

with the temperature the heat of ionization of water has been calculated, and found to be in close agreement with the directly measured heat of neutralization of strong acids and bases.

I wish in closing to acknowledge my great indebtedness to Dr. A. A. Noyes, at whose suggestion this work was undertaken, for aid therein.

## THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF THE ORGANIC ACIDS IN LIQUID HYDROGEN CHLORIDE AND BROMIDE.

BY E. H. ARCHIBALD.  
Received August 23, 1907.

### Introduction.

It has been shown in a previous paper,<sup>1</sup> that the majority of the organic hydroxy bodies dissolve in liquid hydrogen bromide to give solutions which conduct the electric current. It was found however, that, as first pointed out by Steele, McIntosh and Archibald,<sup>2</sup> the behavior of these solutions toward the electric current was very different from that of aqueous solutions of the ordinary electrolytes. As distinguished from these solutions, the molecular conductivity, except in the case of the more dilute solutions, decreased rapidly as the dilution increased. It was found, too, that in a number of cases the specific conductivity decreased with rise of temperature, giving negative temperature coefficients. It was thought that the organic acids would be an interesting class of substances to study as regards their power of forming conducting solutions when dissolved in this medium, and the nature of the variation of the molecular conductivity with dilution, particularly for the more dilute solutions. At the same time it was thought advisable to extend this study to include solutions of these substances in liquid hydrogen chloride, as it has been shown by Steele, McIntosh and Archibald,<sup>3</sup> that in many cases solutions of organic substances in this solvent exceed those formed with the liquid hydrogen bromide in their power of conduction.

It has been pointed out by Walker, McIntosh and Archibald,<sup>4</sup> that several of the organic acids form conducting solutions with liquid hydrogen chloride; but in the case of the hydrogen bromide solutions, the specific conductivity seemed to be so small as to be almost unmeasurable. It will be shown below, that with the form of electrolytic cell here used, the conductivity of a large number of these acids, when dissolved in the liquid hydrogen bromide, can be followed over a considerable range of dilution.

*The Materials Used.*—The preparation of the liquid hydrogen bromide

<sup>1</sup> This Journal, 29, 665 (1907).

<sup>2</sup> Phil. Trans., A. 205, 99 (1905).

<sup>3</sup> Loc. cit. p. 132.

<sup>4</sup> J. Chem. Soc., 85, 1098 (1904).

has been already described in the paper referred to above. The hydrogen chloride was generated from sulphuric acid and a saturated solution of sodium chloride. The resulting gas was thoroughly dried by passing through concentrated sulphuric acid, and then through a glass tube 50 cms. long, well packed with anhydrous granular calcium chloride. From here the gas passed directly into the condensing tube, which was immersed in a pasty mixture of solid carbon dioxide and ether. The liquid chloride, dried in this way, had a slightly lower conductivity than that dried by means of phosphorus pentoxide, due, perhaps, to the fact that in the latter case some oxochloride of phosphorus may have been formed, as pointed out by Bailey and Fowler<sup>1</sup> and also by Baxter,<sup>2</sup> and dissolved by the liquid chloride.

The organic acids used were nearly all from Kahlbaum's laboratories, and were in all cases the purest that could be obtained. The purity of the different substances was tested by means of boiling and freezing point measurements.

*Apparatus.*—The apparatus used in making the following measurements was essentially the same as that used in the case of the alcohol solutions.<sup>3</sup> Two conductivity cells, one for solutions having a high resistance, and the other for use where the resistance was comparatively low, enabled one to follow the conductivity over a considerable range of dilution.

When working with the hydrogen bromide solutions, the conductivity vessel was immersed in the bath of solid carbon dioxide and ether. This bath, if sufficient attention is paid to the stirring, can be kept within at least two tenths of a degree of  $-80^{\circ}$ .

A lower temperature than  $-80^{\circ}$  was necessary when working with solutions in the liquid hydrogen chloride, as this solvent boils at a temperature of  $-83^{\circ}$ . The necessary condition was secured by connecting the vacuum tube containing the carbon dioxide and ether with a good water pump, and in this way keeping a partial vacuum over the cooling mixture. With a steady stream of water passing through the pump, the temperature of the bath remains surprisingly constant for a long time; in the present case at about  $-96^{\circ}$ . So vigorously does the carbon dioxide boil away, that it serves to keep the mixture well stirred. The temperatures were, in all cases, indicated by pentane thermometers, standing in a tube half filled with ether, which in turn passed through the rubber stopper of the vacuum tube well down into the pasty mass of carbon dioxide and ether. These thermometers were made especially for working with these solutions; they were graduated to tenths of a degree, and could easily be read to fiftieths of a degree if necessary.

<sup>1</sup> Chem. News, 58, 22.

<sup>2</sup> This Journal, 28, 770 (1906).

<sup>3</sup> This Journal, 29, 666 (1907).

The same method of measuring resistance was employed, as was used in the case of the hydrogen bromide solutions of the alcohols—that is, the Kohlrausch method using telephone and alternating current. In the case of the more concentrated solutions, it was found necessary to pay a great deal of attention to the platinizing of the electrodes, if a sharp minimum was to be obtained. Treating the electrodes after the manner suggested by Griffiths, seemed to be an advantage in some cases, but nothing appeared to be more satisfactory than an even and firm coating of the platinum black.

In the case of the more dilute solutions, where the resistance is very high, the conductivity of the solvent has to be subtracted from the conductivity of the solution. For this purpose the conductivity of the solvent must be known as accurately as possible. As I pointed out in a previous communication, it is very difficult to obtain an accurate value for the specific conductivity of these liquid hydrides, the resistance being so high that the minimum point on the bridge cannot be located within several millimeters. The resistance of each particular portion of solvent used was measured as accurately as possible, and the value found was used in calculating the conductivity, in the case of the solutions prepared with this portion of solvent.

