the atomic weight of neo-ytterbium with great care. The earth was subjected to many fractionations, and each fraction was studied magnetically and spectroscopically. The value found for the atomic weight, the mean of 13 determinations, was 173.50. He suspects that the "aldebaranium" studied by Auer von Welsbach contained an element of lower atomic weight, probably thulium. Urbain's paper will be published in the near future, perhaps before this report appears. F. W. C.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, THE UNIVERSITY OF CHICAGO.]

STUDIES IN CONDUCTIVITY. II. THE CONDUCTIVITY OF SOME FORMATES AND OF HYDROGEN CHLORIDE IN (ANHYDROUS) FORMIC ACID. CASES OF APPARENT AGREEMENT OF STRONG ELECTROLYTES WITH THE MASS LAW.[1]

BY H. I. SCHLESINGER AND A. W. MARTIN.[2]

Received May 12, 1914.

In the first paper of this series, Schlesinger and Calvert[3] showed that the solutions formed when ammonia is passed into formic acid are excellent conductors and that the electrolyte, ammonium formate, obeys the law of mass action, although it is highly ionized. It is well known that strong electrolytes do not, in general, obey this law and these solutions, therefore, are exceptionally interesting. Consequently, we have undertaken to extend this work, with the intention of determining the limiting concentrations within which the law is applicable and of obtaining results of greater accuracy by improving the methods employed. In addition to a study of the conductivity of these solutions, their viscosity was also determined. Since it was possible that the agreement with the mass law in the one case, ammonium formate, might be due to a cancellation of deviations from the law in opposite directions, the validity of the conclusion that the agreement is not accidental in character was tested by studying the behavior of other formates in this solvent. Finally, preliminary determinations of the conductivities and freezing points of solutions of hydrogen chloride in the same solvent were carried out, as there was reason to believe that previous work on this subject by Zanninovich-Tessarin[4] was incorrect.

The formic acid used in this work was purified by a method which is a considerable improvement over that employed by Schlesinger and Cal-

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[1] Presented, in part, at the Cincinnati meeting of the American Chemical Society, April 9, 1914.

[2] The work reported in this article constitutes the basis of a dissertation submitted by A. W. Martin to the faculty of the University of Chicago in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] THIS JOURNAL, 33, 1924 (1911).

[4] *Z. phys. Chem.*, 19, 251 (1896).

vert.[1] They distilled from phosphorus pentoxide, under reduced pressure. While this method yields an acid of fair quality, it is accompanied by considerable decomposition and loss of material and requires a large amount of time, since the distillation has to be repeated from five to ten times to obtain good results. An effort was made to improve this method by carrying out the distillation at still lower pressure, but the results were not much better. Attempts were also made to produce the anhydrous acid directly by heating anhydrous sodium formate mixed with acid salts, such as acid potassium sulfate, in the dry condition as well as in solution in anhydrous formic acid, but these methods gave neither good yields nor good products.[2] The method finally determined upon was distillation of the acid from boric anhydride. The anhydride was prepared by heating boric acid to a high temperature in a furnace until all bubbling and foaming ceased. The resulting melt was poured on an iron plate and allowed to cool in a desiccator. The glassy boric anhydride was then powdered and introduced directly into the formic acid,[3] with which it was allowed to remain in contact for several days. After a few days the powdered material sets into a hard mass, from which the supernatant liquid can be distilled at reduced pressure without bumping. The distillation was carried out in a specially designed apparatus at a pressure of about 12 to 18 mm. and a temperature of about 22° to 25°.

The apparatus used for this distillation is shown in the accompanying sketch (Fig. 1). It was designed to avoid contact of the acid with rubber, for it was soon found that the presence of the latter decidedly affected the quality of the acid. *A*, in Fig. 1, is the distilling flask which is connected

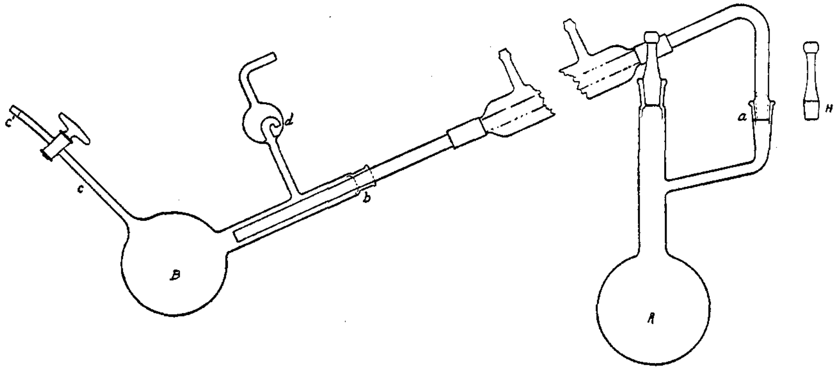

Fig. 1.

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[1] *Loc. cit.*

[2] See *Chem. Zentr.*, 1907, I, 1470; 1908, I, 998.

[3] The formic acid was especially prepared for this work by Baker & Adamson and originally had a conductivity of about 12–15 × 10^{-5} reciprocal ohms.

with the inner tube of the condenser by the ground joint *a*.[1] Into the vertical portion of the side neck of this flask, thoroughly washed and dried glass wool was placed to prevent spattering over of the liquid. *B* is the receiving vessel which is connected with the inner tube of the condenser by means of the ground joint *b*. In order to empty the receiving vessel after the distillation, it was rotated about the joint *b*, until the delivery tube *c* pointed directly downward. The end of this tube is ground to fit into a storage bottle which is shown in the next figure. In this way, the acid could be removed into the vessels in which it was to be used without opening the distillation apparatus or exposing the liquid to air. The tube *c* was always washed out by a little of the acid before the latter was collected. Before the acid was distilled it was allowed to stand for several days with boric anhydride. From this it was poured into the distilling flask which had been previously charged with a fresh portion of the anhydride. After standing for several days in the apparatus, the distillation was begun by simply reducing the pressure. About one-fifth of the acid (about 50 cc.) distilled off before the liquid had cooled sufficiently to stop the distillation. While this was going on the condenser was cooled with ice water and the receiving vessel with ice. When the distillation stopped, as a result of the cooling of the contents of the distilling flask, the contents of the receiver were warmed and the acid therein collected distilled through a second condenser into a second receiving vessel. The second condenser and receiving vessel were connected with the first by rubber through tubulus *d*. This procedure had the advantage of washing the apparatus[2] with formic acid before collecting the portion to be used, as well as of subjecting the acid to a partial fractionation. The second receiver also is useful in catching the small amounts of acid which are not condensed in the first. After the first acid condensed had thus been again distilled away, the first receiver was again cooled and the distilling flask warmed to about room temperature. About one-fifth of the original volume of the acid was allowed to remain in the distilling flask at the close of the operation. This, however, together with that collected in the second receiver and that retained by the anhydride,[3] was again treated with anhydride and mixed with fresh portions of acid and redistilled.

While the above seems like a complicated process, it really is not, for, by keeping acid continually drying over the anhydride, a fresh supply can always be obtained in about an hour's time. Occasionally the acid was distilled twice, but no improvement was noted. The acid thus obtained

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[1] "*H*" is a stopper fitting the flask at "*a*."

[2] The apparatus was, of course, thoroughly washed occasionally, but better results were obtained if the apparatus was opened as seldom as possible. Before each filling, however, dry air was drawn through the whole apparatus for about half an hour.

[3] The boric anhydride seems to form an unstable, crystalline(?) compound with the acid from which the latter can be recovered by heating.

had an average conductivity of about 6.35×10^{-5}, although occasionally an acid having a conductivity as high as 6.6×10^{-5} reciprocal ohms was obtained. The best acid had a conductivity of 6.2×10^{-5}. Practically no acid was used having a conductivity higher than 6.4×10^{-5}, except for the hydrochloric acid work, in which the greatest accuracy was not sought, and for a few of the concentrated solutions where the conductivity of the solvent was practically negligible, as was proved by trial. The acid used by Schlesinger and Calvert had a conductivity of about 6.8×10^{-5}, so that the present method gives a materially better acid, in addition to giving better yields[1] and requiring less time than did the old method.[2]

Two methods were employed for making up the solutions for the conductivity measurements. Each of the concentrated solutions was made up separately, in the manner described below, and was introduced into the cell described by Schlesinger and Calvert. For the dilute solutions, the dilution method was employed and the special cell *F*[3] shown in Fig. 2 was used. In this figure is also shown the storage bottle *S*. It will be seen that by means of the gound joint *c″* this bottle can be connected to the receiving flask of the distillation apparatus at *c′* and, in this way, the conductivity of the acid measured without exposing it to moisture, since the storage bottle is fitted with electrodes *ee*.[4] This same grinding, *c″*, fits one of the two-way pipets *p* shown in the figure. By means of this the acid can be introduced from the bottle into the flask for making up the solution, or into the conductivity cell without exposure to air. In making up the solution, the solute to be used was first weighed[5] out into a thoroughly dried calibrated 25 cc. flask and the flask filled with formic

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[1] The anhydride causes only a very slight decomposition of the acid, as is shown by the slight pressure which is developed in flask when the acid has been standing for some days in contact with the anhydride.

[2] Even the conductivity of the best acid, 6.2×10^{-5} seems very large when compared to other pure solvents. It must be remembered, however, that formic acid is quite unusual in that it is not only a good ionizing medium, but is itself fairly highly dissociated when dissolved in other ionizing media. We have thus far not been able to reduce the conductivity of the acid below the values stated although we have subjected the best acid to freezing, etc. However, there is some evidence pointing to a somewhat lower value for the conductivity of pure acid (see p. 1598) and experiments are under way to obtain a better acid by freezing the acid purified in the manner described above. Thus far the improvement has been very small.

[3] This cell is referred to in the paper as cell No. 2.

[4] When the acid stands above a certain level the cell constant of the storage bottle is no longer affected by the amount of acid contained in the bottle. When the bottle is full the conductivity of the acid can, therefore, be measured with great accuracy. At lower levels a number of cell constant values were determined and by using a suitable one the conductivity of any acid in the bottle can be determined with sufficient accuracy. It was found, however, that the acid could be kept in the bottle for days without undergoing noticeable change.

[5] Weights were reduced to vacuum when necessary.

