures. The scale of abscissas for the plots is shown below each figure. The scale of ordinates varies from salt to salt, the value of

[1] See foot-note, page 1333.

the ordinates being shown on the figure at the points of intersection of the curves with the parallels to their axis of abscissas. The values of the constants chosen are shown on the plots, and are summarized in Table V. The salts are arranged in the order of increasing values of K. The values
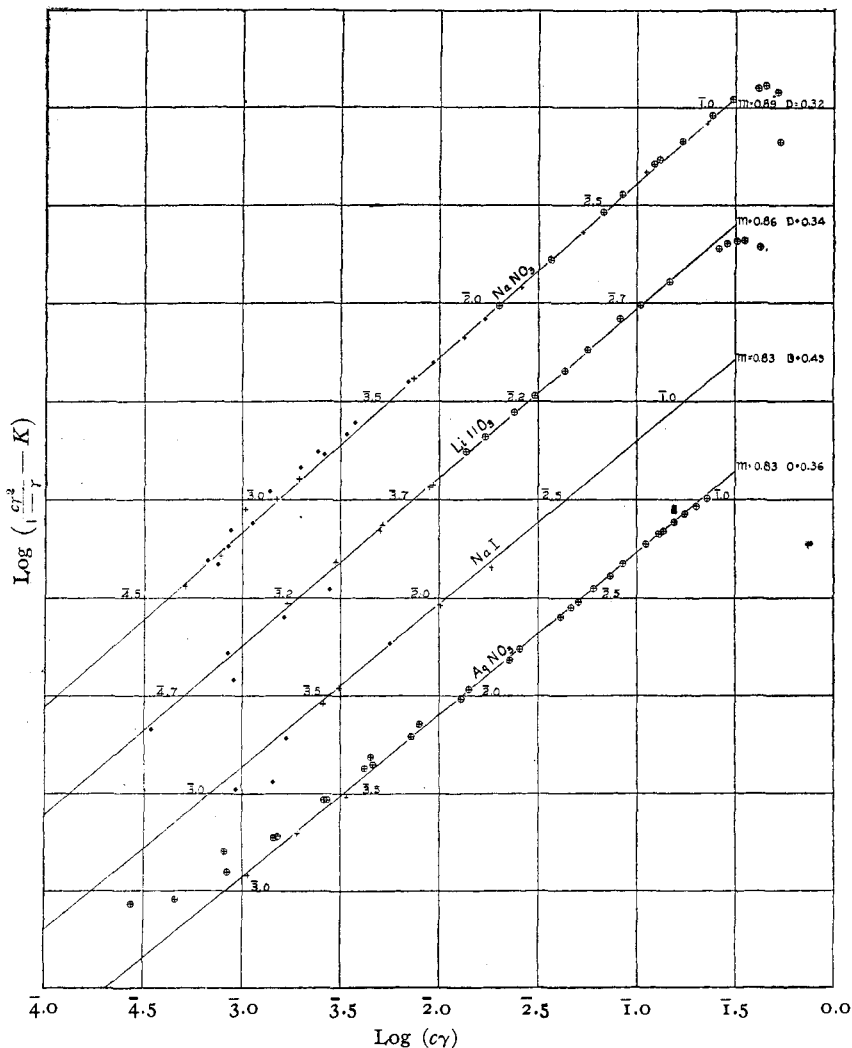

Fig. 10.—m-D Plot.

of Λ_0 given in Table III are included in Table V, and also approximate values of K for NaNH$_2$, calculated directly from Franklin's conductance measurements, and for six other salts, derived from the Λ_0-K plots alone. The plots for four of these electrolytes are reproduced in Fig. 12.

TABLE V.—VALUES OF THE CONSTANTS FOR INORGANIC ELECTROLYTES IN AMMONIA.

Salt.	Figure.	Investigation.	A_0.	10^4K.	m.	D.
NaNH₂	..	F	263	0.056	..	....
KNH₂	1-4	F	301	1.20	1.18	0.095
AgI	6-8	F-K_I, F-K_II, F	287	2.90	0.70	0.0083[1] 0.010[2]
NH₄Cl	6-8	F-K_I, F-K_II	310	12.0	0.84	0.127
NaCl	12	F-K_II	309	14.5	..	....
KNO₃	6-8	F-K_I, F-K_II	339	15.5	0.96[1] 0.89[2]	0.25[1] 0.21[2]
KBr	12	F-K_I	340	21.0	..	....
TlNO₃	..	F-K_II	323	21.0	..	....
NaBrO₃	12	F-K_I	278	23.0	..	....
NaNO₃	9-11	F-K_II, F	301	23.0	0.89	0.32
NH₄Br	6-8	F-K_II	303	23.0	0.82	0.24
LiNO₃	9-11	F-K_II, F	283	26.0	0.86	0.34
NaBr	12	F-K_I	302	27.0	..	....
NaI	9-11	F-K_II	301	28.0	0.83	0.43
AgNO₃	9-11	F-K_I, F	287	28.0	0.83	0.36
NH₄NO₃	6-8	F-K_I, F	302	28.0	0.86	0.39
KI	6-8	F	339	42.0	0.94	0.62

Reference to the third column of the table shows that in seven cases measurements were made in independent investigations; and an examination of the position of the points in the figures marked with circle, cross, and combined cross and circle (corresponding to F-K$_I$, F-K$_{II}$, and F, respectively) shows that the agreement is satisfactory except for AgI and KNO$_3$. In these two cases the lack of agreement is shown in a striking manner in the relatively dilute solutions in the m-D plot, Fig. 7. The displacement of the points really corresponds to an error of only about 2 per cent. in the value of Λ or of c. The agreement in the remaining five cases is convincing evidence of the general accuracy of all the experimental work. The exceptional discrepancies are probably due to lack of purity of the solute. An examination of the results in very dilute solutions, where it was most difficult to obtain accurate measurements, shows that the data obtained by Franklin and Kraus in their first investigation are by far the most reliable. This was to have been expected, since the change of concentration in successive dilutions was much smaller than in the other investigations and since, in general, much greater precautions were observed to ensure accurate results. Franklin's investigation, moreover, was undertaken primarily for the purpose of studying concentrated solutions, and he does not claim great accuracy in the dilute solutions. There appears to be a general tendency towards high results in his Λ values at low concentrations, the most striking example of which is shown in the case

[1] For the concentrated solutions.
[2] For the dilute solutions.

of $AgNO_3$ in the Λ_0-K plot, Fig. 9. The Λ_0 values have accordingly been based, as far as possible, upon the data given in the first paper by Franklin and Kraus.

In Table V two sets of constants are given for AgI and for KNO_3, and in each case the two corresponding lines are shown in the m-D plot, Fig. 7. These lines are drawn to illustrate two different methods of treating results which are not concordant. In the case of AgI, m has been assumed constant and two different values of D determined. The results of F-K_I in dilute solutions are satisfactorily represented by the equation
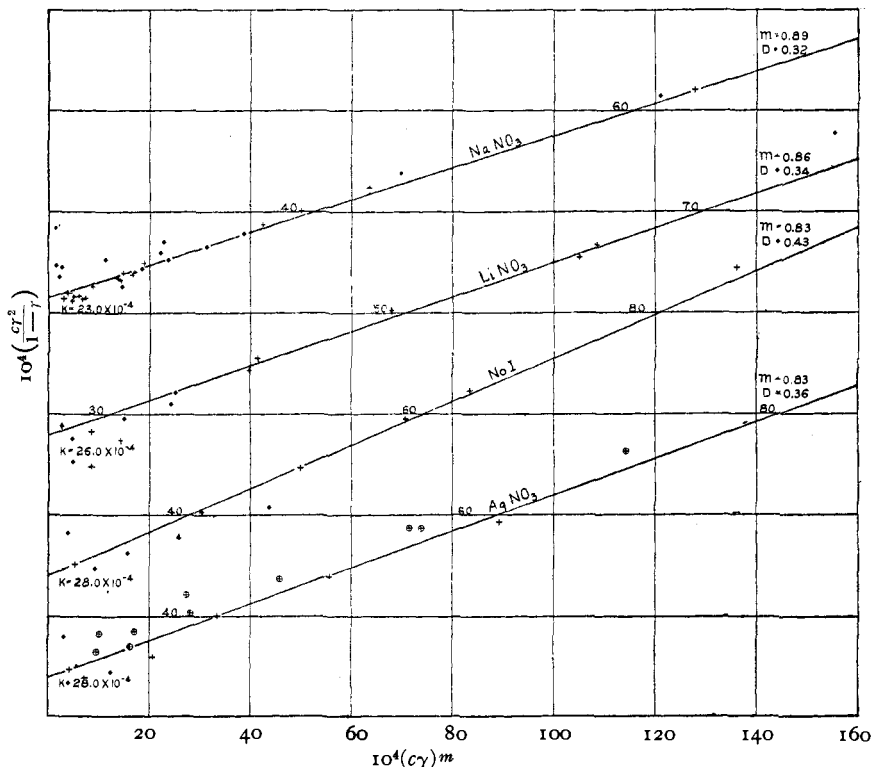
Fig. 11.—K-D Plot.

$c\gamma^2/(1 - \gamma) = 2.90 \times 10^{-4} + 0.010(c\gamma)^{0.70}$; but this equation cannot be used in extrapolating to concentrated solutions, since values of γ and Λ calculated from it would exceed the values found by Franklin by large percentages. It is, therefore, preferable to assume two different values of m, as has been done for KNO_3. According as the results of F-K_I or F-K_{II} in dilute solutions are accepted as correct, the results over the whole range of concentration will be represented by one or other of the equations:

$$c\gamma^2/(1 - \gamma) = 15.5 \times 10^{-4} + 0.21(c\gamma)^{0.89},$$

or

$$c\gamma^2/(1 - \gamma) = 15.5 \times 10^{-4} + 0.25(c\gamma)^{0.96}.$$

The constants for these electrolytes must necessarily remain somewhat uncertain until concordant conductance measurements are available.

To assist in the examination of the plots, some information regarding them has been presented in Table VI:

TABLE VI.—SUMMARY OF DETAILS RELATING TO FIGS. 1–12 AND TABLE V.

Salt.	Figure.	Number of Series.	Number of Points.	Dilution v in liters. Maximum.	Dilution v in liters. Minimum.	Λ_0-K plot ends.	m-D plot begins.	K-D plot ends.	Law ceases to hold.
NaNH₂......	..	1	5	196.5	12.91	..	..	...	...
KNH₂.......	1–4	6	55	15050	0.1202	250	65	10	0.4
AgI.........	6–8	7	50	80000	0.1408	480	1650	300	0.5
NH₄Cl......	6–8	2	28	77660	9.84	1300	770	150	...
NaCl........	12	1	10	30330	66.3	1400	..	...	...
KNO₃........	6–8	2	27	40360	3.13	1400	1460	324	...
KBr.........	12	1	19	52640	301.9	1400	..	...	...
TlNO₃.......	..	1	7	8144	155.0	..	..	...	...
NaBrO₃......	12	2	31	84040	323.4	1400	..	...	...
NaNO₃.......	9–11	5	62	64650	0.1368	1400	1600	62	0.8
NH₄Br.......	6–8	1	10	5751	21.47	1400	2800	300	...
LiNO₃.......	9–11	3	38	74150	0.4595	1400	1500	100	2.0
NaBr........	12	2	29	74580	3.97	1200	..	...	...
NaI.........	9–11	2	13	16600	26.45	1400	530	100	...
AgNO₃.......	9–11	5	56	30800	1.365	1400	1500	100	...
NH₄NO₃.....	6–8	3	40	22660	105.1	1400	1430	200	1.0
KI..........	6–8	6	49	3183	0.2087	1400	800	8	1.0

The number of independent series of experiments and the total number of measurements are shown in the third and fourth columns. The values of v for the most dilute and the most concentrated solutions are given in the fifth and sixth columns. The approximate range of concentrations covered by the plots is shown in the next three columns. The Λ_0-K and K-D plots extend from the greatest dilution to that given in the seventh and ninth columns, respectively, and the m-D plot extends from the dilution shown in the eighth column to the minimum dilution (column 6). The last column shows the approximate value of v at which the deviations from Equation III become appreciable in concentrated solutions on the m-D plots. It is to be noted that in Figs. 3, 7 and 10 the deviations in concentrated solutions are regular and similar for different salts. The law holds satisfactorily up to the high concentrations of about 2.5 normal for KNH₂, normal for NH₄NO₃ and KI, and between normal and 0.5 normal for LiNO₃.

The nature of the agreement with the law may be judged by the position of the points with reference to the straight lines shown in the differ-

ent figures.   More detailed information in specific instances may be ob-
tained by consulting the original articles, and by examining Table VI
and the detailed notes given below.   For the electrolytes treated in these
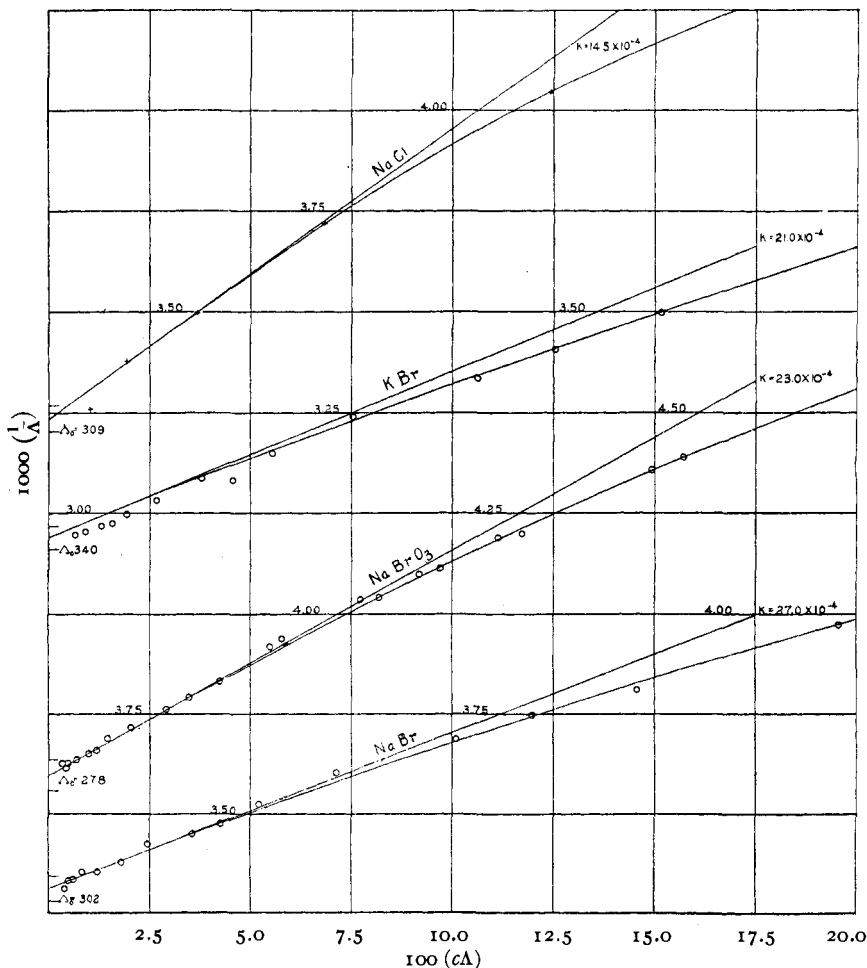
Fig. 12.—Λ_0-K Plot.

notes and in those on organic electrolytes, the data are concordant among
themselves except when otherwise stated.

The relationships among the constants for the different salts will be dis-
cussed later in Section III C, after the results for organic electrolytes in
liquid ammonia have been presented.

Notes Accompanying Figs. 6–12.

Figs. 6, 7 and 8.   AgI....F-K$_I$.—One series, 21 points, v = 80000–212.1.   At
v = 2881, Λ is too high, as shown in the Λ_0-K and K-D plots.   At v = 439.8 and 314.1,

Λ is too high, as shown in the K-D and m-D plots. The large deviations in the m-D plot in dilute solutions correspond to an error of only about 1%.

F-K_{II}.—One series, 8 points, $v = 10310$–62.4. The Λ values are approximately 2% lower than in the preceding series, as shown in the Λ_o-K and m-D plots.

F.—Five series, 21 points. IV, 4 points, $v = 80.97$–40.99; III, 1 point, $v = 22.40$; II, 4 points, $v = 6.855$–3.471; I, 4 points, $v = 1.299$–0.3329; V, 7 points, $v = 0.3397$–0.1408. Series IV agrees fairly well with F-K_{II}. The Λ values in Series II appear to be low, as shown in the m-D plot.

NH_4Cl....F-K_I.—One series, 21 points, $v = 77660$–2989. The three most dilute solutions are omitted in the m-D plot, since Λ is shown to be much too low in the Λ_o-K plot.

F-K_{II}.—One series, 7 points, $v = 597.3$–9.84. Λ is too high in the two most dilute solutions, as shown in the K-D and m-D plots.

KNO_3....F-K_I.—One series, 18 points, $v = 40360$–324.0. Λ is too low at $v = 13330$, as shown in the Λ_o-K and K-D plots.

F-K_{II}.—One series, 18 points, $v = 1966$–3.13. Λ is lower than in F-K_I, and especially so at $v = 1966$ and 880.2. It is possible that all the results except in the two most concentrated solutions are in error.

NH_4Br....F-K_{II}.—One series, 10 points, $v = 5751$–21.47. Λ is a little low at $v = 3486$, as shown in the Λ_o-K and K-D plots, and at $v = 709$, as shown in the K-D and m-D plots.

NH_4NO_3....F-K_I.—One series, 20 points, $v = 22660$–105.1. Λ is too low in the most dilute solution, as shown in the Λ_o-K and K-D plots. The smooth curve in the Λ_o-K plot should be drawn lower than is shown in the figure.

F.—Two series, 20 points. II, 7 points, $v = 13110$–220.8; I, 13 points, $v = 220.8$–0.1234. Λ is too high at $v = 13110$, as shown in the Λ_o-K plot and at 6636.3, as shown in the Λ_o-K and K-D plots.

KI....F.—6 series, 49 points. I, 12 points, $v = 3183$–2.153; IV, 10 points, $v = 407$–0.775; V, 10 points, $v = 159.2$–2.446; VI, 6 points, $v = 69.13$–0.4369; III, 7 points, $v = 0.976$–0.2692; II, 4 points, 0.3300–0.2087. Series III agrees with other series, but is omitted in the plots. Λ is too high in the most dilute solution; it is shown in the K-D plot but not in the Λ_o-K plot.

Figs. 9, 10, and 11. $NaNO_3$....F-K_{II}.—4 series, 43 points. LVII, 15 points, $v = 64650$–648.7; LVI, 9 points, $v = 10120$–257.3; LIV, 10 points, $v = 1644$–1.1988; LV, 9 points, $v = 1227$–22.9. The 4 most dilute solutions in LVII are not plotted in the K-D plot, since Λ is shown to be too high in the Λ_o-K plot. In the same series Λ is too high at $v = 1755$ (K-D plot).

F.—1 series, 17 points, $v = 18.80$–0.1368 and two check measurements at $v = 3.682$ and 2.483. The points in the most concentrated solutions are not shown in the m-D plot.

$LiNO_3$....F-K_{II}.—2 series, 24 points, LIII, 15 points, $v = 74150$–25.86; LII, 9 points, $v = 6965$–25.88. In Series LIII, Λ is much too high in the 5 most dilute solutions. These points are plotted in the Λ_o-K plot but not in the K-D plot. In Series LII, Λ is too low at $v = 218.0$ and in the three most dilute solutions as shown in the K-D plot.

F.—One series, 14 points, $v = 34.40$–0.4595. Λ is too high in the most dilute solution.

NaI....F-K_{II}.—2 series, 13 points. LXI, 7 points, $v = 16600$–271.9; LX, 6 points, $v = 877.1$–26.45. Series LX and the most concentrated solution in LXI agree fairly well, but Λ for the remaining points in LXI seems to be relatively a little low.

$AgNO_3$....F-K_{II}.—One series, 12 points, $v = 30800$–69.95. Λ is too high in the

4 most dilute solutions. The two most dilute are not shown in the m-D plot. Λ is too low in the two most concentrated solutions and these are not shown in any plot.

F.—4 series, 44 points. IV, 15 points, $v = 58240$–251.4; III, 6 points, $v = 4031$–134.1; II, 8 points, $v = 150.6$–2.535; I, 13 points, $v = 140.6$–1.365. The Λ values in IV and III seem to be too high, especially in the dilute solutions in IV, as shown in the Λ_0-K plot. All the points corresponding to the dilute solutions are omitted in the K-D plot. Λ is too high in the two most dilute solutions of Series I, as shown in the m-D plot. *Fig. 12. NaCl*....F-K_{II}.—One series, 10 points, $v = 30330$–66.3. Λ in the most dilute solutions is a little over 1% too high.

KBr....F-K_I.—One series, 19 points, $v = 52640$–301.9. Λ is irregular in the 10 most dilute solutions ($v > 4099$), and is usually too high; but the deviation from the values chosen is less than 1% except at $v = 7093$.

NaNO₃....F-K_I.—2 series, 31 points. I, 21 points, $v = 84040$–323.4; II, 10 points, $v = 44648$–342. The two series are concordant at concentrations higher than $v = 2500$. The values of Λ for the three most dilute solutions of Series II and at $v = 4392$ in Series I agree with each other and are a little lower than those of the remaining points. It is possible that Λ_0 may be 1% lower than 278.

NaBr....F-K_I.—One series, 21 points, $v = 74580$–200.—The points lie irregularly, but the deviations of Λ from the values chosen are never greater than 1%.

F-K_{II}.—One series, 8 points, $v = 1117$–3.97. Λ is relatively low in comparison with F-K_I.

B. Organic Electrolytes in Liquid Ammonia.

The general law was tested for a number of organic electrolytes by constructing the Λ_0-K, m-D and K-D plots in the usual way. The results for all the substances examined, six in number, are shown in Figs. 13, 14 and 15. Since for cyanacetamide (I), the weakest organic electrolyte, $K = 0.045 \times 10^{-4}$ and for trinitraniline (VI), the strongest, $K = 30 \times 10^{-4}$, it is evident that representative substances have been chosen. The agreement with the law is satisfactory in all six cases and it therefore seemed unnecessary to test the law further by constructing the m-D and K-D plots for other substances.

In the preliminary investigation values of Λ_0 and K had been determined for eleven other organic electrolytes by means of the Λ_0-K plots; and, of these, seven are reproduced in Fig. 16 to illustrate the agreement with the mass law at low ion-concentrations. The remaining four substances are strong electrolytes.

All the Λ_0 values are collected in Table VII, column 4, and an approximate estimate of the possible error is given in each case. The Roman numerals in the first column are the numbers of the curves on the plots, and serve to identify the different substances in the figures and in the tables. The formulas of the cation and anion are shown in the fifth and sixth columns, respectively, and the conductance of the anion Λ_A- is given in the last column. These values were calculated by assuming the conductance of NH_4^+ and Na^+ to be 130 (see Section IV). The substances are arranged in the table in the order of increasing values of the anion-conductances.

TABLE VII.—Λ₀ VALUES FOR ORGANIC ELECTROLYTES.

Number.	Figure.	Solute.	Λ_0.	Cation.	Anion.	Λ_{A^-}.
VII	16	Thiobenzamide	204 ± 10	NH_4^+	$C_6H_5CSNH^-$	73
XV	...	Benzoicsulphinide	206 ± 6	NH_4^+	$C_6H_4\!\!\begin{smallmatrix}C-O\\ SO_2\end{smallmatrix}\!\!N^-$	75
VIII	16	Orthomethoxybenzenesulphonamide				
IX	16	Paramethoxybenzenesulphonamide	208 ± 4	NH_4^+	$CH_3OC_6H_4SO_2NH^-$	77
X	16	Metamethoxybenzenesulphonamide				
II	13–15	Benzenesulphonamide	208 ± 20	NH_4^+	$C_6H_5SO_2NH^-$	77
IV	13–15	Metanitrobenzenesulphonamide	231 ± 2	NH_4^+	$NO_2C_6H_4SO_2NH^-$	100
XVII	...	Trinitrobenzene	234 ± 5	NH_4^+	$(NO_2)_3C_6H_2^-$	103
VI	13–15	Trinitraniline	234 ± 1	NH_4^+	$(NO_2)_3C_6H_2NH^-$	103
XVI	...	Potassiummetanitrobenzenesulphonate	275 ± 3	K^+	$NO_2C_6H_3SO_2O^-$	107
XIII	16	Orthonitrophenol	246 ± 2	NH_4^+	$NO_2C_6H_4O^-$	115
XIV	...	Phthalimide	248 ± 3	NH_4^+	$C_6H_4\!\!\begin{smallmatrix}CO\\ CO\end{smallmatrix}\!\!N^-$	117
III	13–15	Methylnitramine	256 ± 3	NH_4^+	$CH_3N.NO_2^-$	125
I	13–15	Cyanacetamide	260 ± 20	NH_4^+	$CH_2CNCONH^-$	129
V	13–15	Nitrourethaneammonium	262 ± 1	NH_4^+	$C_2H_5OCON.NO_2^-$	131
XI	16	Nitromethane	278 ± 5	$\left\{\begin{smallmatrix}NH_4^+\\ Na^+\end{smallmatrix}\right.$	$NO_2CH_2^-$	147
XII	16	Sodiumnitromethane				

Evidence of the accuracy of the experimental work is furnished by the fact that the same Λ_0 values were obtained by extrapolation for the three isomeric substances, ortho-, para-, and metamethoxybenzenesulphon-amide (numbers VIII, IX, and X, Fig. 16). The actual values obtained independently for the three substances were 200 $\pm$ 8, 208 $\pm$ 8, and 212 $\pm$ 4,
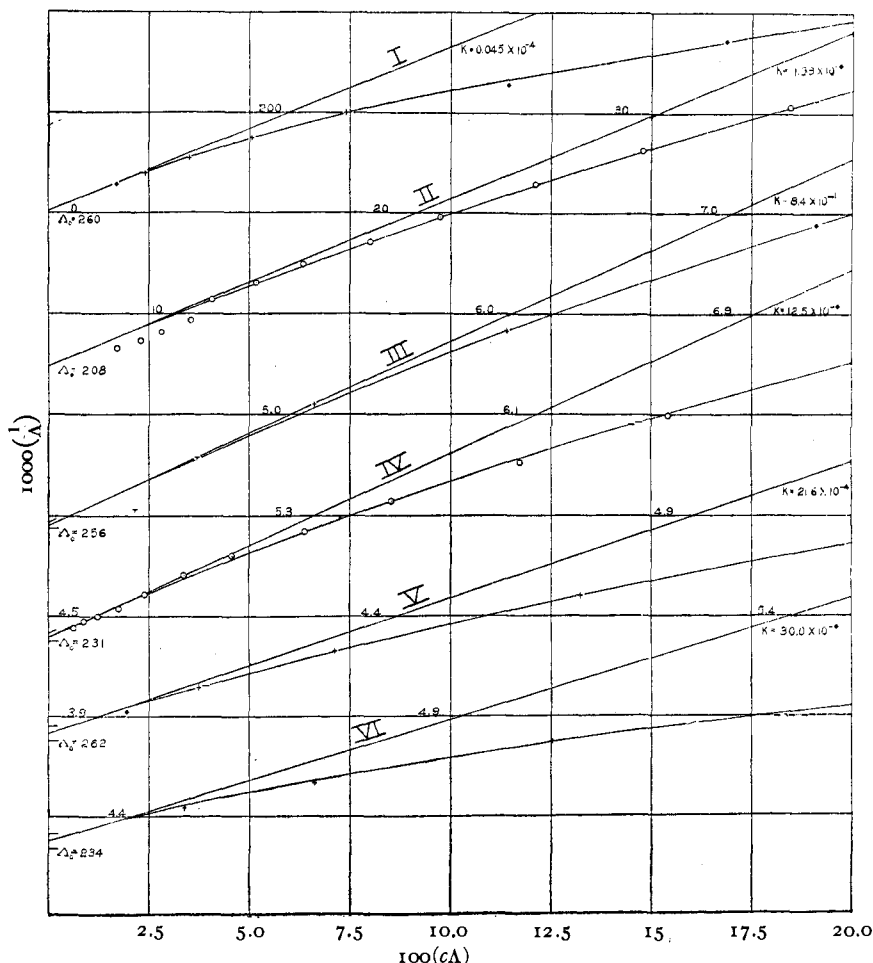
Fig. 13.—Λ_0-K Plot.

respectively, from which 208 $\pm$ 4 was chosen as the final value. An equally satisfactory example is furnished by nitromethane and sodium-nitromethane (XI and XII, Fig. 16), where the data were taken from two different papers, F-K_I and F-K_{II}, respectively. Here identical values of Λ_0 were obtained independently in the two cases.

An examination of the conductances and the chemical formulas of the

anions show that there is a progressive decrease of mobility with increasing complexity of the anion. This not unexpected regularity furnishes further evidence of the reliability of the experimental results and of the correctness of the method of obtaining Λ_o. There is an evident irregularity in the case of benzenesulphonamide (II), where the Λ_o value (208) given is the same as that for the more complex substance methoxybenzene-
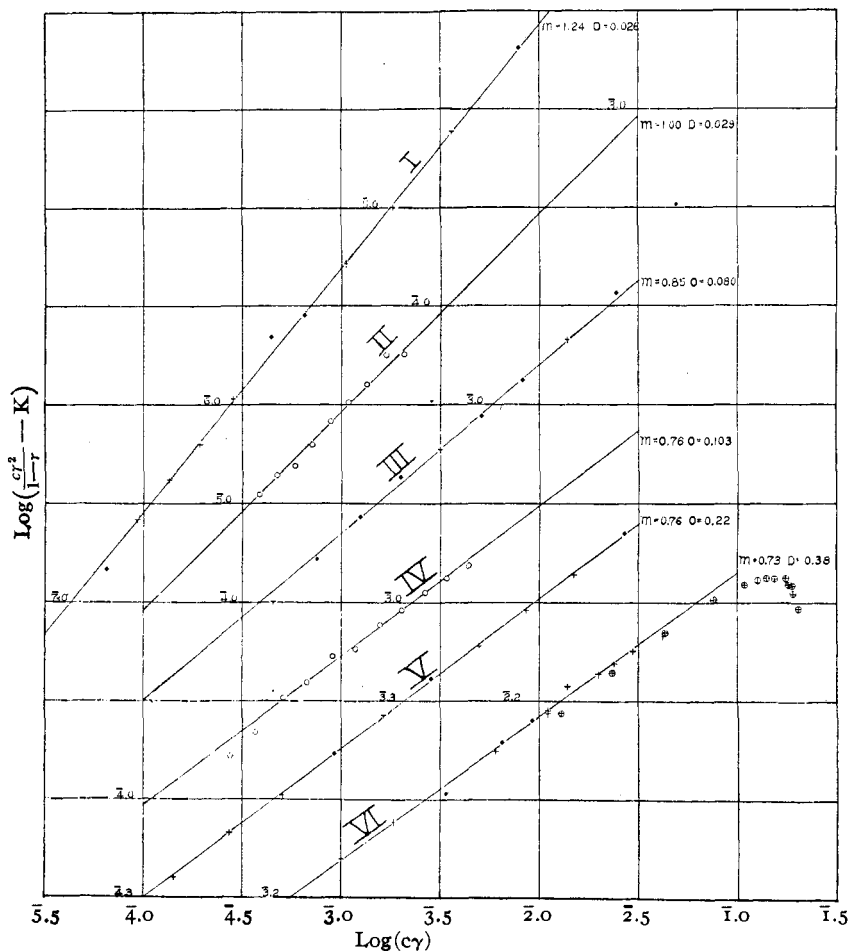
Fig. 14.—m-D Plot.

sulphonamide. Since it is to be expected that the replacement of the methoxy group by hydrogen would lead to a considerable increase in the anion mobility, the Λ_o-K plot (II), Fig. 13, was again examined. It was found that the low value of Λ_o, 208, had been obtained by neglecting the results in the four most dilute solutions, and a second independent extra-

polation led in fact to a much higher value, 228 ± 20, which corresponds
to an anion conductance of 97.   The final figures had, however, been drawn
before this error was discovered and the m-D and K-D plots were not re-
constructed.
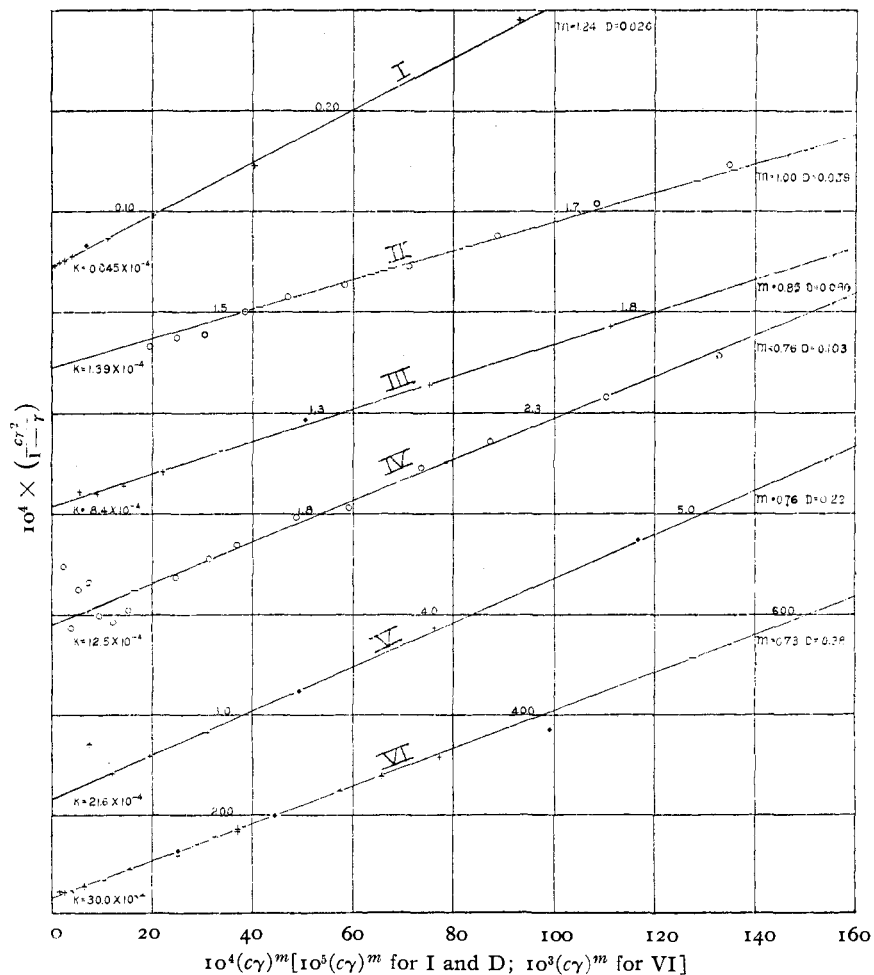
Fig. 15.—K-D Plot.