The specific conductivity of the liquid hydrogen bromide, as stated in the paper referred to above, was, as an average value, about  $0.008 \times 10^{-6}$  in reciprocal ohms, while the corresponding value for the liquid hydrogen chloride was slightly higher, being  $0.010 \times 10^{-6}$  in the same units.

Although not of vital importance in the present research, it may be asked if this greater conductivity on the part of the liquid hydrogen chloride is due to the presence of impurities, or if it is due to the nature of the hydrogen chloride itself. It will be seen from the results given below, that substances dissolved in this solvent conduct better than when dissolved in the liquid hydrogen bromide. The same amount of impurity present, in the case of the hydrogen chloride, might give a solution which would conduct many times better than the corresponding solution with the liquid hydrogen bromide. As it is practically impossible to prepare any substance absolutely pure, the greater conductivity of the hydrogen chloride might be accounted for in this way. However, it is not very apparent what this impurity can be. As shown by Steele, McIntosh and Archibald,<sup>1</sup> very few of the inorganic salts dissolve in the liquid halogen hydrides, and fewer still give conducting solutions. Among those which do give such solutions, are some phosphorus compounds; but one can hardly imagine phosphorus compounds being present in the liquid chloride prepared after the manner stated above, or in

<sup>1</sup> Loc. cit., p. 122.

fact any other body, inorganic or organic, which would give a conducting solution. It seems more likely that it is the hydrogen chloride itself which is conducting the electric current, the lower viscosity<sup>1</sup> of the hydrogen chloride accounting, perhaps, for the greater conducting power of this solvent.

In estimating the accuracy with which the molecular conductivity of any given solution could be determined, we should consider first, the error which may be involved in the measurement of the resistance, due to an unknown change in the temperature of the solution. As we see from the table of temperature coefficients given below, the resistance of some of the solutions may change as much as 3 per cent. for a difference in temperature of 1°. As we pointed out above, the temperature may vary as much as 0.2°. An error therefore of 0.6 per cent. might be made on this account alone. It is not likely that the resistance of any definite solution, provided the temperature remained constant, could be determined within 0.2 per cent, while a still greater error might be made in determining the concentration of the dissolved substance. This error might possibly amount to as much as 0.3 per cent. If now, we assume that these errors all affected the conductivity in the same direction, it is apparent that the measurement of the conductivity might be in error somewhat over 1.0 per cent. ; while in the case of the molecular conductivity, the observed values may be in error as much as 1.5 per cent. For a few of the more dilute solutions, of those substances which give the poorest conducting solutions, the error may be somewhat larger than this ; as there the conductivity of the solvent has been subtracted from that of the solution, and this procedure in itself may lead to an erroneous result ; while an appreciable error in the measurement of the conductivity of the solvent would cause a slight error in the value of the specific conductivity of the dissolved substance.

### Qualitative Results.

A large number of the acids were first examined in a qualitative manner only, to ascertain what ones formed conducting solutions with the solvents in question. In preparing the solutions for these measurements, about 20.0 cc. of solvent were used for each determination. The substance, if not a liquid, was always finely powdered before adding it to the solvent. In the case of those substances which either did not dissolve at all or dissolved only in traces, the organic acid was left in contact with the solvent—with frequent stirring—for a long time, in order to allow the solvent to become as nearly saturated with the substance in question as possible. It is worth noting, that in all cases so far met with, solution takes place a great deal more rapidly and equilibrium is

<sup>1</sup> McIntosh and Steele. *Loc. cit.*, p. 118.

reached much more quickly, than is the case with substances dissolving in water.

In tabulating the results of these experiments, each of the substances examined is considered as belonging to one of three classes, according as it forms a good conducting solution, one which conducts only slightly, or does not give a conducting solution at all. It may be further stated, that the first class would form solutions which have about the same conducting power as that of a fiftieth normal solution of potassium chloride in water; while those in the second group would conduct the current to about the same extent as a sample of ordinary conductivity water.

A blank appearing in the table, indicates that no determination was made to ascertain whether or not that particular acid formed conducting solutions with the solvent in question.

While no absolute measurements were made to determine whether or not a certain substance was soluble in either solvent, almost certain indications could be obtained as to its solubility or non-solubility, by adding, at first, a very small portion of the substance in question to the pure solvent, leaving it for some time—with repeated stirring—and noting whether or not it had dissolved. The amount of heat given out, too, when the organic acid is added to the liquid hydride, serves as a very good indication of whether or not the acid has dissolved; as in all cases where solution is known to take place, there is a marked evolution of heat. It should be stated here, that I have not met with any case where solution of an organic substance is known to have taken place without causing a marked increase in the conductivity above that of the pure solvent.

It will be noticed at once, that, in general, the acids of the paraffin series form conducting solutions with both solvents; the exceptions being, formic acid in the case of hydrogen bromide, and the higher members of the series with both solvents. It is apparent, too, that the conductivity falls off as we approach the higher members of the series; caprylic acid forming solutions which conduct only slightly, while palmitic acid does not conduct at all in hydrogen bromide. The behavior of formic acid is rather anomalous, as, judging from the rest of the series, we would expect it to be the best conductor of them all. However, it is a rather poor conductor when dissolved in hydrogen chloride, while it will apparently not dissolve in hydrogen bromide, and certainly does not conduct at all.

The dibasic acids, belonging to the oxalic acid group, do not conduct with either solvent; indeed, these acids did not appear to dissolve at all in the liquid hydrides. The dibasic acids of the ethylene group, while not forming conducting solutions with hydrogen bromide, have fair conducting power when dissolved in hydrogen chloride. In fact, at the con-

TABLE I.—QUALITATIVE RESULTS.