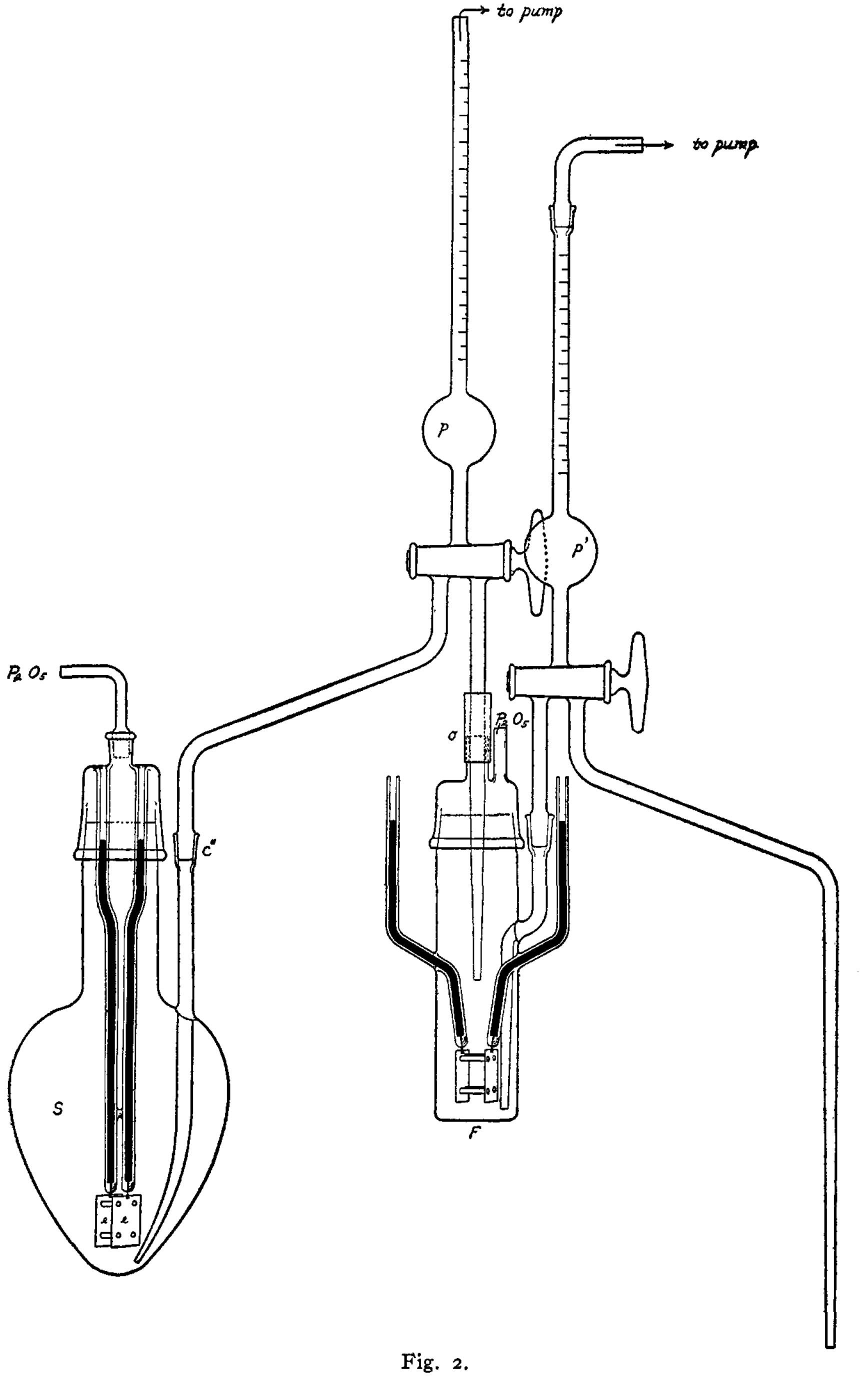

Fig. 2.

acid almost to the mark, by means of the pipet just mentioned. The mixture was thoroughly shaken and then placed in the constant temperature bath. When sufficient time had elapsed for temperature equilibrium to be attained, the acid was filled in up to the mark from the same pipet and the contents again shaken. While not in use, the exposed end of the pipet was protected from moisture by means of a test tube and stopper and the acid remaining in the tip of the pipet was always discarded. From the 25 cc. flask the solution was transferred to the conductivity vessel by means of a pipet, p'', similar to those shown in the figure but of twice their volume. By the use of these pipets all of these steps could be carried out with practically no exposure to moisture.

As stated, the dilution method was employed for the dilute solutions. In these cases the apparatus was set up as shown in Fig. 2 and will need no further description. Pipet p delivers into the cell exactly as much liquid as pipet p' withdraws. Pipet p'' which was used to place the original portion of solution into the cell, delivers just twice as much as does p. The amounts were respectively, 10.02 and 20.04 cc.[1] The procedure of making the dilution measurements is as follows: As described, 20.04 cc. of solution are placed into the cell by means of pipet p'' through the opening *o*. The pipet is then quickly withdrawn and the apparatus set up as shown in Fig. 2 and placed into the bath. This takes only a little over a minute. From now on exposure to air is avoided and it has been found that solutions[2] in the cell remain unchanged for many hours. After the solution has attained the temperature of the bath (25° ± 0.01)[3] a conductivity measurement is made. Then 10 cc. are withdrawn from the cell by means of pipet p' and the stopcock of the pipet turned so as to disconnect the upper portion from the cell. The material withdrawn is run out of the other end of the pipet and the pipet washed with water. Of course, the stem of the pipet which enters into the cell is not allowed to become moist. When the washings are no longer acid the pipet is thoroughly dried by drawing hot, dry air through it. In the meantime, 10 cc. of pure solvent have been transferred from the storage bottle into the cell. The added pure solvent is now thoroughly mixed with the residual solution in the cell by repeatedly drawing the mixture into the withdrawal pipet up to the stopcock and allowing the withdrawn liquid to flow back into the cell. This process is repeated about fifty times, which

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[1] The discharge from these pipets is astonishingly regular, being fully as reliable as that of ordinary pipets. By means of the stopcocks the flow can be excellently regulated and the liquid can be very easily drawn to the mark. For convenience, the upper portion of the pipets was graduated instead of having but one mark. The liquid was drawn into the pipets by means of a pump connected through phosphorus pentoxide tubes.

[2] Except for the aniline solutions. See p. 1614.

[3] Hydrogen scale.

takes about five minutes. The conductivity is then measured and the stirring repeated until constant values for the resistance of the solution are obtained. By setting up the apparatus suitably, all of these processes can be made almost automatic and very good results can be obtained. That the method of stirring is efficient and that no losses of solution occur in the stopcocks was tested by making a series of measurements with aqueous solutions of potassium chloride. The agreement with the known values for this salt was excellent. Usually this method of making up the various solutions was employed only for the dilute solutions. As these solutions gave somewhat peculiar results, one or two sets were also made with more concentrated solutions and the results agreed very well with the data obtained from independently made up solutions. Furthermore, these peculiar results were obtained also by Schlesinger and Calvert, whose apparatus was somewhat different, and have received a very satisfactory explanation.

The resistances of the solutions were measured by the Wheatstone-Kohlrausch method, using the small high frequency machine with appropriate capacities in the circuit as described by Washburn and Bell.[1] The roller bridge employed was calibrated, as were also all of the resistances. As no very high resistances were measured it was found unnecessary to use the capacity free resistances described in the paper referred to above. All resistances were measured to within 0.1% which is an accuracy great enough in view of the other possible errors when one is dealing with a solvent like formic acid.

In the following are given the results of the conductivity measurements for solutions of sodium, potassium, ammonium and phenyl ammonium formates and for hydrogen chloride. A number of other data have also been determined, as will appear in the discussion.

Sodium Formate.

The sodium formate used was Kahlbaum's best grade, which gave an analysis corresponding to the anhydrous salt. Before it was used, it was kept for several months in a desiccator with phosphorus pentoxide. Table I gives the results of the conductivity measurements and some calculations based upon them.

Column 1 of the table gives the number of the experiment. The numbers 1_s to 5_s refer to a series made by the dilution method in cell number 2 as described above; the other data are from entirely independent determinations. Column 2 gives the concentrations, c, in gram molecules per liter; Column 3, the observed specific conductivities, χ, in reciprocal ohms; Column 4, χ_a the observed specific conductivity minus the conductivity of the solvent; Columns 5 and 6 the value 100/*equivalent conductivity*,

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[1] THIS JOURNAL, 35, 177 (1913).

as calculated from the concentration and the specific conductivities given in Columns 3 and 4, respectively. From these values of 100/*equivalent conductivity*, the equivalent conductivity λ can readily be ascertained. The value $100/\lambda$ is extensively used in the discussion of the results, and it is for this reason that it was included in the tables rather than the more commonly employed equivalent conductivities themselves. The other data in the table will be discussed below.

TABLE I.—CONDUCTIVITY OF NaOCHO AT 25°.

No.	c.	χ.	χ_a.	$100/\lambda$.	$100/\lambda_a$.	α.	α_a.[1]	K.	K_a.[1]
0	0	.....	.....	1.500	1.530	...	...	...	...
5*s*	0.00548	0.0003896	0.0003193	1.428	1.715	...	...	...	...
4*s*	0.01095	7457	6814	1.469	1.607	...	...	...	...
3*s*	0.02190	0.001445	0.001381	1.516	1.586	...	...	...	...
2*s*	0.04381	2789	2724	1.571	1.608	0.955	0.951	0.884	0.816
8	0.06670	4115	4052	1.621	1.646	0.925	0.930	0.766	0.817
1*s*	0.08763	5279	5215	1.660	1.680	0.904	0.910	0.742	0.814
1	0.1046	6197	6129	1.688	1.707	0.889	0.896	0.742	0.811
7	0.1484	8439	8376	1.758	1.772	0.853	0.864	0.735	0.812
9	0.1718	9606	9544	1.788	1.800	0.839	0.850	0.751	0.827
4	0.2043	0.01112	0.01106	1.837	1.847	0.817	0.828	0.742	0.815
6	0.2351	0.01252	0.01245	1.878	1.887	0.799	0.811	0.745	0.816
3*a*	0.2760	0.01429	0.01423	1.931	1.940	0.777	0.789	0.746	0.816
13	0.2974	0.01517	0.01511	1.960	1.969	0.765	0.777	0.742	0.805
11	0.3338	0.01661	0.01655	2.010	2.017	0.746	0.758	0.733	0.795
14	0.3968	0.01902	0.01896	2.086	2.093	0.719	0.731	0.730	0.788
2[2]	0.4500	0.02096	0.02089	2.147	2.154	0.699	0.710	0.729	0.784
15	0.5157	0.02304	0.02298	2.238	2.244	0.670	0.682	0.703	0.753
12	0.5933	0.02546	0.02539	2.3305	2.336	0.644	0.655	0.690	0.737
16	0.9867	0.03440	0.03433	2.871	2.877	0.522	0.532	0.564	0.596

As has been recently pointed out by Kraus and Bray[3] conductivity data can be very conveniently examined by a graphical method in order to determine whether the electrolyte in question obeys the mass law. By substituting $1/\lambda$ for α, the mass law, $\alpha^2c/1 - \alpha = K$, can be transformed into the equation $1/\lambda = 1/\lambda_0 + (1/K\lambda_0{}^2)c\lambda$, which is a linear relation between $1/\lambda$ and $c\lambda$. We have preferred, merely for convenience, to plot the value $100/\lambda$ against the specific conductivity ($= \lambda c/1000$). This can, of course, not affect the conclusions.