The values of the constants are collected in Table VIII, where the sub-
stances are arranged in the order of increasing values of K.   Some details
relating to the tables and the experimental data are given in Table IX.
The arrangement of this material is the same as in Table VI.   Further
information may be obtained in the original articles and in the detailed
notes given below:

TABLE VIII.—VALUES OF CONSTANTS FOR ORGANIC ELECTROLYTES.

| Number.	Figure.	Solute.	Investigation.	Λ_o.	$10^4 K$.	m.	D.
I	13-15	Cyanacetamide	F-K$_{II}$	260	0.045	1.24	0.026
VII	16	Thiobenzamide	F-K$_{II}$	204	0.40	. .	. . .
VIII	16	Orthomethoxybenzenesulphonamide	F-K$_{II}$	208	0.40	. .	. . .
IX	16	Paramethoxybenzenesulphonamide	F-K$_{I}$	208	0.50	. .	. . .
XI	16	Nitromethane	F-K$_{I}$	278	0.53	. .	. . .
XII	16	Sodiumnitromethane	F-K$_{II}$	278	0.78	. .	. . .
II	13-15	Benzenesulphonamide	F-K$_{I}$	208	1.39	1.00	0.029
X	16	Metamethoxybenzenesulphonamide	F-K$_{II}$	208	1.81	. .	. . .
XIII	16	Orthonitrophenol	F-K$_{I}$	246	3.90	. .	. . .
III	13-15	Methylnitramine	F-K$_{II}$	256	8.4	0.85	0.080
XIV	. . .	Phthalimide	F-K$_{II}$	248	8.7	. .	. . –
XV	. . .	Benzoicsulphinide	F-K$_{II}$	206	12.0	. .	. . .
IV	13-15	Metanitrobenzenesulphonamide	F-K$_{I}$	231	12.5	0.76	0.103
XVI	. . .	Potassiummetanitrobenzenesulphonate	F-K$_{I}$	275	15.0	. .	. . .
V	13-15	Nitrourethaneammonium	F-K$_{II}$	262	21.6	0.76	0.22
XVII	. . .	Trinitrobenzene	F-K$_{II}$	234	30.0	. .	. . .
VI	13-15	Trinitraniline	F-K$_{II}$, F	234	30.0	0.73	0.38

TABLE IX.—SUMMARY OF DETAILS RELATING TO FIGS. 13–16 AND TABLE VIII.

Number.	Figure.	Number of Series.	Points.	Dilution in liters. Maximum.	Minimum.	A_0-K plot ends.	m-D plot begins.	K-D plot ends.
I.	13–15	1	11	1029	1.11	17.0	1029	20.0
VII.	16	1	14	11980	1.675	50.0	..	..
VIII.	16	1	23	44610	101.2	101.2	..	..
IX.	16	1	18	22620	55.5	70	..	..
XI.	16	1	23	22410	8.99	150	..	..
XII.	16	1	11	10090	10.89	160	..	..
II.	13–15	1	16	8916	42.0	170	731	80
X.	16	1	17	26280	57.96	200	..	..
XIII.	16	1	19	63860	366.2	500	..	..
III.	13–15	1	12	11610	6.34	760	1500	40
XIV.	...	1	14	47630	6.66	..	..	..
XV.	...	1	17	35060	118.1	..	..	..
IV.	13–15	1	18	36930	85.68	1100	3100	100
XVI.	...	1	17	53160	144.8	..	..	..
V.	13–15	1	11	12990	14.02	1600	6600	200
XVII.	...	1	9	12190	52.35	..	..	..
VI.	13–15	4	30	6537	0.982	1600	850	11.1[1]

Notes Accompanying Figs. 13–16.

Figs. 13–15. I. *Cyanacetamide*....F-K_{II}.—Two series, XXIX, 11 points, $v =$ 1029–1.11; XXVIII, 9 points, $v = 316$–1.32. The results in series XXIX are concordant except that at $v = 34.11$, Λ is too high, as shown in the K-D and m-D plots. Series XXVIII has been rejected because the results are not concordant among themselves; the Λ values are relatively much lower than in XXIX.

II. *Benzenesulphonamide*....F-K_I.—One series, 16 points, $v = 8916$–42. The results in the four most dilute solutions are not concordant with those at higher concentrations, and the Λ values were assumed to be too high, as shown in the Λ_0-K plot. The corresponding points are omitted in the K-D plot. It was later decided that the value chosen for Λ_0 (208) might be about 20 units too low, but the plots were not altered.

III. *Methylnitramine*....F-K_{II}.—One series, 12 points, $v = 11610$–6.34. Λ is too high at $v = 11610$. This point is shown in the Λ_0-K plot, but is omitted in the K-D plot.

IV. *Metanitrobenzenesulphonamide*....F-K_I.—One series, 18 points, $v = 36930$–85.68. The points lie irregularly, especially in dilute solutions, as shown in the K-D plot.

V. *Nitrourethaneammonium*....F-K_{II}.—One series, 11 points, $v = 12990$–14.02. Λ is too high for the most dilute solution, as shown in the Λ_0-K and m-D plots.

VI. *Trinitraniline*....F-K_{II}.—Two series, 16 points. I, 8 points, $v = 6537$–54.58; II, 8 points, $v = 103.1$–11.1. The Λ values in the two series agree within less than 1% where they overlap. Λ is a little too high in the most dilute solutions as shown in the K-D plot.

F.—Two series, 14 points. I, 10 points, $v = 44.0$–1.355; II, 4 points, $v = 1.717$–0.982. The usual deviation from the law in concentrated solutions is to be seen in the m-D plot above about 0.2 normal concentration. The Λ values in the two most dilute solutions are somewhat lower than the corresponding values of F-K_{II}.

[1] In the case of this electrolyte the effect of viscosity becomes appreciable at a dilution of 5.0 liters.

Fig. 16. VII. *Thiobenzamide*....F-K_{II}.—One series, 14 points, $v = 11980$–1.675. Λ is a little too high in the most dilute solutions.

VIII. *Orthomethoxybenzenesulphonamide*....F-K_I.—One series, 23 points, $v = 44610$–101.2. The same Λ_o values were obtained from the plots for the ortho,- para,- and meta-compounds (Nos. VIII, IX, and X).

Fig. 16.—Λ_o-K Plot.
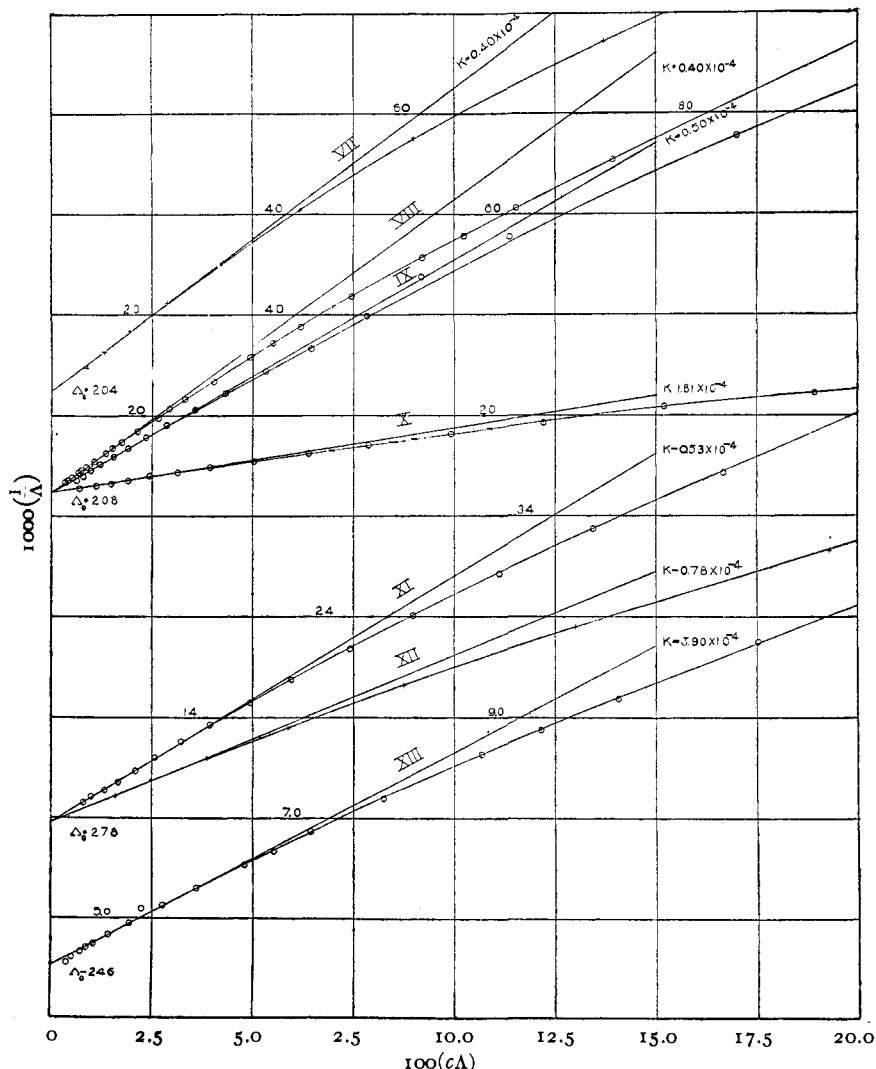
IX. *Paramethoxybenzenesulphonamide*....F-K_I.—One series, 18 points, $v = 22620$–55.5. The points are somewhat irregular. Λ is a little too high in the two most dilute solutions, and too low at $v = 122.8$. The latter point is not shown in the plot.

X. *Metamethoxybenzenesulphonamide*....F-K_I.—One series, 17 points, $v = 26280$–57.96. Λ is a little too low at $v = 5149$.

XI. *Nitromethane*....F-K_I.—One series, 23 points, $v = 22410$–8.99. The same Λ_0 value was obtained as for sodiumnitromethane (XII).

XII. *Sodiumnitromethane*....F-K_{II}.—One series, 11' points, $v = 10090$–10.89.

XIII. *Orthonitrophenol*....F-K_I.—One series, 19 points, $v = 63860$–366.2. Λ is a little too high in the two most dilute solutions, and much too low at $v = 8604$.

C. Discussion of the Results.

Accuracy of the Data.—In Sections A and B, in connection with the presentation of the results of our calculations, some reasons were mentioned for considering the experimental work to be accurate. These were: first, the concordant nature of the Λ_0 values obtained independently for the different inorganic salts (Tables II and III); second, the identity of the Λ_0 values for the three isomeric methoxybenzenesulphonamides, and for nitromethane and sodiumnitromethane (Table VII); third, the regular decrease of the anion conductances with increasing complexity of the anions (Table VII); and fourth, the agreement, in the majority of cases, of the experimental results obtained for the same substance in independent investigations. The most important reason, however, is the fact that in nearly every case the results are concordant among themselves, as shown by the regular arrangement of the points in the plots. That the concordance of results is evidence of their accuracy is obvious, and no one will question the necessity of rejecting results which are not concordant. Stress is here laid upon this point because many conductance results have been published which, when plotted, are at once seen to lack concordance.

Validity of the General Equation.—The proof that Equation III holds in solutions in liquid ammonia is based upon the fact that the separate points in the m-D and K-D plots lie very close to the straight lines corresponding to this general relation. There are, of course, some exceptions, of which the most striking example is silver iodide in the m-D plot, Fig. 6. But with this salt, as was pointed out above, the experimental results are not very satisfactory, and those obtained in different investigations do not agree. In examining the plots, it is to be borne in mind that all the results obtained have been presented, and that none have been suppressed because of lack of agreement with the law. From a study of all the plots it is apparent that the results which are most nearly concordant among themselves agree most closely with the general equation.

It is evident, from a survey of the figures, that the plots of one type are strikingly similar for all the different substances. The plots have the same general appearance for strong and weak electrolytes and for inorganic and organic substances, and the general law holds equally well for the different classes of compounds. The results will therefore be discussed as a whole, the separate substances and classes of substances being referred to as examples. The cyanides of the heavy metals will, however, be

treated in a separate section (Section D), since these probably exist largely in the form of complexes.

Validity of the Mass-Action Law at Small Concentration.—One of the most important results of the present investigation is that in many instances the Λ_0-K plot furnishes a direct proof that the law of mass action is obeyed in very dilute solutions. It has already been pointed out that in this plot two experimentally determined quantities, the reciprocal of the molecular conductance and the specific conductance, are plotted against each other; and that therefore the test of the mass-action law is independent of the values chosen for any of the constants. The following examples afford satisfactory illustrations of agreement with the law, since in these cases the smooth curves certainly approach straight lines in dilute solutions. Values of the mass-action constant K are given in order to show which substances are slightly and which highly ionized.

In each of the following cases it may be seen that the points in dilute solutions lie sensibly on a straight line:

Fig. 2: KNH_2 ($K = 1.20 \times 10^{-4}$); *Fig. 6:* AgI ($K = 2.9 \times 10^{-4}$), NH_4Cl ($K = 12.0 \times 10^{-4}$), KNO_3 ($K = 15.5 \times 10^{-4}$), NH_4NO_3 ($K = 28.0 \times 10^{-4}$); *Fig. 12:* $NaBrO_3$ ($K = 23.0 \times 10^{-4}$), $NaBr$ ($K = 27.0 \times 10^{-4}$); *Fig. 13:* I, Cyanacetamide ($K = 0.045 \times 10^{-4}$), IV, Metanitrobenzenesulphonamide ($K = 12.5 \times 10^{-4}$); *Fig. 16:* All seven examples, organic electrolytes VII–XIII, where K lies between 0.40×10^{-4} and 3.90×10^{-4} (see Table VIII). To these may also be added two less satisfactory examples, KBr ($K = 21.0 \times 10^{-4}$), Fig. 12, and benzenesulphonamide ($K = 1.39 \times 10^{-4}$) II, Fig. 13, where the points in dilute solutions, though lying below the smooth curve, show that there is a definit tendency to approach a straight line with increasing dilution.

This list includes 8 inorganic and 10 organic electrolytes, which is an unexpectedly large proportion of the 15 inorganic and 13 organic substances plotted. It is to be noted that the values of K are less than 4×10^{-4} for 11 of the listed substances and greater than 10×10^{-4} for the remaining 7, the extreme variations of K being from 0.045×10^{-4} to 40×10^{-4}. It is therefore evident that the mass-action law is obeyed in dilute solutions by both weak and strong electrolytes.

All the remaining substances which are shown in the plots were investigated by Franklin (F) and by Franklin and Kraus (F-K_{II}); and, as has already been pointed out, there are independent reasons for expecting their measurements in dilute solutions to be less satisfactory than those of Franklin and Kraus(F-K_I). It is therefore not surprising that Franklin's measurements for $AgNO_3$ ($K = 28.0 \times 10^{-4}$), Fig. 9, show a continuous deviation from mass-action law agreement with increasing dilution, in the direction of too high values of Λ; and that the measurements of Franklin and Kraus(F-K_{II}) for the same substance and for two other nitrates

shown in the same figure, $NaNO_3(K = 23.0 \times 10^{-4})$ and $LiNO_3(K = 26.0 \times 10^{-4})$, show similar, though less marked, deviations. For four other substances investigated by Franklin and Kraus (F-K$_{II}$), namely, $NaI(K = 28.0 \times 10^{-4})$, Fig. 9, $NaCl(K = 14.5 \times 10^{-4})$, Fig. 12, methylnitramine $(K = 8.44 \times 10^{-4})$ III, Fig. 13, and nitrourethaneammonium $(K = 21.6 \times 10^{-4})$ V, Fig. 13, there are only a few points in dilute solutions, and the last point in each case shows a deviation in the same direction as the nitrates, i. e., towards too high a value of Λ. There can evidently be no objection to rejecting the last point in these four cases, and all the points for the dilute solutions of the three nitrates. Finally, in the three remaining cases, $NH_4Br(K = 23 \times 10^{-4})$, and $KI(K = 42 \times 10^{-4})$, Fig. 6, and trinitraniline $(K = 30 \times 10^{-4})$ VI, Fig. 13, there are no points for very dilute solutions, and the values of K have been determined by means of the K-D plots. The Λ_o-K plots for the 10 substances considered in this paragraph have accordingly been drawn to conform with the plots for the 18 other substances; but they are not presented as evidence regarding agreement with the mass-action law in dilute solutions.

The Λ_o-K plots for one other inorganic salt and four other organic substances were prepared in the preliminary investigation; but the experimental results were not concordant enough to furnish evidence as to the applicability of the mass-action law. The K values for these substances, Tables V and VIII, show that all are strong electrolytes. This is also true of the 10 substances discussed in the preceding paragraph.

We thus see that evidence in favor of agreement with the mass-action law in dilute solutions is furnished by 7 of the 22 relatively highly ionized substances investigated; while, as mentioned above, all 11 of the less ionized substances yield satisfactory results. The direct connection between the degree of ionization and the ease with which the mass-action law is tested is easily understood. It is simply a question of the necessary difference of scale in plotting the results for strong and weak electrolytes in the Λ_o-K plot. For a given change in $c\Lambda$ in dilute solutions, there is a much greater relative change in Λ and therefore in $1/\Lambda$ for a slightly ionized substance than for a more highly ionized one, and this necessitates the use of a much larger scale in the latter case. In the case of a strong electrolyte, small accidental errors, say of less than 1 per cent., thus cause the points in a Λ_o-K plot to lie irregularly with reference to the smooth curve, while similar errors can scarcely be detected in a weak electrolyte. It is therefore not surprising that many of the more highly ionized substances do not furnish satisfactory evidence as to the agreement in dilute solutions; and it is evident that these examples can not be cited to prove that the mass-action law does not hold in such cases.

To assist in the proper interpretation of the apparently discordant results for strong electrolytes and to show that Λ_0 can be accurately determined in such cases, the points on the ordinate axis corresponding to a 1 per cent. variation in $1/\Lambda_0$ have been marked on the plots. In the case of the slightly ionized substances, these points lie so close to the $1/\Lambda_0$ point that they have not been shown. Although the mass-action law is more readily tested in the case of solutions of weak than of strong electrolytes, the accuracy with which Λ_0 may be determined is greater for strong electrolytes. The latter result is illustrated by the magnitude of the values of the possible error in Λ_0 given in Tables II and VII.

Ion-Concentration at which the Deviation from the Mass-Action Law becomes Appreciable.—The general equation shows that the deviation from the law of mass action depends upon the ion-concentration of the solution $c\gamma$ and that it increases proportionally with $(c\gamma)^m$. This is shown by the m-D and K-D plots, but the nature of the deviation is also clearly shown in the Λ_0-K plots. In each case the smooth curve representing the experimental results lies below the mass-action law line, and the divergence from this straight line is seen to become appreciable in the plots between values of $c\Lambda$ equal to 0.02 and 0.04. This is equivalent to an ion-concentration of between 1×10^{-4} and 5×10^{-4} normal, since the corresponding values of Λ_0 vary between 240 and 300. This method of determining the "limiting ion-concentration" above which the deviation is appreciable is, however, an arbitrary one, because the result depends on the scale used in plotting $1/\Lambda$, and also because the smooth curve has been drawn in an arbitrary manner through the experimental points without any reference to the general equation.

More definit values of "the limiting concentration" may be obtained in various ways; for example, by determining the concentration at which the mass-action function $c\gamma^2/(1 - \gamma)$ exceeds K by a definit percentage amount, or that at which the actual conductance exceeds by a definit amount the value required by the mass-action law. The results obtained by means of the first method are shown in Table X for all cases in which K, m, and D are known. The ion-concentrations, at which $c\gamma^2/(1 - \gamma)$ exceeds K by 5 and 20 per cent., were calculated from Equation III and are given in the second and sixth columns, respectively. The corresponding values of c are given in the third and seventh columns and those of γ in the fourth and eighth columns. The fifth and ninth columns show the corresponding percentage amounts by which the equivalent conductance Λ, corresponding to the mass-action constant K, must be increased to give the actual conductance at the same ion-concentration. The inorganic and organic electrolytes are arranged separately according to increasing values of K,

TABLE X.—DEVIATIONS FROM THE MASS-ACTION LAW IN RELATION TO THE SALT- AND ION-CONCENTRATIONS.

Inorganic.	Values at which $c\gamma^2/(1-\gamma)$ exceeds K by 5%.				Values at which $c\gamma^2/(1-\gamma)$ exceeds K by 20%.			
	$10^4 c\gamma$.	$10^4 c$.	100γ.	Percentage increase in Δ.	$10^4 c\gamma$.	$10^4 c$.	100γ.	Percentage increase in Δ.
KNH$_2$	2.76	8.82	31.3	3.47	8.97	65.0	13.8	17.2
AgI	0.86	1.14	77.6	1.15	6.38	18.03	3.54	12.8
NH$_4$Cl	1.10	1.19	92.0	0.40	5.70	7.99	71.4	5.73
KNO$_3$	1.35	1.46	92.3	0.36	6.89	10.80	73.0	5.41
NaNO$_3$	1.35	1.42	94.7	0.24	6.52	8.06	80.9	3.78
NH$_4$Br	0.89	0.92	96.4	0.19	4.85	5.70	85.0	3.00
LiNO$_3$	1.06	1.10	96.2	0.19	5.33	6.32	84.3	3.13
NaI	0.63	0.64	97.9	0.10	3.33	3.66	91.0	1.79
AgNO$_3$	0.78	0.80	97.4	0.13	3.38	3.80	89.0	2.21
NH$_4$NO$_3$	0.98	1.02	96.8	0.16	4.92	5.64	87.2	2.58
KI	2.03	2.12	95.6	0.17	8.91	10.50	84.9	3.03
Organic.								
I	0.83	15.4	5.4	4.85	2.53	120.0	2.1	19.7
II	2.40	6.34	37.8	3.28	9.59	64.8	14.8	17.0
III	1.32	1.52	87.0	0.64	7.08	12.04	58.8	8.3
IV	0.58	0.61	95.8	0.21	3.62	4.49	80.6	3.86
V	0.44	0.45	98.1	0.09	2.74	3.03	90.4	1.92
VI	0.22	0.22	99.3	0.03	1.45	1.49	97.1	0.58

A striking result of these calculations is the low value of the ion-concentration at which the deviation from the mass-action law becomes appreciable. For a 5 per cent. difference between $c\gamma^2/(1-\gamma)$ and K, the values of $c\gamma$ lie between 0.22×10^{-4} and 2.76×10^{-4}, and all but three of them lie between 0.58×10^{-4} and 2.40×10^{-4}, *i. e.*, do not differ greatly from 1×10^{-4}. The corresponding values of c show much greater variation, so that, for this method of measuring deviations from the mass law, the ion-concentration is the determining factor, rather than the total salt-concentration. With the exception of four electrolytes, the variation in the value of $10^4 c\gamma$, for a 5 per cent. variation in K, does not exceed a ratio of 1 to 4. The exceptions are either very strong or very weak electrolytes, and in some cases the value of K is somewhat uncertain. Making a comparison for a 20 per cent. variation in K, which is perhaps a more representative test, the corresponding values of $10^4 c\gamma$ for all electrolytes vary between 1.45 and 8.97, thus in the ratio of $1 : 6.2$, the corresponding ratio of the values of $10^4 c$ (those of the total salt-concentration) is $1 : 80$.

It is evident from these results that the deviation from the mass law begins at approximately the same ion-concentration for all electrolytes[1] in ammonia.

[1] The only cases in which the mass-action law fails to apply for values of $c\gamma$ less than 1×10^{-4} is for the cyanides, which are discussed in Section III D. It will be observed, however, that the significance of the result for these salts is doubtful because of uncertainties as to the nature of the equilibrium involved.

The great range of the percentage ionization of the different electrolytes shown in the table, namely, from 5.4 to 99.3 in the fourth column and from 2.1 to 97.1 in the eighth column, should be noted. These extreme values correspond to the lowest value of the mass-action constant, 0.045×10^{-4}, for cyanacetamide (I), and to one of the highest values, 30×10^{-4}, for trinitraniline (VI).

An examination of the values of the percentage ionization at the different ion- and salt-concentrations will assist in understanding the significance of the magnitude and variation of the values of K. For cyanacetamide the mass-action law is sensibly obeyed up to a concentration of 0.02 normal. A substance with a much lower mass-action constant would obey the mass law at still higher concentrations. It is evident, therefore, that strong and weak electrolytes differ in no wise save in degree, which difference is completely accounted for by the magnitude of the constant K. A physical difference, such as is often implied in these terms when speaking of aqueous solutions, is entirely lacking in ammonia. This familiar distinction, which is made in aqueous solutions on the basis of agreement or disagreement with the mass law, has no significance in ammonia; and it is highly probable that it is a purely arbitrary distinction in water also.[1] It merely happens that in water a large number of electrolytes (the weak acids and bases) are dissociated to such a slight extent that at ordinary concentrations the ion-concentration is below that at which deviations from the mass law become sensible. The strength of an electrolyte is defined by the constant K. A strong electrolyte is therefore one whose dissociation constant is high relative to that of other electrolytes in the same solvent.

In the case of the inorganic electrolytes, the values of 100γ do not increase steadily, although the substances are arranged in the order of increasing values of K (compare Table V). This is due to the fact that the values of γ are also dependent on the values of m and D. For two salts having the same value of D and K, the deviations from the mass-action law will be equal for the value of $c\gamma$ equal to unity. In the more dilute solutions the term $D(c\gamma)^m$ will fall off more rapidly for larger values of m. Other things being equal, therefore, the deviations from the mass law in dilute solutions will appear to be the larger for the smaller values of m, while in very concentrated solutions the deviations will be larger for larger values of m. In most cases concentrations are not reached where $c\gamma$ is as large as unity. When m is unusually high, as in the case of KI (see Tables V and VIII), the deviations from the mass-action law will be relatively smaller in dilute solutions than when m is low, and relatively lower values of γ will result.

The results in the fifth and ninth columns of Table XI may be used to

[1] See Section IX.

illustrate another method of measuring deviations from the mass-action law. These numbers show the percentage amounts by which the values of Λ or γ, as calculated from the mass-action constant at the ion-concentrations given in the table, must be increased to give the values of Λ or γ corresponding to a 5 or 20 per cent. increase in K at the same ion-concentration. The results may be used to estimate the ion-concentrations at which the percentage deviations of Λ or γ would be, say, 1 per cent. It is evident that the values of the ion-concentration given in the second column must be considerably decreased in the case of the weakest electrolytes and increased in the case of the strongest. These values of $10^4 c \gamma$ calculated for the six organic electrolytes in order are: 0.3, 1,1, 1.6, 1.6, 1.8, and 1.9.[1]

Value of the Constants of the General Equation.—Inspection of Table V shows that a large number of salts have constants whose values differ but little. Excluding silver iodide,[2] the values of $K \times 10^4$ for fourteen salts lie between 12.0 and 42.0, while those of D lie between 0.13 and 0.62. The values of D for these salts thus vary slightly more than those of K. For these same salts m lies between 0.82 and 0.94. For ten of these salts $K \times 10^4$ lies between 21.0 and 28.0, D lies between 0.24 and 0.43, and m lies between 0.82 and 0.89. For typical salts the mean values of the constants are therefore approximately: $m = 0.85$, $K = 26.0 \times 10^{-4}$, and $D \doteq 0.35$.[2]

Such variations of the constants as exist in the case of the inorganic substances appear to be more or less irregular.[3] The constants for some of the organic electrolytes, however, show much greater regularity. All these constants can be arranged in a regular sequence in the case of the six electrolytes investigated (Table VIII), values of K and D increasing in the same order, while, for the same order of the electrolytes, the values of m decrease. With the exception of cyanacetamide, whose dissociation

[1] If it be assumed that the deviation from the mass-action law is merely apparent and due to change in the speed of the ions, an increase in speed amounting to 1% would have to be assumed to have taken place at these concentrations (see Section XII).

[2] The values of the constants for potassium iodide are somewhat high. This may in part be due to uncertainties in the experimental data for this salt, since reliable data in dilute solutions are not available.

Silver iodide seems to be somewhat exceptional in its properties. Its mass-action constant is much lower than that of the typical salts. The value of D relative to K is much below the mean and the value of m is abnormally low, being the lowest investigated, only 0.70. Since K is low, a high value of m was to have been expected. In this connection, however, we must bear in mind that silver salts generally are somewhat exceptional. In water, for example, some of the silver salts are dissociated to a much smaller degree than other binary electrolytes.

[3] Thus the values of K decrease in the order: K, Na, Ag in the iodides; Na, NH₄, K in the bromides; Na, NH₄ in the chlorides; and NH₄ or Ag, Na, K in the nitrates.

is very small, the values of D and K are roughly proportional to each other. The larger the mass-action constant K, the larger the constant D, and the smaller m. It is interesting to note that for the strongest electrolyte of this series m is as low as 0.73, a value differing not greatly from that of salts in water.[1]

It is to be noted that in Table VII, NH_4^+ is assumed to be the positive ion in the solution of nearly all the organic substances investigated. The equality of the Λ_o values found for nitromethane and sodiumnitromethane furnishes a striking proof of this assumption, since the mobilities of the ions NH_4^+ and Na^+ are equal (see Section IV). This thus confirms the views of Franklin and Kraus[2] that the ammonium salts are, in fact, "acids" when dissolved in ammonia, and we must conclude that all these organic substances when dissolved in ammonia behave in a manner similar to that of the common acids, such as HCl in water.

The dependence of the constant K on the constitution of the electrolyte, as shown in Table VIII, possesses some interest. The number of substances investigated is too small to admit of a detailed comparison being made with other solvents. In general, however, the value of K is determined by the constitution of the electrolyte, much as we might expect from the behavior of the organic acids in water. On the whole, it would seem that for the organic acids K varies less in ammonia than it does in water. It should be borne in mind in this connection that in some cases temporary or permanent molecular rearrangements result when the substances are dissolved in ammonia. Some of the substances appearing in the table are practically non-conductors in water. The reason for this is to be looked for in the stronger basic character of ammonia as compared with that of water. It is probable that when an acid is dissolved in water dissociation results only if the acid combines with water to form what may be called an oxonium salt;[3] for the hydrogen ion is doubtless hydrated[4] and corresponds, at least in part, to the formula OH_3^+. This ion is similar in nature to the ammonium ion, save that it is less stable and probably less solvated than the corresponding ammonium ion. It is not surprising, therefore, that many substances (for example, the acid amides) are more strongly dissociated in ammonia than in water.

One further fact may be pointed out here, namely, that all the polybasic ammono-acids act as monobasic acids at the dilutions for which conductance measurements are available; for the conductance curve in every case corresponds to that of a binary equilibrium.

Deviation from the General Equation at High Concentration,—It should

[1] For KCl, m = 0.673 (See Section IX).
[2] F-K$_I$ (14), pp. 302 *et seq.*
[3] Compare Section VIII.
[4] Compare Buchbök (68).

further be stated that, although the general equation fails to hold beyond a concentration of approximately 1.0 normal, there is good reason for believing that the failure is only the result of a change in the speed of the ions owing to the increasing viscosity of the solution.[1] It will be seen from Tables V and IX that the applicability of the law ceases at a smaller concentration in the same measure as the complexity of the solute increases, whether due to the complexity of the dissolved substance itself or to a strong tendency to solvation. It should not be forgotten in this connection that the viscosity change is for the most part due, not to the ions, but to the un-ionized fraction, since the dissociation is not large. The equation ceases to be applicable to solutions of KNH_2 and AgI at 2.5 and 2.0 normal, to $NaNO_3$ at 1.25 normal, to NH_3NO_3 and KI at 1.0 normal, to $LiNO_3$ at 0.5 normal, and to trinitraniline at 0.2 normal. These figures corroborate what has just been said in a striking manner.[2] Still more convincing evidence as to the influence of viscosity is furnished by aqueous solutions. These results will be the subject of a separate communication by one of us in the near future.