Name of organic acid	Conducting power of solution formed with the halogen hydrides	
	Hydrogen bromide	Hydrogen chloride
Formic acid .....	no conduction	good
Acetic acid .....	good	good
Propionic acid.....	good	good
Butyric acid .....	good	good
Isovaleric acid.....	good	.....
Caprylic acid.....	.....	slight
Palmitic acid .....	no conduction	.....
Oxalic acid.....	.....	no conduction
Malonic acid .....	no conduction	no conduction
Sebacic acid.....	no conduction	no conduction
Glycollic acid.....	.....	no conduction
Lactic acid .....	no conduction	.....
Malic acid .....	no conduction	no conduction
Tartaric acid.....	no conduction	no conduction
Racemic acid .....	no conduction	no conduction
Citric acid.....	no conduction	no conduction
Saccharic acid.....	.....	no conduction
Amino-succinamic acid.....	.....	no conduction
Fumaric acid.....	no conduction	slight
Maleic acid .....	.....	good
Mesaconic acid .....	.....	no conduction
Sorbic acid.....	.....	slight
Benzoic acid.....	good	good
Ortho-nitro benzoic acid.....	no conduction	.....
Meta-nitro benzoic acid .....	slight	slight
Para-nitro benzoic acid.....	no conduction	.....
Ortho-amino benzoic acid .....	no conduction	.....
Hippuric acid.....	no conduction	slight
Ortho-toluic acid.....	good	good
Meta-toluic acid.....	good	good
Para-toluic acid.....	good	good
Ortho-phthalic acid.....	no conduction	good
Meta-phthalic acid.....	no conduction	no conduction
Ortho-hydroxy benzoic acid.....	good	good
Para-hydroxy benzoic acid .....	no conduction	slight
Tannic acid .....	no conduction	.....
Cinnamic acid .....	slight	good
Cumaric acid.....	no conduction	.....

centration examined, maleic acid had as good conducting power as any other acid examined at this particular concentration.

It is worth noting that the monobasic acids, carrying an hydroxyl group, as in the case of lactic and glycollic acids, do not form conducting solutions with the halogen hydrides.

In the case of the acids of the benzene series, conducting solutions seem to be formed with both solvents, as shown in the cases of benzoic

and the toluic acids. The behavior of the hydroxy benzoic acids seems to vary with the position of the hydroxyl radical. When this radical is ortho to the carboxyl group (salicylic acid) we have good conducting solutions formed with both solvents, while the para acid conducts slightly when dissolved in hydrogen chloride, but not at all when treated with the liquid hydrogen bromide. The same is true of the phthalic acids: *o*-phthalic acid gives good conducting solutions with hydrogen chloride, while the meta acid does not apparently dissolve at all. The same behavior is noticed in the case of the oxybenzoic acids when dissolved in water, for there the conductivity of the ortho acid is many times greater than that of the meta, while the meta acid in turn, is a much better conductor than the para.

It will be remembered, that, in the case of the hydrogen bromide solutions of the alcohols, it was generally true, that when the hydroxyl radical was in the meta position the alcohol gave a better conducting solution than when this radical had any other position. In the case of the present solutions, it would seem to be the ortho acid which forms the best conducting solutions. At least this is what one would conclude from the qualitative results, as shown for instance in the case of the phthalic and hydroxy benzoic acids.

The mono and dihydroxy dibasic acids do not form conducting solutions with either solvent.

Solutions of the nitro benzoic acids show only slight conducting power, while ortho-amino-benzoic acid does not form conducting solutions, at least not with hydrogen bromide.

It appears, then, that the action of these solvents is somewhat selective, as in the case of formic, salicylic and ortho-phthalic acids. It seems safe to say, however, that more of the organic acids will form conducting solutions with hydrogen chloride than with hydrogen bromide. Is this due to the lower temperature, or to the nature of the hydrogen chloride itself?

It has been shown by Archibald and McIntosh<sup>1</sup>, that, in all cases where organic bodies dissolve in the liquid hydrides to give conducting solutions, there is present some element which may increase in its power of combining with others. Thus, in the case of the ethers, aldehydes and alcohols, it has been shown that when these substances dissolve in the liquid hydrides, compounds are formed between the hydrides and the organic substances, in which the oxygen probably functions as a quadrivalent element. It would seem from the above measurements, however, that the presence of oxygen atoms in the molecule is not a sufficient reason for supposing that the substance will dissolve or form conducting solutions with these solvents. Thus, if we examine the above table, we see, that, in general, the greater number of carboxyl groups or of hy-

<sup>1</sup> Pr. Roy. Soc. Canada, [2], III, 10, 43 (1904).

droxyl radicals present in the molecule, the less likely is the substance to dissolve. Thus we may instance citric acid, a mono hydroxy tribasic acid; and tartaric and racemic acids, dihydroxy dibasic acids; also the dibasic acids of the oxalic acid group. On the other hand, the monobasic acids of both the paraffin and benzene series form good conducting solutions.

This behavior, on the part of those acids which contain a larger number of oxygen atoms in the molecule, might at first seem to be opposed to the idea that the valence of the oxygen has increased at the lower temperature here obtaining. But, if we look further into the matter, it seems to me that the fact that these acids do not form conducting solutions, rather supports this idea than otherwise.

If we consider an hydroxy polybasic acid, when the temperature of such a substance is lowered, while this may be attended with an increase in the valence of the oxygen, there is here some likelihood that the free valences of one oxygen may be satisfied by the free bonds of another, there being a great many ways in which such a combination can take place. While, in the case of a monobasic acid, the number of ways in which such a neutralization may occur is greatly reduced. The valence then of the oxygen belonging to the polybasic acid may increase, but it does not necessarily follow that the substance will dissolve in the liquid hydride, to give addition compounds which undergo ionic dissociations.