In Fig. 3 are found a number of such plots drawn to the data found in Table I. The curve labeled *AA* corresponds to the data in Columns 4 and 6 of the table; namely, to the conductivities obtained by subtracting the conductivity of the pure solvent from the observed conductivity of

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[1] Calculated from the conductivities from which the conductivity of the solvent has been subtracted.

[2] The measurements for number 2 were made while the bath was 0.05° too low.

[3] THIS JOURNAL, 35, 1324 (1913). See also Noyes, *Carnegie Publications*, 63.

the solutions.[1] It will be seen that for concentrations lying between 0.0438 and 0.3 the data conform very well to a straight line.[2] The plot on which these curves were originally made was drawn to such a scale that deviations

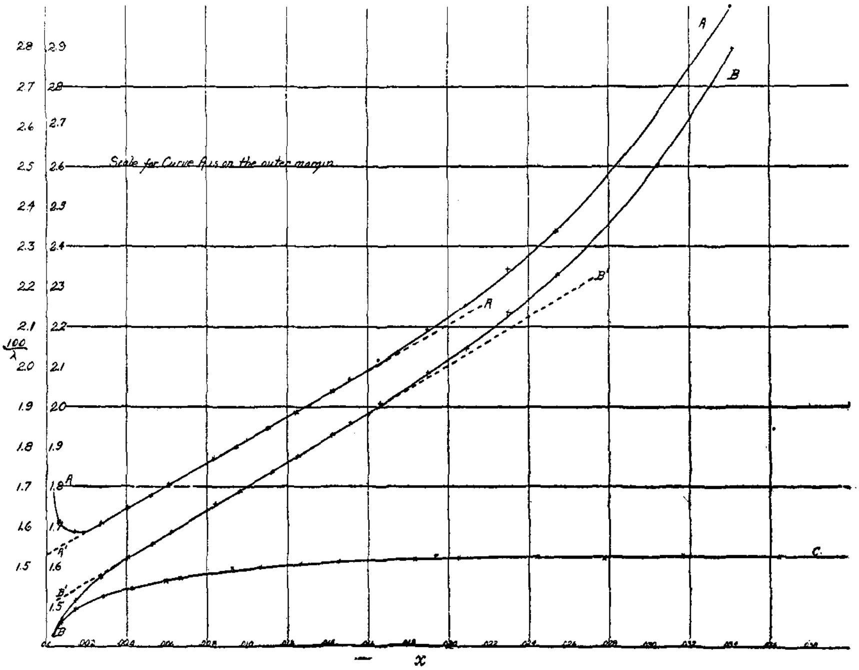

Fig. 3.

from the straight line corresponding to 0.1% could readily be observed and none of the values departed from the straight line by more than 0.2%, which is within the experimental error when one is dealing with a solvent so sensitive to moisture as is formic acid.

It is further to be noted that the conductivities corresponding to concentrations above and below these limits depart from the straight line. The higher concentrations are to be discussed below. It is self-evident from the character of the plot that the deviations in the low concentrations mean that the observed conductivities are smaller than is required for conformity to the mass law. Now it will be recalled that the conductivities used in plotting Curve *AA* were the values obtained by subtracting the conductivity of the pure solvent from the observed conductivity of the solutions. But the solutions contain highly ionized sodium formate and the effect of the presence of the formate ion would be to repress the

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[1] The scale of ordinates for this curve is found on the outer left-hand margin of the plot.

[2] The dotted line *A'A'* is this straight line extended.

ionization of the formic acid, and, therefore, to diminish its conductivity. Hence, the conductivity obtained by subtracting the total conductivity of the acid should be too small, and the values of 100/λ too large, which would account for the upward trend of the curve in the dilute solutions. Of course, the same thing would be true for the more concentrated solutions, but in these the conductivity of the solution is so large that the role played by the conductivity of the solvent is of less importance. This point will receive further elaboration in the next paragraph. By neglecting the upward turn of this curve and extending the straight line portion to the axis of ordinate, a value for the equivalent conductivity at infinite dilution may be obtained.[1] This is found to be 65.4, and from it, or from 100 over this value, the degree of ionization, α_a, for the concentrations in the range just discussed and the ionization constant, K_a, can be calculated.[2] These values are found in Columns 8 and 10 of the table.

In view of the probability that the presence of formate ion in the solutions represses the ionization of the solvent and, therefore, decreases its conductivity, a second curve, *BB* in Fig. 3,[3] has been plotted, using the conductivities uncorrected for the conductivity of the solvent.[4] The lower concentrations again deviate from the straight line, this time, however, in the opposite direction. This deviation indicates that the conductivities employed for these concentrations in making this curve are too large. Two possible explanations can be offered for this phenomenon. In the first place, it is possible that in the more dilute solutions the concentration of formate ion, resulting from the ionization of sodium formate, is sufficient to repress the ionization of the acid partially, but not sufficiently great to repress it completely. The other possible explanation is that the observed conductivity of the solvent is not entirely due to its ionization, but is in part due to impurities present even in our best acid. A preliminary calculation which we have made shows that really both causes are operative in producing the deviation noted, but that the presence of an impurity, whose conductivity is not affected by the ions of sodium formate, seems to be the most important factor.[5] This impurity is

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[1] On the assumption that the mass law really holds to infinite dilution. It is shown below that the deviations in the dilute solutions do not indicate deviation from the law, as they are due solely to the high conductivity of the solvent.

[2] Owing to the fact that the values of λ occur several times in the equilibrium law equation, the deviations of the constants from the mean (about 1%+) are greater than the deviations of the conductivities from the straight line. There is no deviation in the constants which cannot be accounted for by an experimental error of less than 0.2%.

[3] A portion of this curve is repeated in Fig. 4, labeled "Na," This enables a comparison with the other curves there given.

[4] The scale of ordinates for Curve *BB* in Fig. 3 is found on the inner left-hand margin of the plot.

[5] The calculation was made as follows: We assumed that the conductivity of the

probably water into which the formic acid seems to be continuously decomposing. This conclusion receives strong support in the fact that the deviation under discussion is not observed in the solutions of hydrogen chloride, which contain hydrogen ion capable of repressing the ionization of both the formic acid and of the water. Since, therefore, the conductivity of the solvent is due chiefly to an impurity unaffected by the presence of the salt, the decrease in the conductivity due to the latter can only be very small, and we should expect that the data corrected for the conductivity of the solvent should more closely represent the true conductivity of the solute. An inspection of the curves shows that the one for the corrected conductivities deviates less from the straight line in the dilute solutions than does the other.[1] Nevertheless we have calculated the degrees of ionization and the ionization constants from the data uncorrected for the conductivity of the solvent and have presented them in Columns 7 and 9 of the table. It will be seen that they do not differ very much from the others. On this account we have occasionally used these data in the discussions, as they are a little simpler to handle; but whenever it is important to use absolute values for these data, the conductivities corrected for the conductivity of the solvent should be used.

It appears, therefore, that sodium formate, when dissolved and ionized in (anhydrous) formic acid, obeys the law of mass action up to a concentration of about 0.3 molar when the degree of ionization is calculated directly from the conductivity of the solutions. Above this concentration the degree of ionization calculated in this way is less than it should be for continued agreement with the law, and as the concentration increases the deviation gradually becomes greater. This is the reverse of the kind of deviation observed in dilute aqueous solutions of strong electrolytes. It is, however, the kind of deviation which is to be expected according to the kinetic theory, for in the higher concentrations the volume actually occupied by the dissolved substance must become appreciably large in comparison with the total volume of the solution.[2] Should this be the correct interpretation of the deviation which we have observed in the concentrated solutions, it should be possible to make a correction for the volume

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solvent (6×10^{-5}) is entirely due to its ionization and calculated from this the ion product constant of the solvent, using for the equivalent conductivity at infinite dilution the value 75 which we have obtained for hydrochloric acid. (A calculation made using 220 led to the same results.) From the ion product constant thus found, we calculated the degree of ionization of the solvent in the presence of the amount of sodium formate contained in the dilute solutions and from this the conductivity of the solvent in these solutions. The maximum value thus found was only 8×10^{-6}, which, while not entirely negligible, is not sufficient to account for the whole deviation.

[1] In examining the curves of Fig. 3 it must be borne in mind that the axis of abscissae is different for the two curves under discussion. If drawn to the same origin of axes, the two curves would be very close together.

[2] See Ostwald, *Z. physik. Chem.*, 2, 270 (1888).

b, of dissolved substance by writing the equilibrium law in the form of the equation

$$\frac{\alpha^2}{(1-\alpha)(v-b)} = K' \qquad (1)$$

in which v is the volume of the solution. The volume b is the sum of the volume of the undissociated molecules plus that of the ions and, unless we make some assumptions in regard to the relative values of these volumes, the equation cannot be solved. The simplest assumptions to make in order to test the equation are: (1) that the sum of v_p, the volume of one gram ion of the positive ion, plus v_n, the volume of the corresponding quantity of the negative ion, is very large compared to v_m, the volume of one gram molecule of undissociated salt; (2) that v_p plus v_n is twice as large as v_m; (3) that v_p plus v_n is equal to v_m and, (4) that v_p plus v_n is negligibly small compared to v_m. Calculation shows that the first two assumptions lead to values for K' which are not even approximately constant. In Table II are given the equilibrium constants K_a without correction taken directly from Table I, the constants, K'_3, for the whole range of concentrations all recalculated on the basis of the third assumption and the corresponding constants K'_4, calculated on the basis of the fourth assumption. The equation resulting from the assumption that v_p plus v_n is equal to v_m is

Table II.