D. Cyanides of the Heavy Metals.

In their first investigation on the conductance of ammonia solutions, Franklin and Kraus(14) found that the conductance curve of mercuric cyanide in ammonia passes through a minimum. Subsequently they found (29) that the cyanides of zinc and silver exhibit a similar behavior.[3] Gold cyanide was found not to yield a minimum, but its behavior was found to resemble that of the other cyanides in that its conductance changes but little with concentration. These salts appear to form a distinct class. It is true that other electrolytes in ammonia, such as KNH_2, for example, exhibit a minimum conductance in concentrated solutions; but in these cases the conductance in the more dilute solutions increases very rapidly. In the case of the cyanides considered in this section, the increase in conductance in dilute solutions is extremely small. This means, of course, that the K-term in Equation III is extremely small in comparison with the D-term, assuming a binary equilibrium to exist.

The experimental results for the cyanides are shown graphically in Fig. 17. The m-P plots are shown for the cyanides of silver, zinc, and mer-

[1] See Franklin (28), p. 693; Franklin and Gibbs (27), and the next foot-note below.

[2] Fitzgerald (65) has recently published measurements of the viscosities of solutions of a number of substances in ammonia and in methylamine, and has shown that there is in general a very great increase of viscosity in the very concentrated solutions. His results show, in fact, that in solutions of KI, $NaNO_3$ and AgI in ammonia (page 660) the increase of viscosity with the concentration becomes very great at or near the concentration values mentioned above.

[3] A number of other electrolytes were found by Franklin (26) which exhibit minima when dissolved in ammonia. In other respects, however, the conductance curves for these electrolytes differ greatly from those of the cyanides.

cury. For gold cyanide, the m plot is shown. The scale of abscissas for the m-P plots is shown at the top of the figure. The scale of ordinates for each plot is shown on the figure by numbers which appear where the curves cut the parallels to the axis of abscissas. The scale employed in
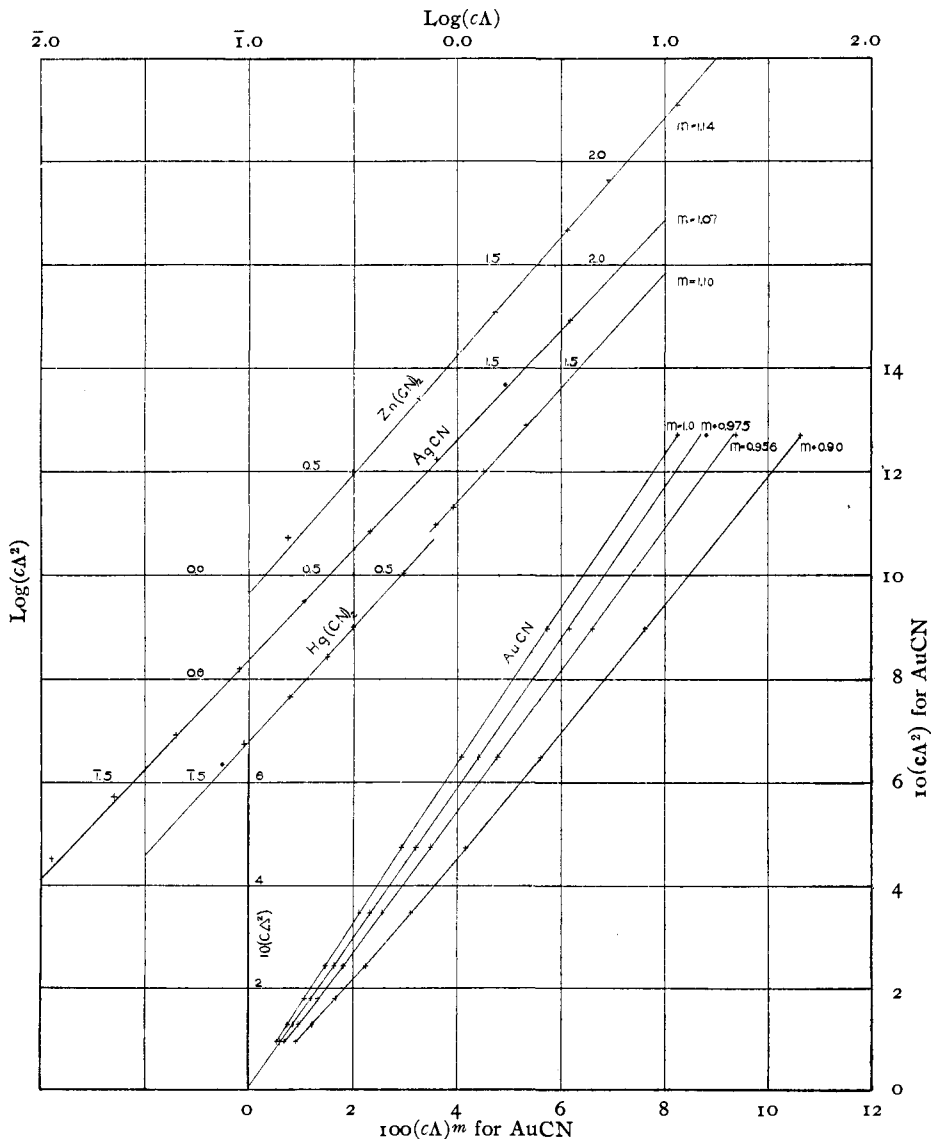
Fig. 17.—m-P Plots for Zn (CN)$_2$, AgCN and Hg(CN)$_2$ and m Plot for AuCN.

the m plot is shown at the bottom of the figure. All the data are taken from the second paper of Franklin and Kraus(29). For silver cyanide, the conductances differ somewhat from those given by Franklin(26).

For purposes of comparison it seemed best to use the results of a single investigation. The constants are summarized in Table XI.

TABLE XI.—CONSTANTS FOR CYANIDES DISSOLVED IN AMMONIA.

Solute.	m.	D.	K.	Λ at minimum.	v at minimum.	Concentration range v-maximum.	v-minimum.
AuCN......	0.975	0.047	7.7×10^{-8}	minimum lacking		3220.0	185.3
AgCN......	1.07	0.056	....	1.63	21.8	55.6	1.16
Hg(CN)₂....	1.10	0.057	....	12.0	538.0	1063.0	4.48
Zn(CN)₂....	1.14	0.102	....	9.86	64.0	977.0	1.43

The values of P were obtained from the plots of Fig. 17. The values of Λ_o may be approximated with sufficient accuracy for present purposes by comparison with other salts. The conductance of the gold ion was assumed to be the same as that of the silver ion: that of CN^- to be the same as that of Br^-. For the cyanides of mercury and zinc the value $\Lambda_o = 250$ was chosen as lower limit. This value should doubtless be lower than that of AgCN, since it is highly probable that the cations are complex for the cyanides of bivalent metals. With the aid of the Λ_o values, the values of D were determined from the values of P by means of Equation VII. For AuCN, where the m plot was utilized, the value of K as well as that of D was estimated from the plot, since $K\Lambda_o(\Lambda_o - \Lambda)$ is the intercept of the straight line on the $c\Lambda^2$-axis in the m plot, while D was obtained from the slope of the line, making use of Equation VII.

It is evident, on examining the plots, that the general equation is applicable to these salts within the limits of experimental error. It must not be forgotten, in this connection, that the m-P plots should show deviations in the concentrated solutions owing to the viscosity effect mentioned previously in this paper. The fact that three of the salts exhibit minima is conclusive evidence that in the region of the minimum the K-term of Equation III is becoming appreciable, and it is not to be expected that the points should conform to the m-P plot for dilutions as high or higher than the minimum. That the K-term is appreciable in the case of gold cyanide is shown by the fact that the curve intersects the axis of $c\Lambda^2$ at a value greater than zero.

There can be no question as to the applicability of Equation VI to the solutions under consideration. There may, however, be some question as to the interpretation of the results in dilute solutions. As may be seen from an inspection of the values in Table XI, the magnitude of D is what might be expected for salts having an ionization in the neighborhood of those found here. The K values, judging by the value of K for AuCN and the position of the minima for the other salts, are abnormally low. In all other cases so far examined in this paper, the D and K values run parallel. In the case of the cyanides the K values are extremely low.

There is considerable evidence that, in the presence of ammonia in aque-

ous solution, silver cyanide forms complex anions[1] according to the equation: $2AgCN.NH_3 = Ag(NH_3)_2{}^+ + Ag(CN)_2{}^-$. It is not improbable that in the case of all the cyanides here considered in ammonia solution such processes come into play, which must be taken into account in the equilibrium equation. If the dissociation is not that of a simple binary electrolyte, it is not to be expected that the value of K obtained by extrapolation will be the true value.

There can be no question, however, as to the applicability of Equation III at higher concentrations, where the state of the solute is presumably constant. These solutions have a bearing on the question of complex formation in other cases; for we see that in this case, where there is reason for believing that complex ions may result, the form of the conductance curve is very different from that of the great majority of electrolytes in ammonia or in other solvents. The crucial test as to the formation of complex ions is given by transference measurements. As we shall see in Section IV, transference experiments prove the absence of complex ions in the case of the common electrolytes in ammonia solution.

IV. Ion-Conductances and Transference Numbers in Liquid Ammonia.

Data Available.—The only transference data in liquid ammonia which we have been able to find are contained in an article entitled "On the Velocities of the Ions in Liquid Ammonia Solutions" published in 1904 by Franklin and Cady(25). Fortunately, these measurements were made very carefully with a large number of substances in some cases over a large range of concentration. The agreement of the numerous check measurements and the general concordance of the results furnish satisfactory evidence of the accuracy of the experimental work. Since this work in liquid ammonia involved many serious experimental difficulties and required exceptional manipulative skill, the authors cannot be given too much credit for the successful accomplishment of their task.

The method of moving boundaries, first suggested by Lodge in 1886, was employed. The work was completed and described[2] in 1902, and Franklin and Cady therefore deserve equal credit with Steele(30), Abegg and Gaus(31), and Denison and Steele(32) for the development of this method of determining transference numbers. The theory of the moving boundary method of determining transference numbers is given in each of the articles cited above.

Method of Computation.—The quantities measured by Franklin and Cady were:

u, the observed velocity of the boundary in centimeters per second.

a, the cross-section of the tube in square centimeters.

I, the current in amperes (the current density being I/a).

[1] Abegg u. Auerbach, *Handbuch der anorganischen Chemie*, 2 [1] 699 (1908).

[2] *Proc. A. A. A. S.*, 51, 366 (1902).

$c = 1/v$, the concentration of the solution in mols per liter.

The potential-gradient in the solution was not measured directly, and its actual value was not used in the calculations. It could be calculated from the expression $(1/a) \times (1000 \, v/\Lambda)$, where Λ, which is the conductance at concentration c, could be determined by interpolation from the measurements of Franklin and Kraus.

In any solution the absolute velocity of the cation-constituent U_C or of the anion-constituent U_A is equal to the observed velocity u of the respective boundary divided by the potential-gradient. That is:

$$U_C \text{ or } U_A = \frac{ua\Lambda}{1000 \, v \, I}.$$

From the separate values of U_C and U_A thus obtained the relative velocities of the two ions and the transference number can be determined without introducing any assumption whatever.

From their measurements Franklin and Cady calculated values of U_o for each ion where U_o is defined as U/γ, γ being the degree of ionization given by the conductance ratio Λ/Λ_o. It follows that

$$U_o = ua \, \Lambda_o / 1000 \, v \, I,$$

a formula which does away with the necessity of determining Λ. In their original paper, Franklin and Cady tabulate these values of U_o as absolute velocities of the ions at zero concentration. This is not strictly true, for, as was pointed out by these authors themselves, it involves the assumption that Λ/Λ_o gives a correct measure of the degree of ionization. Only for solutions of zero concentration does the above method yield the true velocities of the ions at zero concentration. It is, however, very convenient to use these values of U_o, since, in general, they change but little with the concentration, and since the trouble of determining Λ by interpolation is avoided. It is easy to obtain from them, by averaging or by extrapolation, the values at zero concentration. The conductances of the cation and anion, Λ_C^+ and Λ_A^-, may then be calculated from the values of U_o by the equation:

$$\Lambda_C^+ \text{ or } \Lambda_A^- = 96540 \, U_{oC} \text{ or } U_{oA}.$$

Preliminary values of the ionic conductances were calculated in the way just described from the experimental values of the boundary velocity u. Now, for each salt Λ_C^+ and Λ_A^- must satisfy the relation: $\Lambda_C^+ + \Lambda_A^- = \Lambda_o$, where Λ_o is the conductance at zero concentration, whose values have already been derived from conductance data and tabulated in Table III, above. Therefore, as soon as the conductance of one ion is fixed, the values for all the other ions may be calculated. Accordingly, several series of corresponding ion-conductances were tabulated; and the corresponding ion-velocities were calculated by the above relation and compared with the values of U_o for each ion derived from the transference experiments.

That series of ion-conductances for which the agreement was most satisfactory was chosen. The final values of the ion-conductances thus obtained are shown in the last column of Table XII.

Ion-Conductance Values.—The experimental results[1] and the values calculated from them are summarized in Table XII A–XII B. The solute investigated is shown in the second column, and the ion whose velocity controlled the motion of the boundary is named in the first column. The volume v, in liters per mol of salt, is given in the third column; the concentration ($1000c$) in millimols per liter, in the fourth column; the number of readings in each series, in the fifth column; and the average of all the values of U_o, obtained by Franklin and Cady in each series, in the sixth column. In the cation experiments the results derived from the final measurements in some series were relatively high, and the mean values obtained by Franklin and Cady, after rejecting these results are shown in the next column of Table XII A under the heading "Revised." A correction must, however, be applied to these numbers owing to the fact that the Λ_o values used by Franklin and Cady were not the same as those given by us in Table III, the percentage differences being shown in the fourth last column of the table. (Thus, our value of Λ_o for NH_4NO_3 (302) is 0.7 per cent. larger than 300, the value used by Franklin and Cady, and the Franklin and Cady values of U_o given in the table for the ions of NH_4NO_3 should therefore be increased by this percentage amount.)

In order to check the results of Franklin and Cady, the values of U_o were recalculated by us from the original experimental data. The original results were carefully examined; and some of the final measurements, and in some cases the initial measurements also, were rejected before calculating the mean for the series. The results of this revision are shown in the third last column under the heading "$10^5 U_o$, K-B, Recalculated." It will be seen that there is good agreement between these values of the ion-velocities and those of Franklin and Cady, after the above-mentioned correction has been applied to the latter.[2]

The values of the ion-conductances $\Lambda_C{}^+$ and $\Lambda_A{}^-$ finally chosen by us are shown in the last column of the table. To assist in the comparison with the remaining numbers in the table, the corresponding ion-velocities (multiplied by 10^5) were obtained by dividing $\Lambda_C{}^+$ and $\Lambda_A{}^-$ by 0.96540, and are shown in the second last column. There is in general good

[1] Only two series of measurements given in the original article have been omitted in the table: that for $NO_3{}^-$ in $NaNO_3$ at $v = 35.6$, where the indicator was considerably mixed with the $NaNO_3$ solution, and u was found low, as expected; and that for Br^- in $NaBr$ at $v = 45.7$, where u was low as a result of a current leak.

[2] Iodide ion in potassium iodide is the only striking exception, and here there is some evidence that all the results were low because a slow destruction of the boundary seemed to be taking place. The lowest results were accordingly rejected by us before taking the mean.

agreement between the values shown in the second last and third last columns, derived respectively from conductance and transference measurements; this question will be discussed in detail below.

From the variation of the separate results at each concentration, the probable error in each value of U_o was estimated to lie in general between 2 and 5 units, but it seemed to be considerably greater for Cl⁻ in NH₄Cl, Br⁻ in NH₄Br, and I⁻ in KI.

To make clearer the significance of the results shown in the second and third last columns, these values of U_o are shown in Fig. 18, plotted as ordinates against the concentration as abscissas. The values of the ion-velocities (multiplied by 10^5), $\Lambda_{C}^{+}/0.96540$ and $\Lambda_{A}^{-}/0.96540$ in the second last column, are plotted on the ordinate axis, and a horizontal line is drawn through each of these points. The results for the cations are shown in the upper part and those for the anions in the lower part of the plot. The nitrates, bromates, and iodides are distinguished by means of a circle, cross, and combined cross and circle, respectively. The same symbols are used to distinguish the sodium, ammonium, and potassium salts in the lower part of the plot.

TABLE XII A. CATION-VELOCITIES AND CONDUCTANCES IN AMMONIA.

Ion.	Solute.	z.	1000c.	Readings.	$10^5 U_o$, F-C. Mean.	$10^5 U_o$, F-C. Revised.	Percentage correction to be added.	$10^5 U_o$. Recalculated. K-B.	$\Lambda_c^{+}/0.96540$.	Λ_c^{+}.
NH₄⁺	NH₄NO₃	58.7	17.04	8	135	133	+0.7	135	136	131
		14.06	71.1	7	133	133	+0.7	134	...	...
		6.28	159.2	18	133	131	+0.7	134	...	...
NH₄⁺	NH₄I	31.05	32.2	11	130	129	—0.7	129	136	131
		29.8	33.6	4	126	126	—0.7	125	...	...
K⁺	KNO₃	187.5	5.33	6	176	191	+0.3	174	174	168
		56.2	17.8	6	176	175	+0.3	175	...	...
		23.52	42.5	8	179	174	+0.3	176	...	...
		9.62	104.0	11	181	177	+0.3	178	...	...
		9.61	104.1	11	180	178	+0.3	179	...	...
		8.02	124.7	13	174	172	+0.3	174	...	...
Na⁺	NaNO₃	62.3	16.05	7	138	132	+1.0	139	135	130
		59.8	16.72	6	138	131	+1.0	134	...	...
		35.15	28.45	8	135	132	+1.0	134	...	...
		11.97	83.5	10	131	130	+1.0	132	...	...
		9.53	104.9	7	132	130	+1.0	131	...	...
		4.42	226.2	5	127	127	+1.0	128	...	...
		4.16	240.4	6	126	126	+1.0	128	...	...
Na⁺	NaBrO₃	109.3	9.15	3	135	135	+0.7	136	135	130
		85.7	11.67	9	130	129	+0.7	131	...	...
		33.5	29.85	7	131	129	+0.7	130	...	...
Ag⁺	AgNO₃	24.2	41.3	8	111	111	—2.7	108	120	116

TABLE XII B.—ANION-VELOCITIES AND CONDUCTANCES IN AMMONIA.

Ion.	Solute.	$\tilde{v}$	1000ς	Readings.	10^5U_0 Mean. F-C	Percentage correction.	10^5U_0 K-B Recalculated.	$J_A^-/0.96540$	J_A^-
NO₃⁻	NH₄NO₃	25.17	39.73	7	175	+0.7	176	177	171
NO₃⁻	KNO₃	94.6	10.57	9	176	+0.3	177	177	171
		35.6	28.1	11	178	+0.3	178	...	...
NO₃⁻	NaNO₃	28.8	34.7	10	174	+1.0	176	177	171
		27.0	37.0	13	175	+1.0	177	...	...
Cl⁻	NH₄Cl	52.75	18.96	7	217	+2.0	222	185	179
		40.7	24.6	6	222	+2.0	227	...	...
		18.23	54.9	6	229	+2.0	234	...	...
		8.46	118.2	8	280	+2.0	286	...	...
		4.98	200.8	7	309	+2.0	315	...	...
Cl⁻	NaCl	58.5	17.09	9	180	+2.2	185	185	179
		29.45	33.95	11	180	+2.2	184	...	...
Br⁻	NH₄Br	41.75	23.95	6	188	—0.3	187	178	172
		19.1	52.4	11	188	—0.3	188	...	...
		17.01	58.8	6	196	—0.3	195	...	...
Br⁻	NaBr	59.75	16.74	9	178	0.0	178	178	172
		21.35	46.84	10	176	0.0	176	...	...
I⁻	NH₄I	60.0	16.67	8	176	—0.7	175	177	171
I⁻	KI	128.0	7.81	5	164	—0.6	169	177	171
		57.6	17.36	4	161	—0.6	165	...	...

Variation of U_0 with the Concentration.—An examination of the values of U_0 in the third last column of the table or in the figure shows that only in one case is there a large variation of the ion-velocity with the concentration. (U_0 for Cl⁻ in ammonium chloride increases rapidly with the concentration, and there is also a less marked increase in the case of Br⁻ in NH₄Br.) It is highly probable, however, that these cases are affected by some unknown source of error, since there is no evidence of a change in U_0 for Cl⁻ or Br⁻ in the sodium salt, nor in U_0 for NH₄⁺ in NH₄NO₃. In the case of Na⁺ in NaNO₃, where the experiments extend over the largest range of concentration, there appears to be a slight decrease of U_0 with increasing concentration, but it is impossible to decide whether this is a real decrease or simply an apparent one due to some error in the more concentrated solutions. In any event, it is evident that the change in the transference number is small, even at as high a concentration as 0.25 normal. As far as the remaining measurements are concerned, there is no distinct indication of a change of the ion-velocities, and therefore of the transference numbers, with the concentration.

The agreement between the values of U_0 derived from the transference experiments and those assumed at zero concentration from conductance data is very satisfactory except in the case of Ag⁺ in AgNO₃. But only

one solution of this substance was studied, and it will be recalled, more-over, that the determination of Λ_0 from the conductance data was less accurate for the silver salts, and especially for AgNO$_3$, than for the other salts investigated. It is evident that the experimental values of U_0 for the halide ions are too high in NH$_4$Cl and NH$_4$Br and too low in KI. Reasons for rejecting these results have already been given in the pre-
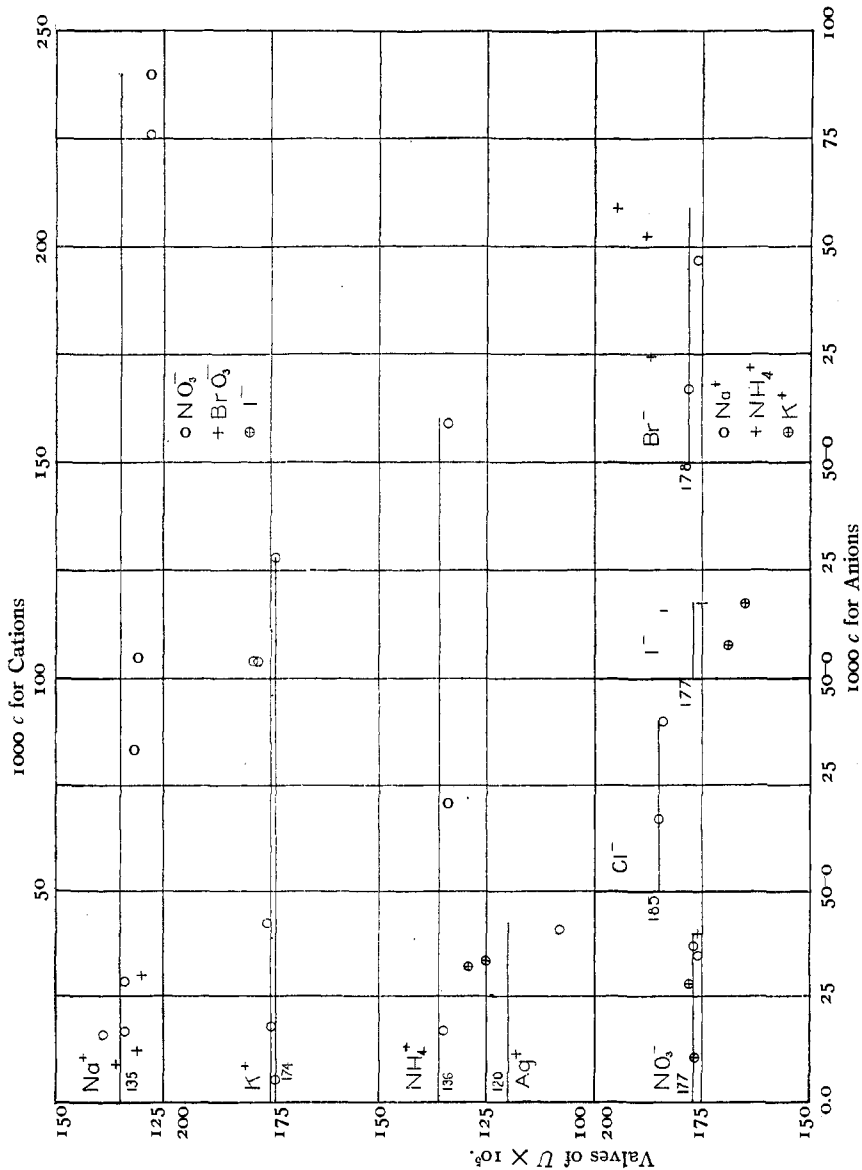

Fig. 18.—Change of U with Concentration.

ceding pages. The best evidence that these three sets of measurements are in error is furnished by the fact that the U_0 values for the halide ions in NaCl, NaBr and NH$_4$I are in good agreement with those derived from the conductance values at zero concentration.

The transference numbers may be calculated from the ionic conductances or from the ionic velocities. Thus the anion transference number for NH$_4$NO$_3$ is $171/(131 + 171) = 0.566$. It is interesting to note that an independent determination of this quantity by Franklin and Cady, in an experiment with the most concentrated NH$_4$NO$_3$ solution ($v = 6.28$), in which the motion of both the cation and the anion boundaries was followed, gave the value 0.58. This is as good an agreement as was to have been expected, since this experiment extended over a period of two hours and only the initial and final readings were given. The smallest anion transference numbers are those for KNO$_3$ and KI, $171/339 = 0.504$; the highest is that for AgNO$_3$, $171/287 = 0.598$. The corresponding value for AgNO$_3$, based on the actual boundary velocity measurements, is $177/(177 + 108) = 0.621$. This lack of agreement corresponds to the difference between the experimental and assumed values of U_0 for Ag$^+$. Similar calculation of the transference numbers have not been made in the other cases because no additional information would be gained thereby.

The final conclusion to be drawn from the available experimental material is that there is at present no evidence of any large change in the transference numbers with increasing concentration. The fact that the U_0 values derived from the boundary velocities are in agreement with the values obtained from conductance results at zero concentration is strong presumptive evidence that the assumptions underlying the calculations of the former are correct. It is desirable, however, that the present results be checked by independent experiments, that the measurements with the ammonium halides be repeated, and that additional measurements be made in more concentrated solutions and with other substances than these typical salts.

Comparison of the Ion-Conductances in Ammonia and Water.—Since ammonia and water are the only solvents for which a large number of ion-conductances are known, it is interesting to compare the corresponding values in the two solvents. In Table XIII, the values of the ion-conductances in ammonia at $-33.5°$ are shown in the second column, those in water at $18°$ (33) are shown in the third column, and the ratios of the two are given in the fourth column.

The velocities of the ions in ammonia are evidently much greater than in water, which corresponds to the fact that the viscosity of ammonia is much less than that of water. An as yet unpublished determination made in this laboratory by Kraus and Abbott shows the viscosity of NH$_3$

at $-33.5°$ to be 2.558×10^{-3}, while that of water at $18°$ is 10.63×10^{-3}. The ratio is 4.15.

TABLE XIII.—COMPARISON OF ION-CONDUCTANCES IN AMMONIA AND IN WATER.

Ion.	In NH$_3$ at $-33.5°$.	In H$_2$O at $18°$.	Ratio.
Li$^+$	112	33.3	3.36
Ag$^+$	116	54.0	2.15
Na$^+$	130	43.4	3.00
NH$_4^+$	131	64.7	2.03
Tl$^+$	152	65.9	2.31
K$^+$	168	64.5	2.61
BrO$_3^-$	148	47.6	3.11
NO$_3^-$	171	61.8	2.77
I$^-$	171	66.6	2.57
Br$^-$	172	67.7	2.54
Cl$^-$	179	65.5	2.73

An examination of the results in the last column of the table shows that the ratio of the ion-velocities is by no means constant. It is very high for Li$^+$, and considerably above the average for Na$^+$ and BrO$_3^-$. This indicates a specific effect of one or both solvents on these three ions. The most probable explanation is that the relative solvation of these ions is greater in water than in ammonia, especially in the case of the lithium ion. On the other hand, the ratios for Ag$^+$ and NH$_4^+$ are exceptionally low, which indicates that the relative solvation of these ions is greater in ammonia than in water. Such effects as these are not surprising; for the tendency of lithium salts to take up water is well known, as is also that of silver salts to form complexes with ammonia, even in water solutions. The exceptionally low value of the ratio for the ammonium ion is of especial significance in connection with present conceptions regarding the constitution of the hydrogen ion.

The average value of the ratio of the ionic conductances for the remaining six ions is 2.59, and this ratio may possibly be of value in determining approximate Λ_0 values in ammonia from those in water. It is to be noted that this value is much smaller than the viscosity ratio given above, and it is evident that the product Λ_0 times viscosity is nearly 1.6 times larger in water than in ammonia. There are a number of solvents in which this product is approximately constant, but ammonia, like water, furnishes an exception to this rule, although ammonia is much less exceptional than water. This question will be discussed by one of us in a subsequent publication.

It is to be noted that the conductance of the ammonium ion is not larger than that of the other cations in liquid ammonia. It is in fact equal to the conductance of the sodium ion and much smaller than that of the potassium ion. The conductance of the amide ion NH$_2^-$ (Table IV) is also smaller

than that of the anions of typical inorganic salts. These results are of importance, since there is a time-honored tradition anong physical chemists that the abnormally high conductance of the H^+ and OH^- ions is related to the fact that water dissociates into these ions. In some cases a kind of modified Grotthus-chain effect has been postulated whereby the high conductance of these ions is considered to be due to their combination with neutral water molecules and the simultaneous dissociation of the ions on the other side of the water molecules. NH_4^+ and NH_2^-, however, are the ions of pure ammonia; and yet the velocities of these ions is not larger than those of other ions, indeed, as we have seen, the NH_4^+ ion actually moves more slowly than might otherwise be expected. Similarly, the alcoholate ion in alcohol possesses a lower conductance than the common univalent ions.[1]

The important conclusion may therefore be drawn that the speed of certain ions in a given solvent is not related to the possible dissociation of this solvent into ions of the same character as those of the dissolved substance. This question will be discussed more fully by one of us in a subsequent publication.

A number of investigators have advanced the hypothesis that in those cases where the conductance increases with increasing concentration,[2] the solutes form aggregates which dissociate into complex ions. If complex ions are present in a solution, their complexity must change with concentration and it follows that, in general, the transference numbers for these ions must likewise change. For the purpose of proving the falsity or correctness of the hypothesis just mentioned, the preceding transference results in liquid ammonia are of the utmost importance.

In the first place, it is to be borne in mind that the phenomenon involved in the deviations from the mass law is doubtless the same whether m is less or greater than unity, since the general equation applies equally well in both cases. In ammonia we find some electrolytes with m greater than unity and others with m less than unity. Moreover, the value of m is a function of the temperature; thus in the case of solutions in sulfur dioxide considered in the next section, we shall find that it increases with the temperature. It is evident, therefore, that any explanation advanced must not be confined to the very special case where m is greater than unity. In addition to the difficulty, already pointed out, that m has no definit value, but varies over a considerable range, the hypothesis in question meets with more serious objections in the light of the results discussed in the present section. Although in all cases, the electrolytes investigated deviate largely from the mass-action law at the concentrations at which

[1] In ethylalcohol at $25°$, Turner (69) found the Λ_o values for KI and LiCl to be 48.4 and 38.0, respectively. For sodiumethylate in ethylalcohol at the same temperature, Robertson and Acree (70) found $\Lambda_o = 33.2$.

[2] Steele, McIntosh and Archibald (34), p. 148, et seq.; Sachanov (35), p. 20, et. seq.

transference measurements were made,[1] the transference numbers obtained are in excellent agreement with the conductance values obtained in extremely dilute solutions where the mass-action law is obeyed. In addition to this, the transference measurements show that there is little, if any, change of the transference numbers with concentration.

The results of transference measurements are of crucial importance to the hypothesis of complex formation which we are considering and they show conclusively that it is untenable. There are doubtless cases in which complex ions are formed; for there are numerous such instances in aqueous solutions, and some in other solvents (thus probably in the case of the cyanides in ammonia). The phenomenon is not a general one, however, and has no bearing on the question of the deviation from the mass-action law.

V. Solutions in Liquid Sulfur Dioxide.

Data Available.—Aside from ammonia, sulphur dioxide is practically the only other solvent for which data are available in both dilute and concentrated solutions. Dutoit and Gyr(19) measured the conductance of dilute solutions in sulfur dioxide at $-15°$, and Franklin(28) measured the conductance in both dilute and concentrated solutions at a number of temperatures. Unfortunately, the results in dilute solutions in both these investigations are far from satisfactory. Accidental errors seem to have been large; and the curves, in very dilute solutions, develop a trend which indicates either that the conductance of the solvent was not wholly corrected for or that leakage currents were not excluded. At any rate, it is impossible to obtain a satisfactory value of Λ_0 from the results in dilute solutions. Because of the unsatisfactory nature of the data for solutions in this solvent, final calculations were made only on the results of Franklin for potassium iodide at $-10°$, for which temperature the data are most numerous.

Results with Potassium Iodide at $-10°$.—An initial estimate of the value of Λ_0 and K gave the values: $\Lambda_0 = 207$, $K = 7.3 \times 10^{-4}$. But on making the m-D plots and K-D plots for this value of Λ_0 satisfactory results could not be obtained, nor could agreement be obtained by adjustment of the values of K, m, and D. This was most plainly shown on the K-D plot. The value of Λ_0 was therefore adjusted so as to bring the plots into agreement with the experimental data, particularly in solutions of moderate dilution. To do this the value of Λ_0 had to be reduced to 199.[2] The other constants were then found to be: $m = 1.14$, $K = 8.5 \times 10^{-4}$, and $D = 0.403$.

[1] See Section III C.