#### Quantitative Measurements.

*Results with Hydrogen Bromide.* The results of the quantitative measurements carried out with solutions in liquid hydrogen bromide, are set forth in Table 2. Under the heading, dilutions, are given the number of liters which contain a gram of molecule of the dissolved substance. While the molecular conductivities—expressed in reciprocal ohms—will be found in the remaining columns. The values here given were obtained from the dilution—molecular conductivity curves, shown below, where the original measurements, by aid of which these curves were drawn, are indicated, at least over the greater part of the dilution examined.

In Table 3 are shown the temperature coefficients of the conductivity for the hydrogen bromide solutions, expressed as percentage values of the conductivity at  $-80^{\circ}$ . The first column of the table shows the dilutions of the particular solutions examined.

It has been already noted that formic acid does not form a conducting solution with hydrogen bromide. The other members of this series, however, which have lower molecular weights than that of caprylic acid, do form conducting solutions with this solvent. And here, as in the case of the corresponding alcohol solution, the conductivity, particularly



TABLE 2.

HYDROGEN BROMIDE SOLUTIONS—VALUES OF THE MOLECULAR CONDUCTIVITIES.

Dilutions	Acetic Acid	Butyric Acid	Isovaleric Acid	Benzoic Acid	<i>o</i> -Toluic Acid	<i>m</i> -Toluic Acid	<i>p</i> -Toluic Acid	Salicylic Acid
250.0	.....	.....	.....	.....	.....	.....	.....	80.0
200.0	.....	.....	.....	.....	.....	.....	.....	76.2
125.0	.....	.....	.....	.....	.....	.....	.....	72.0
100.0	.....	.....	.....	.....	.....	.....	.....	70.0
50.0	.....	.....	.....	.....	.....	.....	.....	71.0
40.0	.....	.....	.....	2.794	6.31	.....	.....	76.1
20.0	.....	.....	8.04	4.12	8.12	3.95	6.12	100.5
12.50	5.68	.....	9.22	5.80	10.23	5.79	8.16	141.3
10.00	6.80	5.80	10.12	7.15	12.56	7.27	10.26	168.2
6.66	11.21	10.35	13.75	13.12	18.85	16.61	19.62	233.8
5.00	18.4	15.10	19.90	19.75	29.71	21.81	30.4	294.5
4.00	29.8	23.9	28.2	31.7	39.3	32.1	46.1	354.
3.33	44.8	34.3	39.3	44.2	49.9	48.3	63.5	407.
2.857	62.5	46.2	52.4	58.8	63.8	64.1	82.0	452.
2.500	81.4	61.7	68.2	77.9	81.3	84.5	104.7	490.
2.222	103.0	79.3	88.1	100.9	99.7	107.1	129.5	523.
2.000	123.5	98.5	107.7	127.8	120.0	132.8	155.0	552.
1.666	171.0	143.3	146.8	187.9	164.0	186.1	210.4	604.
1.428	215.0	188.0	183.3	.....	205.6	238.2	262.6	650.
1.250	252.0	225.4	212.0	.....	226.0	294.1	324.4	.....
1.000	332.0	277.4	254.7	.....	150.0	435.	.....	.....
0.833	408.	314.1	285.2	.....	.....	.....	.....	.....
0.714	465.	339.0	307.5	.....	.....	.....	.....	.....
0.666	491.	.....	.....	.....	.....	.....	.....	.....
0.625	511.	.....	.....	.....	.....	.....	.....	.....
0.588	518.	.....	.....	.....	.....	.....	.....	.....
0.555	524.	.....	.....	.....	.....	.....	.....	.....

for the more concentrated solutions, is the greater the lower the acid comes in the series. The opposite seems to be true for the acids of the benzene series, for here benzoic acid does not conduct as well as ortho and para toluic acids. And this again is parallel with the case of the alcohols, where thymol gave better conducting solutions than the lower cresols, and these in turn were better conductors than phenol.

If we examine the values of the molecular conductivities of the more dilute solutions of these acids, it will be seen that only in the case of salicylic acid is there any indication of an increase in the molecular conductivity with dilution. For all the other acids examined, there is a continual rise in the molecular conductivity as the solution becomes more concentrated. In some cases it increases nearly one hundred times, in passing from a tenth normal to a normal solution. It will be remembered that in the case of the dilute solutions of some of the alcohols in hydrogen bromide, the molecular conductivity was found to increase with the dilution. It should be noted in passing, that it is the acid which has the highest conducting power, that shows this interesting variation.



The temperature coefficients seem to vary in a regular manner, increasing slightly with the concentration of the solution. It is noteworthy that the magnitude of this quantity should be so different for the different acids. In some instances it is larger than for water solutions of the inorganic electrolytes, while in other cases it has practically disappeared; the temperature having apparently no effect on the conductivity within the narrow range here examined. As opposed to the above water solutions, where the temperature coefficient of conductivity almost invariably increases with the dilution, we see that here the variation is in the opposite direction. This would seem to be further evidence to show that we are here dealing with a much more complex electrolyte than in the case of the water solutions.