No.[1]	*c*.	K_a.[2]	K'_3.[2]	K'_4.[2]
2*s*	0.04381	0.816	0.816	0.816
8	0.06670	0.817	0.818	0.817
1*s*	0.08763	0.814	0.816	0.814
1	0.1046	0.811	0.814	0.812
7	0.1484	0.812	0.817	0.814
9	0.1718	0.827	0.834	0.829
4	0.2043	0.815	0.825	0.819
6	0.2351	0.816	0.829	0.821
3*a*	0.2760	0.816	0.834	0.823
13	0.2974	0.805	0.825	0.815
11	0.3338	0.795	0.820	0.808
14	0.3968	0.788	0.824	0.809
15	0.5157	0.753	0.812	0.793
12	0.5933	0.737	0.816	0.796
16	0.9867	0.596	0.814	0.820
17	1.017	0.584	0.817	0.830
		Mean,	0.821	0.815

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[1] Number 2 has been omitted since the measurements were made at a somewhat lower temperature than was used for the others. Number 17 is from measurements made by Mr. Coleman who is continuing the work herein reported.

[2] The constants are calculated from the conductivities which have been corrected for the conductivity of the solvent.

$$\frac{\alpha^2 c}{(1 - \alpha)(1 - c^2 v_m)} = K'_3 \qquad (2)$$

and the values found for K'_3, in the table, are calculated by means of this equation, using the value 0.275 for v_m. The assumption that the volume of the ions is negligible leads to the equation

$$\frac{\alpha^2 c}{(1 - \alpha)(1 - c^2 v_m(1 - \alpha))} = K'_4 \qquad (3)$$

which was used in obtaining the values for K'_4, the value of v_m for this calculation being 0.6. All of the other data required for the calculations were taken from Table I. The calculations were made for the dilute solutions in which the uncorrected mass law holds as well as for the concentrated ones, in order to make sure that the volume correction introduces no discontinuities.

It will be noted that, up to the concentration 0.3, the original uncorrected values for the equilibrium constant are a little better than either of the corrected constants but that in the higher concentrations, for which the uncorrected mass law gives very rapidly falling values for K_a, both of the corrected equations yield fairly good constants. The maximum deviation of the values of K'_4 from the mean is 2.7%, which corresponds to an error in the measurement of the conductivities of about 0.6%, while the maximum deviation of K'_3 from the mean is 1.6% corresponding to an error of measurement of only 0.3%. In spite of this apparently fairly good agreement between the data and the demands of the equations, too much stress must not be laid upon these calculations. In the first place, while the mean deviations, especially in the case of K'_3, are not much larger than might be expected from the probable errors of measurement, they are not as irregular as might be expected from deviations which are due entirely to experimental error. In the second place, the values of the term v_m are larger than one would expect. Thus, if we accept the results as meaning that the deviations observed in the concentrated solutions are completely explicable on the basis of the volume occupied by the solute, we must conclude that in a molar solution the dissolved substance occupies about 0.3 of the total volume. This, of course, would not be probable unless the molecules are extensively solvated. Finally, in making deductions from these equations, the fact that the volume correction introduces a third constant, v_m, into the equations must not be overlooked, because an equation with three constants in general fits a given set of data better than does a two constant equation. Consequently, we can now go no farther than to say that very likely the deviations in concentrated solutions are at least partially[1] due to the volume occupied by the solute, that this volume is probably quite large and that the volume of

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[1] It is not unlikely that the effect of the viscosity will have to be taken into consideration in the more concentrated solutions. See p. 1606.

the ions is probably considerably less than that of the undissociated molecules. It is hoped that further work, to be carried out on more concentrated solutions of the formates, will definitely settle these points.

Thus far the conductivities have been discussed without reference to the viscosities of the solutions. It seems quite impossible that the agreement found for the conductivity, uncorrected for the viscosity, of sodium formate solutions in formic acid with the mass law can be accidental in character. Furthermore, we have found, as is to be shown, that what is true of sodium formate is true likewise of potassium formate, of ammonium formate, of phenyl ammonium formate and of hydrogen chloride in the same solvent and no accident could be responsible for this array of evidence. Hence, we believed that these solutions might be particularly favorable for deciding on the nature of the effect produced by viscosity changes and some preliminary measurements were therefore made. The viscosities were measured in a small Ostwald viscometer of such dimensions that the pure acid flowed out in about 100 seconds. From the type of instrument employed, results of the highest degree of reliability cannot be expected, but the results are sufficiently accurate to give a preliminary survey of the field. At the same time, it was necessary to determine the densities of the solutions. This was done in a special 25 cc. flask with narrow graduated neck and gave measurements accurate to about 0.1% or better, which is fully adequate for our purpose. The results of these measurements are tabulated in Table III. Column 1 gives the concentration; Column 2 the density d; Column 3 the viscosity η, and Column 4, a constant, A, calculated from the viscosities on the basis that the variation of these with the concentration is a linear function. The experimental values for the densities can be very accurately reproduced by the equation:

$$d = 1.2142 + 0.0356c.$$

TABLE III.—THE RELATIVE VISCOSITIES AND DENSITIES OF SODIUM FORMATE SOLUTIONS IN FORMIC ACID AT 25°.

c.	d.	η.[1]	A.
0.0000	1.2142	0.0162	...
0.04228	1.2156	0.01669	0.01182
0.06941	1.2162	0.01700	0.01153
0.1124	1.2183	0.01743	0.01094
0.2382	1.2228	0.01892	0.01142
0.4460	1.2298	0.02139	0.01164
0.5759	1.2342	0.02302	0.01182
0.7435	1.2400	0.02532	0.01227
0.9876	1.2497	0.02926	0.01325

[1] These viscosities are only relative values. No effort was made to determine the absolute value for the pure acid, and as the data found in the literature differed considerably from each other, the rounded figure 0.0162 was chosen for the pure acid. Since we have no means of determining the accuracy of the viscosity data until they have been, at least in part, repeated with a more reliable instrument, we have given the number of decimal places which correspond to the "reproducibility" of the results.

It will be observed that the values of A show a decided minimum. The deviation from a straight line is not very great, amounting to a few per cent. In calculating the viscosities corresponding to the concentrations required for the conductivities, a value for the constant A was chosen from the table by interpolation and the viscosity calculated by a straight line formula of the form:

$$\eta = 0.0162 + Ac. \qquad (2)$$

By choosing for each concentration suitable values for A the experimentally determined viscosities can thus be very well reproduced. Table IV gives the results of the viscosity calculations. Column 1 again gives the number of the conductivity determination; Column 2 the concentration; Column 3, the value for A for the respective concentrations calculated as described above; Column 4 the viscosities calculated according to equation 2; Column 5, the value of a hypothetical, corrected conductivity calculated on the basis of the equation

$$\chi_\eta = \chi \cdot \eta/\eta_0$$

in which η is the viscosity of the solution, η_0 the viscosity of the pure solvent, χ the specific conductivity of the solution not corrected for the conductivity of the solvent, and χ_η the hypothetical, corrected specific conductivity. Column 6 gives the value of $100/\lambda_\eta$ as calculated from the "corrected specific conductivity" of Column 5 and the concentration.

TABLE IV.—CONDUCTIVITIES OF NaOCHO AT 25° CORRECTED FOR VISCOSITY.

No.	C.	A.	η.[1]	χ_η.	$100/\lambda_\eta$.
0	0	...	0.01620	.....	...
5*s*	0.005477	0.012	0.01627	0.0003852	1.427
4*s*	0.01095	0.012	0.01633	0.0007517	1.457
3*s*	0.02190	0.012	0.01646	0.0014685	1.492
2*s*	0.04381	0.0118	0.01672	0.002878	1.522
8	0.06670	0.0113	0.01697	0.004310	1.548
1*s*	0.08763	0.0112	0.1718	0.005598	1.565
1	0.1046	0.0110	0.01735	0.0066375	1.576
7	0.1484	0.0111	0.01785	0.009298	1.596
9	0.1718	0.0112	0.01812	0.010745	1.599
4	0.2043	0.0113	0.01851	0.01270	1.608
6	0.2351	0.0114	0.01888	0.01459	1.611
13	0.2974	0.01145	0.01960	0.018355	1.620
11	0.3338	0.0115	0.02004	0.02055	1.624
14	0.3968	0.0116	0.02080	0.02442	1.625
2[4]	0.4500	0.01165	0.02144	0.02774	1.622
15	0.5157	0.01174	0.02225	0.03166	1.628
12	0.5933	0.01187	0.02324	0.03652	1.625
16	0.9876	...[2]	0.02928	0.06217[3]	1.589

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[1] See footnote 1, Table III.

[2] This concentration is one for which the viscosity was directly determined.

[3] There was no room for this value on the plot.

[4] The measurement of the conductivity was made while the bath was 0.05° too low.

The values of $100/\lambda_\eta$, taken from Table IV, have been plotted against the specific conductivities "corrected for viscosity" taken from the same table. The curve is labeled *CC*[1] on Fig. 3. The portion of the curve corresponding to concentrations up to 0.3 molar is not a straight line.[2] Above this concentration the curve is almost a straight line. Up to about 0.6 molar the maximum deviation from the straight line is only about 0.5% and even at the most concentrated solution measured, 0.9876 molar, the deviation may be due to error in the viscosity measurements, as it is well known that the small viscometers of the type used may deviate quite a little from Poiseuille's law when the relative viscosities measured differ as much as they do in the case of these solutions.[3] We may, therefore, treat the curve, for the present, as if it were a straight line, parallel to the axis of specific conductivities. Such a line does not, however, indicate agreement with the demands of the equilibrium law. For the curve means, if the conductivities corrected for viscosity are to be used in calculating the degree of ionization, that, as we go from dilute to concentrated solutions, the degree of ionization first decreases and then becomes constant and remains constant to very high concentrations.[4] Such a conclusion is not even qualitatively in agreement with our ideas of chemical equilibrium.[5] Consequently, it seems very doubtful to us

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[1] The scale of ordinates for this curve is found on the inside of the left-hand margin of the plot.

[2] This cannot be due to the effect of the conductivity of the solvent. In the first place, the corresponding curves for the data which have not been "corrected" for viscosity are straight lines at much lower concentrations. In the second place, it can be shown that the influence of the conductivity of the solvent upon the character of the curve ceases above 0.05 molar. The data given in Table IV have not been corrected for the conductivity of the solvent. If this correction is made and the resulting data are plotted and compared with curve *CC*, it will be found that the two curves are entirely similar until we get considerably below the concentration 0.05 molar, where the doubly corrected curve flattens out and gradually turns upward. From this it is clear that it is only below 0.05 molar that the conductivity of the solvent affects the character of the curve.

[3] On the other hand, it is possible that these deviations from the straight line are real and that there is a true maximum at about 0.5 molar. The deviation can be only very slight, however. The data for potassium formate show a similar, but even less-pronounced maximum (deviation from the straight line only 0.2%), while in the case of ammonium formate there is a more clearly defined maximum. It will require more accurate data, which are now being obtained, to decide the question. The conclusions which we have tentatively reached in the main body of this paper would not be affected if the curves show a maximum instead of being horizontal straight lines.

