alkaline metal formates, in anhydrous formic acid solutions, and the demands of the mass law is a real, and not an accidental one.

3. As is to be expected, when the total concentration of mixed solutions becomes relatively great, deviation from the mass law occurs also in the solutions which contain only uni-univalent formates. It has been found that this deviation seems to begin when the concentration of the undissociated molecules of one of the salts reaches the same value as that at which deviation begins in the solution of that salt by itself. This seems to be independent of the concentration of the other molecular species present and to indicate that in the concentrated solutions it is the undissociated molecules and not the ions which cause deviation from the mass law or at least that the undissociated molecules cause deviation at lower concentrations than do the ions.[1]

CHICAGO, ILL.

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

STUDIES IN CONDUCTIVITY. VII. TRANSFERENCE NUMBERS OF THE FORMATES OF SODIUM, POTASSIUM AND CALCIUM IN ANHYDROUS FORMIC ACID.

BY H. I. SCHLESINGER AND E. N. BUNTING.[2]

Received July 28, 1919.

The work of the preceding papers of this series,[3] particulary that of the sixth one, has proved that the agreement in the behavior of the formates of the alkali metals, when dissolved in formic acid, with the demands of the mass law, is a real and not an accidental one so far as it is possible to establish this conclusion by the use of conductivity data alone. The only weakness in the argument lies in the fact that from the conductivity data two constants must be calculated for each salt—the ionization constant and the conductivity at infinite dilution, the latter of which must be obtained by extrapolation. If, however, we assume that the conductivity at infinite dilution obtained in this way for one of the salts is correct, we can calculate from this value and the transference numbers of this and the other salts the conductivity at infinite dilution for those

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[1] It must be recalled that the deviation herein referred to is of a different type from that commonly known in moderately dilute aqueous solutions of strong electrolytes (see the second paper of the series) in which the undissociated molecules are likewise frequently believed to be the deviating species.

[2] The work herein reported has been presented to the Faculty of the Ogden Graduate School of Science of the University of Chicago by E. N. Bunting in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was completed in the summer of 1918.

[3] Schlesinger and collaborators, THIS JOURNAL, 33, 1924 (1911); 36, 1589 (1914); 38, 271 (1916); 41, 72, 1727, 1921 (1919).

salts without the use of conductivity data or extrapolation. By carrying out measurements of transference numbers we have in the work reported in this paper finally confirmed the conclusion mentioned above.[1] We have included also measurements of the transference number of calcium formate in order to gain further information concerning the alkaline earth formates which, as has been shown in the fourth paper of the series, display an anomolous behavior. In addition to establishing the points mentioned above, this work has resulted in data which it is hoped will be of aid in shedding light on the problem of the solvation of ions.

The analysis of formic acid solutions of the alkali metal formates by the usual methods with the degree of accuracy required for even fairly reliable measurements of transport numbers, presents difficulties which it seemed unlikely that we would overcome readily. It was therefore decided that the most convenient and most accurate method would be found in measurement of the conductivity of the solutions before and after the electrolysis. Before carrying this plan into effect it was necessary, however, to make sure that no products are formed at the electrodes during electrolysis which might influence the conductivity. Solutions of the 3 salts for which transport numbers were to be determined were therefore separately electrolyzed between platinum electrodes, the quantity of current used was measured by a silver coulometer and the gaseous products were analyzed. The hydrogen given off at the cathode was found to correspond to a 100% yield according to the electrolytic equation

$$2Na^+ + 2\ominus + 2HCOOH \longrightarrow 2HCOONa + H_2.$$

At the anode the amount of carbon dioxide given off was found to correspond to 97% of that calculated on the basis of the equation

$$2COOH^- + 2\oplus \longrightarrow CO_2 + HCOOH.$$

Carbon dioxide is extremely soluble in formic acid and, while the electrolysis was run for a considerable length of time before beginning the measurements in order to saturate the solution, it is possible that some carbon dioxide was lost on this account. It is more likely, however, that some carbon monoxide and some oxygen may have been formed at the anode by secondary reactions as has been reported by Hopfgartner.[2] It is therefore clear that at the cathode no new ions or other products which might affect the conductivity are formed. At the anode the production of carbon monoxide is in all likelihood accompanied by the formation of water according to the equation

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[1] It was our intention to compare the transference numbers obtained by the Hittorf method with those obtained from concentration cells, but the latter part of this program was interrupted by duties arising out of the war.