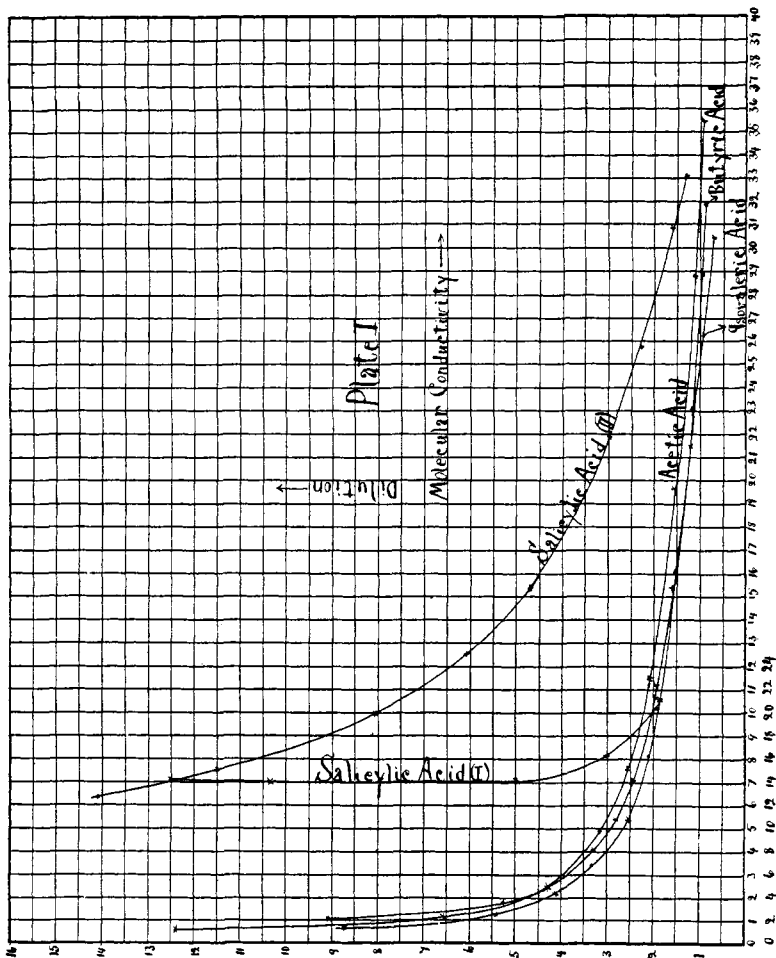
A change in the conductivity of a solution, following a change in the temperature, may be due, either to a change in the degree of the ionization of the electrolyte, a change in the viscosity of the solution, or a change in the mobility of the ions, to any one, or to all of these combined. Now the change in the viscosity of the solutions, within the range of temperature here considered, must be practically the same for all these solutions. However, it is conceivable that the change in the speed of the ions, due to this change in viscosity, might be very different in the case of an ion of which acetic formed a part, from what it is in the case of a toluic acid ion. But it is the acetic acid which has the larger temperature coefficient of conductivity; while if the change in viscosity has much influence in changing the conductivity, we would expect the more complex ion to be effected the more. It would seem then, that the change in conductivity, caused by the change in temperature, must be due chiefly to a change in the degree of ionization of the electrolyte.

In working with hydrogen bromide solutions of the alcohols, a number of cases were found where the solutions had negative temperature coefficients. No such cases were met with in the work with the organic acids, although in some instances the coefficient was exceedingly small.

The relation between the dilution and the molecular conductivity is shown graphically in Plates I and II, where the ordinates represent the dilutions and the abscissae the molecular conductivities. The values here indicated are the experimental ones, and those previously given, for the round numbers, were obtained from such curves as these, except that they were plotted on a larger scale.

The relative conducting power of the several acids is here clearly shown, particularly for the more concentrated solutions. Attention should be called to the curves for isovaleric and acetic acids. These are seen to cross each other at a dilution of about 4.5 liters the isovaleric acid solutions being better conductors than those of acetic acid, in the more dilute solutions while in the case of the more concentrated solutions,

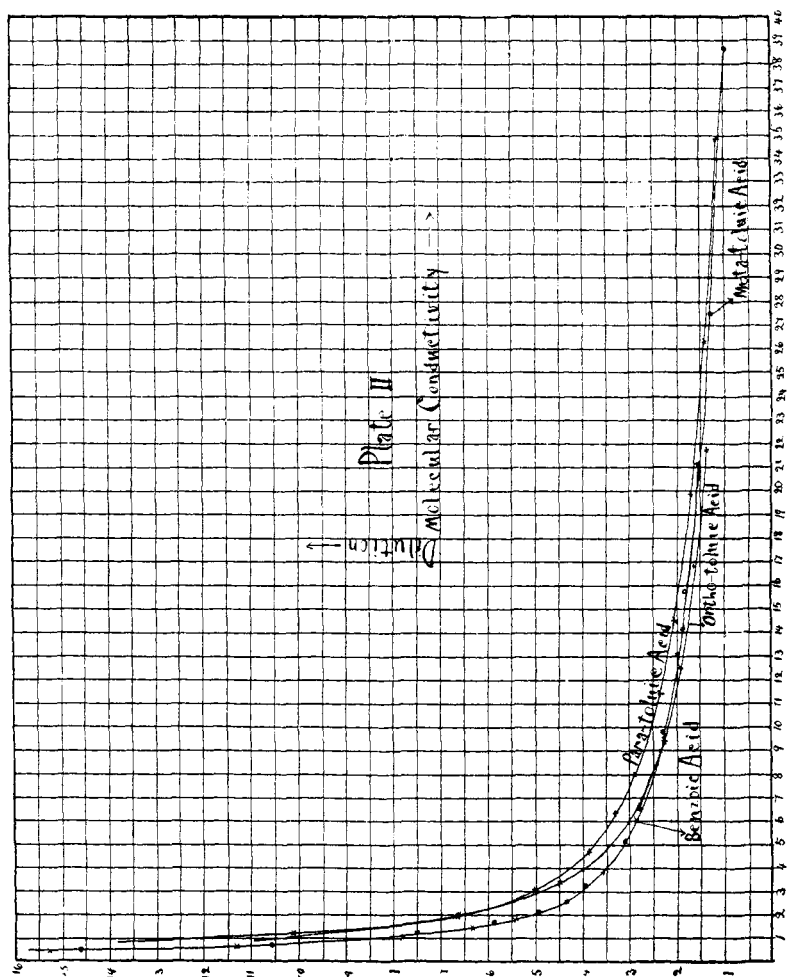
the acetic acid is the better conductor. This is parallel to the behavior of acetic and butyric acids in water solutions, as we will show further on,



the butyric acid being the better conductor in the dilute solutions, but the acetic acid being the better in the more concentrated.