[4] If we consider the curve to have a real maximum, we must conclude that the degree of ionization has a minimum at about 0.5 molar.

[5] Robertson and Acree, *Am. Chem. J.*, 49, 502 (1913) have found that when they applied the viscosity correction to some of their conductivity data somewhat similar results were obtained.

that the application of the viscosity correction[1] is justified in these solutions.

Since there is, however, a great deal of evidence that the viscosity has, in many solutions, a decided effect upon the mobilities of the ions, there must be a reason why, in the case of the solutions of the formates in formic acid which we have investigated, the viscosity should have no such influence. There are a number of conceivable explanations. In the first place, it is possible that in the dilute solutions the ions are extensively solvated and that as the concentration increases they lose their formic acid of solvation and thus become smaller.[2] Such a progressive change in the volume of the ions could, of course, counteract the increase in viscosity. It does not seem, however, as if this could be the correct interpretation, as the decrease in volume necessary to produce the required result is greater than we have reason to believe likely to occur.[3]

A much more reasonable explanation for the absence of a noticeable viscosity effect is the following: Kraus[4] has suggested that in many organic solvents the great increase in viscosity with increasing concentration is due to the presence in the solutions of a relatively small number of very large undissociated molecules and that these, while they greatly decrease the fluidity of the solution as measured by the rate of flow through a capillary tube, do not greatly affect the mobility of the ions. This explanation is not in contradiction to any of the commonly cited theories concerning the flow of particles through viscous media, since these theories are based on the assumption that the molecules of the diffusing substance are large compared to the molecules of the viscous medium. Furthermore, the direct experimental evidence of these theories has been obtained under conditions in which these assumptions are justified. We have some evidence that, in the solutions now under discussion, the reverse of these assumptions is true. In the first place, the increase of the viscosity as the concentration increases is very large, indicating that the molecules which produce the viscosity change are very large. In the second place, although the evidence is indirect and not yet definitely established, the behavior of the concentrated solutions[5] seems to indicate that the ions

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[1] A number of modifications of the simple viscosity correction have been suggested by Green, Johnston, Washburn, Kraus and others. For references, see the articles by Kraus cited below. We have, so far as the data permit, applied such modified viscosity corrections, but have found that no essential changes have resulted. These calculations are therefore not given.

[2] The same suggestion has been made for aqueous solutions. See for example, Hartley, Thomas and Applebey, *J. Chem. Soc.*, **93**, 555 (1908); Green, *Ibid.*, **93**, 2033; Bousfield, *Z. physik. Chem.*, **53**, 257 (1903); Washburn, *Trans. Am. Electrochem. Soc.*, **21**, 128 (1912).

[3] See Kraus, THIS JOURNAL, **36**, 35 (1914).

[4] *Loc. cit.* See also Washburn, *loc. cit.*, p. 30, *et seq.*

[5] See page 1602.

are considerably smaller than the undissociated molecules. These are exactly the conditions which, according to Kraus, tend to make relatively small the effect of viscosity increase upon the conductivity of solutions.

In view, therefore, of the possibility of explaining the apparent absence of viscosity influence and especially because of the excellent agreement between the data for uncorrected conductivities and the demands of the law of chemical equilibrium, we believe that the usual viscosity correction should be not applied in these solutions.[1] As has been already mentioned this conclusion receives added confirmation from the fact that thus far in all of the solutions investigated by us in this solvent the same conditions are found.[2]

Potassium Formate.

The potassium formate was prepared by treating pure potassium carbonate with a large excess of boiling formic acid, which had been purified by the method described. The resulting salt was recrystallized several times from the pure acid. When apparently dry, the salt was found still to contain as much as 20% of the acid. This was removed by heating the substance to about 150° (which is a little below the melting point of the pure salt) for several days until it reached constant weight. The resulting solid analyzed to 99.6% potassium formate. The residual acid, which it probably contained, could doubtlessly have been driven out by melting the salt, but as the presence of acid could not affect the results, it was thought better to leave the salt in the condition described rather than to risk the danger of decomposition by further heating.

The solutions were made up as was described for sodium formate. The potassium salt is, however, far more hygroscopic than the sodium salt and consequently there is much greater liability of slight deviations. In spite of this, the data for this salt are as concordant as they are for the sodium formate. The data for the conductivity measurements will be found in Table V, the arrangement of this table being the same as for Table I.

It will be seen from the table that the conductivity data agree very well with the mass law whether they be "corrected" for the conductivity of the solvent or not. As in the case of sodium formate, deviation from the straight line, which represents the behavior in case agreement with the

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[1] It is not unlikely that in the concentrated solutions the viscosity effect becomes noticeable.

[2] Solutions of other uni-univalent formates are being investigated in the hope that in some of them the viscosity conditions will not be like those thus far met with. This may lead to a definite means of proving our conclusions. Furthermore, conductivity determinations of mixed solutions will be made in order to see whether the conductivities thus found will agree with the mass law and the degrees of ionization as calculated in this paper. Finally, transference experiments are planned to complete the data necessary for a complete elucidation of the points discussed.

TABLE V.—CONDUCTIVITY OF KOCHO AT 25°.

No.[1]	c.	χ.	χ_a.	$100/\lambda$.	$100/\lambda a$.	α.	α_a.	K.	Ka.
0	0	...	...	1.430	1.452	...	...	...	...
5_s	0.01056	0.000759	0.000696	1.391	1.514	...	...	...	...
4_s	0.02112	0.001482	0.001419	1.425	1.488	...	...	...	...
14	0.4052	0.002756	0.002693	1.470	1.505	...	...	...	...
3_s	0.4224	0.002864	0.002801	1.475	1.508	...	...	...	...
3	0.5480	0.003667	0.003603	1.495	1.521	...	...	...	...
13	0.06342	0.004210	0.004147	1.506	1.529	[0.95]	...	[1.11]	...
9	0.07661	0.005000	0.004974	1.533	1.552	[0.93]	[0.935]	[0.992]	[1.036]
2_s	0.08448	0.005474	0.005411	1.543	1.561	[0.927]	[0.930]	[0.991]	[1.05]
10	0.09464	0.006065	0.006002	1.560	1.577	0.917	0.921	0.955	1.006
8	0.1059	0.006901	0.006638	1.581	1.596	0.904	0.910	0.907	0.9761
15	0.1137	0.007171	0.007108	1.585	1.599	0.902	0.909	0.946	1.027
4	0.1270	0.007917	0.007854	1.604	1.617	0.891	0.898	0.930	1.004
16	0.1712	0.01036	0.01030	1.652	1.662	0.866	0.874	0.954	1.035
5	0.2121	0.01249	0.01243	1.698	1.706	0.842	0.851	0.953	1.008
11	0.2627	0.01499	0.01493	1.751	1.759	0.817	0.825	0.956	1.026
12	0.3043	0.01696	0.01690	1.793	1.800	0.797	0.807	0.955	1.024
6	0.3195	0.01765	0.01759	1.810	1.816	0.790	0.800	0.950	1.019
19	0.3917	0.02086	0.02080	1.877	1.883	0.762	0.771	0.954	1.017
17	0.4432	0.02301	0.02295	1.922	1.927	0.744	0.753	0.948	1.021
18	0.6104	0.02918	0.02912	2.094	2.098	0.683	0.692	[0.898]	[0.950]

law exists, is found above and below certain limits, the range of agreement in this case being from 0.09 to above 0.45 molar. Since the nature of the deviation in the low concentrations is of exactly the same kind as in the case of the sodium salt, we may again assume that it is due to a small residual conductivity of the acid, a residual conductivity caused chiefly by some impurity whose degree of ionization is not repressed by the ions of the potassium formate.

The concentrated solutions also are entirely analogous, the deviation from the law of mass action of both being in the sense that the degree of ionization is *too small.* In the case of the potassium salt the deviation begins at a higher concentration than in the case of the sodium salt. On account of the similarity of the two cases, only one curve is shown for potassium formate, namely, the one for the conductivities "uncorrected" for the conductivity of the solvent. It is found in Fig. 4 and is labeled *K*.

The viscosities and densities were determined in the manner described for the sodium salt. The viscosities corresponding to the concentrations were calculated from the values found in Table VI just as has been described for the other solutions and a set of conductivities "corrected for viscosity" calculated as before. These, and the corresponding values of $100/\lambda_\eta$, are found in Table VII.

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[1] Nos. 1 and 2 were made with a salt containing 20% acid and are, therefore, not included. Number 1_s was practically identical with number 16 and is not included. Numbers 8 and 4, do not lie well on the curve but they are practically duplicated in numbers 15 and 16 which agree very well.

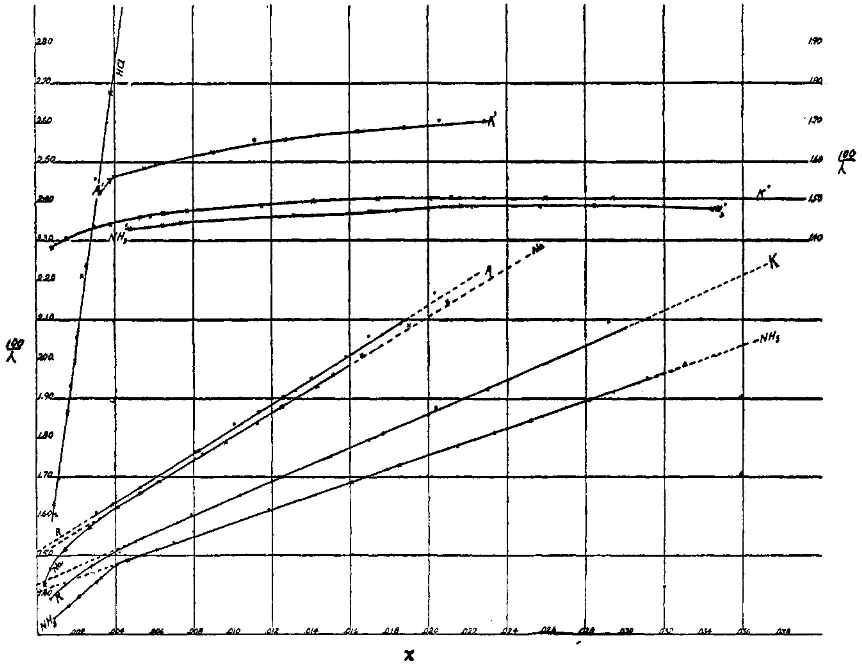

Fig. 4.