[2] This value of Λ_0 at $-10°$ is less than the value given by Dutoit and Gyr at $-15°$, and the discrepancy becomes greater when a correction is applied for the difference in temperature. However, unless the errors in concentrated solutions are unexpectedly large, it is improbable that our value is in error by as much as 2%.

In Fig. 19 are shown the plots for solutions of potassium iodide in sulfur dioxide at $-10°$. The upper curve is the K-D plot. Values[1] of $(c\Lambda)^m$ and $c\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda)$ are plotted as abscissas and ordinates, respectively. The scale of abscissas is shown at the top of the figure and that of ordinate on the left-hand margin. The intermediate curve is the m-D plot and
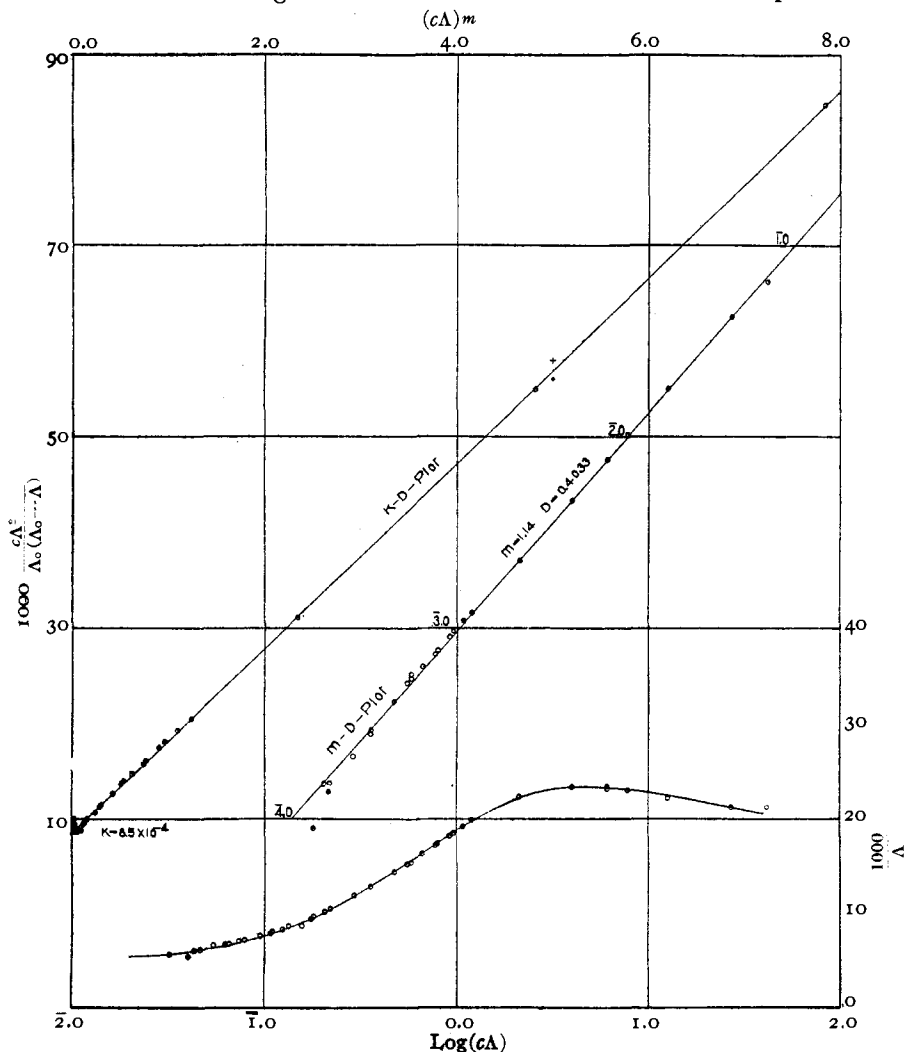
$$(c\Lambda)m$$

Fig. 19.—Plots for KI in SO$_2$.

[1] The "modified" K-D and m-D plots shown in Fig. 19 differ from those previously employed in that γ has now been replaced by Λ/Λ_0. It is obvious that the two sets of plots will serve equally well to test the validity of the general relation (Equation III). In the modified plots, however, $D/\Lambda_0{}^m$ and not D will be determined directly from the plots. When the values of Λ_0 can be accurately determined from the Λ_0-K plots as in

the lower curve is a plot of $1/\Lambda$ against $\log(c\Lambda)$. Values of $\log(c\Lambda)$ are plotted as abscissas for both these curves on a common scale which is shown at the bottom of the figure. The scale of ordinates of the m-D plot is shown on the figure at the points where the curve crosses the parallels to the axis of abscissas. The scale of $1/\Lambda$ is shown on the right-hand margin of the figure. The curve drawn in the $(1/\Lambda) - \log(c\Lambda)$ plot was calculated from Equation III, employing the constants given above.

It is evident that the general equation expresses the experimental results well within the limits of error. All the points plotted are experimental points and not averaged points from a smoothed curve. Values beyond 6000 liters were not plotted, since they do not even approximately accord with the rest of the measurements.

From the constants, the minimum point in the conductance curve (or the maximum when $1/\Lambda$ is plotted) is found by means of Equations VIII and IX. This gives: $c'\gamma' = 0.0252$, $c' = 0.1169$, and $\gamma' = 0.2154$. In the concentrated solutions the experimental values of $1/\Lambda$ rise above the curve, doubtless owing to viscosity. This explanation for the trend of the conductance curve was first advanced by Franklin and Gibbs(27), and is unquestionably correct.[1] It appears in the case of all solutions, and always in the neighborhood of normal concentration. In the case of potassium iodide in sulfur dioxide it is appreciable above 0.5 normal.

TABLE XIV.—IONIZATION OF POTASSIUM IODIDE IN SULFUR DIOXIDE AT $-10°$.

$c\gamma$.	c.	100γ.	Λ.
0.5	1.865	26.81	53.37
0.2	0.8162	24.50	48.76
0.1	0.4326	23.11	46.01
0.05	0.2272	22.01	43.80
0.0252	0.1169	21.54	42.87[2]
0.01	0.04373	22.87	45.51
0.005	0.01880	26.59	53.16
0.002	0.005367	37.27	74.16
0.001	0.001997	50.07	99.65
0.0005	0.0007719	64.79	128.9
0.0002	0.0002458	81.37	161.9
0.0001	0.0001116	89.62	178.3
....	....	100.00	199.0

Table XIV will assist in gaining an idea of the ionization relations of solutions in sulfur dioxide. In the first column are given the values of liquid ammonia solutions, it is perhaps better to use the regular plots; but when the Λ_0 values are uncertain, as in sulfur dioxide solutions and in aqueous solutions (Section IX), several trials may have to be made to determin values of Λ_0 consistent with the K-D plot. Therefore it is then preferable to employ $c\Lambda$ rather than $c\gamma$ as variable, since the former is independent of Λ_0. Compare Section IX.

[1] See last paragraph of Section III C.
[2] Conductance minimum.

the ion-concentrations $(c\gamma)$; in the second, third, and fourth columns are given, in order, the corresponding values of the total salt concentration c, the percentage ionization 100γ, and the equivalent conductance Λ.

It will be seen in this table that the lowest ionization, at 0.1169 normal, is 21.54 per cent., and that in a normal solution the ionization is not far from 25 per cent. This is striking in view of the fact that sulfur dioxide is usually considered to be a poor ionizing agent. The correctness of this view is shown, however, by the data in dilute solutions; for at a dilution of 10,000 liters the ionization is only about 90 per cent. This is much lower than in ammonia, acetone, and similar solvents at the same concentration.

Comparison with Typical Salts in Ammonia.—The constants for potassium iodide in sulfur dioxide differ considerably in relative values from those in ammonia. The value of K (which is the chief determining factor for the ionization in very dilute solutions) is much smaller than for the typical salts in ammonia, but the value of D is relatively much larger. Thus, for typical salts in ammonia, K is about 26×10^{-4} and D is 0.35; while for potassium iodide in sulfur dioxide K is only 8.5×10^{-4} and D is 0.40. Because of the large value of D relative to that of K the deviations from the mass-action law appear in more dilute solutions than in ammonia.[1]

An examination of the conductance curves obtained by various investigators for other salts in sulfur dioxide shows that the mass-action constants vary greatly for different electrolytes. Indeed, the range of the conductance curves in moderately dilute solutions is so great that Walden and Centnerszwer[2] were somewhat inclined to question the law of the additivity of ionic conductances. The low degree of ionization of potassium iodide in dilute sulfur dioxide solutions makes it practically certain that this apparent discrepancy is due to the differences in the degree of ionization of different electrolytes at a dilution of about 2000 liters.

Effect of Temperature.—The influence of temperature on the conductance of solutions in sulfur dioxide is worthy of note. From a preliminary examination of the constants of potassium iodide in sulfur dioxide, it was found that for the temperature interval from $-35.5°$ to $+10°$ the value of m increases from about 1.06 to 1.21, the value of K decreases very considerably, while that of D remains nearly constant. This change in the value of the constants accounts completely for the peculiar relations observed by Franklin(28) between the conductance and the temperature of sulfur dioxide solutions, as will be seen from the following considerations.[3]

[1] This makes it correspondingly difficult to determin the Λ_0 value correctly in sulfur dioxide solutions from measurements in dilute solutions alone.

[2] Walden and Centnerszwer (38), p. 530.

[3] This analysis of the effect of temperature on the conductance curves is practically the same as that of Franklin (28), except that here the results are interpreted in terms of the constants of the general equation.

On solving Equation III for $\gamma/\mathrm{i} - \gamma$ we obtain:

$$\frac{\gamma}{\mathrm{i} - \gamma} = D\,(c\gamma)^{m-1} + \frac{K}{c\gamma}. \qquad (IIIa)$$

Bearing in mind, now, the fact that with increasing temperature m increases, K decreases, and D changes but little, we may follow out the influence of temperature on the conductance curve. For the value of $c\gamma$ equal to unity, $\gamma/(\mathrm{i} - \gamma)$ and therefore γ is practically independent of the temperature, since $(c\gamma)^{m-1}$ equals unity, D changes but little, and K is negligible. As a result, with increasing temperature, the conductance of this concentrated solution increases because of the increased value of Λ_0 arising from increased fluidity of the solvent. In very dilute solutions, where the ionization is practically complete, and therefore nearly constant, the conductance will likewise increase because of increasing fluidity. For certain intermediate concentrations, however, where $c\gamma$ is less than unity, but still large enough so that the term $D\,(c\gamma)^{m-1}$ is a major term in Equation IIIa, the ionization decreases with increasing temperature owing both to the increase of m and the decrease of K. The effect on the conductance of this decrease in γ may be greater than that due to the increase of Λ_0, in which case the conductance must fall as the temperature rises.

In certain cases, therefore, the conductance-concentration curves for two different temperatures will intersect each other twice. In other cases the curves will not intersect but will lie much closer together in the middle than at either end. This is well illustrated by the plots in Franklin's original paper(28).

With increasing temperature the minimum point will be shifted toward higher dilutions. The shift of the minimum point is best shown by the equation for the minimum point:

$$(c'\gamma')^m = \frac{K}{D(m-\mathrm{i})}, \qquad (IX)$$

where $c'\gamma'$ is the ion-concentration at that point. Since D does not change very rapidly with temperature, it follows that $c'\gamma'$ is dependent upon the change in $K/(m-\mathrm{i})$. When the value of m lies near unity, $m-\mathrm{i}$ increases very rapidly with temperature, and, at the same time, K is also decreasing considerably, so that the minimum point is shifted toward higher dilutions.

The above considerations show how little significance is to be attached to measurements of temperature-coefficients of the conductance of solutions, particularly in non-aqueous solvents. The results cannot be interpreted except when the entire conductance curve is shown. Further conductance measurements for a given solvent at different temperatures are much needed; and there can be no doubt that such measurements

will serve to shed some light on the physical factors underlying the constants K, D, and m.

VI. Dilute Solutions in Organic Solvents.

Introduction.—In the preceding sections we have seen that a large variety of electrolytes dissolved in liquid ammonia conform to the mass-action law in very dilute solutions. We shall now examin the remaining experimental material in order to determin whether the mass-action law is generally applicable, especially to solutions of the so-called "strong electrolytes."

Practically the only experimental material which fulfils the necessary conditions of accuracy is that of Dutoit and his associates at the University of Lausanne. Much of this has been published only in the original theses; and we are greatly indebted to Professor Dutoit for his kindness in forwarding us the reprints. Walden has measured the conductance of salts in a very large variety of solvents. With a few exceptions, he has confined his investigations to moderately concentrated solutions, so that his results cannot be utilized for our purpose. In the case of epichlorhydrin and ethylene chloride, he has determined the conductance of solutions of the substituted ammonium salts at dilutions where the mass law is clearly obeyed.

The following is a list of the papers from which data have been taken in this section, the initials being appended for the sake of brevity in references:

Dutoit and Levrier (D–L), *acetone*(15); Dutoit (D), preliminary summary of conductances in various solvents (16); Dutoit and Rappeport (D–R), *ethylalcohol*(17); Dutoit and Duperthuis (D–D), *ethyl-, isoamyl-, isobutyl-*, and *propylalcohols, pyridine*, and *acetone*(18); Benz (B), *acetone* (20); Nicollier (N), *methylethylketone, acetophenone*, and *benzonitrile*(21); Gagnaux (G), *acetoaceticester, isoamyl-* and *isobutylalcohols*(22); Ottiker(O), *propylalcohol* and *pyridine*(23); Walden (W$_I$), *epichlorhydrin*(36); Walden (W$_{II}$), *ethylene chloride*(37).

Nearly all the data recorded in the above papers relate to very dilute solutions. In the introduction, and later in presenting the results in liquid ammonia, we referred to the necessity of careful experimental work in such researches. The investigations considered in this section meet the requirements of concordance and reproducibility.[1] In most cases,

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[1] The experimental methods employed in the Lausanne laboratory are described in the article of Dutoit and Levrier (15). It is to be noted that, in addition to the "method of successive dilutions," the "method of concentration" was also employed. In this method the conductance of the pure solvent was first determined, after which solutions of successively increasing concentration were made by adding small amounts of a solution of high concentration.

the various sources of error were investigated,[1] and the investigations were continued until satisfactory results were obtained.

In the original articles all the results, excepting those of Dutoit and Gyr and of Walden are expressed in Siemens' units. A 0.2 normal solution of KCl at 18° was assumed to have an equivalent conductance of 112.2. We have adopted for this solution the value 119.96, given by Kohlrausch and Maltby(49). Expressed in 1912 atomic weights this becomes 119.9. In converting the results of Dutoit from the Siemens' to the customary unit, the factor 1.069 must therefore be employed. The symbol Λ_s will be employed in this paper to denote that the data are expressed in Siemens' units.

As has already been stated, Dutoit concluded from his work on dilute solutions that the mass-action law holds in nearly all cases. It seemed worth while, however, to examin the results graphically, making use of the Λ_0-K plot, in which values of $1/\Lambda$ and of $c\Lambda$, when plotted against each other, yield a straight line if the mass-action law applies.

Results for a Typical Electrolyte in Various Solvents.—Solutions of sodium iodide have been studied in a larger variety of solvents than any other electrolyte. This salt has accordingly been chosen as a typical electrolyte whereby to compare the electrolytic properties of various solvents. The Λ_0-K plots for sodium iodide in seven different solvents are shown in Figs 20 and 21. In the case of two solvents, *viz.*, acetone and isoamylalcohol, plots are reproduced for lithium bromide and lithium iodide, respectively. In the case of an eighth solvent, acetoaceticester, only two measurements were made with sodium iodide in very dilute solutions and the plot is reproduced for another salt, NaSCN. ·The name of both solvent and solute appears on the plots, save in the case of sodium iodide, for which the name of the salt is omitted. For epichlorhydrin and ethylene chloride, solutions of NaI have not been studied, and the results for substituted ammonium salts were used instead.

Since nearly all the data of the investigations at the Lausanne laboratory are taken from the theses, which are not readily accessible, the original data are given here. At the head of the various parts of the table are given: the name of the solute, that of the solvent, the temperature at

[1] Dutoit and Levrier (15) discuss the following sources of error: the use of platinized electrodes and errors in concentration due to adsorption on the electrode surfaces, chemical reactions between solvent and solute, and errors due to the presence of impurities in the solvent. Nicollier (21) studied a number of cases in which irregular and variable results were obtained as a result of photochemical reaction. The conductance change (decrease) was found to be a function of the intensity of the light and the concentration of the solutions, being relatively greater at higher dilutions. It was found that reproducible results could be obtained in the dark. Such reactions were found in solutions in methylethylketone, acetophenone, benzonitrile, and acetoaceticester, but not in pyridine and the alcohols.

which the measurements were made, the initials of the investigators, and the number of the figure in which the results have been plotted. In the first column are given the series numbers as they appear in the original papers. The letter "C" signifies that the "method of concentration" was employed. The second and third columns contain, respectively, the dilutions and the corresponding equivalent conductances in Siemens' units. The fourth column gives the percentage correction applied for the conductance due to the solvent, and the fifth and sixth columns give respectively the values of $100 \, c \Lambda_s$ and $1000/\Lambda_s$.

TABLE XV.—CONDUCTANCE DATA. FIGS. 20 AND 21.

NaI in Propylalcohol, $18°$ (O), Fig. 20.

Series.	V. ∞.	Λ_s. 19.25 ± 0.2.	Percentage correction.	$100C\Lambda_s$. 0.	$1000/\Lambda_s$. 51.95.	Remarks.
I-C	16700.0	18.93	11.0	0.1134	52.82	
	5870.0	18.51	4.0	0.315	54.02	
	2466.0	17.77	..	0.721	54.27	
II-C	5860.0	18.64	4.0	0.318	53.65	
III	3610.0	18.2	..	0.504	54.95	
	604.7	15.43	..	2.55	64.8	
	159.5	12.27	..	7.595	81.5	
	31.8	8.85	..	27.8	113.0	Not shown
IV	1759.0	17.6	..	1.005	56.82	
	817.0	15.8	..	1.935	63.29	
	284.0	13.5	..	4.755	74.07	
	52.5	10.13	..	19.3	98.7	Not shown

NaI in Acetone, $18°$ (D-L), Fig. 21.

	∞.	156 ± 1.		0.	6.41.	
I	64827.0	156.0	2.8	0.2406	6.411	
	39700.0	155.2	1.7	0.3909	6.443	
	18660.0	154.8	..	0.8297	6.460	
	8874.0	151.0	..	1.702	6.622	
	4083.0	147.7	..	3.617	6.770	
	1030.0	131.1	..	12.73	7.628	
	292.6	112.8	..	38.55	8.865	

LiBr in Acetone, $18°$ (D-L), Fig. 21.

	∞.	154 ± 1.		0.	6.494.	
I	306900.0	148.4	21.0	0.0483	6.739	Rejected
	87850.0	150.8	5.8	0.1717	6.631	
	24100.0	143.0	1.7	0.5933	6.994	
	7087.0	127.4	..	1.798	7.849	
	2137.0	100.3	..	4.694	9.970	
	593.5	68.7	..	11.58	14.55	
	161.1	43.5	..	27.00	22.99	
	51.0	27.7	..	54.31	36.10	Not shown

TABLE XV (*continued*).

Series.	V. ∞.	Λ_s. 154 ± 1.	Percentage correction.	100 $c\Lambda_s$. 0.	1000/Λ_s. 6.494.	Remarks.
II	73340.0	152.5	5.6	0.2080	6.557	
	22074.0	144.7	1.8	0.6556	6.910	
	6040.0	124.4	..	2.060	8.039	
	1787.0	97.4	..	5.451	10.27	
	490.5	64.7	..	13.19	15.46	
	163.1	44.0	..	26.98	22.73	
	56.2	28.0	..	51.25	34.71	Not shown

NaI in Acetophenone, 25° (N), Fig. 20.

	∞.	33.3±0.7.		0.	30.0.	
I	24713.0	33.7	16.0	0.1364	29.67	Λ is high
	9966.0	32.6	6.7	0.327	30.67	
	4784.0	31.2	3.4	0.652	32.05	
	2313.0	28.1	1.8	1.214	35.59	Rejected
	775.8	26.6	..	3.43	37.59	
	324.4	22.8	..	7.03	43.86	Λ is low
	123.3	18.9	..	15.33	52.91	Not shown
	67.0	16.8	..	25.1	59.52	Not shown
II	32743.0	34.0	21.0	0.104	29.41	Λ is high
	12143.0	32.6	8.2	0.268	30.67	
	1558.0	28.8	..	1.85	34.72	
	700.0	26.5	..	3.79	37.74	
	275.4	22.6	..	8.20	44.25	Not shown
	123.0	18.2	..	14.80	54.95	Not shown
III	27380.0	29.0	21.0	0.106	34.48	Rejected
	5387.0	28.5	4.2	0.530	35.09	Rejected
	2569.0	30.2	1.9	1.175	33.11	
	998.0	27.9	..	2.79	35.84	
	437.0	25.0	..	5.72	40.00	Λ is high

NaI in Methylethylketone, 25° (N), Fig. 21.

	∞.	130.0±2.		0.	7.69.	
I	110860.0	129.0	15.0	0.1164	7.752	
	30244.0	127.4	4.0	0.4213	7.849	
	7534.0	123.4	..	1.638	8.104	
	2730.0	114.1	..	4.179	8.764	
	876.5	98.9	..	11.28	10.11	
	387.3	84.6	..	21.84	11.82	

NaI in Pyridine, 18° (O), Fig. 21.

	∞.	57.0±0.5.		0.	17.54.	
I-C	210100.0	57.47	19.0	0.02736	17.40	
	90480.0	56.8	8.0	0.0638	17.61	
	44160.0	56.24	4.0	0.1274	17.78	
	26000.0	55.5	2.4	0.2134	18.02	
	13863.0	53.9	..	0.3886	18.55	
II-C	47770.0	55.8	5.2	0.1168	17.92	
	15515.0	54.1	..	0.3485	18.48	
	8752.0	52.6	..	0.601	19.01	

TABLE XV (continued).

NaI in Pyridine, 18° (O), Fig. 21.

Series.	V. ∞.	Λ_s. 57.0 ± 0.5.	Percentage correction.	100 $c\Lambda_s$. 0.	1000/Λ_s. 17.54.	Remarks.
III	23630.0	54.5	..	0.2305	18.35	
	2736.0	47.6	..	1.738	21.01	
	383.4	34.7	..	9.06	28.82	Not shown
	57.7	23.6	..	......	.....	
IV	11042.0	53.8	..	0.487	18.59	
	3987.0	50.0	..	1.254	20.00	Λ is high
	1461.0	43.5	..	2.977	22.99	
	507.5	36.73	..	7.24	27.23	
	114.6	27.28	..	......	.....	
V	6879.0	51.36	..	0.806	19.47	
	4184.0	48.80	..	1.166	20.49	Λ is low
	1970.0	44.53	..	2.260	22.45	Λ is low
	814.7	39.30	..	4.825	25.45	
	215.5	30.68	..	14.23	32.45	Not shown

NaI in Isobutylalcohol, 25° (G), Fig. 20.

	∞.	12.8±0.2.		0.	78.1.	
I	11220.0	12.12	5.7	0.108	82.5	
	4970.0	11.14	2.8	0.224	89.8	
	1986.0	9.71	..	0.489	103.0	
	990.0	8.06	..	0.814	124.1	Λ is low
	438.4	6.84	..	1.556	146.2	
II	23106.0	12.47	4.6	0.054	80.2	
	5750.0	11.27	1.3	0.196	88.7	
	1643.0	9.35	..	0.569	107.0	
	567.0	7.46	..	1.315	134.0	Λ is high
	170.4	5.28	..	3.10	189.4	
III-C	36220.0	12.51	9.3	0.0345	79.95	
	8907.0	11.84	2.5	0.133	84.45	
	3751.0	10.78	..	0.287	92.8	

NaI in Acetoaceticester, 18° (G).

	∞.	28.7 ± 1.0.		0.	34.8.	
I-C	12457.0	27.86	8.7	0.2237	35.93	K cannot be ob-
	7461.0	27.30	5.3	0.3660	36.63	tained from Λ_0-K plot

NaSCN in Acetoaceticester, 18° (G), Fig. 20.

	∞.	30.0±0.5.		0.	33.3.	
I	20690.0	28.46	6.4	0.1375	35.14	
	7380.0	27.03	2.4	0.366	37.00	
	2688.0	23.10	..	0.860	43.29	
	826.0	17.35	..	2.100	57.63	
	300.0	13.04	..	4.347	76.7	
	131.7	10.09	..	7.66	99.1	

TABLE XV (continued).

Series.	V. ∞.	Δ_S. 30.0±0.5.	Percentage correction.	100 $c\Delta_S$. 0.	1000/Δ_S. 33.3.	Remarks.
II	17540.0	28.25	6.1	0.161	35.4	
	6131.0	26.28	2.3	0.427	38.06	
	2411.0	22.81	..	0.946	43.84	
	644.3	16.41	..	2.545	60.93	
	204.3	11.73	..	5.74	85.25	

LiI in Isoamylalcohol, 25° (G), Fig. 20.

	∞.	8.6±0.2.		0.	116.	
I	13303.0	7.98	6.6	0.060	125.3	
	4350.0	6.81	2.5	0.1565	146.8	
	1440.0	5.44	..	0.378	183.8	
	3568.0	3.60	..	1.01	277.8	Not plotted
II	64704.0	8.35	30.0	0.0129	119.8	
	19790.0	8.07	9.5	0.0416	123.9	
	4672.0	6.98	2.6	0.1493	143.3	
	1205.0	5.11	..	0.424	195.7	

NaI in Isoamylalcohol, 25° (G), Fig. 20.

	∞.	8.9±0.3.		0.	112.	
I	18410.0	8.07	5.6	0.0438	123.9	
	9018.0	7.15	3.1	0.0793	139.9	
	4604.0	6.25	1.8	0.1357	160.0	
	2225.0	5.32	..	0.240	188.0	
	1068.0	4.20	..	0.393	238.1	
II	54185.0	·8.41	19.0	0.0155·	118.9	
	28091.0	8.30	10.0	0.0295	120.5	
	12482.0	7.70	5.0	0.0617	129.9	
	5133.0	6.36	2.4	0.124	157.2	
	2084.0	5.15	..	0.247	194.2	

Since the results of Walden are readily accessible, they are not reproduced here. It should be stated, however, that in the case of $(C_2H_5)_4NI$ in epichlorhydrin the highest dilution measured was 25,600 liters; and, for $(C_3H_7)_4NI$ in ethylene chloride, the highest dilution reached was 30,000 liters. The maximum correction due to conductance of the solvent did not exceed 2.5 per cent. in the former case and was negligible in the latter. For $(C_2H_5)_4NI$ in epichlorhydrin, the value found for Λ_0 is 62.1 ≠ 0.3, and for $(C_3H_7)_4NI$ in ethylene chloride 66.7 ≠ 2.0.

The Λ_0-K plots are reproduced in Figs. 20 and 21. It should be noted that in Fig. 20, for NaI and LiI in amylalcohol (the first and last plots on the figure), values of 1000 $(c\Lambda)$ are plotted as abscissas instead of 100 $(c\Lambda)$, as shown in the scale for the remaining plots. In the case of LiI in amylalcohol, the smooth curve is drawn so as to pass through a point which lies outside the figure. In Fig. 21 for NaI in pyridine (the first plot) and for $(C_2H_5)_4NI$ in epichlorhydrin and $(C_3H_7)_4NI$ in ethylene chloride (last two plots), the scale differs from that of the remaining plots as is shown at the top of the figure.

In some cases the points are not shown on the plot for the reason that the concentrations extend beyond the region as reproduced in the figure; such points are marked "not plotted" in the table. In case the deviations of any point from the mean position is so large as to indicate an error far beyond what might be expected, is is marked "rejected."
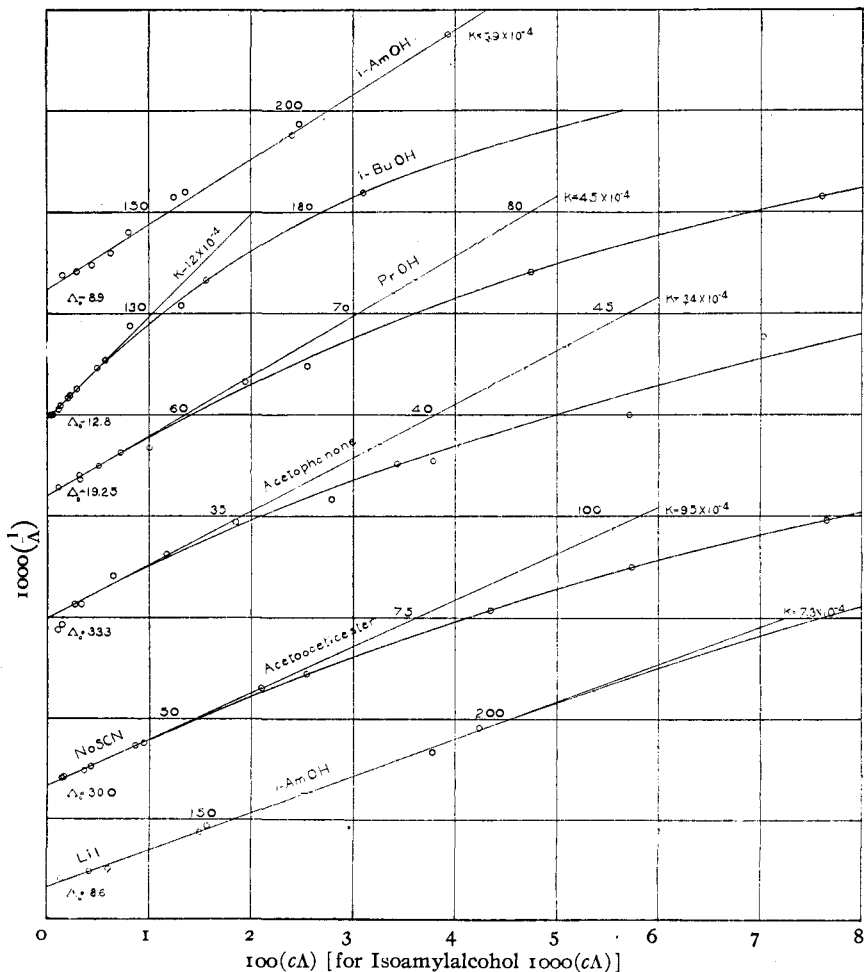

Fig. 20.—Λ_0-K Plot for NaI in different Solvents and NaSCN in Acetoaceticester and LiI in Amylalcohol

The values of Λ_0 (in Siemens' units) and of K were calculated from the plots and are shown in the figures. Λ_0, corresponding to $v = \infty$, is given for each substance in Table XV, and the estimated error is shown. These errors lie between 1 and 3 per cent., but they may be larger, if the deviations from the mass law are appreciable at lower concentrations, than we have

assumed.   The results of Walden are expressed in the customary Kohl-rausch units.

An examination of the data and of the corresponding figures shows that the results are fairly regular, except in one or two cases.[1]
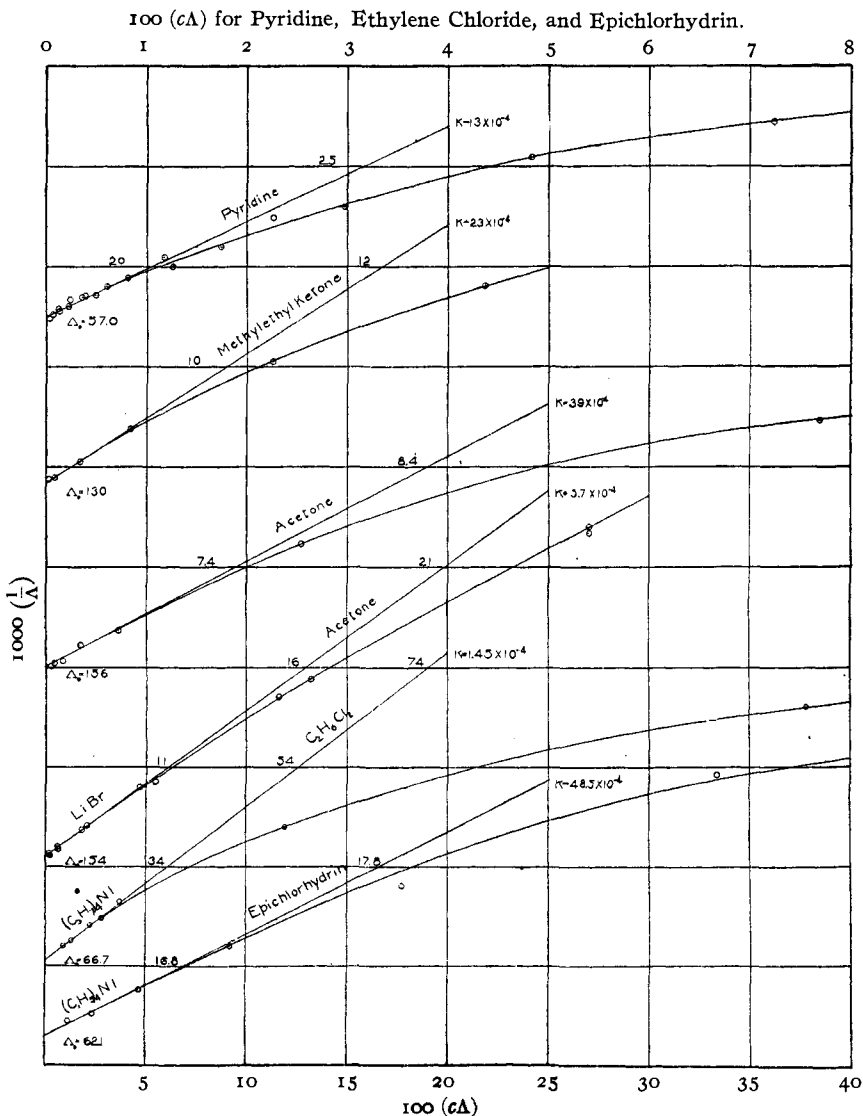
Fig. 21.—Λ_0-K Plots for NaI in Different Solvents and for LiBr in Acetone.