As the different curves, with the exception of the first part of the salicylic acid curve, are all plotted to the same scale, it will be seen that the acids of the acetic acid group, have almost the same conducting power as those of the benzoic acid group. It is also noticeable that salicylic acid exceeds all the others in conducting power.

*Results with Hydrogen Chloride.*—The quantitative results for solutions in the liquid hydrogen chloride are given in Table 4. The different values are expressed in terms of the same units as employed in the



previous table; the values for the molecular conductivity being taken from the dilution—molecular conductivity curves shown below.

The temperature coefficients of conductivity, for the hydrogen chloride solutions, expressed in terms of the same units as the corresponding values for the hydrogen bromide solutions, are given in Table 5. The dilutions to which these measurements refer are also included in the table.

The temperature coefficients can be dismissed with a few words. Here, as in the case of the hydrogen bromide solutions of these substances, they seem to vary in a regular manner, and are all positive, although some are very small. It is noticeable that benzoic and toluic acids have much a larger temperature coefficients here than in the case of the hydrogen



It is noteworthy that in this solvent the conductivity of the paraffin series of acids, for all dilutions, increases from the higher members of the series down, until we reach formic acid, which is much below acetic acid in its conducting power. It will be recalled that this substance did not conduct at all, or apparently dissolve in the liquid hydrogen bromide. In the hydrogen chloride it has about the same conducting power as acetic acid in hydrogen bromide. It is apparent, too, that there is a much greater difference in conductivity between the acids in this series, in the present instance, than was the case with the hydrogen bromide solutions.

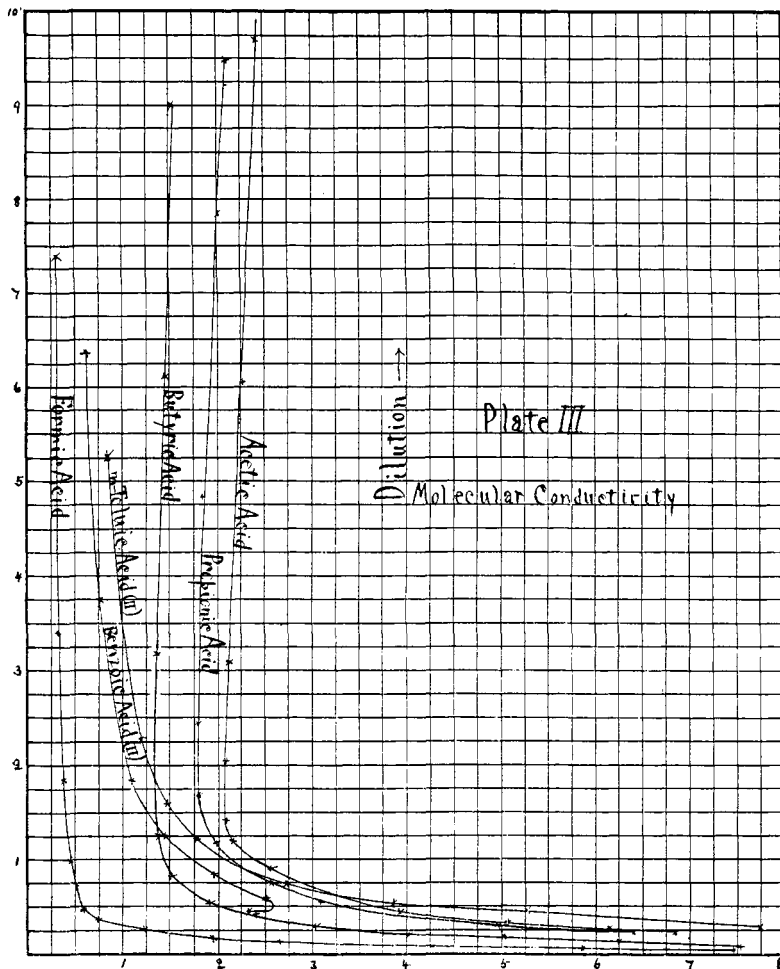
It will further be seen, that here the acids of the paraffin series are much better conductors than those of the benzene series, while, in the case of the hydrogen bromide solutions, they were about equal in conducting power. It will be noticed, too, that salicylic and phthalic acid solutions surpass all the other solutions of equal concentration, in their power of conducting the current; the molecular conductivity, in the case of these two acids, having about eight times as great a value as it has in any other case.

If we examine the variation of the molecular conductivity with the dilution, for these hydrogen chloride solutions, we notice at once, that, for the dilute solutions, if we except the three acids, formic, *p*-toluic and benzoic, the molecular conductivity always increases as the dilution increases. This interesting variation, which is the same as we have in the case of water solutions of the ordinary electrolytes, is much more marked than in the case of the hydrogen bromide solutions of the alcohols. However, after a certain concentration is reached which is very much the same for all the acids, the molecular conductivity begins to increase with decreasing dilution; a variation which we have found for solutions of most of the organic substances in the liquid hydrides.