TABLE VI.—DENSITY AND RELATIVE VISCOSITY[1] OF KOCHO SOLUTIONS AT 25°.

c.	d.	A.	η.
0	1.2142	....	0.0162
0.0548	1.2166	0.0109	0.01680
0.0733	....	0.0108	0.01699
0.0176	....	0.0105	0.01743
0.1270	1.2201	....	....
0.1787	....	0.01063	0.01810
0.1888	....	0.0106	0.01820
0.2099	....	0.0101	0.01832
0.2121	1.2230	....	....
0.2619	....	0.01008	0.01884
0.2878	1.2266	0.0097	0.01899
0.3195	1.2282	0.01004	0.01941
0.3832	1.2324	....	....
0.3917	....	0.01009	0.02015
0.4445	....	0.01005	0.02067
0.6104	1.2420	0.01030	0.02237

The density data of Table VI can be reproduced with an accuracy of better than 0.01% by the equation

$$d = 1.2142 + 0.045c.$$

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[1] See footnote, Table III.

Table VII.—Conductivity of $KOCHO$ Solutions "Corrected for Viscosity" at 25°.

No.[1]	c.	η.[2]	χ_η.	$100/\lambda_\eta$.
0	0	0.0162	....	...
5*s*	0.01056	0.01632	0.000765	1.381
4*s*	0.02112	0.01643	0.001503	1.405
3*s*	0.04224	0.01664	0.002945	1.434
3	0.05480	0.01680	0.003803	1.441
13	0.06342	0.01690	0.004392	1.444
9	0.07661	0.01703	0.005256	1.458
2*s*	0.08448	0.01710	0.005778	1.462
10	0.09464	0.01721	0.006443	1.469
15	0.1137	0.01741	0.007707	1.474
16	0.1712	0.01801	0.01152	1.487
5	0.2121	0.01834	0.01414	1.500
11	0.2627	0.01885	0.01745	1.506
12	0.3043	0.01927	0.02008	1.508
6	0.3195	0.01943	0.02117	1.509
19	0.3917	0.02016	0.02596	1.509
17	0.4432	0.02068	0.02937	1.509
18	0.6104	0.02249	0.04051	1.507

The curve, K′ (Fig. 4) for the conductivities "corrected for viscosity" is just like the corresponding one for sodium formate. It becomes parallel to the axis of specific conductivities at the concentration 0.26 molar and remains so to the highest concentration measured, 0.61 molar, which, however, is not nearly so high a concentration as the highest for sodium formate. It is not impossible that, at a corresponding concentration, the potassium formate curve might fall off from the straight line as does the other. The line as drawn deviates, in the parallel portion, only by 0.2% from the straight line.

Ammonium Formate.

Solutions of this salt have already been investigated by Schlesinger and Calvert.[3] It was deemed advisable to repeat this work for several reasons. In the first place, owing to the fact that their solutions were made by passing ammonia into the acid, only one or two analyses of the original solution could be made and the remaining solutions had to be made up by the dilution method. This is objectionable in the concentrated solutions, because of possible volume changes upon dilution which cannot readily be taken into account[4] as was pointed out in the earlier paper.

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[1] Those experiments which on the curve for conductivities uncorrected for viscosity, appeared not to be in concordance with the others have been omitted in this table. There are practically duplicates for all such points. Also points lying very close to one another have been represented here by only one of the two.

[2] See footnote 1, Table III.

[3] *Loc. cit.*

[4] In the more dilute solutions such changes cannot be of importance.

In the second place, the analyses were difficult to make because of the large excess of very volatile acid present in the solutions. In order to avoid these difficulties,[1] we prepared ammonium formate by saturating the purest acid with ammonia and recrystallizing the salt from formic acid solution. The salt thus prepared, was kept for weeks in a desiccator over potassium hydroxide. The final product was analyzed by distilling off the ammonia in the presence of sodium hydroxide. All of the usual precautions to prevent spattering of the alkali and of removing all of the ammonia by a current of pure air, etc., were observed. The acid in which the ammonia was collected was carefully standardized. The salt used showed 100% ammonium formate within the limits of analytical error. From this salt the solutions were made up as in the case of the previously described salts.

The results of the measurements are given in Table VIII and in the curve labeled NH_3 in Fig. 4. This is the curve for the actually observed conductivities, those corrected for the conductivity of the solvent not being plotted because of their similarity to the sodium formate curve. The arrangement of Table VIII is identical with that of Table I.

TABLE VIII.—CONDUCTIVITY OF NH_4OCHO AT 25°.

No.[2]	c.	χ.	χ_a.	$100/\lambda$.	$100/\lambda_a$.	α.	α_a.	K.	K_a.
0	0	....	....	1.410	1.430	...	...	...	...
4*s*	0.01162	0.000866	0.000803	1.340	1.447	...	...	...	...
3*s*′[3]	0.02197	0.001598	0.001535	1.375	1.431	...	...	...	...
14	0.02962	0.002125	0.002062	1.395	1.438	...	...	...	...
2*s*′	0.04394	0.003065	0.003002	0.434	1.464	...	...	...	...
2*s*	0.04646	0.003220	0.003157	1.443	1.472	...	...	...	...
13	0.06821	0.004581	0.004515	1.489	1.511	0.947	0.946	1.15	1.14
1*s*	0.09293	0.006134	0.006071	1.515	1.531	0.931	0.934	1.16	1.23
2	0.1070	0.006988	0.006923	1.532	1.546	0.920	0.925	1.14	1.22
6	0.1914	0.01184	0.01177	1.617	1.636	0.872	0.879	1.14	1.23
1	0.2711	0.01609	0.01603	1.685	1.691	0.837	0.845	1.16	1.23
12	0.3207	0.01855	0.01848	1.728	1.735	0.816	0.824	1.16	1.24
10	0.3220	0.01858	0.01852	1.732	1.739	0.814	0.822	1.15	1.23
5	0.3822	0.02154	0.02147	1.775	1.780	0.794	0.803	[1.17][4]	[1.25][4]
11	0.4236	0.02336	0.02329	1.813	1.819	0.778	0.786	1.15	1.23
4	0.4643	0.02519	0.02512	1.843	1.848	0.765	0.774	1.16	1.23
3	0.5351	0.02825	0.02819	1.894	1.898	0.744	0.753	1.16	1.23
8	0.6081	0.03115	0.03108	1.952	1.956	0.723	0.731	1.15	1.21
7	0.6575	0.03304	0.03298	1.990	1.994	0.709	0.717	[1.13]	[1.20]

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[1] Our procedure is not as reliable for the dilute solutions as will be shown below.

[2] Two series were made in this case because the data did not agree with those of Calvert and the curve was not just like the sodium formate curve in the dilute solutions. The corresponding data have been numbered *s* and *s*′, respectively. They are seen to be concordant.

[3] Made up in a calibrated 50 cc. flask.

[4] This point is apparently incorrect. This can be seen by reference to the plot.

It is evident that the results for ammonium formate are, in general, like those for sodium and potassium formate and that they fully confirm the results of Schlesinger and Calvert.[1] The deviation in the more concentrated solutions begins above 0.55 molar.[2] A slight difference between the ammonium salt and the others is found in the dilute solutions, which fall away from the straight line much more rapidly than do the corresponding points for the other salts. We ascribe this to impurity in the ammonium formate, because Schlesinger and Calvert's results were entirely analogous to ours on sodium and potassium formates and because we obtained a similar result with an ammonium formate sample which had been freshly prepared. This sample of salt was not then used because it still contained an excess of formic acid. The somewhat different result obtained after the salt has been kept for some time can be explained by assuming partial (very slight) transformation into formamide. This impurity would not affect the concentrated solutions because its conductivity is very small.[3] But in the more dilute solutions, where it would be more highly ionized, its effect would be to make the apparent conductivity of the ammonium formate too large. This explanation is offered only as a suggestion; further work would be required to settle the point. It is, however, a matter of little importance, since the agreement with data for the salts in the more concentrated solutions is excellent.

The viscosity and density data are given in Table IX.

TABLE IX.—VISCOSITY AND DENSITY OF NH_4OCHO SOLUTIONS AT 25°.

c.	*d.*	η.[4]	*A.*
0.8847	1.2273	0.02418	0.00903
0.8290	1.2269	0.02356	0.00888
0.5221	1.2222	0.02063	0.00848
0.3676	1.2203	0.01923	0.00824
0.3207	....	0.01888	0.00835
0.2868	1.2189	0.01859	0.00833
0.2495	1.2186	0.01841	0.00886
0.1422	1.2166	0.01745	0.00907
0.05978	1.2152	0.01680	0.01004
0	1.2142	0.0162[1]	.....

In Table X are given the calculations for the "corrected conductivities," calculated as before.

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[1] The line drawn from their data does not fall exactly on ours, probably because of the more accurate analysis permitted by our method of making up the solutions.

[2] The last one of our points to fall on the straight line is for the concentration 0.535. The next point 0.608, lies slightly above the line, but S. and C. found that the point for 0.55 was still on the line.

[3] The concentrated solutions of the fresh and the old salt showed good agreement.

[4] See footnote 1, Table III.

TABLE X.—CONDUCTIVITY OF NH_4OCHO "CORRECTED" FOR VISCOSITY AT 25°.

No.	c.[1]	A.	η.[2]	χ_η.	$100/\lambda_\eta$.
0	...	...	0.162	...	...
13	0.06821	0.01000	0.01688	0.004774	1.429
1	0.09293	0.00965	0.01710	0.006475	1.435
2	0.1070	0.00919	0.01718	0.007410	1.444
6	0.1914	0.00896	0.01791	0.01309	1.462
1	0.2711	0.00855	0.01852	0.01840	1.473
12	0.3207	.....	0.01888	0.02162	1.483
10	0.3220	0.00833	0.01888	0.02165	1.487
5	0.3822	0.00826	0.01935	0.02573	[1.486][3]
11	0.4236	0.00834	0.01973	0.02845	1.489
4	0.4643	0.00838	0.02009	0.03124	1.486
3	0.5351	0.00850	0.02075	0.03618	1.479
8[4]	0.6081	0.00859	0.02143	0.04120	1.476
7[4]	0.6575	0.00866	0.02189	0.04464	1.473

The curve corresponding to the data in Table X is found in Fig. 4 and is labeled NH_3'. It is very similar to the corresponding curves for sodium and potassium formates. The portion corresponding to the concentrated solutions does not lie quite on a straight line parallel to the axis of specific conductivities, but shows a slight maximum. The deviation from a straight line is about 1%, but, since the maximum is quite regular, it may not be due to experimental error. If the data are correct, they would mean that the degree of ionization has a minimum at about 0.4 molar. A similar trend has been pointed out in the data for the other salts.

Phenyl Ammonium Formate.