[1] Thus, the two points shown in the plot for the most dilute solutions of sodium iodide in acetophenone (Fig. 20) have been rejected since the percentage correction due to the conductance of the solvent amounts to 16 and 21%, respectively.   Series

The results of the graphical examination are summarized in Table XVI. Here Λ_o is expressed in reciprocal ohms, its value being obtained by means of the conversion factor (1.069) previously given. The fluidity[1] of ten of the solvents at the temperature at which the conductance measurements were made is also given in the table (column 5).

TABLE XVI.—VALUES OF Λ_o AND K, FIGS. 20 AND 21.

Solvent.	Solute.	Figure.	Temper-ature.	Fluidity.	Λ_o.	$K \times 10^4$.
Benzonitrile............	NaI	..	25°	80.0	49.0	55.0
Epichlorhydrin..........	$(C_2H_5)_4NI$	21	25°	97.1	62.1	48.5
Propylalcohol	NaI	20	18°	42.5	20.6	45.0
Acetone................	NaI	21	18°	304.0	167.0	30.0
Acetophenone..........	NaI	20	25°	...	35.6	34.0
Methylethylketone......	NaI	21	25°	249.0	139.0	23.0
Pyridine...............	NaI	21	18°	101.0	61.0	13.0
Isobutylalcohol	NaI	20	25°	29.6	13.7	12.0
Acetoaceticester	NaI	..	18°	59.4	30.7	...
Acetoaceticester	NaSCN	20	18°	...	32.1	9.5
Isoamylalcohol	NaI	20	25°	27.2	9.2	3.9[2]
Isoamylalcohol	LiI	20	25°	...	9.2	7.3
Ethylenechloride	$(C_3H_7)_4NI$	21	25°	127.9	66.7	1.45

The mass-action constant for sodium iodide in benzonitrile is only a rough approximation. In the case of sodium iodide in acetoaceticester, the data do not admit of a reliable determination of the constant. Since the data for NaSCN in this solvent are concordant, the constant for this salt is included in the table. In the case of isoamylalcohol, the value of K seems abnormally low for NaI. The value of K for LiI is accordingly included in the table.

III is unsatisfactory, but in this case the solutions were prepared by adding to the acetophenone a small quantity of a concentrated solution of sodium iodide in another solvent, acetone. Later investigations at the Lausanne laboratory have shown that this method does not give reliable results. Finally, it is to be noted that acetophenone is one of those solvents which is very sensitive to the action of light. In such cases it seems to be difficult to obtain concordant results, even when precautions are taken to exclude light. The results for sodium iodide in benzonitrile are so unsatisfactory that the plot has been omitted; they are not sufficiently concordant to admit of their serving as evidence with regard to the applicability of the mass-action law. Assuming this law, however, it is possible to approximate the values of Λ_o and K (see Table XVI).

[1] The fluidity is expressed as the reciprocal of the viscosity in absolute units. It is to be noted that the Λ_o values (column 6) are approximately proportional to the fluidities for the solvents shown in Table XVI, and that the average value of this ratio for such organic solvents is 0.517. This ratio is abnormally large in some inorganic solvents, as ammonia and water, as was pointed out in Section IV. Compare Walden (72).

[2] As a result of an investigation in this laboratory, by Dr. F. G. Keyes and Mr. W. J. Winninghoff, it appears that this value of K is too low. The work will be published shortly.

The results here tabulated will be discussed more fully later in this article. It may, however, be pointed out in this place that the mass-action law holds in all these solvents at sufficiently high dilutions, and that at somewhat higher concentration deviations from this law appear which increase rapidly with increasing concentration. Since the constants m and D are not known, it is not possible to make an exact comparison of the concentrations at which a given deviation appears in the different solvents. We can, however, estimate roughly the points on the plots at which the deviations from the straight line exceed the experimental error. In Table XVII are given the values of $100\,c\Lambda$ and $10^4 c\gamma$ resulting from such an approximation:

TABLE XVII.—APPROXIMATE LIMITS AT WHICH DEVIATIONS FROM THE MASS-ACTION
LAW BECOME APPRECIABLE.

Solvent.	Solute.	Figure.	$100\,c\Lambda$.	$10^4\,c\gamma$.
Propylalcohol	NaI	20	1.2	6.0
Acetone.....................	NaI	21	8.0	5.0
Acetone.....................	LiBr	21	7.0	4.5
Acetophenone...............	NaI	20	1.2	3.6
Methylethylketone...........	NaI	21	4.5	3.5
Pyridine....................	NaI	21	1.0	1.7
Isobutylalcohol	NaI	20	0.7	5.5
Acetoaceticester	NaSCN	20	1.8	6.0
Isoamylalcohol	LiI	20	0.7	8.0

From an inspection of the table it appears that the deviation from the mass-action law becomes appreciable in different solvents at approximately the same ion-concentration, namely, at 4 to 6×10^{-4} normal. The ion-concentration appears somewhat above the average for isoamylalcohol (8×10^{-4}) and somewhat below it for pyridine (1.7×10^{-4}); but these differences may be due, in part, to the errors inherent in the method employed for determining the point at which the deviation becomes appreciable.

It is to be noted that the values of Λ_0 which we find for solutions in epichlorhydrin and in ethylene chloride differ considerably from those given by Walden in his papers; thus for $(C_2H_5)_4NI$ in the epichlorhydrin he gives the value 66.6, and for $(C_3H_7)_4NI$ in the ethylene chloride 78.6. These discrepancies are due to the fact that different functions were employed for the purpose of extrapolation. Walden employs for this purpose the function which Kohlrausch has used to express the results for water solutions, namely: $\Lambda = \Lambda_0 - ac^{1/3}$, when a is a constant. Walden's method of applying this function consists in eliminating a between two points and solving for Λ_0. This was done, in general, for successive points, and the results were averaged. It is obvious that, since the mass-action law applies to dilute solutions, the Kohlrausch function must lead

to false results. An inspection of the results obtained by Walden indicates that this function gives much too large values for Λ_0.[1]

Results for Other Electrolytes in Acetone.—The results of earlier investigations on the conductance of acetone solutions have been discussed by Dutoit(39). As has been stated previously in this section, measurements in acetone are liable to be seriously affected by several sources of error. Since these were not taken into account in the earlier investigations, the results obtained are not concordant and cannot be utilized in testing the applicability of the mass-action law. In this section we shall limit the discussion to the data furnished by Dutoit and Levrier, by Benz, and by Dutoit and Duperthuis.

The material in question was examined in the usual way by means of the Λ_0-K plot. It seemed unnecessary, however, to reproduce the plots, since several examples have already been given for solutions in acetone (Fig. 21). The results have accordingly been collected in Table XVIII. All the data are due to Dutoit and Levrier except the last three, which are due to Benz. The Λ_0 values are expressed in Siemens' units.

TABLE XVIII.—SUMMARY OF RESULTS IN ACETONE AT 18°.

Solute.	Number of		Values of Λ_0.			$K \times 10^4$.		Mass law agreement.
	Series.	Points.	Previous investigator.	K–B, preliminary.	K–B. adopted.	Investigator.	(K–B).	
KI	1	7	157.5	156 ± 1	156	43.0	51.0	Poor
NaI	1	7	155.5	156 ± 1	156	..	39.0	Fair
LiI	1	6	157.0	155 ± 1	154	..	31.0	Poor
NH₄I	1	7	157.5	160 ± 1	159	16.4	15.0	Fair
KSCN	1	7	170.0	169 ± 1	169	..	31.0	Fair
LiSCN	1	7	...	169 ± 3	167	..	18.0	Poor
NH₄SCN	1	7	171.0	172 ± 3	172	..	8.3	Poor
KBr	2	10	155.5	157 ± 1	156	..	16.0	Good
NaBr	2	12	158.0	156 ± 1	156	..	13.0	Good
LiBr	2	14	155.0	154 ± 1	154	..	5.7	Good
NH₄Br	2	13	157.5	157 ± 6	159	..	2.3	Good
LiNO₃	2	10	132.0	125 ± 3	125	1–2	2.6	Good
AgNO₃	2	10	...	100 ± 5	100	..	0.28	Good
LiCl	3	16	...	154 ± 6	154	..	0.94	Good

The formula of the solute is given in the first column, and the number of series of measurements made and the total number of points determined are given in the second and third columns, respectively. In the fourth column are given the values of Λ_0 derived by the original investigators from their experiments. In the fifth column are given the values as originally determined by us from Λ_0-K plots together with the estimated error. The error was determined from the plots by assuming the extreme position of the straight line which might be drawn through the points with-

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[1] We shall see below (Section IX), that in aqueous solutions, also, this function has led to values of Λ_0 which are too large.

out exceeding what appeared to be the limit of concordance of the experimental values. In the sixth column are given the values of Λ_o finally adopted as being mutually consistent with the law of additivity of ionic conductances. In the seventh and eighth columns are given the values of $K \times 10^4$, and in the last column is indicated the nature of the agreement with the mass-action law.

It is seen that the agreement with the law of mass action is much more satisfactory for the weaker than for the stronger electrolytes, the reason for which has already been discussed at length in Section IIIC. In general, taking into account the errors by which measurements in dilute acetone solutions are liable to be affected, the agreement is as good as could be expected. The divergences are probably largely due to experimental errors.[1]

It is to be noted that in every case the values finally adopted for Λ_o come within the limits of error of the preliminary estimate. As was to be expected, the error in Λ_o is greater the smaller the dissociation constant of the electrolyte. In six out of eleven cases, the Λ_o values given in the original papers lie outside the limits of error which we have given. This is not surprising, since the values seem to have been chosen more or less arbitrarily, presumably from a plot of Λ against $\log v$. The uniform mutual consistency of the Λ_o values obtained from the Λ_o-K plots illustrates the advantage of this method of determining these values.

Inspection of the table shows that the ion-conductances are the same for chloride, bromide, and iodide ions. The ion-conductance of the nitrate ion is much lower, while that of the sulfocyanate ion is considerably higher than that of the halide ions. The conductance is the same for Na^+ and K^+, but for Li^+ it is slightly lower and for NH_4^+ slightly higher. On the other hand, the conductance of the silver ion is much smaller than that of the Na^+ ion.

As was pointed out in speaking of ammonia solutions, the order of the conductance values of the different ions differs from solvent to solvent. In ammonia K^+ has a much greater conductance than Na^+, while that of

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[1] Thus in the case of LiCl (B), the Λ values for one series, while concordant with one another, are not in agreement with those of the first and third series. Either set of values is in good agreement with the mass law. The value of Λ_o from the second series is in the neighborhood of 148. It seems probable that the discrepancy is due to an error in concentration.

It should also be stated that the Λ values of NH_4I and NH_4SCN (D–L) were found to decrease on standing. The data given relate to values obtained when the measurements were carried out rapidly. The second series for NH_4SCN was rejected on account of this error. The Λ values for the three most dilute solutions of KI and LiI were rejected, since they were found to lie far above the straight line on the Λ_o-K plot. The points for LiSCN and NH_4SCN were found to be rather irregular when plotted on the Λ_o-K plot. In fact, the results for sulfocyanates, in general, were found to be less satisfactory than for iodides and bromides.

NH_4^+ is practically the same as that of Na^+. In acetone the conductances of Na^+ and K^+ are the same while that of NH_4^+ is greater. On the other hand, in ammonia NO_3^- has the same conductance as Br^-, while Cl^- has the greatest conductance of any anion in ammonia. It is clear that the conductance of any ion is a function of the characteristic properties both of the solvent and of the fundamental element or group of elements that constitutes the essential invariant structure of the ion.

As regards the mass-action constants, acetone solutions are striking because of their regularity. While, in the case of ammonia, we found many transpositions in the order of the K values for different salts, in acetone the same order holds throughout without exception. Thus, the mass-action constant K decreases in the order of K, Na, Li, NH_4, Ag for all the salts with a common anion. For salts with a common cation the order of decreasing values of K is I, SCN, Br, NO_3, Cl.

The variation of the constant K for the typical salts in acetone is much greater than in ammonia. For fourteen common salts in ammonia $K \times 10^4$ varies from 12 to 42 and for ten of these the value of $K \times 10^4$ lies between 21 and 28. For the fourteen salts in Table XVIII, $K \times 10^4$ varies from 0.28 to 51, the ten highest values vary from 5.7 to 51, and only the four highest lie between 31 and 51.

It is thus seen that the dissociation of salts in different solvents is greatly influenced by the individual relationship of solvent to solute. At the same time, it is evident that in different solvents certain solutes always appear among the most highly dissociated in all cases.

Dutoit and Duperthuis have measured the conductance of NaI in acetone at intervals of 10°, from 0° to 40°. Not more than four dilutions were measured at any one temperature; and, while the results agree with those of Dutoit and Levrier as well as could be expected, the number of measurements is too small to be of value in testing the mass-action law.

Results for Other Electrolytes in Pyridine.—For solutions in pyridine, much less material is available than is the case with solutions in acetone. The best results are due to Ottiker(23). The following table is based on Ottiker's experimental values. The arrangement of the table is the same as that of Table XVIII and the meaning of the different quantities will be clear from the captions of the columns.

TABLE XIX.—SUMMARY OF RESULTS IN PYRIDINE AT 18°.

Solute.	Number of		Λ_0: Ottiker.	$\Lambda°$ (K–B).		$K \times 10^4$.		Mass law agreement.
	Series.	Points.		Preliminary.	Adopted.	Investigator.	(K–B).	
NaI......	5	22	57.3	57.0 ± 0.5	57.0	12.0	13.0	Fair
RbI......	5	17	61.3	....	..	5.5	..	...
KI.......	7	20	60.0	59.5 ± 1.0	59.5	5.3	5.2	Poor
KSCN....	3	10	62.6	62.5 ± 0.5	62.5	4.1	4.1	Fair
NaSCN...	5	16	59.2	59.2 ± 0.5	60.0	2.0	1.9	Fair

The Λ_0 values in this table are expressed in Siemens' units. Ottiker's values were obtained by eliminating K from the mass-action law expression between pairs of points and solving for Λ_0. Actually, Ottiker first drew a smooth curve through his points and then calculated Λ_0 from a number of pairs of points on this curve in dilute solutions, averaging the results. The Λ_0-K plot is preferable to this method, since it gives a weighted mean. In any case, it is not allowable to average results of conductance measurements by means of a smooth curve unless the curve approaches a straight line very closely.

In the main, the Λ_0 values obtained by Ottiker are in good agreement with the values which we have obtained. An estimate of the nature of the agreement with the mass-action law may be made by consulting Fig. 21.

The four salts NaI, KI, KSCN, and NaSCN have also been investigated by Dutoit and Duperthuis(18) at intervals of 10°, from 0° to 80°. Since only four or five measurements were made for each salt, the values of Λ_0 and K may be affected by considerable error. Dutoit and Duperthuis calculated the Λ_0 values from pairs of experimental points; but all possible pairs of points were not computed, and this undoubtedly introduced some error into their Λ_0 values.

On examining the Λ_0 values given by these investigators it was found that the difference in the Λ_0 values for KI and NaI is not equal to that for KSCN and NaSCN. Also, when the Λ_0 values of each salt were plotted against temperature, some errors were at once detected. The following table embodies some of the results based on preliminary values of the Λ_0-K plots which are concordant among themselves.

TABLE XX.—VALUES OF Λ_0 AND K FOR PYRIDINE SOLUTIONS AT DIFFERENT TEMPERATURES.

Solute.	Λ_0 in Siemens' Units				10^4K			
	10°.	18°.	20°.	30°.	10°.	18°.	20°.	30°.
NaI.....................	50.8	57.9	59.9	69.3	12.0	10.3	9.9	8.8
KI.....................	53.0	60.2	62.1	71.5	5.9	5.3	5.2	4.6
KSCN.................	54.8	62.3	64.2	73.9	4.9	4.3	4.1	3.6
NaSCN...............	52.6	60.0	62.0	71.7	2.1	1.9	1.9	1.7

The values given under 18° were obtained by interpolation from plots of Λ_0 and K against temperature. Comparison with the results of Ottiker at 18° shows that the agreement is satisfactory except, perhaps, for NaI. But even in this case the agreement is fully as good as was to have been expected, since the results of Dutoit and Duperthuis for NaI at 0° and at 10° are not concordant among themselves. The same is true for some of the other substances at these temperatures.

A sufficiently large number of electrolytes has not been investigated in pyridine to enable us to draw any conclusions as to the regularity of

the Λ_0 and K values for different substances. As is the case in ammonia, the Λ_0 values for potassium salts in pyridine are considerably higher than those of sodium salts. The conductivity of the SCN$^-$ ion is greater than that of the I$^-$ ion, a result similar to that obtained in the case of acetone solutions.

The most striking feature of the K values is the abnormally high value of K for NaI as contrasted with that for KI. This appears to be quite exceptional so far as our knowledge goes; for, both in ammonia and in acetone, the value of K is markedly greater for KI than for NaI. This is the more remarkable, since pyridine is closely related to ammonia in constitution. Moreover, in the case of the sulfocyanate, the value of K for the potassium salt is much greater than for the sodium salt. Judging by the variation of K for the five salts appearing in Table XIX, the dissociation constants for typical salts in pyridine are subject to a much wider range of variation than they are in ammonia.

VII. General Discussion of Dilute Solutions.

Having presented all the available data relating to the conductance of dilute solutions in various solvents, it remains to consider the problem in its broader aspects. That the mass-action law is applicable in the case of all the solutions for which data have been presented is clear from what has already been said, and we may therefore conclude that the fundamental principles underlying the ionic theory are correct. It is scarcely conceivable that the results obtained for so many and so great a variety of electrolytes in dilute solutions could be explained on any other basis than that of an ionic equilibrium. Not only is the mass-action law obeyed whenever the ionization of the salt is sufficiently low to permit of determining the concentrations of the different molecular species with a reasonable degree of precision, but whenever sufficient data are available, the law of Kohlrausch relating to the additivity of ionic conductances is also corroborated in a most striking manner.

In one respect, however, current conceptions must be modified. The concentration of a solution at which it may be considered as behaving substantially as a perfect solution is far smaller than has commonly been assumed to be the case. As a rule, a 0.1 normal solution has been considered as being sufficiently near to ideal conditions for practical purposes. This conclusion seems to have been reached from a consideration of the analogous behavior of gases at the same concentration. For certain properties of solutions, viscosity for instance, this concentration may perhaps be looked upon as a limiting region below which correction factors may be neglected; but when we consider that in electrolytic solutions we are dealing with an equilibrium involving charged particles between which, under certain conditions, forces may come into play which are enormously greater than those acting between neutral molecules, it becomes clear

that the concentration limit beyond which electrolytic solutions may be treated as perfect solutions can only be determined from an examination of electrolytic solutions themselves.

From a consideration of the results presented in this paper it follows that the concentration limit below which electrolytic solutions may be treated as perfect solutions is determined, not by the total concentration of the electrolyte, but by the concentration of the ions themselves. The laws of perfect solutions are not applicable to electrolytic solutions above an ion-concentration varying between 1×10^{-3} and 1×10^{-4} normal. It is evident that, for electrolytes which are strongly dissociated, the laws of perfect solutions may not be applied when their concentration exceeds 1×10^{-3} to 1×10^{-4} equivalents per liter. On the other hand, weak electrolytes will in general obey the laws of perfect solutions up to much greater total concentration.

This explains the behavior of the weak acids and bases in water. It also shows that it is not to be expected that the mass-action law should be found to apply to solutions of strong electrolytes in water; for, in the region where the mass-action law should hold, the dilution is so great and the un-ionized fraction is so small that this fraction cannot be determined with the degree of precision necessary in testing the law. This matter will be more fully discussed in Section IX.

In the discussion of the results in ammonia (Section IIIC) it was shown that the general relation (Equation III) is obeyed by both the highly and the slightly ionized substances. It was pointed out that strong and weak electrolytes in this solvent evidently differ in no wise save in degree, and that this difference is completely accounted for by the magnitude of the mass-action constant K. It is a very striking fact that the ionization constants for ten inorganic salts in ammonia lie between the narrow limits 21 and 28×10^{-4}, and that only in the case of potassium iodide was a higher value of K obtained. It seems natural to regard these most highly ionized salts as "typical strong electrolytes" in ammonia, and to accept this value of K as an approximate measure of the ionizing power of the solvent ammonia. In this connection it may be noted that a large number of uni-univalent salts in aqueous solution are ionized to nearly the same extent and that these are regarded as the typical strong electrolytes in water. In general, salts which are among the most highly ionized in water are also among the most highly ionized in ammonia.

In the other solvents investigated, fewer examples are available and the ionization constants of ordinary salts show greater variation than in ammonia; but there is no reason for doubting that the ionizing power of each solvent may be measured by the ionization constants of the most highly ionized substances in that solvent. In acetone the ten highest values of $K \times 10^4$ lie between 5.7 and 51, and four of these (for KSCN,

LiI, NaI and KI) are greater than 31; from which it follows that acetone is to be regarded as a slightly better ionizing agent than ammonia. On the other hand, in pyridine the three highest values of $K \times 10^4$ (for KI, RbI and NaI) lie between 5 and 12.0, and in sulfur dioxide the value for KI is 8.5; and these two solvents are thus poorer ionizing agents than ammonia.

We have thus been led to the conclusion that the best measure of the ionizing power of a solvent is obtained by determination of the ionization constants of several of the substances most highly ionized in it. An examination of the available data shows that certain salts appear almost uniformly among the most highly ionized substances in each solvent, for example, sodium iodide, potassium iodide, potassium chloride and the tetra-substituted ammonium salts. One of these may therefore be taken as a typical strong electrolyte, and a fair approximation of the ionizing power of solvents may be made by comparing its K values in different solvents. Such a comparison has been made in Table XVI for sodium iodide in several organic solvents. These solvents have been arranged in order of decreasing values of K, and it is probable that the ionizing powers decrease in the same order.

Such a comparison of the ionizing power of solvents by means of the mass-action constants of typical electrolytes, however, is reliable only in dilute solutions, that is, in solutions in which the law of mass action holds. In the more concentrated solutions the ionization of a given salt is a function not only of K, but also of D and m. Thus, it has been pointed out that in concentrated solutions potassium iodide is more highly ionized in sulfur dioxide than in ammonia, although the converse is true in dilute solutions. The phenomenon is therefore completely described only when all the constants are known. This matter will be fully considered in a later section of this article.

The difficulty of choosing a salt which will act as a typical strong electrolyte in all solvents is well illustrated by the following examples of transposition in the order of K values from solvent to solvent and in a single solvent. In pyridine K is smaller for potassium iodide than for sodium iodide, while the converse is true in acetone and ammonia. Certain salts which are among the most highly ionized substances in ammonia, as silver nitrate, lithium nitrate, ammonium bromide, etc., have strikingly low ionization constants in acetone. In ammonia the values of K vary irregularly; for example, they decrease in the order of Ag, Na, K in the nitrates, and in the reverse order in the iodides. The case of silver iodide in ammonia is interesting because its ionization constant is very small, while both potassium iodide and silver nitrate are typical strong electrolytes in this solvent.

From these and other examples it is evident that the ionization con-

stant K depends upon the specific properties of both solvent and solute, and doubtless upon a specific action between each solvent and each solute. It seems, indeed, highly probable that it is only by virtue of this action that ionization becomes possible, and that this action is closely related to the process of solvation which takes place when the salt dissolves.

Considering again the fact that the ionization constants of the most highly ionized susbtances in each solvent do not differ greatly, it would seem that in these cases K is determined mainly by the properties of the solvent. From the kinetic standpoint, the value of K depends upon the rates of two reactions, the union of the two ions, and the breaking up of the un-ionized portion into ions. One reaction is a second-order reaction depending mainly upon the number of collisions between the positive and negative ions, while the other is a first-order reaction which depends upon the specific properties of the un-ionized substance. It is possible that in a given solvent the rate of combination of ions will be approximately the same for a number of pairs of ions, and in that event the velocity constant for the decomposition of the un-ionized portion will have its maximum value for the most highly ionized susbstance in that solvent, and will have a smaller value for the less ionized substances. For example, the small value of K for silver iodide in ammonia may be due to an abnormally slow rate of decomposition of the un-ionized substance, and may thus be referred to the specific properties of the compound of ammonia and the un-ionized silver iodide. Finally, even if the above kinetic considerations are not valid, it still seems highly probable that the low ionization constant of silver iodide in ammonia is related to the specific properties of the un-ionized substance.

It is not our purpose to enter here into a discussion of the relation between conductance and fluidity, but we wish to point out the fact illustrated by Table XVI that the limiting conductance (Λ_0) values in nearly all organic solvents are approximately proportional to the fluidities. This fact indicates that the relative dimensions of the ions and the solvent molecules or aggregates of solvent molecules are approximately the same in all these cases. It shows, moreover, that at the dilutions considered in this section all electrolytes are approaching a limiting degree of ionization which is practically the same for all electrolytes.

Certain writers have recently expressed the views that the deviations from the laws of ideal solutions arise as a result of the formation of complex molecules and ions. It may well be that in concentrated solutions complexes are formed in some instances; but the fact that a binary equilibrium exists in the case of all the solutions which we have considered is practically conclusive evidence that in the dilute solutions complexes are not present. The bearing of complexes on the question of deviations

from the mass-action law will be discussed more fully after further data have been presented with regard to concentrated solutions.

VIII. Concentrated Solutions.

Method of Treatment.—Having examined the conductance curves of dilute solutions in a variety of solvents and having demonstrated the applicability of Equation III to the conductance curve of electrolytes in ammonia and sulfur dioxide over a wide range of concentration, we shall now consider the conductance curves of a number of solvents for which data are available in concentrated solutions only, and, in particular, those solvents which exhibit a form of conductance curve differing greatly from that found in solvents of high dissociating power.

For a large number of solutions in solvents of very low ionizing power Λ_0 and K cannot be determined, at any rate not from the data at present available. As was pointed out in Section II, the general equation may be expressed (by substituting Λ/Λ_0 for γ and transposing) in the following form:

$$c\Lambda^2 = D\Lambda_0^{1-m}(\Lambda_0 - \Lambda) \ (c\Lambda)^m + \Lambda_0(\Lambda_0 - \Lambda)K. \qquad \text{(VI }b)$$

In the case of slightly ionized electrolytes, $\Lambda_0 - \Lambda$ may be treated as a constant and placed equal to Λ_0 itself. Moreover, in all the cases considered in the present section the values of K are so small as to be negligible at the concentrations for which accurate data are available. Omitting the term containing K and substituting P for $D\Lambda_0^{1-m}$ (see Equation VII), the above equation may be written in the following simple form:

$$\log (c\Lambda^2) = m \log (c\Lambda) + \log P. \qquad \text{(VI }c)$$

If Equation VIc holds true, a straight line will result on plotting values of $\log (c\Lambda^2)$ against $\log (c\Lambda)$. The constant m is given by the slope of the curve and $\log P$ by the intercept or the axis of $\log (c\Lambda^2)$.

Sources of Material.—Twelve solvents in all have been examined; and the m-P plots for 64 electrolytes in these solvents are given in Figs. 22–26. The following is a list of the papers from which the data have been obtained, together with the initials of the investigators, the name of the solvent, and the number of the figures and the curves in which the plots are reproduced:

Hydrochloric acid, McIntosh and Archibald (McI–A) (34), Archibald (A_{11}) (40) and (A_{111})[1] (41), Fig. 22, I–XIII; *Hydrobromic acid,* Archibald (A_1) (42) and (A_{11}) (40), Fig. 23, XIV–XXIX, and McIntosh and Archibald (McI–A) (34), Fig. 24, XXX–XXXV; *Hydriodic acid,* McIntosh and Archibald (McI–A) (34), Fig. 24, XXXVI–XXXVIII; *Hydrogen sulfide,* McIntosh and Archibald (McI–A) (34), Fig. 24, XXXIX and XL;

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[1] It appears that the values of Λ, the molecular conductance, as given in Archibald's two earlier papers (40, 42), are expressed in units 1000 times smaller than the unit customarily employed for this purpose. Although not specifically corrected in the third paper (41), comparative numerical values are given which show this to be the case.

Mercuric chloride, Foote and Martin (F–M) (43), Fig. 25, XLI–XLIII, XLV and XLVI; *Iodine*, Lewis and Wheeler (L–W) (44), Fig. 25, XLIV; *Amylamine*, Kahlenberg and Ruhoff (K–R) (45), Fig. 25, XLVII; *Ethylamine*, Shinn (Sn) (46), Fig. 25, XLVIII–L; *Aniline*, Sachanov (Sa) (47), Fig. 26, LX–LXIV; *Methylaniline*, Sachanov (Sa) (47), Fig. 26, LI and LII; *Acetic acid*, Sachanov (Sa) (48), Fig. 26, LVI–LIX; and *Propionic acid*, Sachanov (Sa) (48), Fig. 26, LIII–LV.

Treatment of the Experimental Material.—In Figs. 22–26 values of log
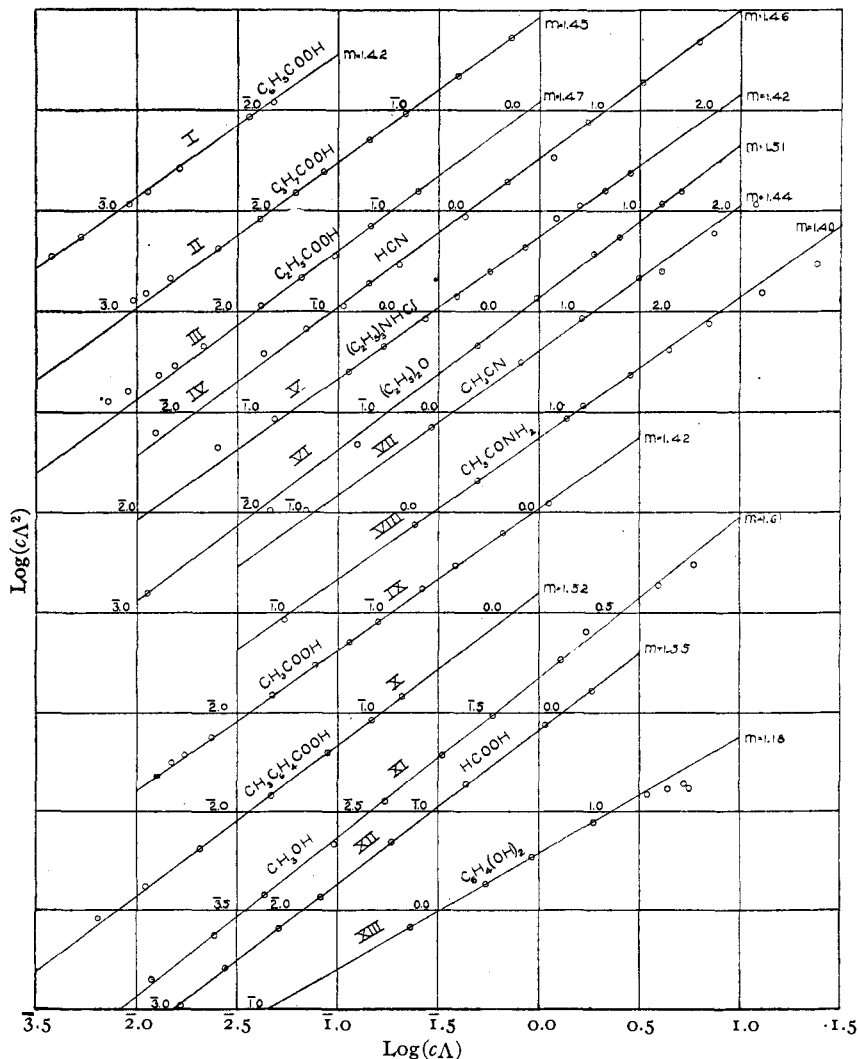
Fig. 22.—*m-P* Plots for Solutions in HCl.