[2] *Monatsh.*, **32**, 523 (1911). No data on the current yields are given in this paper. This work, however, made it unnecessary to investigate the products further.

$$2COOH^- + 2\oplus \longrightarrow CO + CO_2 + H_2O.$$

The amount of water formed in this way is apparently too small to affect the results except perhaps in the most concentrated solutions. It was also feared that the great solubility of the carbon dioxide in the solutions might result in a change of the conductivity but experiments showed that neither the conductivity of the pure acid nor that of the salt solutions was appreciably affected by saturating with the dry gas. The conductivity method of analysis was several times checked by gravimetric analysis of the solutions after electrolysis and the two methods gave the same results within the limit of analytical error.

The transport cell employed,[1] of the usual W type with an inlet for filling at the top of the middle bend, had a capacity of about 200 cc., the column of liquid was about 70 cm. in length; the electrodes were of platinum foil about 3 sq. cm. in area, and the current used was 0.03–0.05 amperes. It could be run from 4 to 5 hours without appreciably changing the middle portion. The ordinary form of coulometer, consisting of a platinum dish, 15% silver nitrate solution and a silver disk anode wrapped in filter paper, was used; this form has been shown to be accurate within 0.05%.

The method of making a transference run was as follows: The apparatus containing about 200 cc. of a solution of known concentration was immersed in a thermostat at 25.00° ± 0.01° and the current was passed through the solution for 4 to 5 hours, depending on the concentration. The conductivity of the solution was measured before any of it was subjected to electrolysis and also at the end of the run. For this latter purpose 15 cc. was removed from the mid-portion through the opening in the apparatus provided for this purpose. In general the conductivity of the mid-portion remained unchanged or changed by less than 0.1%; runs in which the difference was greater were rejected and are not included in the tables given below. At the close of the run, 50 cc. was withdrawn from both the cathode and the anode portion by means of a pipet and transferred to two glass stoppered bottles in which the contents of each could be thoroughly mixed by shaking. After this the conductivity of each solution was measured. As a result of the withdrawal of solution from the ends of the columns, the latter had of course separated in the middle and had become divided into two parts, which may be called the

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[1] The first cell made had electrodes of platinum deposited on the glass at various points within the cell in order that the conductivity of the solutions might be measured at various distances from the electrodes without removing the solution from the cell. While these electrodes were very small, local electrolysis nevertheless occurred and the resulting evolution of gas stirred up the solution. On this account and because the method of pipetting out a portion of the liquid proved satisfactory the scheme was abandoned. We now believe, however, that this plan can be carried out and that it would lead to accurate results, if successful.

sub-anode and the sub-cathode portions; these portions were run into bottles, and weighed, and their conductivities measured after each was thoroughly shaken.[1] After the removal of these various portions of solution from the cell, the latter was weighed in order to determine how much of the solution remained. This quantity of solution, usually from 0.3 to 0.4 cc., was assumed to be equally divided between anode and cathode portion and was added to the two portions in this way in the calculations. It was shown by experiment and by calculation that the amount of liquid lost during electrolysis by volatilization and spraying of the solution at the electrodes was small enough to be negligible.

As has been pointed out, the conductivity was used to determined the concentrations of the various portions of the solution after electrolysis. For this purpose equations based on the data of Schlesinger and Reed[2] and of Schlesinger and Mullinix[3] were used. For the sodium formate solutions the equation is:

$$1/\lambda = 0.01510 + 0.2815\chi,^{4}$$

for the potassium formate

$$1/\lambda = 0.01451 + 0.1936\chi,$$

and for calcium formate,

$$1/\lambda = 0.018185 + 0.7818\chi,$$

where λ is the equivalent conductivity, χ_1 the specific conductivity in reciprocal ohms corrected for the conductivity of the solvent. The first constant is $1/\lambda_0$, *i. e.*, the reciprocal of the conductivity at infinite dilution as determined by the method described in the earlier papers of this series; and the second constant is equal to the fraction $1000/K\lambda^2{}_0$, in which K is the ionization constant. From the value of λ obtained by the use of these equations and our experimental data the concentration in equivalents was directly calculated. The specific conductivities were measured in the cells and by the methods described in the fifth paper of this series. The densities of the solutions which were needed for the calculations could be found from the concentrations by means of equations of the type:

$$D = A + BC,$$

in which A and B are constants, D is the density of the solutions and C the concentration. The values for B for sodium, potassium and calcium formate solutions, respectively, are 0.036, 0.041 and 0.038 at 25° and