The work was carried out exactly as for the other salts, except that aniline was used to make up the solutions instead of the salt itself. The accuracy of the work was somewhat interfered with by the fact that the solutions are not stable, probably because of anilide formation. By working rapidly, however, good results could be obtained, excepting that occasionally a reading was taken before temperature equilibrium was established. Usually, however, the change due to temperature adjustment could be distinguished from the other, slower change in the solutions. It took some experience before this was learned and for this reason the data found in the table are from the later experiments, as can be seen from the numbers. Because of this tendency of the solutions to undergo change, dilute solutions were not studied as a dilution series takes several hours at the best. In all other respects the experiments and the results

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[1] The calculations for those concentrations at which the deviation due to the conductivity of the solvent are noticeable, have not been included in the table.

[2] See footnote, Table III.

[3] Concerning this point see footnote 3 on p. 1610.

[4] These points are not plotted on the curve, as they lie beyond the field covered by the plot, but the curve is drawn so that it would include these points if it were extended.

are entirely analogous to the ones for the sodium and potassium salts. They require therefore, no further discussion. The data are found in Tables XI, XII and XIII, which correspond to analogous tables in the preceding and the curves are drawn in Fig. 4. The one labeled *A* is for the conductivity data without correction for the conductivity of the solvent and the one labeled *A′* is for the conductivity corrected for viscosity.

TABLE XI.—CONDUCTIVITY OF PHENYL AMMONIUM FORMATE AT 25°.

No.	c.	χ.	χ_a.	$100/\lambda$.	$100/\lambda_a$.	α.	α_a.	K.	K_a.
0	0	......	......	1.514	1.545	....	....	.....	.....
8	0.04866	0.003022	0.002960	1.610	1.644	0.940	0.940	0.719	0.714
28	0.06238	0.003828	0.003764	1.6295	1.657	0.929	0.932	0.742	0.802
29	0.08758	0.005231	0.005166	1.674	1.695	0.904	0.911	0.748	0.822
30	0.1466	0.008295	0.008231	1.768	1.782	0.856	0.867	0.748	0.829
22	0.1845	0.01006	0.009995	1.834	1.846	0.825	0.837	0.720	0.792
42	0.2105	0.01130	0.01124	1.863	1.874	0.813	0.824	0.742	0.815
21	0.2395	0.01260	0.01253	1.9015	1.911	0.796	0.808	0.745	0.817
26	0.2740	0.01404	0.01400	1.9515	1.960	0.776	0.788	0.736	0.804
20	0.3174	0.01582	0.01575	2.007	2.015	0.754	0.767	0.736	0.800
25	0.3494	0.01700	0.01694	2.055	2.063	0.737	0.749	0.721	0.780
31	0.3894	0.01865	0.01859	2.088	2.095	0.725	0.737	0.744	0.806
34	0.4391	0.02026	0.02026	2.167	2.174	0.699	0.711	[0.711]	[0.767]

TABLE XII.—DENSITY AND VISCOSITY OF PHENYL AMMONIUM FORMATE SOLUTIONS AT 25°.

c.	d.	η.[1]
1.0410	1.2133	0.02668
0.6276	1.2143	0.02231
0.4070	1.2148	0.02000
0.3316	1.2147	0.01943
0.1587	1.2146	0.01775
0.08122	1.2140	0.01704
0	1.2142	0.0162

TABLE XIII.—CONDUCTIVITIES OF PHENYL AMMONIUM FORMATE AT 25°, "CORRECTED" FOR VISCOSITY.

No.	c.	η.[2]	χ_η.	$100/\lambda_\eta$.
8	0.04866	0.01673	0.003121	1.559
28	0.06238	0.01689	0.003991	1.563
29	0.08758	0.01712	0.005528	1.584
30	0.1466	0.01764	0.009033	1.623
22	0.1845	0.01797	0.0116	1.653
24	0.2105	0.01832	0.01272	1.655
21	0.2395	0.01850	0.01438	1.665
26	0.2740	0.01890	0.01638	1.672
20	0.3174	0.01932	0.01886	1.683
25	0.3494	0.01958	0.02055	1.700
31	0.3894	0.01988	0.02289	1.702

[1] See footnote 1, Table III.

[2] See footnote to Table III.

The latter is not a straight line, and shows no portion parallel to the axis of specific conductivity, probably because the work was not extended into sufficiently concentrated solutions. Deviation in the higher concentrations begins between 0.3 and 0.4 molar. The actual point of deviation is not definitely settled, because it is quite difficult to be sure that apparent deviation is not due to the changes occurring in the solutions, as was mentioned above. Judging from the curve, the most probable point is at about 0.3 molar.

Hydrogen Chloride.

Zanninovich-Tessarin[1] concluded from his measurements of the conductivity of solutions of hydrogen chloride in formic acid that there was practically no ionization, and from his measurements of the depression of the freezing point of formic acid by hydrogen chloride that the latter was associated in this solvent. As has already been pointed out by Schlesinger and Calvert,[2] if these conclusions are correct, salts such as ammonium chloride should be practically completely decomposed in formic acid solution into a formate and hydrogen chloride and the conductivity of the salt should, therefore, be practically the same as that of the corresponding formate. The work of Schlesinger and Calvert showed that the conductivity of ammonium chloride was entirely different from that of ammonium formate. For this reason, it seemed necessary to repeat the work of Zanninovich-Tessarin. On account of certain difficulties, which would have required the construction of a new conductivity cell to obtain results of the degree of accuracy reached in the measurements on the formates, results accurate to only about one to 2% were sought. This degree of accuracy was sufficient to decide the question of the hydrolysis of salts, as well as to give a fairly definite idea of the behavior of hydrogen chloride in the solvent.

The measurements were made in cell No. 2, the solutions being made from one another by the dilution method. The original solution was prepared by passing carefully dried hydrogen chloride gas through formic acid contained in the conductivity cell. The undissolved gas was displaced by a current of dry air. Since the volume of the resulting solution was not the same as that of the original formic acid, both because of loss of acid by volatilization and because of the change in volume resulting from the dissolution of the gas, the concentrations could not be calculated in the ordinary way. Consequently, the portion of solution withdrawn from the cell in order to make the dilution was analyzed each time by precipitation of the chlorine as silver chloride. Two difficulties stood in the way of attaining great accuracy in the type of cell used for our other work. In the first place, the more concentrated solutions seem to lose hydrogen chlo-

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[1] *Z. physik. Chem.*, 19, 251 (1896).

[2] *Loc. cit.*

ride rapidly and the measurements are, therefore, made under great disadvantages. The more dilute solutions have a conductivity which is not sufficiently greater than that of the pure solvent to give very trustworthy results. Furthermore, the amount of silver chloride precipitated from 10 cc. of the dilute solutions is too little to allow of an analytical accuracy of more than 1%, or less, without the use of the nephelometer. However, no attempt was made to refine the analytical method because of the other difficulties mentioned. The results obtained, which are given in Table XIV, show that the data of Zanninovich-Tessarin are incorrect and that formic acid solutions of hydrogen chloride are good conductors. The reason for this divergence between our results and those of the former investigator doubtless lies in the fact that the acid used by him as solvent was very impure, as judged from its high initial conductivity. In the table are given the results of three series of measurements made as described. The first column gives the number of the series from which the data are taken; the second the concentrations; the third the specific conductivity uncorrected[1] for the conductivity of the solvent; the fourth, the equiva-

Table XIV.—Conductivity of HCl in Formic Acid at 25°.

No. of series.	c.	χ.	λ.	α.	K.
0	0	......	80.0	..	......
2	0.0080	0.000566	70.0	0.88	[0.0520]
3	0.0111	0.000768	69.2	0.86	[0.0449]
2	0.0150	0.000936	62.3	0.78	0.0415
1	0.0152	0.000931	61.4	0.77	0.0388
3	0.0195	0.00115	58.9	0.74	0.0407
2	0.0276	0.00148	53.7	0.67	0.0376
3	0.0328	0.00170	51.8	0.65	0.0392
2	0.0518	0.00234	45.2	0.57	0.0385
3	0.0570	0.00255	44.7	0.56	0.0404
2	0.0951	0.00355	37.4	0.47	0.0392
3	0.101	0.00377	37.4	0.47	0.0415
1	0.137	0.00454	33.1	0.41	0.0398
2	0.174	0.00528	30.0	0.38	0.0405
1	0.281	0.00732	26.0	0.32	[0.0438]
2	0.317	0.00801	25.3	0.32	[0.466]

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[1] The uncorrected value is used, since the hydrogen ion would tend to repress the ionization of the solvent. A curve drawn for the corrected conductivities was exactly of the same character as the one shown. The extrapolated value of λ_0 from this curve is about 69. Two slight differences from the data for the formates are to be noted. In the first place, the correction for the conductivity of the solvent has a greater effect on the constants and on the value of λ_0 than it has in the case of the salts. This is due to the much smaller conductivity of the hydrogen chloride solutions. In the second place, the deviation in the dilute solutions observed in the case of the formates is not so noticeable here. There are probably two reasons for this. In the first place, the data are not so accurate for hydrogen chloride solutions and the plot is drawn to a smaller scale, so that small

lent conductivity in the usual units, and the fifth the degree of ionization, α. This latter value was obtained by plotting $100/\lambda$ against the specific conductivity and extending the straight line portion of the resulting curve to to the axis of ordinate as has already been described. This, of course, gives an extrapolated value for λ_0, namely, about 80. The plot obtained was practically a straight line between the concentrations 0.174–0.015. The points deviate from the line irregularly by the amount to be expected from the probable error of measurement—at most by 3%. Both above and below these concentrations the curve seems to depart from the straight line but it is very probable that this is due to experimental error—due in the concentrated solutions to loss of hydrogen chloride by volatilization in the course of the transfer of the solution from the cell to the water in which it was analyzed, and in the dilute solutions to the insufficient amount of silver chloride available for the analysis. The deviation in the dilute solutions begins at exceedingly low concentrations and is, in this respect, not like the deviation observed in the case of the formates