If we compare the values for the molecular conductivity, obtained with the hydrogen bromide solutions, with those given above for the hydrogen chloride, we see that the solutions in the latter solvent conduct much better than those in the former. Phthalic acid, which would not conduct in hydrogen bromide, gives solutions of high conductivity with hydrogen chloride. This difference is much greater for the dilute solutions than for the more concentrated. In fact, the molecular conductivity for hydrogen chloride solutions of acetic acid, at a dilution of 10.0 liters, is about forty times as great as for the corresponding hydrogen bromide solutions, while, at a dilution of 1.0 liters, it is only about three times as large.

The variation of molecular conductivity with dilution, for the hydrogen chloride solutions, is shown graphically in Plates III and IV; where the dilutions as ordinates are plotted against the molecular conductivities as abscissae. Here the curve for butyric acid is seen to be behind that

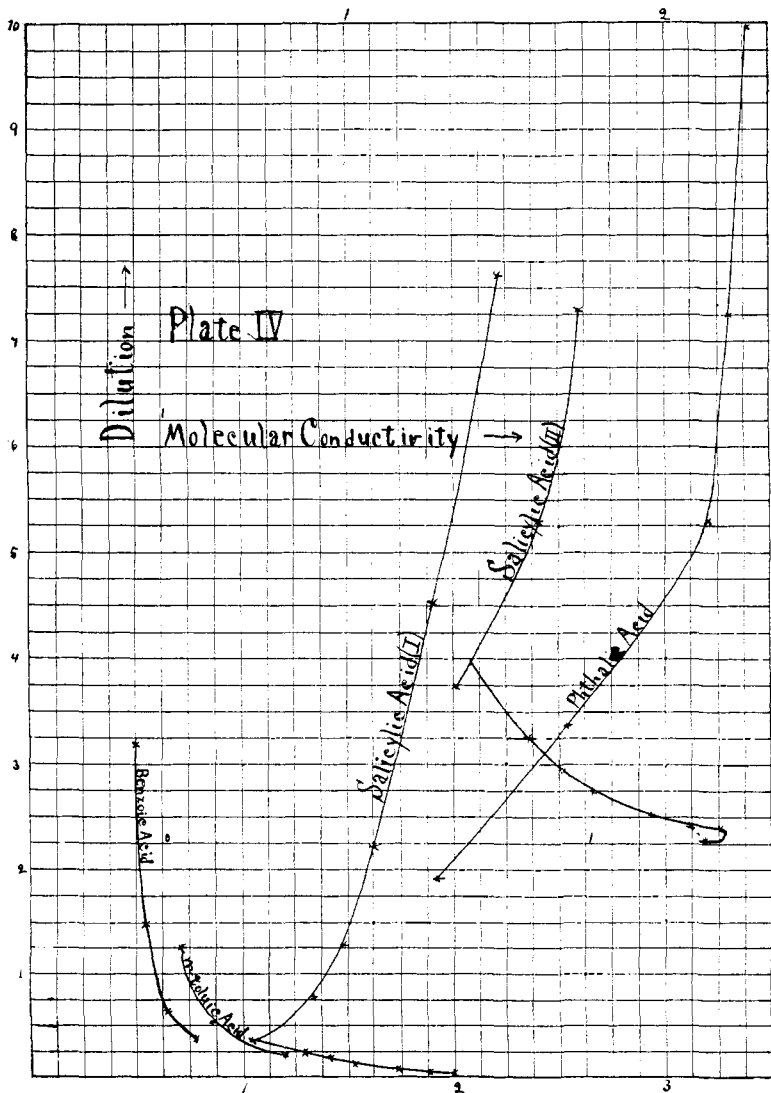
for propionic, throughout its entire length. The same may be said of the propionic acid curve as compared with the acetic; the formic acid curve, however, lies far behind the others.



The increase of the molecular conductivity with dilution for the more dilute solutions, is here shown by the slope of the first part of the curve backward, toward the  $y$ -axis. This is exaggerated in the case of salicylic acid, until we have here apparently two curves meeting at a dilution of about 380.0 liters. There is here probably some radical change in the addition body which forms, and which undergoes ionic dissociation. It should be stated that no change could be noticed in the solution at this point; it appeared perfectly homogeneous.



From an examination of the curves for the hydrogen chloride solutions, it appears that the variation of molecular conductivity with dilution changes its character at almost the same dilution in each case. It seems



probable that in the case of these acids, in the dilute solutions, and up to a certain concentration, the addition substance which is formed between the organic acid and the hydrogen chloride, and which subsequently undergoes ionic dissociation, has a very simple structure; perhaps one molecule of the hydrogen chloride uniting with one molecule of the or-

ganic acid. In such a case the molecular conductivity would be given by the expression  $\kappa V$  where  $\kappa$  is the specific conductivity, and  $V$  the dilution; and here the molecular conductivity, as given by this expression, should increase with the dilution. On the other hand, in the more concentrated solutions, it is not unlikely that we have a much more complex addition compound formed, and, supposing it contained  $n$ -molecules of the dissolved substance, the concentration of the compound will be proportional to the  $n$ th power of the concentration of the dissolved substance, and the molecular conductivity, as pointed out by Steele, McIntosh and Archibald<sup>1</sup>, will be given by the expression  $\kappa V^n$ , rather than by  $\kappa V$ . The molecular conductivity as calculated from the expression  $\kappa V$ , will, in such a case, decrease with the dilution. And this is what we find to be the case for these acids, in their more concentrated solutions.