($c\Lambda$) are plotted as abscissas and the corresponding values of log ($c\Lambda^2$) as ordinates. The scale of abscissas is shown at the bottom of the figures, unless otherwise specified. The scale of ordinates for any curve is shown by numbers appearing on the figures where the curve crosses the parallels to the axis of abscissas. The plots corresponding to Equation VIc are throughout known as "m-P" plots, since they are employed in determining
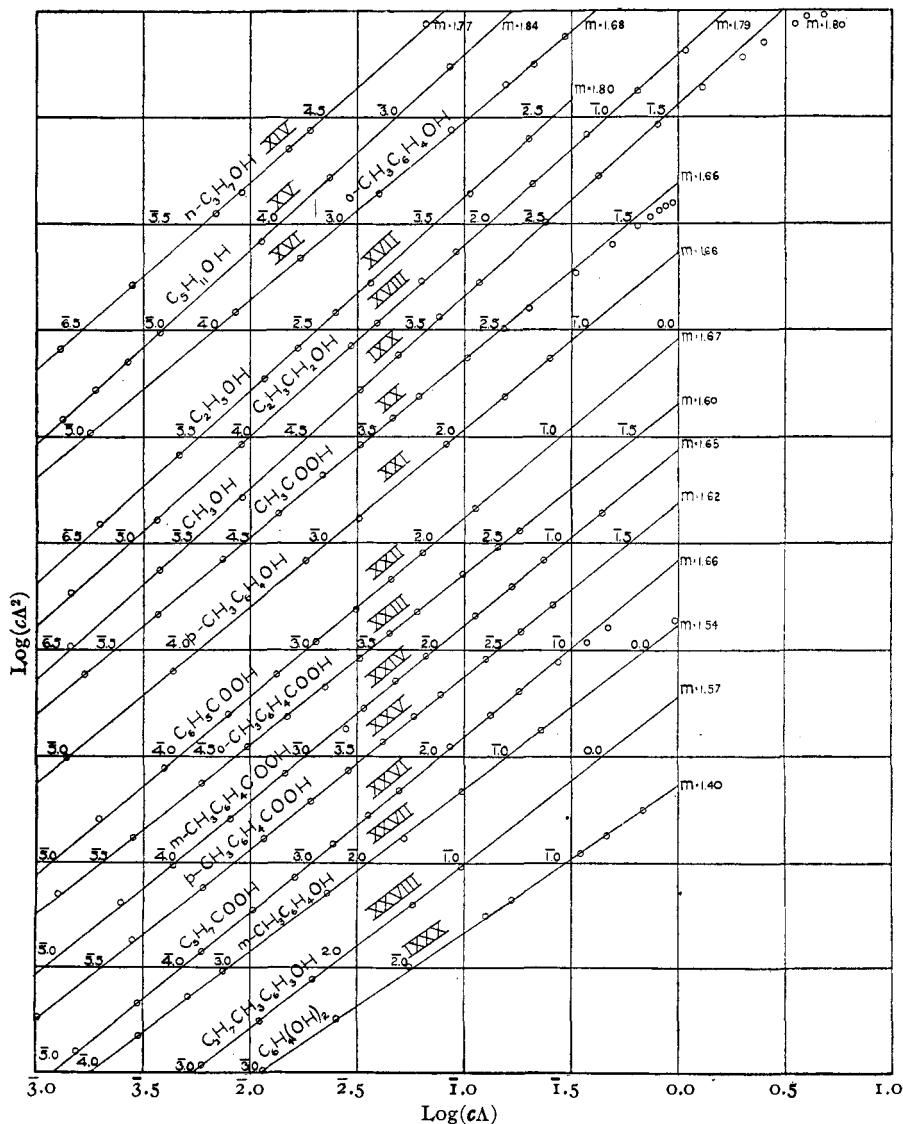
Fig. 23.—m-P Plots for Solutions in HBr.

the values of m and P. The value of m corresponding to each curve is shown on the plot. In the case of substances of simple formula, the formula is shown on the plot. Each curve is also numbered in Roman numerals. In case the formula for the solute does not appear on the plot, the name of the solute may be found by referring to Table XXI. Where more than one solvent appears in a single figure, the formula or name of the solvent appears on the plot near the lower end of the curves.

In connection with Curve XLIV for potassium iodide in iodine (44), it
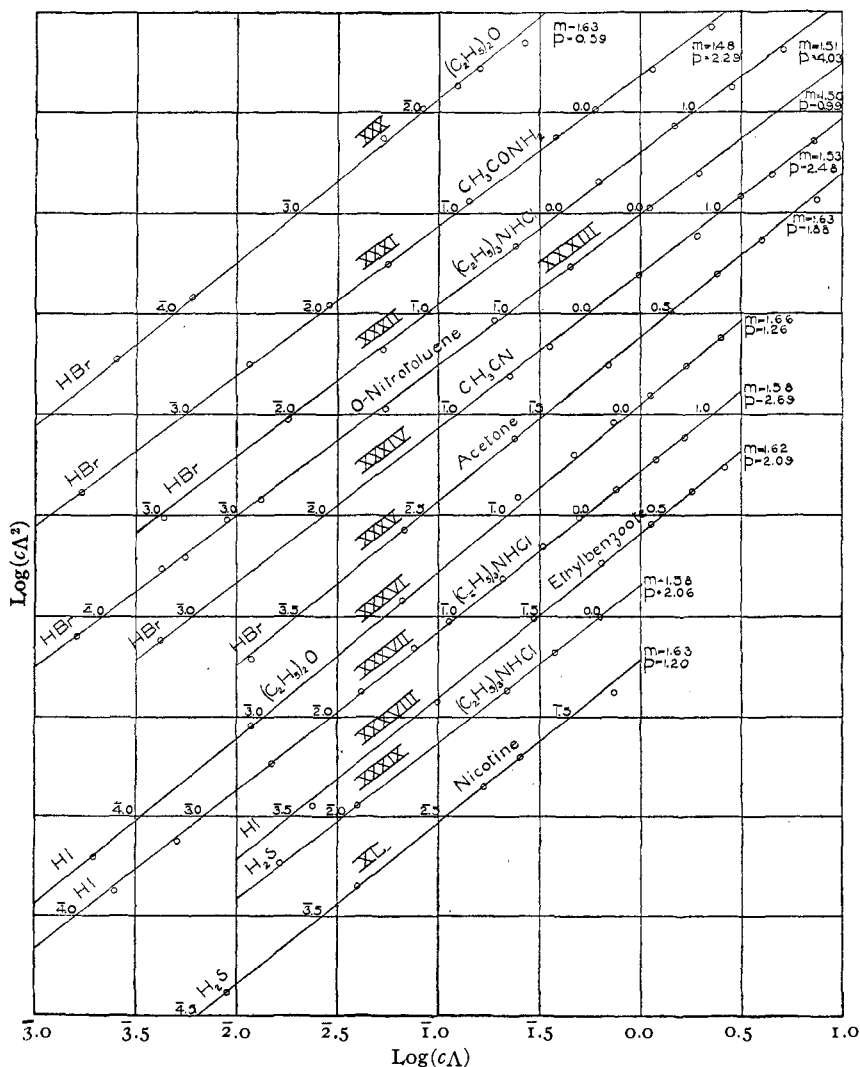
Fig. 24.—m-P Plots for Solutions in HBr, HI and H_2S.

should be stated that all the points plotted for the more dilute solutions
are from Series 2, Table III, and the more concentrated from Series 3,
Table IV, in the original article. The remaining series agree with those
plotted, but they contain fewer points and are less consistent among
themselves. It should also be stated that for silver nitrate in amyl-
amine, Fig. 25, XLVII, two points in dilute solutions were omitted be-
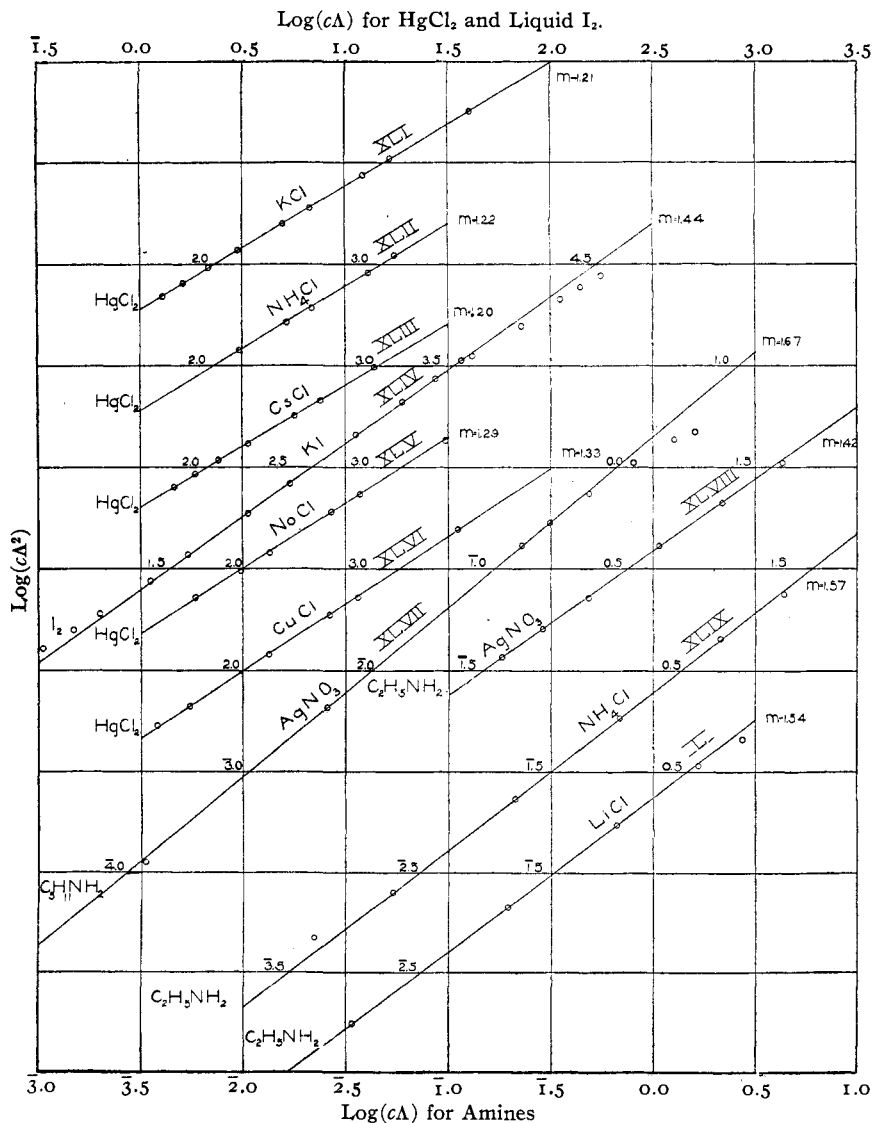
Fig. 25.—m-P Plots for Solutions in $HgCl_2$, Liquid I_2, $C_5H_{11}NH_2$ and $C_2H_5NH_2$.

cause they lie outside the figure.   Both are in agreement with the straight line as drawn in the figure.   For mercuric chloride and iodine, Fig. 25, XLI–XLVI, the scale of abscissas is shown at the top of the figure, while that for the two amines appears at the bottom of the figure.

Validity of the General Equation.—An examination of Figs. 22–26 shows that, without exception, the *m-P* plots yield straight lines over a large range of concentration. As a rule the points fall on a straight line for a
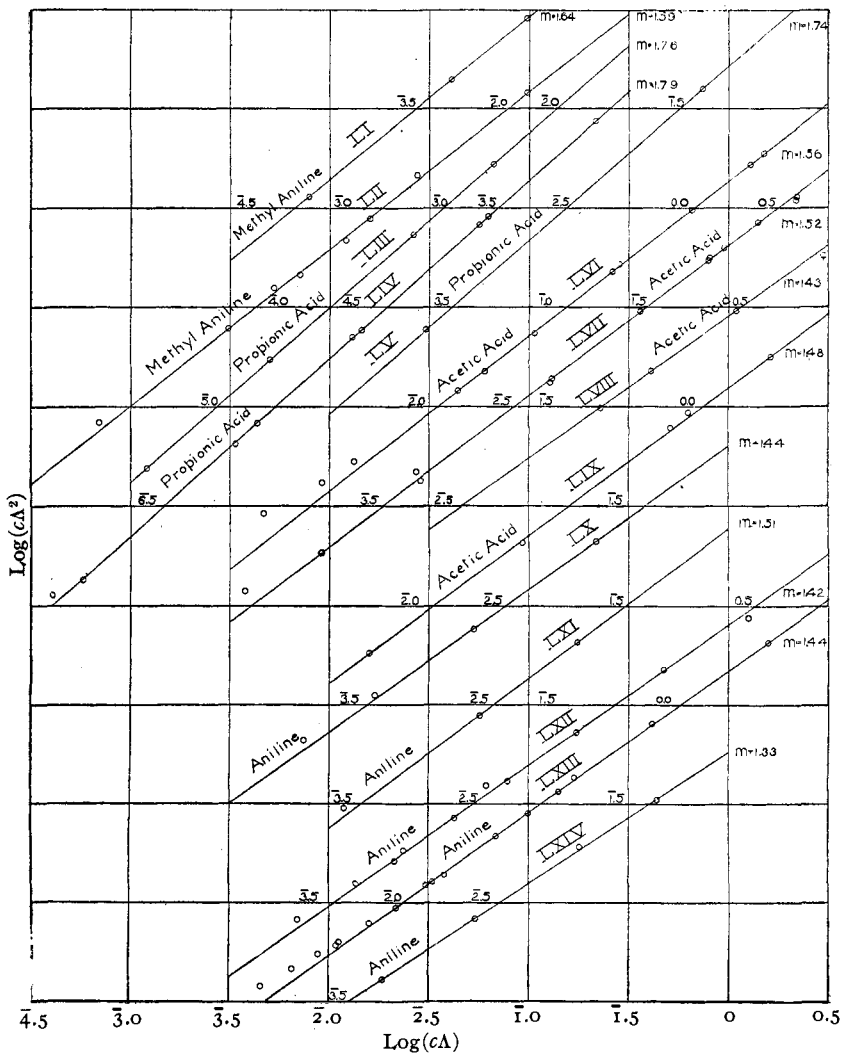

Fig. 26—*m-P* Plots for Solutions in Methyl Aniline, Propionic Acid, Acetic Acid and Aniline.

change in the value of $c\Lambda$ between 100- and 1000-fold. This demonstrates the applicability of Equation VIc and consequently also of the more general equation (III) from which it is derived. This result appears all the more striking when we take into consideration the fact that some of the solvents are acidic, others basic substances, while one is a neutral element. Some of the measurements were made with solvents boiling at —100°, while others were carried out at 282°, a temperature sufficiently high to melt some electrolytes. The dissolved substances include a large variety of different compounds. Some of the electrolytes are common salts, while others are substances not commonly classed as being electrolytic in nature.

In the more concentrated solutions, usually beginning in the neighborhood of normal concentration, the points begin to depart from a straight line, and always in the direction corresponding to too small a value of Λ. This is well illustrated in the case of KI in I_2 (Fig. 25, XLIV), of AgNO$_3$ in amylamine (Fig. 25, XLVII), of CH$_3$OH in HBr (Fig. 23, XIX), and of acetamide in HCl (Fig. 22, VIII). This trend of the curves corresponds to that observed in concentrated solutions in liquid ammonia (see last paragraph of Section III, C), and there is good reason for believing that it is due to the gradually increasing viscosity of the solution with concentration.[1] An examination of the data shows that, in agreement with this explanation, the deviations in a given solvent appear at relatively lower concentrations for the more complex solutes. Thus for methyl-alcohol in HBr the points fall on a straight line up to a concentration of 2.5 normal, while for acetic and butyric acids in the same solvent the deviations become appreciable below normal concentration.[2]

In a few cases it is possible also that the curvature of the plots in concentrated solutions is due to the fact that Λ is undergoing so large a change that $\Lambda_0 - \Lambda$ can no longer be treated as a constant; thus, this may well be true for the solutions of KI in iodine. That it is not generally true is shown by the following considerations: If the viscosity of the solvent is known, its Λ_0 value may be approximated with sufficient accuracy to determin whether the change in $\Lambda_0 - \Lambda$ may be neglected. The fluidities of HCl, HBr, HI and H$_2$S, at the temperature where the conductance measurements were carried out, are 196, 119, 70 and 194, respectively(34). For most solvents the ratio of the conductance Λ_0 to the fluidity lies very near to the value 0.517. Since in these solvents the molecular conductance

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[1] Compare Franklin and Gibbs(27), p. 1395; and Franklin(28), p. 693. Kahlenberg and Ruhoff(45), p. 257, remark on the high viscosity of concentrated solutions of AgNO$_3$ in amylamine.

[2] It may be noted in this connection that in solvents of low dielectric constant the viscosity change (increase) due to a dissolved electrolyte is much greater than it is in solvents of high dielectric constant. This is well illustrated by solutions in water, ammonia and methylamine. Compare Fitzgerald(65).

rarely exceeds 10 units and usually is much lower, it is evident that the variation of $\Lambda_0 - \Lambda$ may safely be neglected in comparison with the corresponding change in Λ. An examination of the viscosity data for aniline, acetic acid and propionic acid shows that in these cases, too, the change in $\Lambda_0 - \Lambda$ is not such as to cause serious error in the application of Equation VIc. It is probable that this is true up to normal concentration in the remaining cases.

In dilute solutions there is a well-defined tendency for the points to rise above the straight line with increasing dilution. This might seem to be due to the fact that the term involving K in Equation VIb is no longer negligible, especially since Archibald has found a number of cases in which the equivalent conductance passes through a minimum and then increases with increasing dilution, and since it is obvious that Equation VIc cannot be applicable in the region of the minimum or beyond. A study, however, of Archibald's data, particularly of those for the solutions in HBr, in which a large number of substances were studied, leads us to doubt whether the rise in the conductance curve is really due to the K-term. In the first place, the minima were observed for solutes of very low values of P, $i.$ $e.$, for solutions of very low conducting power. If the curves plotted for HBr solutions in Fig. 23 are extended to values of $\log (c\Lambda)$ between $\bar{4}.0$ and $\bar{3}.0$, it will be found that in all cases the points begin to rise above the straight line plots in the neighborhood of $\log (c\Lambda) = \bar{3}.0$. That is to say, deviations from the straight line begin for different solutes when their solutions possess the same specific conductance. Now, the dissociation of the different solutes varies very greatly, and we ·should expect the minimum to be more apparent in solutions of electrolytes of high rather than of low ionization. It seems, probable therefore, that the rise in the conductance curve recorded by Archibald for very weak electrolytes in HBr and HCl is due to the conductance of impurities present in the solvent or to external leakage of the current. This accounts for the fact that the deviations always occur for solutions of the same specific conductance. Of course, we should expect that at sufficiently high dilutions the K-term of Equation VI will become appreciable. We should, however, expect this to occur in the case of the stronger electrolytes, such as the substituted ammonium salts. Unfortunately, these electrolytes have not been studied in very dilute solution in the liquid halogen acids.

Values of the Constants of Equation VIc.—From the plots the values of m and P were determined. In Table XXI are summarized the values of the constants together with such data as it seems worth while giving. The names of the solvents are given as sub-headings. The name of the solute is given in the first column. Its chemical formula representing the substance actually weighed out is given in the second column. (The nature of the electrolyte may be quite different from that of the substance originally

put into the solvent.)   In the third, fourth, fifth, and sixth columns are given, in order, the number of the figure in which the m-P plot appears, the number of the curve on this figure, the initials of the investigators, and the temperature at which the measurements were carried out.   The value of m is given in the seventh column and that of P in the eighth.   In each solvent the dissolved substances are arranged in the order of decreasing values of P.   Since the values of Λ_0 for the different electrolytes in any one solvent are of the same order of magnitude, it follows that the order of the P values is substantially that of the D constants.[1]   In the ninth column is given the molecular conductance Λ, corresponding to the dilution given in the tenth column.   In the last two columns are given, respectively, the maximum and minimum dilutions for which measurements are recorded.   The data in the more dilute solutions, however, are not always reliable.

Three substances are included in the table for which curves are not shown in the figures.   These are: ethyl- and butylalcohols in HCl and phenol in HBr. These were omitted for the reason that the data are not sufficiently concordant to afford evidence as to the applicability of the dilution law.   Approximate values of the constants are included in the table for purposes of discussion.   Any errors in the constants will not materially affect their position in the table.

Discussion of the Values of the Constant m.—It will be seen from Table XXI that for any given solvent the value of m does not vary greatly with the nature of the dissolved substance, although the specific characteristics of certain substances are plainly evident.   The approximate constancy of the value of m for any solvent is shown also by the fact that the m-P plots for different electrolytes are nearly parallel.

From the table it will also be seen that in a given solvent there is a rough relationship between the values of m and P.   The smaller the value of P, the greater is the value of m.   There are, to be sure, exceptions; but a very high value of m is invariably accompanied by a low value of P.   This is noticeably the case with the alcohols both in HCl and HBr.

It may also be pointed out that the value of m increases as the solvent has a higher position in a homologous series, like that of the amines; thus, for silver nitrate in ammonia, m has a value of 0.83, in methylamine 1.22 (as shown by calculations nor recorded in this paper), in ethylamine 1.42, and in amylamine 1.67.

That the solute may have a specific influence on the value of m is shown very strikingly in the case of resorcinol.   In both hydrochloric acid and

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[1] In Table XXIII, Section XI, will be found some values of D as calculated from the values of P given above.   The important result is there obtained that the value of D, for a given solute, is practically independent of the solvent, and it does not approach the value zero as the dielectric constant of the solvent approaches unity.

TABLE XXI.—CONCENTRATED SOLUTIONS.

Solute.	Formula.	Figure.	Curve No.	Investigator.	Temperature.	m.	p.	Conductance Λ at dilution v.	Dilution v.	Range of dilution investigated. v max.	v min.
Liquid Hydrochloric Acid (HCl).											
Triethylammonium chloride	(C₂H₅)₃N.HCl	22	V	McI-A	—100°	1.42	5.75	8.51	2.99	71.4	2.99
Acetamide	CH₃CONH₂	22	VIII	McI-A	—100°	1.40	5.53	8.20	2.86	29.4	0.51
Methylcyanide	CH₃CN	22	VII	McI-A	—100°	1.44	4.17	6.25	1.54	21.7	0.81
Resorcinol	C₆H₄(OH)₂	22	XIII	A_III	— 89°	1.18	3.89	4.11	2.19	12.6	0.54
Hydrocyanic acid	HCN	22	IV	McI-A	—100°	1.46	3.33	5.81	1.79	41.4	1.23
Toluic acid	CH₃.C₆H₄COOH	22	X	A_II	— 96°	1.52	1.58	0.70	3.33	125.0	3.33
Diethylether	(C₂H₅)₂O	22	VI	McI-A	—100°	1.51	1.38	1.41	1.45	12.5	0.61
Propionic acid	C₂H₅COOH	22	III	A_II	— 96°	1.47	1.21	0.62	2.50	200.0	2.50
Acetic acid	CH₃COOH	22	IX	A_II	— 96°	1.42	1.09	0.95	1.43	100.0	1.00
Benzoic acid	C₆H₅COOH	22	I	A_II	— 96°	1.42	0.94	0.240	6.66	333.0	5.00
Butyric acid	C₃H₇COOH	22	II	A_II	— 96°	1.45	0.85	0.56	1.43	25.0	1.00
Methylalcohol	CH₃OH	22	XI	A_III	— 89°	1.61	0.71	0.156	1.61	33.2	0.13
Formic acid	HCOOH	22	XII	A_II	— 96°	1.55	0.67	0.267	1.43	66.0	0.50
Ethylalcohol	C₂H₅OH	..	......	A_III	— 89°	1.70	0.50	0.049	1.48	48.8	0.12
Butylalcohol	C₄H₉OH	..	......	A_III	— 89°	1.62	0.38	0.036	1.53	29.4	0.13
Liquid Hydrobromic Acid (HBr).											
Triethylammonium chloride	(C₂H₅)₃N.HCl	24	XXXII	McI-A	— 81°	1.51	4.03	8.19	1.61	143.0	1.61
Thymol	CH₃.C₃H₇.C₆H₃OH	23	XXVIII	A_I	— 80°	1.57	3.60	0.97	10.0	500.0	10.0
Methylcyanide	CH₃CN	24	XXXIV	McI-A	— 81°	1.53	2.48	4.62	1.47	33.0	0.72
Acetamide	CH₃CONH₂	24	XXXI	McI-A	— 81°	1.48	2.29	3.15	1.41	90.9	1.41
Acetone	(CH₃)₂CO	24	XXXV	McI-A	— 81°	1.63	1.88	2.32	1.64	83.3	0.75
Metacresol	m-CH₃.C₆H₄OH	23	XXVII	A_I	— 80°	1.54	1.70	0.77	3.33	125.0	2.00
Orthonitrotoluene	o-CH₃.C₆H₄NO₂	24	XXXIII	McI-A	— 81°	1.50	0.99	0.67	1.50	25.0	0.66
Benzoic acid	C₆H₅COOH	23	XXII	A_II	— 80°	1.67	0.82	0.188	1.67	40.0	1.67
Acetic acid	CH₃COOH	23	XX	A_II	— 80°	1.66	0.78	0.171	1.67	12.5	0.55
Metatoluic acid	m-CH₃.C₆H₄COOH	23	XXIV	A_II	— 80°	1.65	0.77	0.186	1.67	20.0	1.00

Liquid Hydrobromic Acid (HBr).

Paratoluic acid	p-CH$_3$.C$_6$H$_4$COOH	23	XXV	A$_{II}$	— 80°	1.62	0.76	0.210	1.67	20.0	1.25
Butyric acid	C$_3$H$_7$COOH	23	XXVI	A$_{II}$)	— 80°	1.66	0.71	0.143	1.67	10.0	0.71
Orthotoluic acid	o-CH$_3$C$_6$H$_4$COOH	23	XXIII	A$_{II}$	— 80°	1.60	0.65	0.164	1.67	40.0	1.00
Diethylether	(C$_2$H$_5$)$_2$O	24	XXX	McI-A	— 81°	1.63	0.59	0.129	1.54	16.6	0.47
Paracresol	p-CH$_3$.C$_6$H$_4$OH	23	XXI	A$_I$	— 80°	1.66	0.55	0.0535	1.67	16.7	0.83
Resorcinol	C$_6$H$_4$(OH)$_2$	23	XXIX	A$_I$	— 80°	1.40	0.52	0.275	1.67	125.0	0.67
Orthocresol	o-CH$_3$.C$_6$H$_4$OH	23	XVI	A$_I$	— 80°	1.68	0.45	0.0282	1.67	10.0	0.67
Methylalcohol	CH$_3$OH	23	XIX	A$_1$	— 80°	1.80	0.41	0.0024	1.67	7.69	0.12
Allylalcohol	C$_2$H$_3$.CH$_2$OH	23	XVIII	A$_1$	— 80°	1.79	0.39	0.0024	1.67	16.7	0.36
Ethylalcohol	C$_2$H$_5$OH	23	XVII	A$_I$	— 80°	1.80	0.35	0.0013	1.67	12.5	0.50
Amylalcohol	C$_5$H$_{11}$OH	23	XV	A$_1$	— 80°	1.84	0.27	0.0002	1.67	20.0	0.36
Normal propylalcohol	n-C$_3$H$_7$OH	23	XIV	A$_I$	— 80°	1.77	0.27	0.0010	1.67	20.0	0.55
Phenol	C$_6$H$_5$OH	..	......	A$_1$	— 80°	1.61	0.27	0.0095	2.00	7.69	0.55

Liquid Hydriodic Acid (HI).

Triethylammonium chloride	(C$_2$H$_5$)$_3$N.HCl	24	XXXVII	McI-A	— 50°	1.58	2.69	3.58	2.17	27.8	2.17
Ethylbenzoate	C$_6$H$_5$COOC$_2$H$_5$	24	XXXVIII	McI-A	— 50°	1.62	2.09	2.98	1.66	16.6	1.37
Diethylether	(C$_2$H$_5$)$_2$O	24	XXXVI	McI-A	— 50°	1.66	1.26	1.11	1.49	10.0	0.88

Liquid Hydrogen Sulfide (H$_2$S).

| Triethylammonium chloride | (C$_2$H$_5$)$_3$N.HCl | 24 | XXXIX | McI-A | — 81° | 1.58 | 2.06 | 1.58 | 2.50 | 71.4 | 2.50 |
| Nicotine | C$_{10}$H$_{14}$N$_2$ | 24 | XL | McI-A | — 81° | 1.63 | 1.20 | 0.50 | 1.92 | 66.7 | 1.03 |

Mercuric Chloride (HgCl$_2$).

Caesium chloride	CsCl	25	XLIII	F-M	282°	1.20	14.5	70.0	5.0	30.0	5.0
Potassium chloride	KCl	25	XLI	F-M	282°	1.21	14.3	62.0	5.0	30.0	2.0
Ammonium chloride	NH$_4$Cl	25	XLII	F-M	282°	1.22	14.3	64.5	5.0	15.0	4.0
Sodium chloride	NaCl	25	XLV	F-M	282°	1.29	13.7	43.0	5.0	15.0	2.0
Cuprous chloride	CuCl	25	XLVI	F-M	282°	1.33	13.6	42.0	5.0	20.0	2.0

Liquid Iodine (I$_2$).

| Potassium iodide | KI | 25 | XLIV | L-W | 140° | 1.44 | 13.5 | 107.4 | 1.72 | 261.0 | 0.12 |

TABLE XXI (*continued*).

Solute.	Formula.	Figure.	Curve No.	Investigator.	Temperature.	m.	p.	Conductance Λ at dilution v.	Dilution v.	Range of dilution investigated.	
										v max.	v min.
				Ethylamine ($C_2H_5NH_2$).							
Silver nitrate	AgNO$_3$	25	XLVIII	Sn	0°	1.42	4.68	7.96	1.85	75.1	0.93
Ammonium chloride	NH$_4$Cl	25	XLIX	Sn	0°	1.57	1.97	3.04	1.42	78.8	0.95
Lithium chloride	LiCl	25	L	Sn	0°	1.54	1.80	2.16	1.28	95.6	0.511
				Amylamine ($C_5H_{11}NH_2$).							
Silver nitrate	AgNO$_3$	25	XLVII	K-R	25°	1.67	1.97	1.38	1.68	81.6	0.400
				Aniline ($C_6H_5NH_2$).							
Ammonium iodide	NH$_4$I	26	LXIII	Sa	25°	1.44	2.19	2.69	1.69	70.5	1.69
Silver nitrate	AgNO$_3$	26	LXII	Sa	25°	1.42	2.02	1.96	1.56	44.9	1.56
Pyridine hydrobromide	C$_5$H$_5$N.HBr	26	LXI	Sa	25°	1.51	1.91	0.79	4.50	19.3	4.50
Aniline hydrobromide	C$_6$H$_5$NH$_2$.HBr	26	LX	Sa	25°	1.44	1.29	0.65	2.98	25.2	2.98
Lithium iodide	LiI	26	LXIV	Sa	25°	1.33	1.04	0.79	1.80	27.8	1.8
				Methyl Aniline ($C_6H_5NHCH_3$).							
Pyridine hydrobromide	C$_5$H$_5$N.HBr	26	LI	Sa	25°	1.64	1.19	0.27	2.72	6.85	2.76
Aniline hydrobromide	C$_6$H$_5$NH$_2$.HBr	26	LII	Sa	25°	1.59	0.59	0.15	1.54	14.5	1.54
				Acetic Acid (CH_3COOH).							
Lithium bromide	LiBr	26	LVIII	Sa	25°	1.43	2.60	3.55	1.19	42.8	1.19
Pyridine	C$_5$H$_5$N	26	LVI	Sa	25°	1.56	1.86	2.15	1.67	38.2	0.80
Dimethylaniline	C$_6$H$_5$N(CH$_3$)$_2$	26	LIX	Sa	25°	1.48	1.53	1.96	1.20	13.1	1.20
Aniline	C$_6$H$_5$NH$_2$	26	LVII	Sa	25°	1.52	1.32	1.26	1.57	31.8	0.81
				Propionic Acid (C_2H_5COOH).							
Lithium bromide	LiBr	26	LV	Sa	25°	1.74	0.84	0.063	2.06	9.52	0.90
Aniline	C$_6$H$_5$NH$_2$	26	LIV	Sa	25°	1.79	0.37	0.004	1.19	2.44	0.51
Pyridine	C$_5$H$_5$N	26	LIII	Sa	25°	1.76	0.32	0.002	1.66	3.12	0.613

hydrobromic acid the value of m for this solute is the lowest in the table and is far lower than that of other organic solutes. Unfortunately, no other dibasic phenols have been investigated, so that it is impossible to determin whether an abnormally low value of m is characteristic of these compounds.

Discussion of the Values of the Constant P.—The values of this constant may be taken as a rough measure of the relative conductance of the different solutes in the same solvent at normal concentration; for $P = \Lambda^{2-m}$ when $c = 1$, and, as just shown, m does not vary greatly with the nature of the solute. In Table XXI the solutes in each solvent are arranged in the order in which the values of P decrease, and the strongest electrolytes are thus placed first in each list. It is apparent at a glance that the strongest electrolytes in the acidic solvents are those that contain nitrogen; thus the triethylammonium salts are the most highly ionized of the electrolytes studied in the liquid halogen acids and hydrogen sulfide, and acetamide, hydrocyanic acid, and methylcyanide are also among the best conductors in these solvents.

This difference between the nitrogen compounds and those of oxygen is doubtless due to the more pronounced basic properties of nitrogen as compared with those of oxygen. This naturally brings up the question as to the nature of the electrolytes in these solutions. In the liquid halogen acids the organic compounds in question are to be looked upon as salts of basic oxygen and nitrogen. That is to say, in these compounds the functions of oxygen and nitrogen are entirely similar to those of nitrogen in the common ammonium salts. The formula for an ammonium salt is: R_4N—X, where R represents a univalent element or group, such as H, CH_3, C_6H_5, etc., and X is a strongly negative element or group of elements. The group NR_4^+ acts as the positive ion in solution while X^- functions as negative ion. In the case of oxygen the corresponding substituted oxonium compound is: R_3O—X, and the resulting ions are OR_3^+ and X^-. The basic properties of oxygen are well recognized by organic chemists.[1] Compounds of this type are well known in the case of sulfur. The analogy between this element and oxygen is even more striking than it is in the case of nitrogen and oxygen.