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[1] In a number of experiments no liquid was withdrawn by pipet from the anode and cathode portions, but the whole of each was collected in bottles, as were the portions described as sub-anode and sub-cathode portions above.

[2] THIS JOURNAL, 33, 6445 (1911).

[3] See the fourth paper of this series, *Loc. cit.*

[4] Equations of this type represent a form of the Ostwald dilution law. See the second paper of this series.

the constant *A* is the density of the pure acid, 1.2142. The values of these constants were determined by a series of density determinations and reproduce the densities of the solutions within 0.05%, which is ample for the present purpose.

In order to avoid the necessity of tabulating all of the data required for the calculations and thus making the tables unduly long, the method of calculating the transference numbers will be illustrated in the following:

In one of the runs on potassium formate the conductivity of the original solution, corrected for the conductivity of the solvent was 0.011871 reciprocal ohm; the conductivity of the mid-portion at the close of the run was the same. The conductivities of the cathode and sub-cathode portions were, respectively, 0.013614 and 0.012642, whence the concentrations of the original solution of the cathode and of the sub-cathode portions are calculated to be, respectively, 0.19953, 0.23343 and 0.21439; the corresponding densities are 1.22238, 1.22377 and 1.22299. The volume of the cathode portion was 50 cc.; from the concentration and density just given we find that it contained 60.207 g. of formic acid and 0.011672 gram equivalents of potassium formate. The weight of the sub-cathode portion was 31.370 g. From the concentration and density of this portion we find that it contained 30.907 g. of the acid and 0.005499 gram equivalents of the salt. The total weight of the solvent in the cathode portion was therefore 91.114 g. and the total weight of the salt was 0.017171 gram equivalents. As a result of electrolysis, however, some of the acid in the cathode portion is decomposed. In the run under discussion 0.007832 Faraday was passed through the solution. From the equation $2K^+ + 2HCOOH + 2\ominus = 2HCOOK + H_2$ we calculated the amount of acid decomposed to be $0.007832 \times 46.01 = 0.360$ gram. The original weight of the solvent in the cathode portion was therefore 91.475 g. From the concentration and the density of the original solution we find that this weight of solvent had contained 0.015140 gram equivalents of the salt before electrolysis. The amount of potassium transferred was then 0.017171 — 0.015140 or 0.002031 equivalents. This number divided by the number of Faradays which caused the transference is the transference number of the potassium ion. The number of Faradays is equal to the number of equivalents of silver, *G*, deposited in the coulometer if a correction for the current carried by the solvent is made. This is done by multiplying the quantity *G* by a fraction obtained by dividing the conductivity of the solution corrected in the usual way for the conductivity of the solvent by the uncorrected conductivity of the solution. The transference number can of course also be calculated from the loss of potassium at the anode. The calculation is like that described except for one point. At the anode, as a result of the reaction $2COOH^- + 2\oplus = HCOOH + CO_2$, $^1/_2$ equivalent of formic acid is produced per Faraday of electricity. The amount of acid calculated from this equation must therefore be subtracted from the weight of the solvent contained in the anode portion at the close of the run. Since the reaction at the anode does not proceed quite quantitatively according to the equation given, as has been shown above, the results at the cathode may be more reliable, but the data on sodium formate show that in moderately concentrated solutions the effect is negligible. Each of the determinations was subjected to 3 tests to check its reliability: first, the closeness of agreement between the results obtained at the anode and those at the cathode; second, the constancy of the conductivity of the mid-portion; third, the sum of the amounts of salt contained in all of the portions analyzed at the close of electrolysis had to be within 0.1% of the total amount of salt originally put into the apparatus. Runs which did not satisfy these requirements are, with but one or two exceptions, not included in the tables.