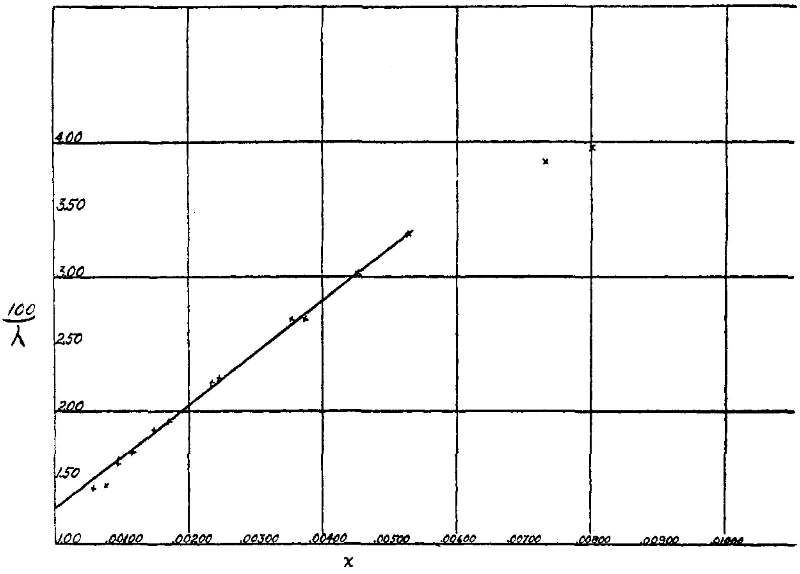

Fig. 5.

deviations are not so noticeable. In the second place, the hydrogen ion in these solutions must suppress not only the ionization of the formic acid but that of the water as well, which is probably present as impurity. (See p. 1599.) Hence there is no reason to suppose that the curves should show the type of deviation found in the case of the formates since this deviation was shown in part to be due to the conductivity of the water which is not affected by the ions of these salts. Since it is probably repressed by the ions of the hydrogen chloride, we believe that here the data uncorrected for the conductivity of the solvent are the ones to use.

as explained in footnote 1, page 1615. The curve is shown in Fig. 5.[1] The agreement of the curve with a straight line is again evidence that this solute, in formic acid solution, obeys the law of mass action. The constants obtained according to this law are given in the last column of the table. They were calculated directly from the conductivities and not from the data for α, which, as given in the table, are rounded in the second decimal place. It will be noted that the constants are fairly good, except for the high and low concentrations where the errors of measurement were large.

It is interesting to note that in formic acid solutions hydrogen chloride is very much less dissociated than are the formates, the results for which are given in the preceding sections. Thus the ionization constant for ammonium formate is 1.15 and for hydrogen chloride only 0.040. This is in agreement with Walden's assumption[2] that acidic substances are not as highly ionized in acid solvents as are basic substances. It is also very interesting to note that the conductivity of hydrogen chloride in this solvent at infinite dilution seems to be only about 80, which is of the same order of magnitude as that of the formates investigated. Hydrogen ion cannot, therefore, occupy the exceptional position in this solvent which it holds in aqueous solutions.[3]

Since our results on the conductivities of these solutions differ so widely from those of Zanninovich-Tessarin, it was natural to question his results on the freezing-point depression. As such measurements were considerably outside of the scope of this paper, only a few determinations were made. They were carried out in an ordinary Beckmann freezing-point apparatus, modified so as to allow the making of dilutions in it without exposing its contents to moisture, as well as to allow of the withdrawal of the solution in equilibrium with the solid solvent for analysis at the time the temperature reading was made. As the Beckmann apparatus is liable to many errors the results will be stated only briefly. Between the concentrations 0.026 and 0.36, the molecular lowering changed progressively from 42 to 29. While no great accuracy is claimed for these values, they at least show qualitative agreement with the results of the conductivity measurements and show that those of Zanninovich-Tessarin are incorrect here also. Not only the nature of the change of the molecular freezing-point depression with change in concentration, but the value

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[1] In order to make comparison with the other curves possible, a part of this one is also shown in Fig. 4. It is labeled "HCl."

[2] *Trans. Far. Soc.*, 6, 71 (1910).

[3] It is evident, therefore, that the exceptionally large migration velocity of hydrogen ion in aqueous solutions cannot be related essentially to the fact that hydrogen ion is a product of the ionization of water, since it is also a product of the dissociation of formic acid. See also Kraus, *loc. cit.*, and Hantzsch and Caldwell, *Z. physik. Chem.*, 58, 578 (1907).

27.7 obtained for the molecular freezing-point depression constant for this solvent by Raoult both indicate ionization and not association. Tessarin's value of about 13 must certainly be in error because of the impurity of his formic acid, which melted at 7.0° whereas the pure acid melts at about 8.4°.

Summary.

(1) The highly ionized solutions of sodium, phenyl ammonium, potassium and ammonium formates in (anhydrous) formic acid obey the law of mass action up to concentrations of from 0.3 to 0.6 molar, if the degree of ionization is calculated from the conductivities[1] to which no correction for the viscosity of the solutions is applied. The ionization constants of the salts in the order in which they are named have the values: 0.816, 0.814, 1.02 and 1.23. The same thing is true of solutions of hydrogen chloride, the ionization constant of which is only 0.04.[2] Above the concentrations mentioned, the formates show deviation from the mass law in the sense that the degree of ionization is less than it should be. This is the kind of deviation which is to be expected from the kinetic theory, if its cause lies in the reduction of the free space by the volume occupied by the solute itself. In this connection it is interesting to note that the data for sodium formate, up to the highest concentrations measured, show fair agreement with the equation

$$\frac{\alpha^2 c}{(1-\alpha)(1-v_m c^2)} = K$$

which is derived on the assumption that the deviation in the concentrated solutions is due to the cause suggested above. It is, however, not considered finally established that this agreement is reliable evidence of the correctness of the assumption.[3] There seems also to be a connection between the value of the highest concentration at which the law of chemical equilibrium holds and the value of the ionization constant. Thus ammonium formate, with a constant[4] of 1.23, begins to deviate above 0.55 molar; potassium formate, whose constant is 1.02, above 0.45 molar, and sodium and phenyl ammonium formates, whose constants are respectively, 0.816 and 0.814, both begin to deviate from the law at about 0.3 molar. It seems, therefore, that the greater the value of the ionization constant, the higher the point at which deviation begins. Of course, four cases is not a sufficiently large number to establish definitely a point

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[1] For a discussion of the conductivity of the pure solvent and its effect on the conductivity of the solutions see p. 1598.

[2] The limiting concentration for hydrogen chloride has not been determined.

[3] It was also assumed in deriving the equation that the volume of the ions is smaller than that of the undissociated molecules. For the complete discussion of this and other similar equations and of the data see p. 1599.

[4] These are the constants from the data uncorrected for the conductivity of the solvent.

of this sort. This regularity is pointed out, nevertheless, because, in view of the probable explanation offered above for the cause of this deviation, a regularity of this sort might prove of considerable theoretical interest. It is evident that it would lead to the conclusion that there is a relationship between the degree of ionization and the volume of the unionized molecule.[1]

(2) When the conductivities of the solutions are corrected in any of the usual ways for the viscosity of the solutions, and the degrees of ionization calculated from these corrected conductivities, the agreement with the mass law disappears. From the fact that the agreement of the uncorrected data in the more dilute solutions is so good and uniform in all of the cases investigated, and because there are possible explanations for the absence of viscosity effect, we conclude that the uncorrected conductivities are the ones to be used in these solutions for the calculation of the degree of ionization. This point has already been discussed in detail in the section in which the data for sodium formate are presented (p. 1604, *et seq.*). In this connection Table XV is of interest. It gives in Column 1 the name of the substance studied, in Column 2 the conductivity of its solution in water at infinite dilution, in Column 3 the observed conductivity at infinite dilution when formic acid is the solvent, and in Column 4 the conductivities of these same substances at infinite dilution in formic acid, calculated on the assumption that this conductivity is inversely proportional to the viscosities of the two solvents.

TABLE XV.

Substance.	λ_0 in H_2O at 25°.[2]	λ_0 in HCOOH at 25°.[3]	λ_0 in HCOOH calc.
NH_4OCHO	127.9	70.4	71.1
KOCHO	128.4	69.4	71.3
NaOCHO	104.9	66.0	58.5
$C_6H_5NH_3OCHO$	85.0	65.4	47.0
HCl	424.0	75.0	236.0

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[1] This is pointed out merely as a possibility which must await further evidence for definite proof. It is, however, in line with some of the more recent views on the nature of the process of dissociation. See Perrin, *Les Atomes*, **1912**, 228–231; Szyszkowski, *Compt. rend.*, **157**, 761.

[2] Except for phenyl ammonium formate, these values are calculated from the migration velocities found in Landolt-Börnstein, Roth, *Physikalich-Chemische Tabellen*, **1912**, 1124. The value for phenyl ammonium formate is obtained from Bredig's value for aniline hydrochloride (*Z. phys. Chem.*, **13**, 216 (1899)), and is, of course, quite uncertain. The value for formate ion is also not exactly known, but would affect all results equally. The rounded values 0.009 and 0.0162 were used for the viscosities of water and formic acid, respectively.

[3] The λ_0 values here used are the averages of those obtained by neglecting the conductivity of the solvent and those obtained when the correction is made. As explained on p. 1615, footnote 1, the difference in the two λ_0 values is large only in the case of hydrogen chloride. In the other cases it is only about 1%.

It is quite clear that the calculated values do not agree at all with those found except in the case of potassium and ammonium formate. This fair agreement in two cases makes the disagreement in the others more striking. If none of the values showed agreement, the disagreement might be explained for the formates by the lack of an accurate value for the migration velocity for formate ion in aqueous solution and in the case of hydrogen chloride by the probable inaccuracy of our value for the formic acid solution (although the inaccuracy could not be nearly large enough to account for the enormous discrepancy in this particular case).[1] Or the disagreement might be explained by saying that the simple viscosity relationship assumed is not correct in any case. But since the relationship gives, in some cases, values which agree and in others values which disagree with the experimental ones, it is clearly shown that the difference in viscosity of the solvents does not affect all ions alike.[2] It is, therefore, not permissible to set up a general equation expressing a relationship between the conductivities at infinite dilution in various solvents and the viscosities alone.[3] In formic acid, for instance, the mobilities of the ions do not seem to differ from each other as much as they do in aqueous solutions.[4]

This work is being continued in this laboratory along the lines indicated in the body of the paper. In addition to the points already mentioned it may be stated that we are repeating some of the measurements at different temperatures from those at which the data herein reported were obtained, and that we are also studying formates of types higher than the uni-univalent ones.

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THE HEAT OF VAPORIZATION OF NORMAL LIQUIDS.

BY JAMES KENDALL.

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The theoretical study of the heat of vaporization of liquids—a branch of physical chemistry long neglected—has recently attracted a great deal of investigation. The subject is of interest from its connection with the equation of van der Waals and the problem of molecular attraction. A number of formulas for representing variation of heat of vaporization with temperature have lately been put forward; some of these claim a theoretical basis, some are admittedly empirical. During the past year,

[1] The data for HCl are discussed on p. 1616.

[2] This may be due to differences in the solvation of the various ions in the two solvents.

[3] See Walden, *Z. physik. Chem.*, 55, 207 (1906) for references.

[4] See Kraus, *loc. cit.*