The relation between the constants of the different solutes and their constitution at once becomes clear in the light of the above considerations. An alcohol, when dissolved in a pure acid, HX, acts as an oxonium base, in which one hydrogen has been substituted by an alkyl group to form the salt RH_2O—X. As in the ammonium bases derived from ammonia, so in the oxonium bases derived from water, the replacement of hydrogen atoms by alkyl groups increases the strength of the base. Thus

[1] Meyer and Jacobson, *Organische Chemie*, **1**, p. 290, *et seq.*, Ed. 2.

ether, which gives a diethyloxonium salt[1] with an acid, forms a solution which conducts much better than ethylalcohol, which is only a mono-substitution product. Water would doubtless prove to be even a weaker base[2] than the alcohols when dissolved in the halogen acids.

Similarly, phenol and phenol derivatives when dissolved in an acid solvent yield oxonium salts, or, more accurately, oxonium bases in this solvent. An examination of the experimental results for these substances shows that the replacement of hydrogen of the benzene ring by an alkyl radical increases the strength of the base. Thus in hydrogen bromide the cresols are all much more highly ionized than phenol; and thymol, which has two hydrogens of the ring replaced by alkyl groups, is a very strong electrolyte. On the other hand, a comparison of the results of benzoic acid with those for its derivatives, such as the toluic acids, shows that the effect of replacing hydrogen in the ring by an alkyl radical is very small. It is to be noted that in this case the oxygen is not directly attached to the benzene ring, as it is in the phenols.

In considering the behavior of organic substances in different solvents the dual behavior of certain atoms or groups of atoms must always be taken into account. Thus, the solute obtained on dissolving acetamide in a halogen acid is undoubtedly very different from that obtained on dissolving it in ammonia; in the latter case the nitrogen of the acetamide is in the anion, while in the former it is in the cation.

The transference experiments of Steele show conclusively that, in solutions of ether and ketones in hydrogen bromide, the oxygen is contained, as assumed above, in the cation.[3] Steele determined the transference numbers of ether, acetone, methylhexylketone, and triethylammonium bromide. At concentrations less than normal the cation-transference number was found to be considerably less than 0.5 for triethylammonium bromide, acetone, and methylhexylketone, though it becomes much larger for the last two substances at higher concentrations. With ether a value much over 0.5 was found at normal concentration, while in more concentrated solutions the value appeared to be smaller. With the exception of ether,[4] then, the transference numbers for the cations in the more dilute solutions are small. This is what we should expect, if the cation is in all cases a large aggregate and the anion is simply Br^-,

[1] The term salt is here used in its broad sense. Strictly speaking, any chloride dissolved in liquid hydrogen chloride is a base, since HCl, in all probability, is capable of dissociating into H^+ and Cl^- ions. Thus, ether and ethylalcohol, when dissolved in HCl, yield the bases diethyloxonium chloride $(C_2H_5)_2HO\text{-}Cl$ and ethyloxonium chloride, $C_2H_5H_2O\text{-}Cl$, respectively.

[2] See preceding footnote, second and third sentences.

[3] Steele, McIntosh and Archibald(34), p. 138, et seq.

[4] What the explanation may be for the high value of the cation transference number in the case of ether is uncertain, but, considering the experimental difficulties involved

a rapidly moving ion in all solvents. Moreover, the transference results indicate that complex cations containing the halogen are not formed to any considerable extent; for, if this were the case, we should expect the transference number of the cation to be abnormally large, even before normal concentration is reached. The results for solutions of triethyl-ammonium bromide are particularly noteworthy, since it is a typical salt and the transference measurements were made in more dilute solutions than was the case with the other solutes.

The ionization relations in the different solvents are so similar in character that a detailed discussion of the data seems unnecessary. Two of the solvents, however, deserve especial attention and are worthy of further study. The curve for potassium iodide in iodine (Fig. 25) is of interest because of the exceptional character of the solvent and the high value of the conductance. The results with substances dissolved in mercuric chloride (given in Fig. 25) are also of interest for the reason that we have here a new type of solvent. The agreement with the linear relation required by Equation VIc is excellent. The values of P and of Λ are very high. Taken in connection with the low values of m, this indicates that measurements in dilute solutions may make it possible to determin the K and Λ_0 values.

In the last-named solvent the similar behavior of different salts is well illustrated: the values of P for the five salts measured in mercuric chloride differ by less than 10 per cent., although the values of m differ considerably. In the other solvents, also, the values of P for the most highly ionized substances do not differ greatly in any given solvent; just as was found to be true of the values of D for typical strong electrolytes in ammonia.

IX. Aqueous Solutions.

In the preceding sections we have seen that the general equation is applicable to solutions of electrolytes in a large variety of solvents. It is presumably applicable also to solutions in water, and it is therefore probable that at sufficiently low concentrations the mass-action law will hold for this solvent also. It is, however, difficult to test the applicability of the mass-action law in the case of water for the reason that before a dilution is reached at which the effect of the D-term has become small in comparison with K, the ionization has reached such a high value that the un-ionized fraction of the electrolyte $(1 - \gamma)$ cannot be determined with a sufficient degree of accuracy.

Among many investigators there has been a tendency to look upon water as an exceptional solvent, the laws governing it being assumed to

in these measurements, it would not be surprising if the results were in error to a greater extent than might be inferred from the agreement of the limited number of individual experiments made. It would be extremely valuable to have transference data over a much larger concentration range, particularly in dilute solutions.

differ from those governing other solvents in something more than in degree. This view is not borne out by the facts. For example, considering water and the alcohols, it is evident that there is a perfect gradation in properties from water to amylalcohol. In water, methylalcohol and ethylalcohol the K values for salts cannot be determined with any degree of certainty from conductance measurements in dilute solution because of the high ionization and the magnitude of the corrections that must be applied for the conductance of the solvents. We have seen, however, (Section VI), that in propyl-, butyl,- and amylalcohols the law of mass action holds true in dilute solutions of typical strong electrolytes; and there is therefore every reason for believing that it is also applicable to ethylalcohol, methylalcohol and water. The difference between these various solvents is merely one of degree. The value of K for sodium iodide in amylalcohol is one of the lowest appearing in Table XVI, 3.9×10^{-4}; in butylalcohol it is 12×10^{-4}, and in propylalcohol it is still higher, 45×10^{-4}. The value of K for a typical salt is undoubtedly much larger in ethyl- and methylalcohols, and, as we shall see later, it has an extremely high value in water.

By applying the knowledge gained from other solvents, we may therefore expect to throw more light on the phenomena in aqueous solution; and it is our purpose in the present section to make a detailed study of aqueous solutions of a single electrolyte (potassium chloride) for which the most accurate data are available. It does not seem necessary to study a large number of such electrolytes in water, for the conductance curves are so nearly similar that what applies to one binary electrolyte will doubtless apply to all.

A serious difficulty is encountered, as just stated, in examining the dilution law of aqueous solutions owing to possible error in $1 - \gamma$. This error arises from uncertainties in the values of Λ_0 and becomes increasingly great with increasing dilution, so that the true form of the law may be completely masked by a small error in Λ_0. Moreover, the values commonly accepted for Λ_0 may well be in error to a much larger extent than is commonly believed. For, in extrapolating for Λ_0, two functions have commonly been employed: one is an equation of the form of Equation II, the other is an equation of the form $\Lambda = \Lambda_0 - ac^{1/3}$, which has been employed by Kohlrausch. Neither of these functions applies to more than a limited interval of the conductance curve, and the presumption, therefore, is that the Λ_0 values obtained by extrapolating these functions are in error to some unknown extent. Moreover, both these functions are in contradiction with the presumption that the mass-action law will hold true at high dilutions.

In testing a dilution law we must therefore endeavor to obtain functions whose constants are independent of Λ_0. This can be done as fol-

lows: The value of m in the general equation may be obtained by plotting against each other the first two logarithmetic terms in the equation

$$\log \frac{c\Lambda^2}{\Lambda_0\,(\Lambda_0-\Lambda)} = m \log\,(c\Lambda) + \log \frac{D}{\Lambda_0{}^m}, \qquad (V\,a)$$

and evaluating m from the slope of the curve.[1] The curve is not a straight line for aqueous salt solutions, since K cannot then be neglected, but at high concentrations (above about 0.5 normal) the curve becomes sensibly linear. This necessitates extending the conductance curve to 3 or 5 normal, and correcting for the viscosity of the solution.[2] It has been found that the value of m so determined is independent of the values adopted for Λ_0. This modified m-D plot will therefore give an accurate value of the ratio $D/\Lambda_0{}^m$, and therefore of D if Λ_0 is known.

If Equation III is applicable and a correct value of Λ_0 is chosen, then a plot of $\dfrac{c\Lambda^2}{\Lambda_0\,(\Lambda_0-\Lambda)}$ against $(c\Lambda)^m$ (the modified K-D plot) must yield a straight line, whose intercept on the ordinate axis gives the value of the mass-action constant K. If, however, the value of Λ_0 is incorrect, then the K-D plot will not give a straight line, but will exhibit curvature in dilute solutions. Now, it may readily be shown by trial that any curvature of the m-D plot cannot be corrected by changing the value of m; it follows that curvature of the K-D plot in dilute solutions can only be due either to an incorrect value of Λ_0 or to the fact that the equation fails to apply in dilute solutions where for theoretical reasons we should consider it most likely to apply.

In this section we shall examin the conductance data for potassium chloride dissolved in water at 18°. The experimental values for this salt are more trustworthy than those of any other electrolyte in water and the transference numbers are known to be constant up to high concentrations. The viscosity correction is small and can be made with practical certainty. The conductance data employed are those of Kohlrausch and Maltby(49). The experimental data are shown in Table XXII, below.

The results are shown graphically in Fig. 27. The three upper curves (I, II, III) are reproductions of modified. m-D plots, the scale for which is shown on the upper and left-hand margins. The scale of ordinates is actually that of the topmost plot only. Since the curves are practically coincident at their upper extremities, Curve II was displaced downward by 0.50 units and Curve III by 0.30 units. The three lower curves on

[1] This is a modified m-D plot, in which γ, Λ/Λ_0, is replaced by Λ as variable. See footnotes, Sections I and V.

[2] It is not always possible to make this correction; but, as will be shown by one of us in a forthcoming publication, this correction may be applied with certainty in some cases.

the figure are K-D plots, the scale for which is shown on the lower and right-hand margins, values of $(c\Lambda)^m$ being plotted as abscissas. For these three plots the same scale of $(c\Lambda)^m$ is employed; but the values of Λ_0 differ, being 128.3, 128.8, and 130.1 for Plots IV, V, and VI, respectively.

The value of m was determined from the m-D plot (I), using for Λ_0 the value 130.1 and neglecting K. As may be seen, the curve is practically a straight line at the upper end of the plot, corresponding to concentrated solutions. The most concentrated solution (uppermost point) does not
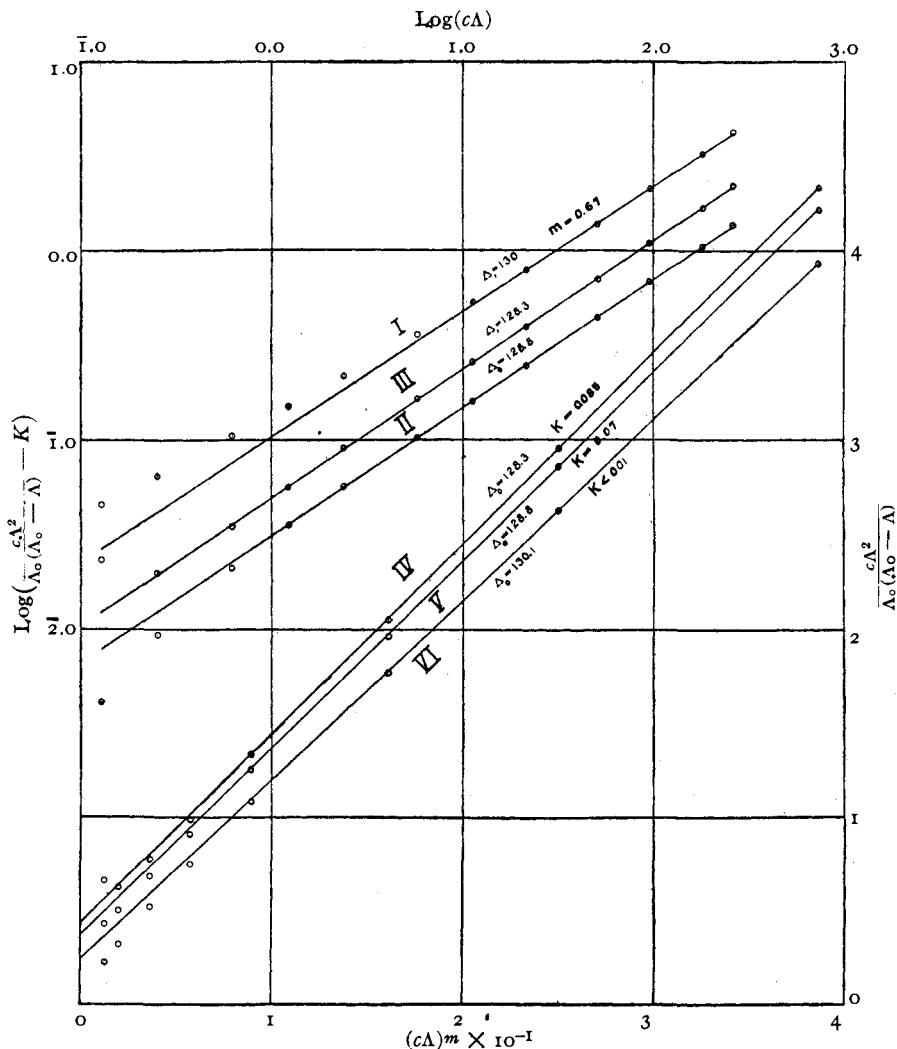
Fig. 27.—m-D and K-D Plots for KCl in H_2O at 18°.

quite accord with the remainder of the points. This is presumably due to inaccuracy in the conductance or viscosity data. This plot gives the value $m = 0.67$. Having determined m, the K-D plot, VI, was next constructed, Λ_0 being assumed equal to 130.1 as in Plot I. This plot, also, gives a straight line in the more concentrated solutions, but in the dilute solutions the curve drops sharply. So far as this curve may be extrapolated in dilute solutions, the value of K would be very small, if not zero. Since, in the more concentrated solutions, the plot is a straight line, it follows that the curvature in dilute solutions cannot be rectified by changing the value of m; for if m were changed, the portion hitherto straight would become curved. We must therefore conclude that the value of Λ_0 is in error, and, judging from the direction of the curvature, Λ_0 is too large.

A new K-D plot, V, was therefore constructed, assuming 128.8 as the value of Λ_0. In this case the points in dilute solutions approach much nearer a straight line. Extending the line until it cuts the axis of ordinates, we obtain 0.07 for the value of K. With this value of K, the m-D plot, II, was constructed, values of $\log \left[\dfrac{c\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)} - K \right]$ being plotted as ordinates. All the points, excepting a few in the most dilute solutions, lie on a straight line. It will be observed that this straight line is parallel to that obtained in Plot I, showing that the value of m as determined for concentrated solutions is practically independent of Λ_0 and K. In considering the K-D plot we are therefore entirely justified in treating m as an independent constant.

The lowest points on Plot II are tending downward very rapidly. In order to understand the significance of this fact, it should be pointed out that K and Λ_0 affect the points in opposit directions. Increasing K tends to lower the points while decreasing Λ_0 tends to raise them. It is obvious, therefore, that the points could not be brought on the line by decreasing K; for, in so doing, the remaining points, already on the straight line, would be raised above the line. The points in dilute solutions can be brought on the line of Plot II only by decreasing Λ_0. Accordingly, the K-D plot, IV, was constructed for $\Lambda_0 = 128.3$. The points in dilute solution lie much more nearly on a straight line than in Plot V. The last point in this case lies above the line. We shall presently discuss the significance of this circumstance. By extrapolating Plot IV, the value of $K = 0.085$ was obtained. With this value of K, and Λ_0 corresponding, the m-D plot, III, was constructed. All the points lie practically on a straight line, with the exception of the last point which lies above it. It is to be noticed again that all the m-P plots are parallel, showing that m is substantially independent of the values of Λ_0 and K.[1]

[1] The above values were slightly modified on fitting the calculated to the experi-

In Table XXII are given the conductance and viscosity data employed in this section. The viscosity data are due to Grüneisen(50) and to Brückner(51). The viscosity values in the third column were read off on a smooth curve drawn through the experimentally determined viscosities at different concentrations. The maximum correction is 2 per cent. There is a possibility that the divergence of the point at 3 normal may be due to an error in the viscosity. Owing to the change in direction of the viscosity concentration curve, the results of different observers cannot be employed to check each other. Results obtained with other salts make it certain that the discrepancy found at 3 normal is due to experimental error and not to failure of Equation III. In the fourth column is given the conductance of KCl corrected for viscosity.[1] Finally, in the last column, are given conductance values calculated from Equation III, the constants being $\Lambda_0 = 128.3$, $K = 0.080$, $D = 2.707$, and $m = 0.763$.[2]

TABLE XXII.—CONDUCTANCE OF KCl IN WATER AT 18°.

Concentration.	Conductance, Λ.	Viscosity.	Corrected conductance.	Calculated conductance.
3.0	88.3	0.9954	87.9	87.4
2.0	92.6	0.9805	90.8	90.9
1.0	98.27	0.9820	96.5	96.4
0.5	102.41	0.9897	101.1	101.1
0.2	107.96	0.9959	107.5	107.6
0.1	112.03	0.9982	111.8	111.9
0.05	115.75	0.9991	115.6	115.5
0.02	119.96	0.9996	119.9	119.8
0.01	122.43	0.9998	122.4	122.4
0.005	124.41	....	124.4	124.4
0.002	126.31	....	126.3	126.3
0.001	127.34	....	127.3	127.2
0.0	....	....	128.3	...

With the exception of the point at 3 normal, the calculated values check the experimental values within 0.1 per cent., which is the limit of experimental error.[3] Beyond 0.001 normal the conductances calculated by means of mental values, the corrected constants giving a slightly better agreement. From the general character of the results we believe that a slightly smaller value of Λ_0 and larger value of K should be assumed for KCl in water at 18°. However, uncertainties in the experimental data are such that it did not seem worth while to extend the calculations further at this time.

[1] The correction is made on the assumption that the speed of the ions is directly proportional to the fluidity of the solvent.

[2] See footnote on preceding page.

[3] From the graphical analysis of the curve, it appears that Λ_0 should be 0.1–0.2 smaller than assumed, and K somewhat larger than the values assumed in the calculations. Since, however, the values of the constants as given above reproduce the results with the limits of error of the conductance experiments, it did not seem worth while to recalculate the results for the lower value of Λ_0. For a more accurate determi-

Equation III are smaller than those determined experimentally by Kohlrausch and Maltby. There is always a possibility that the discrepancy in these dilute solutions is due to experimental error, such as uncertainties in the correction for the conductance of the solvent. An increase of 10 per cent. in the correction for the solvent would bring the conductances between 0.001 N and 0.0001 N into agreement with Equation III. It should be borne in mind that in these dilute solutions we have a highly complex equilibrium between the solute, the solvent and its ions, and an unknown constituent which, in part, probably consists of carbonic acid. Taking all these factors into account, it may well be expected that the corrections made for the solvent are in error by as much as 10 per cent. It certainly would be an unjustifiable procedure to assume, after showing that a certain dilution law holds true from 3 normal to 0.001 normal within the limits of experimental error, that the law suddenly undergoes an enormous change after reaching a dilution where there is good reason, from a theoretical standpoint, for believing that the law must hold.

It should not be forgotten that the general equation has been found to apply to an enormous number of solutions over extreme ranges of concentration in other solvents than water, including the alcohols, which are closely related to water. Moreover, this equation admits of a rational theoretical interpretation in dilute solutions. Further, many electrolytes in water, namely, the organic acids[1] and bases, and mercuric chloride, a weakly

nation of Λ_0, more accurate conductance and viscosity data should be available between 1 and 5 normal.

It is interesting to note that the value of K for KCl, which we have deduced for 18°, agrees well with the value 0.09 at 0° found by MacDougall(52), who independently obtained the same dilution equation. Had the commonly accepted value of Λ_0 been employed, a much lower value of K would have been obtained. In our first calculation, using for Λ_0 the value 130.1, we approximated a value 0.02. Later, by use of the K-D plot, it was found that K would be indeterminate for this value of Λ_0, with 0.02 as a possible upper limit. From the results of MacDougall, it appears that the value of Λ_0 used by him, and determined experimentally by Washburn and MacInnes(24), at 0° is much more nearly correct than that of Kohlrausch at 18°. In this connection it should be noted that, for KNO$_3$ at 18°, MacDougall finds K = 0.01, a value much lower than for KCl at 0°, and one which is nearly the same as our original approximation for KCl at 18°. This value for KNO$_3$ is doubtless much too low, owing to the fact that the Λ_0 value employed is too high. This accounts for the large variation in the constant K between 0.01 and 0.001 normal, as found by MacDougall. MacDougall does not state that the conductance of KNO$_3$ was corrected for viscosity. Unless such a correction is made, agreement in concentrated solutions is not to be expected. Our value of m, 0.673, for KCl is very nearly the same as that found by MacDougall at 0°. He is inclined to attach some significance to the fact that this value is near $^2/_3$. The results of the present investigation in other solvents than water show that no significance is to be attached to the fact that, in some cases, the value of m chances to be nearly equal to a ratio of simple whole numbers. Any theoretical interpretation of Equation III must be capable of accounting for all values of m, at least between 0 and 2.

[1] Kendall(63) has recently shown that the acids do not obey the law of mass

dissociated salt, all obey the mass-action law in water. To cast aside all this mass of positive evidence because of results obtained for strong electrolytes in water at concentration below 0.001 normal would be an irrational procedure.

As a result of this investigation, we must therefore conclude that aqueous solutions of electrolytes obey the same laws as do solutions of the same electrolytes in other solvents, and that with increasing dilution such solutions conform more and more closely to the mass-action law. Moreover, the fact that the exponent m has a smaller value in water than in any of the other solvents investigated shows that aqueous solutions deviate less from the mass-action law than do solutions in other solvents.

Our results also show that the values commonly assumed for Λ_0 for the binary salts are in error to the extent of 1 or 2 per cent., or even more, these values being too high,[1] owing to the fact that the extrapolation functions hitherto employed are not applicable. This change in the value of Λ_0 will serve to harmonize many of the discrepancies hitherto found in aqueous solutions, as will be shown in a subsequent paper.

X. Salts of Higher Valence Types.

For the higher types of salts, but little experimental material is available, save in the case of aqueous solutions. In general, salts of higher types are much less soluble in non-aqueous solvents than are the di-ionic salts. The dissociation in many cases is extremely small, as, for example, in acetone(20). In ammonia the dissociation of some ternary salts is relatively as great as in water(26). Unfortunately, the Λ_0 values for ternary salts are completely lacking in the case of non-aqueous solutions, with the possible exception of some of the lower alcohols.

For the higher types of salts, the test for the applicability of the mass-action law becomes much less simple, and correspondingly less certain, than for binary electrolytes. If, for example, we assume that in a ternary

action exactly except in dilute solutions, and has proved that the deviations from this law in aqueous solutions may be expressed by a dilution law of the form

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

A preliminary examination of Kendall's results indicates that our general equation

$$(c\gamma)^2/c(1 - \gamma) = K + D(c\gamma)^m$$

is applicable to these aqueous solutions, but that Kendall's equation is not generally applicable to solutions in other solvents. This is evident from the fact that, for $K = 0$, Kendall's equation necessarily reduces to the van't Hoff equation $(c\gamma)^{3/2}/c(1 - \gamma) = K'$ (Ib), an equation which is known not to be generally applicable.

[1] Wegscheider(64) has, for a number of years, maintained that the law of mass action holds in dilute aqueous salt solution and that the Λ_0 values ordinarily accepted are too high. Our value for KCl at 18°, 128.3, agrees closely with his, 128.5, page 624. He points out also that the deviation from the law of mass action is related to the ion-concentration, for both strong and weak electrolytes, and concludes that the limiting ion-concentration at which the deviations become appreciable is about 0.03 N. Our results indicate that this concentration is much too high.

salt, MX_2, both negative ions dissociate simultaneously, the mass law expression is:

$$\frac{(M^{++})\ (X^-)^2}{(MX_2)} = K. \tag{X}$$

If, however, dissociation takes place in two stages, with formation of complex cations, we have the equations:

$$\frac{(MX^+)\ (X^-)}{(MX_2)} = K_1 \quad (Xa) \qquad \text{and} \qquad \frac{(M^{++})\ (X^-)}{(MX^+)} = K_2. \quad (Xb)$$

The form of the conductance-concentration curve depends on the values of the constants K_1 and K_2 and on the Λ_0 values for the M^{++}, MX^+, and X^- ions. When, in addition, the deviations from the law of mass action in more concentrated solutions are considered, it is at once apparent that, in general, it will be impossible to analyze the conductance curve for the purpose of testing the mass-action law or the general dilution law. From the experimental data for weak di-basic acids, and also from theoretical considerations, it follows that K_1 is greater than K_2. When this difference is sufficiently great .the conductance curve in moderately concentrated solutions will be similar in form to that of a binary electrolyte and will tend to approach a limiting value corresponding to the conductance of the MX^+ and X^- ions. But when K_2 is appreciable the conductance curve in dilute solutions will rise so as to approach a value approximately twice the limiting value for the first stage of ionization. The first and second stages of ionization will, in general, overlap to such an extent that an analysis of the two portions of the conductance curve is impossible.

It is evident that a solution of the problem is to be expected only in the exceptional case that the first stage of the ionization process is practically complete before the second stage is far advanced. In this case a simple equation results in dilute solution and the dilution law may be tested, provided the conductance of the intermediate ion MX^+ can be estimated with sufficient accuracy. This value can, in general, be approximated from the values for other univalent ions, but the most satisfactory results will be obtained when K_1 is so large and K_2 is so small that the limiting conductance for the first stage of ionization may be estimated from the actual conductance data.

One of the clearest cases showing the presence of intermediate ions is that of solutions of calcium chloride in propylalcohol. These solutions were investigated by Schlamp(9), who found that the molecular conductance of these solutions is intermediate between those of lithium chloride and potassium chloride in the same solvent, and that in dilute solutions it tends to approach a limiting value intermediate between those for these two di-ionic salts. Völlmer(11) was the first to interpret the results in

the way here indicated, as being due to the fact that only the first stage of ionization has taken place. He showed also that the conductance curves for strontium nitrate and barium nitrate in ethylalcohol exhibit a similar behavior; but found that in this solvent the second stage in the ionization process takes place to a large extent, and, in fact, that ultimately the molecular conductance approaches a limiting value corresponding to that of a ternary ionization. It is interesting to note that the conductance curves of strontium nitrate and barium nitrate in liquid ammonia (14, 29) also exhibit certain irregularities which correspond to the phenomena observed by Völlmer in ethylalcohol. These may be due to experimental error, but taken in connection with the results of Völlmer, it appears more probable that they are a result of the dissociation of these salts in stages.

Another complication, met with especially in the case of salts of higher types, is that several molecules of the solute may associate to form a complex molecule which, in turn, dissociates into complex ions. At higher dilution, these complex ions dissociate into simple ions. This behavior, for example, has been demonstrated for solution of cadmium iodide in water by the transference measurements of Hittorf, the cadmium being present in complex anions.[1] Similar results have been obtained in the alcohols, where the complex ions disappear only at much higher dilutions than in water.

Apparently, in solvents of low dissociating power, the stability of the complex is in general much greater than in water; and it is not unlikely that some di-ionic salts form complexes in such solvents. Thus, by means of transference measurements, Serkov(53) has shown that in acetone, lithium chloride forms complex anions of the type: $(LiCl)_xCl^-$. Serkov is inclined to the view that more than two molecules of neutral salt are associated with a single ion. He also seeks to connect the low value of the conductance in concentrated solutions with the complexity of the ion. It is true that, if complexes are formed, the conductance, in general, will fall below that of a similar salt which does not form complexes. At the same time it is doubtful if more than two lithium chloride molecules combine to form the complex. In dilute solutions, lithium chloride in acetone exhibits a perfectly normal behavior(20). As shown in Table XVIII, its ionization constant is small, and this alone is sufficient to account for the low conductance in more concentrated solutions. Incidentally, it may be mentioned that, while polymerization takes place with some salts in certain solvents, the phenomenon is the exception rather than the rule. It is quite out of question to explain all deviations from the mass-action law on the basis of the formation of complexes; for transference measurements clearly show that polymerization is in

[1] Compare also McBain, THIS JOURNAL, 34, 1134 (1912).

most cases lacking,[1] while the deviations from the mass-action law are perfectly general. Serkov is inclined, even, to explain the low value of the conductance of concentrated solutions of lithium salts in water on the assumption that polymerization occurs. This assumption is unnecessary, for the low value of the conductance is certainly in large measure due to the high viscosity of lithium solutions, while at the same time there is reason for believing that the dissociation constants for lithium salts are, in general, lower than for sodium or potassium salts. Transference measurements show an absence of complex ions in water.

In view of the foregoing facts, the formation of intermediate ions by typical ternary electrolytes in non-aqueous solutions seems highly probable, and in some cases it will doubtless be necessary to take into account the formation of complexes by binary electrolytes as well. It was recently shown, as a result of solubility experiments in this laboratory, that there is evidence that intermediate ions exist in aqueous solutions.[2] That the poly-basic acids dissociate in steps has long been known, and there is no good reason for assuming that the processes involved in the case of the salts are materially different from those in the case of the acids.

Finally, there is little doubt but that ternary electrolytes in non-aqueous solutions exhibit deviations from the mass-action law of the same character as those exhibited by binary electrolytes. This is shown by the form of the conductance curves of ternary salts in liquid ammonia(26), which exhibit pronounced minima at about the same concentrations as do the binary salts. In the case of the ternary salts the minima are characterized by a very rapid rise in more concentrated solutions. Further, the conductance at the minimum point is much greater that it is in the case of binary salts in the same solvent. Unquestionably, the higher types of salts present many interesting phenomena, a better understanding of which cannot but lead to valuable results.

Unfortunately, a study of the properties of higher types of salts from a quantitative standpoint presents many difficulties. An accurate and extended study of binary electrolytes seems far more promising. In the present state of our knowledge, the behavior of higher types of salts certainly cannot be looked upon as offering serious objections to the applicability of the general dilution law to electrolytic solutions.

XI. The Constants of the General Equation in Relation to the Dielectric Constants of the Solvents.

We have seen that, for a binary electrolyte, the deviation from the mass-action law is very simply expressed as a function of the ion-concentration. This result indicates that the observed deviation is a consequence of the electrical forces which have their origin in the electrical

[1] For the results in liquid ammonia, see Section IV.

[2] Harkins(54), p. 1860.

charges resident on the ions and which are distributed throughout the body of the solutions in question. If this hypothesis is correct, we should expect a relation between the deviation from the mass-action law, *i. e.*, the constants of the general equation, and the dielectric constant; for the field of force in a medium, due to the presence of charged particles, is a function of its dielectric constant.

The problem presented in the kinetic equilibrium of a system of charged particles is a complex one and at the present time a solution is not available. However, we may test the hypothesis advanced above by examining empirically the relation between the constants of the general equation and the dielectric constants of the various solvents. If the hypothesis is correct, we should expect to find that the constants are continuous functions of the dielectric constants of the media in question. We should bear in mind, however, that one and the same substance added to different solvents may give rise to different electrolytes in different media owing to the formation of compounds (solvates) with the solvent itself. The hypothesis, therefore, would be best tested by comparing the dielectric constant of a given medium under different conditions, as of temperature for example, and the constants of the general equation for the resulting solutions for a given electrolyte under the same physical conditions. The necessary data are not available for a comparison of this kind and we must therefore study the relations of the various constants for different solvents and solutes, bearing in mind the fact that certain discrepancies are likely to appear in the functions connecting the constants of the general equation with the dielectric constants, due to the cause set forth above. We should expect, however, that the more nearly the different solvents approach one another in constitution the more nearly will the constants of the general equation approach the conditions of continuity with respect to the dielectric constant.

That the dissociating power of a solvent is a function of its dielectric constant was first pointed out by Thomson(71) and by Nernst(58); the dissociating power increasing with increasing dielectric constant. Certain cases have been pointed out in the literature where the Thomson-Nernst rule apparently fails. As we shall see presently, these discrepancies disappear when comparison is made in terms of the constants of the general equation rather than in terms of the ionization at some arbitrary concentration.

In Table XXIII are given the values of the constants of the general equation for a variety of solvents. So far as possible, the same solute is employed throughout in this comparison. Where this has not been possible, one of the other typical largely ionized solutes has been employed. Electrolytes that are likely to exhibit an abnormally low degree of ionization have been avoided. The values of D appearing in brackets

were not determined directly but were approximated from Equation VII by assuming that the ratio Λ_0/f_0, of conductance to fluidity is equal to 0.517. In many cases viscosity data are lacking where, otherwise, D might have been determined. In the solvents of stronger dissociating power, D can only be determined from a complete conductance curve. The values of Λ_0 as calculated from the viscosity of the pure solvent are probably too low for the inorganic solvents; for the relationship employed is far less exact for inorganic than for organic solvents and the ratio is usually greater for inorganic solvents. For this reason, the D values given for the liquid halogen acids and for hydrogen sulfide are probably too large.

TABLE XXIII.—CONSTANTS OF THE GENERAL EQUATION AND DIELECTRIC CONSTANTS FOR VARIOUS SOLVENTS.