Tables I, II and III, which contain the data for the experiments on the transference numbers of sodium, potassium and calcium formates, respectively, are arranged as follows: Under C is the original concentration in gram equivalents per liter; under W, the weight in g. of the solvent in the cathode and in the anode portions, respectively, corrected as described above; under M, the gram equivalents of salt contained in W g. of the solvent in the cathode and in the anode portions; under E, the number of equivalents of positive ion constituent transferred to the cathode and from the anode, respectively; under N, the number of equivalents of electricity passed through the solution, corrected for the conductivity of the solvent; under T, the transference number of the positive ion calculated from the change at the cathode and from that at the anode; under T_{av}, the average of the values given under T for each experiment; under T_c, the average of all of the transference numbers obtained for any one concentration. It will be noted that the data for the anode portion are given in the row just below that on which the corresponding concentration is placed and that the data for the cathode are placed on the row above. The data under T_c have been obtained by weighing the results at each concentration in proportion as they appear to meet the requirements mentioned in the preceding paragraph. T_c has been omitted in the case of sodium formate because for this salt all of the data refer to practically the same concentration.

Table I.—Transference Data for NaOCHO in (Anhydrous) Formic Acid.

C.		W.	M.	E.	N.	T.	T_{av}.
	cathode	129.395	0.028212	0.001462		0.221	
0.2494					0.006601		0.220
	anode	135.224	0.026525	0.001430		0.219	
	cathode	128.549	0.028211	0.001593		0.220	
0.2498					0.007232		0.220
	anode	129.651	0.025266	0.001590		0.220	
	cathode	122.883	0.027217	0.001741		0.220	
0.2501					0.007909		0.220
	anode	131.019	0.025426	0.001737		0.220	
	cathode	119.443	0.026803	0.001698		0.226	
0.2536					0.007522		0.220
	anode	123.087	0.024266	0.001615		0.215	
						Mean	0.220

The data show that the method employed is capable of yielding accurate results under favorable conditions since the transference numbers for sodium formate show excellent agreement, not only for the different experiments but also when the results at the anode are compared with those at the cathode, most of them being practically identical with each other. It is clear, therefore, that the formation of a small amount of water at the anode can have but very little effect in moderate concentra-

TABLE II.—TRANSFERENCE DATA FOR KOCHO IN (ANHYDROUS) FORMIC ACID.

C.		W.	M.	E.	N.	T.	$T_{av.}$	T_c.
0.09982	cathode	108.973	0.0099749	0.0009975	0.003660	0.269	0.268	
	anode	105.577	0.0077313	0.0009787		0.267		
0.09981	cathode	104.109	0.0095835	0.0009955	0.003622	0.275	0.270	
	anode	108.794	0.0080161	0.0009584		0.265		0.269
0.1995	cathode	91.475	0.017171	0.002031	0.007832	0.259	0.259	
	anode	116.600	0.017274	0.002024		0.258		
0.2007	cathode	103.203	0.019060	0.001880	0.007230	0.260	0.256	
	anode	104.810	0.015632	0.001815		0.251		0.258
0.3015	cathode	105.328	0.028163	0.001729	0.006992	0.247	.....	
	anode	105.825	0.024753	0.001806		0.258		
0.3038	cathode	110.224	0.030078	0.002202	0.008770	0.251	0.249	
	anode	114.857	0.026877	0.002170		0.247		
0.3149	cathode	108.667	0.030790	0.002295	0.009264	0.248	0.249	
	anode	113.194	0.027374	0.002309		0.249		0.249
0.3906[a]	anode	103.886	0.034063	0.002797	0.01166	0.240		
0.3930	cathode	107.958	0.038163	0.002719	0.01127	0.241	0.244	
	anode	107.825	0.032290	0.002784		0.247		0.244

[a] An error was made in the cathode portion of this run.

TABLE III.—TRANSFERENCE DATA FOR $Ca(OCHO)_2$ IN (ANHYDROUS) FORMIC ACID.

C.		W.	M.	E.	N.	T.	$T_{av.}$	T_c.
0.2494	cathode	110.415	0.024070	0.001267	0.006096	0.208	0.211	
	anode	109.435	0.021291	0.001309		0.215		
0.2541	cathode	127.032	0.028133	0.001392	0.006352	0.219	0.215	
	anode	114.168	0.022690	0.001344		0.212		
0.2544	cathode	115.490	0.025719	0.001384	0.006370	0.217	0.214	
	anode	127.355	0.025488	0.001347		0.211		
0.2585	cathode	123.857	0.027847	0.001330	0.006266	0.212	0.216	
	anode	117.449	0.023772	0.001373		0.219		0.214
0.3995	cathode	106.845	0.037276	0.001806	0.009246	0.191	0.189	
	anode	111.308	0.035240	0.001713		0.188		0.189

tions. The data for potassium formate do not show quite as good an agreement when the results for any given concentration are compared with each other; this is doubtless due to the fact that the salt and its solutions in formic acid are extremely hygroscopic and that during the unavoidable manipulations involved more or less water is taken up. The moisture absorbed would increase the conductivity of the solutions and thus give too high a calculated concentration which would cause the transference number at the cathode to appear too high and at the anode too low; in agreement with this assumption we find that in almost all cases where the two values are not practically identical the cathode value is higher than the anode value, if we except the most concentrated solutions. While the data for potassium formate are therefore not quite as reliable as those for the sodium salt, they are nevertheless quite acceptable when it is considered that the total amount of salt transferred is only from 0.001 to 0.003 gram equivalent and that therefore an error of 0.05% in the determinations of the concentration might readily produce an error of from 1 to over 4% in the transference numbers.

If we compare the transference numbers obtained for potassium formate at different concentrations, it is seen that no experimental error of the type described can account for the large and regular change which occurs when the concentration is progressively increased. Potassium formate in (anhydrous) formic acid solutions appears to obey the law of mass action when the degree of ionization is calculated from the conductivities of the solutions on the assumption that the equivalent conductivity for complete ionization is independent of the concentration.[1] In view of this fact one would expect the transference numbers also to be independent of the concentration. The most rational explanation of this discrepancy is to assume that the Hittorf transference number which we have here measured is not the true transference number because of solvation of the ions. The following calculations show that this assumption can account for the change in transference number observed. If we assume that only the potassium ion is solvated, it is clear that the amount of solvent found in the cathode portion is larger and that in the anode portion smaller than it would have been had none of the solvent been transferred. A correction may then be applied in the following manner. If n is the number of molecules of the solvent, formic acid, associated with each molecule of potassium ion, x the "true" transference number, and N the number of Faradays passed through the solution, the weight of formic acid in g. carried to the cathode is $46.x.n.N$. If W is the corrected weight of solvent in the cathode portions, f the number of equivalents of potassium formate contained in one gram of the solvent

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[1] See the earlier papers of the series, *Loc. cit.*

in the original solution and E the number of equivalents of the salt contained in W g. of the solvent in the cathode portions, we have

$$x = \frac{E - (W - (46.x.n.N))f}{N},$$

which can readily be solved for x if n, the number of molecules of the solvent associated with each molecule of potassium ion, is known. A similar calculation can be made for the anode portions. In Table IV, the results of such calculations with several values of n are reproduced. It will be seen that the assumption that the potassium ion is solvated is sufficient to account for the fact that the Hittorf transference numbers change with the concentration as they do, since the "true" transference numbers calculated in this way are as nearly constant as they can be expected to be when the various sources of experimental error are considered. The data are not accurate enough to determine accurately the number of molecules of solvent associated with the potassium ion since the calculations with different values of n do not show any great difference in constancy. It is clear, however, if this method of calculation is correct, that the value of n probably is not less than 6 nor greater than 8, a conclusion which is to be subjected to further test and which is of interest in view of Werner's theory of complexes and of the process of ionization.[1] In Table IV, the first column contains the approximate value of the concentrations, Col. 2 the transference number when n is zero—in other words, the Hittorf number—which is included for comparison and the remaining columns give the transference number, x, as defined above, when the value for n is respectively taken to be 5, 6, 7, 8 and 9. At the bottom of each column will be found the difference in *per cent.* between the extreme values of the transference numbers in the column.

TABLE IV.

Transference Numbers.