Solvent.	Solute.	Dielectric constant.	m.	D.	$K \times 10^4$.
Hydriodic acid	$(C_2H_5)_3N.HCl$	2.9 (59)	1.58	(0.58)	....
Amylamine	$AgNO_3$	4.5 (61)	1.67	..	....
Propionic acid	LiBr	5.5 ..	1.74	(0.30)	....
Methylaniline	$C_5H_5N.HBr$	5.9 ..	1.64	..	....
Ethylamine	$AgNO_3$	6.2 (61)	1.42	..	....
Ethylamine	NH_4Cl	6.2 ..	1.57	..	....
Hydrobromic acid	$(C_2H_5)_3N.HCl$	6.3 (59)	1.51	(0.54)	....
Aniline	$AgNO_3$	7.5 ..	1.42	(0.44)	....
Aniline	NH_4I	7.5 ..	1.44	(0.51)	....
Hydrochloric acid	$(C_2H_5)_3N.HCl$	9.5 (59)	1.42	(0.39)	....
Acetic acid	LiBr	9.7 ..	1.43	(0.30)	....
Hydrogen sulfide	$(C_2H_5)_3N.HCl$	10.0 (60)	1.58	(0.30)	....
Methylamine	$AgNO_3$	10.0 (61)	1.22	0.30	0.80
Ethylenechloride	$(C_3H_7)_4NI$	10.5 (37)	..	..	1.45
Pyridine	NaI	12.4 ..	..	..	13.0
Pyridine	KI	12.4 ..	..	..	5.2
Acetoaceticester	NaSCN	15.7 ..	..	..	9.5
Isoamylalcohol	NaI	15.9 ..	..	..	3.9
Isoamylalcohol	LiI	15.9 ..	..	..	7.3
Acetophenone	NaI	16.4 ..	..	..	34.0
Sulfur dioxide	KI	16.5[1] ..	1.14	0.40	8.5
Methylethylketone	NaI	18.4 ..	..	..	23.0
Isobutylalcohol	NaI	18.9 ..	..	..	12.0
Acetone	NaI	21.8 ..	..	..	39.0
Ammonia	NaI	22.0 ..	0.83	0.43	28.0
Epichlorhydrin	$(C_2H_5)_4NI$	22.6 (37)	..	..	48.5
Propylalcohol	NaI	23.0 ..	..	..	45.0
Benzonitrile	NaI	26.0 ..	..	..	55.0
Water	KCl	80.0 ..	0.67	2.5	800.0

The values for the dielectric constants, for the most part, have been taken from Landolt-Börnstein's "physikalisch-chemische Tabellen,"

[1] Extrapolated from the results of Eversheim(62).

and form Winkelmann's "Handbuch der Physik," and no further references are required. In other cases, the reference number is given following the constants. In general, preference has been given to constants determined by means of a statical method. In case electric waves were employed, preference has been given to the results obtained by long waves. Some of the constants are doubtless in error, owing to the influence of dispersion. The value for HI is especially doubtful.[1] In making a comparison of the dielectric constant with the constants of the general equation, uncertainties in the values of the dielectric constants must be kept in mind.

Perhaps the most striking result of the comparison made in this table is the fact that for these strong electrolytes the value of D is nearly the same for the different solvents. The variation of the constants which are shown in parentheses may well be due to errors in the values of Λ_0 as explained above. On the other hand, it is to be borne in mind that the values of D for different salts in a given solvent vary greatly as may be seen by referring to Tables V, VIII and XXI. Since nearly all the substances in Table V are typical strong electrolytes, it follows that, while the exact relation between the dielectric constant and D cannot be determined, the value of D is practically independent of the solvent for values of the dielectric constant less than 22.[2] The high value of D for water is remarkable. It is not probable that this high value can be due to an error either in measurement or in calculation. The probable explanation, therefore, is that, for low values of the dielectric constant, D is approaching a fixed value asymptotically and that only for very large values of the dielectric constant does the value of D increase considerably above its lower limit.

[1] Schaefer and Schlundt(59), who determined this constant, found a negative temperature coefficient for the dielectric constant of this solvent. Also, they found a higher constant for the solid than for the liquid. Such a variation of the constant with temperature and condition is distinctly exceptional, and cannot be accepted without confirmatory determinations by other methods.

[2] The fact that D has the same value for different solutions leads to the remarkable conclusion that for the ion-concentration $c\gamma$ equal to unity, the ionization of these electrolytes is the same. The total concentration must therefore be the same also. This follows at once from the general equation on the assumption that the K-term is negligible at high concentrations, which, as we have seen, is substantially correct for concentrations above normal. As may be seen from the table, the value of D for strong typical electrolytes (excepting in the case of water) is approximately 0.35. At the concentration $c\gamma = 1$, their ionization will, therefore, be 26%, at a total concentration of approximately 4 normal. The ionization curves of these solutions will, therefore, intersect in a narrow region in the neighborhood of 4 normal. At concentrations greater than 4 normal, solutions with the larger value of m will exhibit the larger ionization, while, at concentrations less than 4 normal, solutions with the larger values of m will exhibit the smaller ionization. For values of $m > 1$, the curves pass through the region of intersection ascending with concentration, while for $m < 1$, they pass through descending with concentration.

Thus, for KI, D is slightly larger in ammonia than in sulfur dioxide, and the same is true for $AgNO_3$ in ammonia and in methylamine.

In order to determin the exact form of the relation between D and the dielectric constant, further experimental data are necessary. It is certain, however, that *as the dielectric constant approaches unity, D does not approach zero.* This is a result of great importance from a theoretical standpoint. · The power of ionizing a dissolved substance is thus not restricted to solvents of high dielectric constants. Only in relatively dilute solutions, where the K-term predominates, is ionization confined to solvents of high dielectric constants. In concentrated solutions the power of ionizing typical strong electrolytes is a property of all dielectric media. For a given electrolyte the ionization is the same in all solvents having the same value of the dielectric constant, and it is independent (for the most part, at least) of temperature or the chemical nature of the solvent medium.

The value of K clearly decreases very rapidly with decreasing values of the dielectric constant. For water, with a dielectric constant of 80, K has a value approximately 0.1, while for methylamine, whose dielectric constant is 10, the value of K is approximately 0.0001. The general form of the relation between the mass-action constant and the dielectric constant is unmistakable. With increasing values of the dielectric constant, K increases more rapidly the higher the dielectric constant; K is roughly proportional to the cube of the dielectric constant. The exact nature of the relationship cannot be determined from the available data, partly because the values both of K and of the dielectric constant are uncertain, and partly because the mass-action constant is dependent on the specific nature of the solute. It appears certain, however, that *as the dielectric constant approaches unity, K becomes vanishingly small.*

That the value of m is a function of the dielectric constant is very evident, although here, again, considerable variation arises, owing to the fact that different salts enter into the comparison. An idea of the nature of the relationship may be gained from Fig. 28, in which values of m are plotted as ordinates against values of the dielectric constants as abscissas, for solutions of $AgNO_3$ in amylamine, ethylamine, aniline, methylamine, and ammonia. It is evident that the points lie substantially on a smooth curve. The consistency of the values in this case is doubtless due to the fact that the solvents compared are all derivatives of ammonia, and that the solvates formed are consequently similar in nature. *As the dielectric constant approaches unity, the value of m increases to a value at least as great as 2.* Whether or not it approaches a finite limit is uncertain.

Further experimental data are needed in order to determin more exact relations between the dielectric constant and the values of K, D, and m. However, it is beyond question, from what has been said, that these constants are all very intimately related. We see also that the characteristics

of certain solutes are maintained whatever be the nature of the solvent. Thus oxonium salts, whose value of D is often very small in water, also have a small value of D in the liquid halogen acids and in hydrogen sulfide. So also we find that certain silver salts, some of which have a relatively
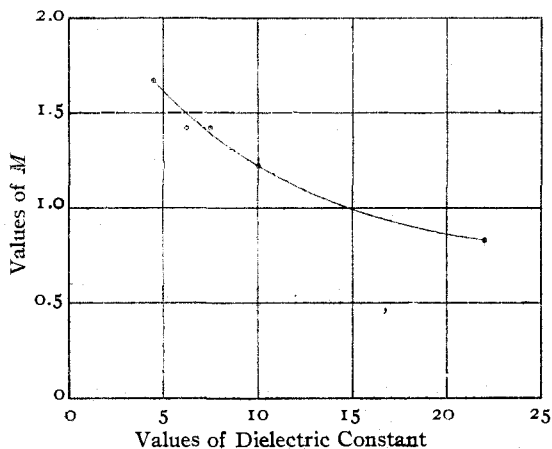

Fig. 28.—Relation between m and Dielectric Constant.

low ionization in water, also have a low ionization in ammonia. On the other hand, the typical inorganic salts, which are among the most strongly ionized electrolytes in water are also among the most strongly ionized in all other solvents.

It should also be noted that the exceptions to the Thomson-Nernst rule which have hitherto been pointed out, lose their significance in the light of the results obtained in this paper; and when the comparison for a given solute is made between the constants of the general equation instead of between conductances directly, no discrepancies appear. There can be little doubt that the dielectric constant is the controlling factor in the process of electrolytic dissociation, both in dilute solutions, where the mass-action law is obeyed, and in concentrated solutions, where the deviation from the mass law determins the form of the conductance curve. Not only is the mass-action constant K determined by the dielectric constant of the medium, but also the deviations from the mass-action law (expressed by D and m) are governed by the same agency. Although the Thomson-Nernst rule is a beginning in the treatment of electrolytic solutions, it remains only a qualitative relation until the ionization of a given solute in dilute solutions can be expressed as a function of the dielectric constant. Until this is done, it seems improbable that a solution will be forthcoming for the much more difficult problem of accounting for the deviations from the mass-action law in more concentrated solutions.

XII. Theoretical Significance of the Results.

It is one of the most important results of this investigation to have shown that *all electrolytic solutions are subject to the same dilution law.* Hitherto, one of the obstacles to the further development of the theory of electrolytic solutions has been the contradictory behavior of different solutions. Thus, the strong electrolytes in aqueous solutions were found to obey certain empirical relations more or less closely, while the weak acids and bases were found to follow the law of mass action. Again, while in aqueous solutions the equivalent conductance invariably decreases with increasing concentration, in non-aqueous solutions a converse relation holds true in many instances. The fact, however, that one general equation is applicable in all cases for which trustworthy data are available shows that the observed differences in the behavior of different electrolytic systems is an apparent, and not a real one; and this conclusion remains true whatever significance be attached to the general equation.

It also follows from this investigation that *at high dilutions the mass-action law applies to the results of conductance measurements.* It is true in certain cases, particularly in solvents of very low dielectric constant, that the mass-action constant K is so small that it cannot be determined by conductance measurements, while other methods of determining it are not available. However, the manner in which the constant K varies with the dielectric constant leaves little room for doubt that, even in the case of very low dielectric constants, K is still a real factor in the dilution equation.

Since the mass-action law is applicable to solutions of binary electrolytes at high dilutions, it follows as a corollary that under these conditions an ionic equilibrium prevails which conforms to the requirements of a binary dissociation.[1] In its fundamental elements, therefore, the ionic theory as originally proposed by Arrhenius is correct. In our search for an explanation of the behavior of concentrated electrolytic solutions we may at once exclude all theories that require a fundamental modification of the prevailing conception as to the nature of electrolytic solutions. Finally, it follows from the present investigation that *in solutions whose ion-concentration exceeds a value lying between 0.001 and 0.0001 normal a divergence from the law of mass action becomes appreciable.* This divergence increases rapidly with concentration and lies in a direction corresponding to a conductance greater than that called for by the law of mass action. The divergence from the mass-action law, is, moreover, a function of the ion-concentration rather than of the total concentration

[1] The discussion throughout this section is restricted to binary electrolytes since sufficient data are not available for higher types. Higher types of salts are discussed in Section X.

of the solute. The problem which remains, therefore, is to account for the divergence from the mass-action law in concentrated solutions. That divergence from the mass-action law should become appreciable at some concentration was to have been expected, since this law, expressed in terms of actual concentrations or pressures, is merely a limiting expression, like the laws of ideal gases, the deviations from which become increasingly larger as the concentration increases. In the case of electrolytic solutions, however, the deviations from the mass-action law become appreciable, as we have seen, at concentrations very much smaller than those at which the deviations occur in ordinary gases or in solutions of non-electrolytes. It is for this reason that the deviations in electrolytic solution deserve special consideration.

Three hypotheses have been suggested to account for the deviations of the measured conductance values from the requirements of the mass-action law, namely: 1. The equilibrium involved is not simply a binary dissociation. 2. A binary equilibrium prevails which conforms to the mass-action law, but the speed of the ions is not independent of concentration, so that the ratio Λ/Λ_0 does not give correctly the degree of ionization of the electrolyte. 3. The ratio Λ/Λ_0 gives correctly the degree of ionization, but owing to the action of forces between the molecules or ions involved in the equilibrium the activities (active masses) of the various molecular species are not proportional to their concentrations. We shall discuss these three hypotheses in order.

1. *The Equilibrium involved is not a Simple Binary Equilibrium.*—To apply the law of mass action to a given system it is essential that the equilibrium reaction be known. If a false assumption be made as to its mechanism, an apparent discrepancy with the law must result. In this connection we should bear in mind the following facts: first, since in very dilute solutions the mass-action law applies, the assumption that the equilibrium reaction is a binary dissociation in such solutions is correct; second, all electrolytic solutions obey the same dilution law; and third, the deviations from the mass-action law in concentrated solutions correspond to conductance values higher than those predicted by this law, and therefore any change in the equilibrium equation must be such as to furnish more carriers than would result from the simple binary dissociation assumed (for, if complex ions are formed, their conductance certainly will not be greater than that of the simple ions).

Steele, MacIntosh, and Archibald(34) have proposed a modification of the equilibrium equation. They had been studying solutions in solvents of very low dielectric constants, in which case, as we have seen, the molecular conductance increases with increasing concentration. They were thus led to suggest that the solute polymerizes at higher concentrations and that only the polymerized molecules are capable of ionic disso-

ciation. This hypothesis has been somewhat further developed by Sachanov(67) in a recent paper. Sachanov assumes that not only the aggregated molecules but also the simple ones are capable of ionization;[1] and he thus attempts to account for the ultimate rise in the molecular conductance of the solutions at high dilutions, as, for example, of solutions in methylamine, ammonia, etc.

The reactions involved in this hypothesis are:

$$(MX)_2 = MX + MX \qquad\qquad (A)$$

$$(MX)_2 = M^+ + MX_2^- \qquad\qquad (B)$$

$$MX \ = M^+ + X^-, \qquad\qquad (C)$$
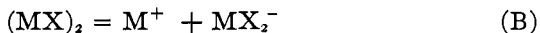
where MX represents an electrolyte dissociating into the normal univalent ions M^+ and X^- and the complex anion MX_2^-. (It is obvious that for the purpose of this discussion it is immaterial whether the anion or cation be assumed to be complex.) The equations here given are for the case in which two molecules of solute associate. It is not necessary to consider more complex cases, since a greater molecular complexity would in many cases lead to conductance values smaller than the observed ones, even if it be assumed that the complex molecules are completely ionized.

Now, according to the hypothesis in question, at low concentration the equilibrium is described by equation (C). In highly concentrated solutions it is described by equations (A) and (B), while for intermediate concentrations all three equations are necessary for a complete description of the equilibrium. It is obvious that in very dilute solutions, where equation (C) applies, the transference numbers of the ions will be determined by their relative speeds, and these numbers will therefore be inde-

[1] Unless we assume that the ionization of the complex molecules into complex ions is much greater than that of the simple molecules into normal ions, the influence of complexes is to lower the conductance of the solution below the value it would otherwise possess. Serkov(53) has suggested that the low conductance values of LiCl solutions in acetone are due to the presence of complex ions. A low value of the conductance does not, however, necessarily indicate the presence of complex ions, as Serkov believes, for more often, as is abundantly shown in this paper, the low conductance values are due to low values of the constants K and D, of the general equation. The independence of the transference numbers of concentration shows conclusively that the presence of complex ions in binary electrolytes is an exceptional rather than a general one. It should also be pointed out that in concentrated solutions the results of transference experiments are enormously affected by solvation. For example, it follows from the work of Washburn(55) that the true transference numbers of Li^+ and Cl^- ions in aqueous solutions change far less with concentration than do the Hittorf numbers. There can be no question that all electrolytic ions are solvated. Thus, Washburn has demonstrated the solvation of K^+, Na^+, Li^+, and Cl^- ions in water. Even the hydrogen ion is hydrated, as was shown by Buchbök(68). Taking into account these facts, together with the approximate proportionality between Λ_0 and the fluidity of various solvents, it follows that all ions are hydrated to a considerable extent. Conclusions based on the results of transference experiments therefore cannot be accepted without question.

pendent of concentration. When, however, concentrations are reached where the proportion of complex ions becomes appreciable, the transference numbers will no longer remain constant, but will change in consequence of the formation of the complex ion. This change will be greater the greater the extent to which reactions (A) and (B) take place; and finally, in very concentrated solutions, very abnormal values of the transference numbers will result.

Thus the dependence of transference numbers on the concentration constitutes a crucial test of the hypothesis that the deviations from the mass-action law are due to the formation of complex molecules and ions, and the fact that the transference numbers as a rule vary very little, even up to fairly high concentrations, enables us to definitly eliminate this hypothesis, so far as its general applicability is concerned. For, since all electrolytic solutions obey the same dilution law, if the hypothesis breaks down·in one case, it breaks down in all others. Now, in ammonia solutions the deviations from the mass-action law are very large, even at concentrations below 0.01 normal. If the hypothesis in question were correct, the transference numbers of the ions in ammonia solutions would have to undergo marked change with the concentrations between 0.001 and 0.1 normal. Yet it follows from the work of Franklin and Cady that little, if any, change takes place in the transference numbers with the concentration. The same holds true of aqueous solutions, where no change takes place with concentration, except in cases in which the viscosity of the solution reaches appreciable magnitude. The transference numbers of solutions in the liquid halogen acids also indicate that complex ions are not present to a considerable extent, if at all.

In the light of these facts, the hypothesis under discussion clearly becomes untenable. This does not mean, of course, that complex ions are never formed,[1] for we have numerous examples of the existence of such ions even in aqueous solutions; but the phenomenon is an exceptional, rather than a general one, and does not account for the universal tendency of solutions to exhibit a conductance higher than that required by the law of mass action.

2. *The Mass-Action Law holds true, but the Ionization is not correctly given by the Ratio* Λ/Λ_0.—Ostwald was the first to suggest that the deviations of strong electrolytes from the mass-action law are merely apparent

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[1] For example, as stated in Section III D, it is probable that complex ions are present in solutions of the cyanides in liquid ammonia. It is to be noted that wherever complex ions are formed their presence is indicated by collateral evidence, and the form of the conductance curve differs from that of typical binary electrolytes. Yet in all cases, the nature of the deviations is the same, when once the influence of the complex ion is taken into account. In the case of the cyanides in liquid ammonia the complex ions are very stable and it is only at extremely high dilutions that the breaking up of the complex ions makes itself evident.

and that they are due to a change in the speed of the ions, as a result of which the ratio Λ/Λ_0 no longer gives the correct value of the ionization. This view was later taken up by Jahn(57)[1]. In a recent paper in THIS JOURNAL, Lewis(66) has pointed out certain evidence which lends a measure of support to this hypothesis.[2]

The first step in an examination of this hypothesis is to determin the magnitude of the change in the speed of the ions which would have to be assumed in order to account for the observed deviations from the mass-action law. The value of the constant K is known for typical strong electrolytes in a number of solvents including water. On the basis of the above hypothesis, therefore, we are able to calculate the ionization of any solution for which K is known. For aqueous solutions the value of K for typical strong electrolytes is approximately 0.1. At normal concentration the ionization is therefore 27 per cent. Assuming the speed of the ions to remain constant, the ionization of this solution at this concentration is approximately 75 per cent. Therefore, in order to account for the observed conductance on the assumption that the speed of the ions increases with increasing concentration, it is necessary to assume that in a normal solution (of KCl, for example) the ions move with a speed approximately three times as great as that of the same ions in very dilute solutions.

This change of speed is not a result of change in viscosity; for the viscosity of a normal KCl solution is only about 2 per cent. less than that of pure water. Also in the case of other electrolytes the viscosity increases with concentration, while the change in speed which would have to be assumed is practically the same as that in the case of KCl solutions. Moreover, it is to be noted that in the case of many electrolytes, such as KCl, the transference numbers of the ions are practically independent of the concentration. We should not expect this to be the case if large changes in speed were to take place.

The changes of speed that would have to be assumed in the case of aqueous solutions are of such a magnitude as to throw doubt on the hypothesis in question. In non-aqueous solutions, even larger changes in speed would have to be assumed. For potassiumamide solutions in ammonia a ninefold increase in speed would have to be assumed to take place between 0.0001 normal and 2.5 normal. Similar changes would have to be assumed for other typical electrolytes in ammonia. In solvents of very low dielectric constant even greater increase in speed would have to be assumed than in ammonia. For example, the observed (molec-

[1] Ultimately, however (although he still maintained that Λ/Λ_0 is not a measure of the ionization), Jahn reached the conclusion that the observed results could only be accounted for on the assumption that there are deviations due to forces acting between the molecules and ions involved in the equilibrium.

[2] Prof. Lewis also calls attention to the fact that additional evidence is necessary before the question can be settled.

ular) conductance increase with increasing concentration is often between 100- and 1000-fold. Assuming the ionization to remain constant, a corresponding increase in speed would have to be assumed. Actually, a greater change in speed would have to be assumed, since, if the mass-action law holds, the ionization does not remain constant but decreases with increasing concentration.

Changes in speed of the order stated in the preceding paragraph could take place only as a result of an enormous decrease in resistance to the motion of the carriers. The viscosity of the solutions in the case of non-aqueous solvents almost invariably increases with concentration so that the only means by which an increase in speed might result would be in consequence of an enormous diminution in the dimensions of the carriers. Such diminution in dimensions is highly improbable.

This argument becomes even more convincing in the light of the relation between viscosity and conductance. In all highly concentrated solutions the molecular conductance decreases as a result of viscosity change. The influence of viscosity becomes appreciable at lower concentrations as the dimensions of the ions become greater. If the speed of the ions increases in any such manner as indicated above, their dimensions must become so small relative to those of the solvent molecules that very little diminution in speed would be expected as a result of viscosity change.

If the deviations from the mass-action law in non-aqueous solutions are not due to change in the speed of the ions, the deviations in aqueous solutions also are not due to this cause; for, as we have seen, aqueous and non-aqueous solutions conform to the same dilution law and the deviations from the mass-action law are therefore of the same nature in the two cases.

It might perhaps be suggested that the deviations are due to a new type of conduction superimposed on the normal type of ionic conduction. For example, it might be assumed that metallic conduction takes place, together with electrolytic conduction. The fact that these solutions obey Faraday's laws proves conclusively, however, that the conduction process is necessarily an ionic one. Moreover, the fact that the deviation is a function of the ion-concentration, or more precisely, of the specific conductance of the solution, indicates that, whatever the conduction process may be, only a single process of conduction prevails in these solutions.

3. *The Degree of Ionization is correctly Measured by the Ratio* Λ/Λ_o.[1]— Having shown the improbability of the first two hypotheses, we shall examin the third, according to which the ionization of an electrolyte is correctly given by the ratio Λ/Λ_o. This hypothesis is one of two main hypotheses underlying the ionic theory as originally proposed by Arr-

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[1] It is assumed that when the viscosity reaches appreciable magnitude, correction has been made for the attendant change in the speed of the ions.

henius, the other hypothesis being that in an electrolytic solution an ionic equilibrium exists. If both hypotheses are correct, their correctness is evidently demonstrable, for in this case the equilibrium must be subject to the mass-action law (at sufficiently high dilutions) and the concentrations of the different molecular species are determinable from conductance measurements. As has been pointed out above, when this test was applied to solutions (which appeared to be dilute) of the so-called strong electrolytes, the correctness of the two hypotheses was not confirmed, and the conclusion was therefore drawn that one of these hypotheses is incorrect, a view which has been largely prevalent up to the present time.

Now, as was pointed out by Nernst(56) and by Jahn(57), the derivation of the mass-action law in its customary form presupposes that the molecular species entering into the equilibrium obey the laws of ideal substances. In order to apply the mass-action law as a test for the correctness of the assumptions underlying the ionic theory, it is therefore necessary that the concentration of the solutions be so small that the forces acting between the different molecules of the dissolved substance be negligible. Taking into account the fact that in electrolytic systems forces may come into play, owing to the presence of charged particles, which are entirely lacking in non-electrolytic systems, it follows that a discrepancy of the observed conductance data with the mass-action law at higher concentrations does does not necessarily imply that the assumptions underlying the ionic theory are incorrect. Only when it had been shown that there is no concentration, however small, at which the results of conductance measurements conform to the mass-action law would it be necessary to assume that these assumptions are false.

It has been shown in the present investigation that at sufficiently low concentrations the mass-action law holds true and that the degree of ionization is correctly measured by the conductance ratio Λ/Λ_o. Under these conditions, then, the fundamental assumptions of Arrhenius are correct. If, now, we assume that in the more concentrated solutions the ratio Λ/Λ_o correctly measures the ionization of the electrolyte, it follows that in these solutions the mass-action law fails to apply for the reason that at these concentrations the underlying laws of ideal substances are no longer applicable. In other words, a concentration has been reached at which the forces acting between the molecules of one or more of the molecular species present in the solution are no longer negligible.

This concentration limit lies between 0.0001 and 0.001 normal, a concentration enormously smaller than that of non-electrolytic solutions in which the concentration limit lies in the neighborhood of 0.1 normal. This result is striking because of the smallness of the value of the limiting concentration; but it is in no wise in contradiction with known facts, for the concentration at which a given solution will show appreciable de-

parture from the laws of ideal solutions cannot be predicted *a priori* but must of necessity be determined by experiment. That the concentration limit should be lower in the case of electrolytes than in that of non-electrolytes is not an unexpected result when we take into account the fact that in the case of electrolytes charged particles are present, the forces between which may well be much greater than those between neutral molecules. That electrical forces play a major role in electrolytic solutions is evidenced by the fact previously pointed out (Section XI) that the constants of the general equation are intimately related to the dielectric constant of the solvent medium; and, moreover, the deviation itself is a simple function of the specific conductance, or, in other words, of the ion-concentration.

It is evident that in electrolytic solutions there is operative an agency which, even at high dilutions, profoundly modifies the mass-action relationship, and which at higher concentrations controls the equilibrium almost completely. This agency comes into play the more, the greater the ion-concentration and the smaller the dielectric constant, *i. e.*, the stronger the electric field surrounding the charged particles. In solvents of very low dielectric constant, such as the liquid halogen acids, iodine, amylamine, etc., ionization appears to be almost entirely due to this agency. That this agency is also operative in other systems containing charged particles in kinetic equilibrium, such as the fused salts and the metals, seems not improbable.

The agency in question manifests itself in a marked deviation of ionized substances from the laws of ideal susbstances and is doubtless due to forces acting either between the charged particles (ions) or between the charged particles and the neutral molecules. The first step in the further development of this question is to determin between what molecular species concerned in the equilibrium the disturbing forces act.[1]

From a theoretical standpoint, much remains to be done in the field of electrolytic solutions, but a serious obstacle in the path of the ready acceptance and further development of the ionic theory has been removed in showing that at high dilutions the mass-action law is generally applicable. The fundamental assumption of Arrhenius that the ionization is correctly determined by the conductance ratio Λ/Λ_0, even at higher concentrations, is greatly strengthened by the results in non-aqueous solutions and serious doubts as to its correctness can no longer be entertained. The innumerable data relative to the conductance of electrolytic solutions are correlated in a simple and surprisingly complete manner by the general equation, and a ready means is thereby afforded for studying the dependence of the condition of electrolytic solutions on various physical

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[1] This problem will be treated more partieularly in forthcoming publications from this laboratory.

factors such, for example, as the dielectric constant of the solvents. Experimental material of this nature is much needed in the further development of theoretical conceptions regarding electrolytic solutions.

XIII. Summary.

It is proposed to express the relation between the concentration and the conductance of electrolytic solutions by the general equation:

$$(c\gamma)^2/c(1 - \gamma) = K + D(c\gamma)^m,$$

where c is the concentration, γ the conductance ratio Λ/Λ_o, and K, D, and m are constants.

In sufficiently dilute solutions, the term involving $(c\gamma)^m$ becomes negligible in comparison with K, and the equation approaches the simple mass-action law as a limit. In concentrated solutions, K becomes negligible in comparison with $D(c\gamma)^m$, and the equation assumes the form of that of Storch. For $m > 1$, the molecular conductance passes through a minimum value; while, for $m < 1$, the conductance decreases continuously with increasing concentration.

Graphical methods are described whereby the constants of the general equation may be conveniently evaluated from the experimental data, and illustrations are given.

A method is provided whereby the mass action law may be tested without assuming a value for Λ_o.

It is shown that the general equation applies to the extensive conductance data available for solutions in liquid ammonia. Values of the constants K, D, m and Λ_o have been calculated and are tabulated. The deviations from the mass-action law become appreciable at ion-concentrations between 0.001 and 0.0001 normal. Accordingly, the smaller the ionization of the electrolyte the higher the total concentration up to which the mass-action law is sensibly obeyed.

With the aid of the transference data of Franklin and Cady the ion-conductances of a considerable number of ions in liquid ammonia solutions have been calculated and these values are compared with those of 'the same ions in water.

The general equation also applies to solutions in liquid sulfur dioxide. The influence of temperature on the conductance of solutions is readily accounted for by the variation which these constants undergo with temperature change.

The applicability of the mass-action law to dilute solutions of strong electrolytes in non-aqueous solvents (including the higher alcohols) has been examined by graphical methods, and it has been found that up to ion-concentrations between 0.0001 and 0.001 normal, this law applies within the limits of experimental error, but that at higher ion-concentrations deviations become measurable. This limiting ion-concentration is approximately the same for solutions of a given electrolyte in different solvents and for different (strong or weak) electrolytes in the same solvent.

In the case of concentrated solutions in solvents of low ionizing power, $1 - \gamma$ does not differ greatly from unity and its change with concentration is negligible in comparison with that of γ. Under these simplifying assumptions the general equation takes the form:

$$c\Lambda^2 = P(c\Lambda)^m,$$

γ having been replaced by the conductance ratio Λ/Λ_0, and P being a constant involving Λ_0. Since Λ_0 does not occur explicitly in this equation, the general equation may be tested without a knowledge of the value of this constant. It has been found that the equation holds for all cases (67 solutions and 12 solvents) for which reliable data exist. The values of P and m have been derived and are tabulated.

The general equation is applicable to aqueous solutions of strong electrolytes. This equation, thus, reproduces the measured conductance of KCl solutions between 0.001 and 2.0 normal within 0.1 per cent. To obtain this agreement in the more dilute solutions it is necessary to assume for Λ_0 the value 128.3 instead of 130.1 as commonly accepted. It seems very probable that the accepted Λ_0 values for all binary electrolytes are from 1 to 2 per cent. too high, the error being due to the fact that in extrapolating for Λ_0 an arbitrary dilution law has been assumed instead of the mass-action law. With the lower Λ_0 values, a ready explanation is found for many discrepancies which have hitherto been observed in dilute aqueous solutions.

In the case of salts of higher valence type, a test of the general equation is at the present time impracticable because of lack of accurate data and because of complications arising from the formation of intermediate ions. It is pointed out that in propylalcohol the presence of such ions has been established previously. There is reason for believing that salts of higher valence type obey the same general relation as do binary electrolytes.

The relation between the ionizing power of a solvent and the values of the constants K, D, and m is discussed and it is shown that, with decreasing dielectric constant, K approaches zero (or, at least, a very small value); D approaches a constant value (0.35) which undergoes but little change as the dielectric constant falls below 22; and m increases approaching a value greater than 2. The marked conductance of concentrated solutions in solvents of low dielectric constant is due to the large value of D.

From a theoretical standpoint, the most important results are: that all electrolytic solutions (of binary electrolytes) obey the same dilution law; that the mass-action law is obeyed at high dilutions; that the divergence from the mass-action law at higher concentrations is a function of the ion-concentration; and that, for a given electrolyte in different solvents, the trend of the conductance curve is determined by the dielectric constant of the solvent. Finally, it is shown that the fundamental hypothesis of Arrhenius, according to which the ionization is measured by the con-

ductance ratio Λ/Λ_o, is in harmony with the observed facts, not only in very dilute solutions, but also in concentrated solutions (up to more than normal when viscosity changes are taken into account). An explanation of the observed deviations from the mass-action law is to be looked for in the interacting forces due to the presence of charged particles (ions) throughout the body of the solution.

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CHEMICAL REACTIONS AND ELECTRICAL CONDUCTIVITY OF NON-AQUEOUS SOLUTIONS.

By H. P. Cady and H. O. Lichtenwalter.

During recent years, Kahlenberg[1] and others have published several papers in which they set forth reasons for not accepting the dissociation theory. For instance, Kahlenberg[2] conducted double decompositions in non-aqueous solutions and states that some instantaneous reactions occur without any conductivity, hence no ionization. It is with a view of studying similar double decompositions that this investigation has been undertaken. Kahlenberg chose benzene as a solvent and copper, nickel and cobalt oleates as the solutes. After drying the benzene very care-

[1] Kahlenberg, J. Phys. Chem., 6, 1 (1902); Sammis, Ibid., 10, 593 (1906); Gates, Ibid., 15, 97 (1911).
[2] Loc. cit.