C.	$n = 0$.	$n = 5$.	$n = 6$.	$n = 7$.	$n = 8$.	$n = 9$.
0.10	0.269	0.273	0.274	0.275	0.277	0.278
0.20	0.258	0.269	0.271	0.271	0.276	0.279
0.31	0.249	0.264	0.268	0.271	0.276	0.279
0.39	0.244	0.265	0.268	0.274	0.279	0.283
Difference...	10%	3%	2%	1.5%	1%	1.7%

We may now use the transference numbers of these two salts to calculate for one of them the conductivity at infinite dilution without the use of conductivity data for that salt. Thus, the conductivity at infinite dilution for the sodium salt obtained by extrapolation of the conductivity data, is 66.225.[2] The transference number, at 0.25 N, was found to be

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[1] See also Kendall and Booge, THIS JOURNAL, **39**, 2323 (1917).

[2] See the sixth paper of this series, *Loc. cit.*

0.220.[1] By the usual method of calculation we derive 14.6 for the equivalent conductance of the sodium ion and 51.6 for that of the formate ion. From the latter and the transference number of potassium formate at 0.25 *N*,[2] we obtain 17.5 for the equivalent conductance of the potassium ion. Since the corresponding value for the formate ion is, as just stated, 51.6, the equivalent conductance of the potassium formate at infinite dilution should be the sum of these two, namely, 69.1, which proves to be practically identical with the value 68.92 derived in our previous work by extrapolation from conductivity data. We have therefore shown that the calculation of both the conductivity at infinite dilution and the ionization constant from the conductivity data alone introduced no error into our conclusion that there is a real agreement between the behavior of the alkali metal formates and the demands of the mass law and this chapter of our work on formic acid as a solvent is therefore considered complete.

One other point of interest appears from the data presented. It is seen that the equivalent conductance of the formate ion is very much greater than that of the positive ions combined with it in the salt molecules. This is like the behavior of the hydroxide ion in aqueous solutions to which the formation in formic acid solutions is analogous. The same explanation as the one usually given for the great mobility of the hydrogen and hydroxide ions in aqueous solutions may be applied to the great relative mobility of the formate ion in our solutions. On the other hand, since some evidence has been presented which tends to show that the positive ions are apparently much more extensively solvated than is the formate ion, we may ascribe to this difference the difference in the mobilities of the ions.

The transport experiments on solutions of calcium formate were included in order to throw further light on the questions raised by the anomalous behavior of the alkaline earth formates which, in formic acid solutions, obey the law of mass action as developed for uni-univalent salts in moderately concentrated solutions but not in dilute solutions.[3] This behavior suggests the possibility that in the range of concentration for which this law is applicable, ionization into an intermediate ion, *e. g.*, $CaOCHO^+$, exclusively takes place. This question can be answered by

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[1] The true transference numbers obtained as described above ought perhaps to be used for these calculations. The results if this is done do not differ materially from those given in the text and since the value of the "true transference numbers" as well as the theory upon which they were calculated need further verification, it has been thought best to proceed as has been done in the text.

[2] This value is obtained by graphical interpolation from the data of Table II, since no data are available for this concentration. The interpolation is over a very short interval.

[3] Schlesinger and Mullinix, THIS JOURNAL, **41**, 72 (1919).

the transference data. It can be shown, if V represents the speed of diffusion of the formate ion in centimeters per second under a potential gradient of one volt per cm., λ_o represents the equivalent conductivity calculated on the assumption that the equivalent weight of calcium formate is $^1/_2$ its molecular weight, n_1 is the transference number of the formate ion if the salt dissociates into formate ion and $CaOCHO^+$ and n_2 the transference number if the salt dissociates into formate and calcium ions, that the two following equations are correct provided either the one or the other mode of ionization occurs exclusively:

$$2\lambda_o = \frac{FV}{n_1} \quad (1), \qquad \text{and} \qquad \lambda_o = \frac{FV}{n_2} \quad (2)$$

Equation 1 applies to ionization into the intermediate ion and Equation 2 to ionization into the simple ions. If dissociation into the intermediate ion occurs, the change in concentration of formate ion constituent at the anode is due (*a*) to formate ion discharged at the electrode, (*b*) to formate ion carried into the anode portion, and (*c*) to calcium formate ion carried from the anode portion. If S_o represents the number of gram equivalents of calcium formate contained in the anode portion before electrolysis, and S_f the number of gram equivalents of the salt in this portion after electrolysis, and N is the number of equivalents of electricity passed,

$$2S_o - N + Nn_1 - (1 - n_1)N = 2S_f \quad \text{or} \quad n_1 = \frac{N - (S_o - S_f)}{N}.$$

If, on the other hand, ionization occurs only into the simple ions, the change in the concentration of the formate ion constituent is due only to the formate ion discharged at the anode and the formate ion carried into the anode portion by transference. Hence,

$$2S_o - N + n_2N = 2S_f \quad \text{or} \quad n_2 = \frac{N - 2(S_o - S_f)}{N}.$$

In Table III, the data under T and T_{av} represent the fraction $(S_o - S_f)/N$. Hence n_1 and n_2 become respectively equal to $1 - T$ and $1 - 2T$. Hence, if ionization into the intermediate ion is the exclusive mode of ionization of the salt, $2\lambda_o = FV/(1 - T)$. FV, the equivalent conductance of the formate ion, has been obtained from the work with sodium and potassium and at 0.25 N has been found to be 51.5 reciprocal ohms. Taking for T, the average value 0.214, $2\lambda_o$ from the equation just given is calculated to be 65. Actually, λ_o was found by Schlesinger and Mullinix to be 55. Hence the transference data do not support the view that calcium formate dissociates exclusively as a uni-univalent salt. On the other hand, if the salt is assumed to ionize exclusively into the simple ions we would have the equation $\lambda_o = FV/(1 - 2T)$. Calculated as before, we get 90 for the value of λ_o. This agrees just as little with the experimentally determined value, 55. Hence the transference data do not decide the question raised, unless we assume that they may be taken to indicate that both modes of dissociation occur—a conclusion already tentatively suggested in the discussion of the work of Schlesinger and Mullinix referred to above.[1]

Summary.

1. The transference numbers of solutions of sodium, potassium and calcium formates in (anhydrous) formic acid have been measured. From the data for the first two salts the equivalent conductance of the formate ion has been calculated and has been found to be 51.5, whereas the corresponding value for the sodium ion is only 14.6 and for the potassium ion 17.5 reciprocal ohms. The significance of these data has been discussed.

2. The transference number of the potassium ion was found to change with the concentration. This is tentatively explained on the assumption that the ion is solvated and a method for calculating the extent of solvation from the transference numbers is suggested. The results so far available indicate that if the assumptions made in the calculations prove to be correct, each potassium ion is combined with from 6 to 8 molecules of formic acid—a finding which is of special interest when viewed in the light of Werner's theory of complex ions and of ionization in general.

3. The transference numbers obtained for calcium formate do not substantiate the view that calcium formate in formic acid solutions ionizes either entirely as a uni-univalent salt nor entirely as a uni-bivalent salt. It is therefore possible that both modes of ionization occur.

CHICAGO, ILLINOIS.

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[1] Two points are to be noted in connection with the calculations upon which these conclusions are based. In the first place the concentration 0.25 equivalent for calcium formate should really be compared with the concentration 0.125 *N* for sodium or potassium formate when the assumption is made that the calcium salt yields only two ions. Or it would be possible in order to avoid confusion to use the "true transference numbers" calculated for potassium formate. Neither of these alternative methods of calculation produces enough change in the results to influence the conclusions and they have therefore not been given in the text. In the second place it must be borne in mind that the "experimental" value for the equivalent conductance of calcium formate at infinite dilution is a value obtained from the data for the conductivity of that salt in solutions more concentrated than 0.1 equivalent and is based on the assumption that the salt obeys the mass law as derived for uni-univalent salts to infinite dilution. As a matter of fact, the salt does not obey this law below the concentration mentioned (see the fourth paper of the series), hence the value of the conductivity at infinite dilution is a fictitious one which has a meaning only if the salt ionizes into two ions only in the range of concentration for which the mass law holds in the form mentioned. Nevertheless, the use of this fictitious value for the purpose for which it is employed in the text is logical as can readily be understood.