Attention should also be drawn to the fact, that the increase of molecular conductivity with dilution, is more marked in the case of those acids which give the best conducting solutions, for instance, the solutions of salicylic, phthalic and acetic acids. This is surely in line with the argument we have used above, for, the conductivity of a solution will depend largely upon the number of ions there are present in a given volume, and this will be the greater, other things being equal, for a given concentration of the dissolved substance, the less the number of molecules of the organic acid there are used up to form one molecule of the electrolyte. In a dilute solution, under these conditions, if you assume one molecule of solute to be associated with one of solvent to give the electrolyte, as more of the solute is added, the molecular conductivity will decrease owing to a decrease in the degree of ionization. As the solution becomes more concentrated, however, and the character of the electrolyte changes, becoming more complex in composition, the effect on the molecular conductivity due to the decrease in ionization, will be overshadowed by the effect due to the change in the concentration of the electrolytic compound which will now be proportional to the  $n$ th power of the concentration of the dissolved substance.

Some reference should be made to the curve for phthalic acid. Here the measurements extend over only a short range of dilution. Apparently the acid was only slightly soluble in the liquid hydrogen chloride, as, at a dilution of about 250.0 liters, the specific conductivity became constant, and the addition of more substance produced no change in the conductivity, and apparently did not go into solution at all.

It is noteworthy, too, that in this case the molecular conductivity continues to increase with the dilution over the whole range investigated.

Those parts of the curves for benzoic and salicylic acids, which correspond to their more concentrated solutions, are seen to turn back and

<sup>1</sup> Loc. cit., p. 152.

downward, showing that the molecular conductivity of their solutions is decreasing with the concentration, although the specific conductivity was still increasing as more substance was added to the solution. This behavior was noticed, too, in the case of hydrogen bromide solutions of methyl alcohol. Either the acid which is dissolved by the solution is only in part used to form more of the electrolytic compound, or of that which is formed, only a small portion is subsequently ionized.

It is interesting to compare the values of the molecular conductivity for some of these organic acids, when dissolved in the liquid hydrogen chloride, or hydrogen bromide, with the corresponding values obtained for solutions in water. Table 6 contains such data for solutions of acetic, butyric and benzoic acids, in the several solvents, as well as for solutions of ethyl alcohol and thymol in hydrogen bromide.

It will be noted, that, for the dilutions which are common to all, the three acids conduct better when dissolved in the liquid hydrides than when dissolved in water. It is almost certain, however, that at greater dilutions than could be examined for the hydrogen bromide solutions, the molecular conductivity of the aqueous solutions of these acids would be greater than those for the hydrogen bromide solutions.

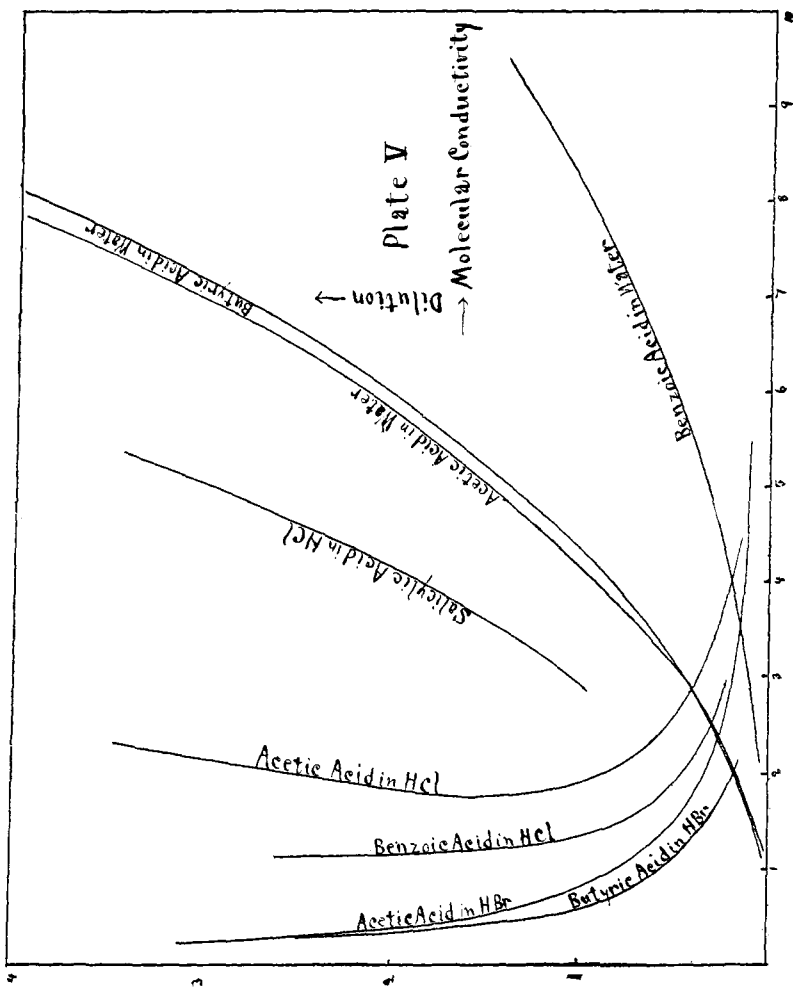
It will be seen, too, from this table, that the hydrogen bromide solutions of ethyl alcohol are much behind, while those of thymol far surpass

TABLE 6.  
MOLECULAR CONDUCTIVITY VALUES FOR VARIOUS SOLVENTS.

Dilutions	Aqueous Solutions			Hydrogen Bromide Solutions					Hydrogen Chloride Solutions		
	Acetic Acid	Butyric Acid	Benzoic Acid	Acetic Acid	Butyric Acid	Benzoic Acid	Ethyl Alcohol	Thymol	Acetic Acid	Butyric Acid	Benzoic Acid
2500.	64.8	66.5	...	...	...	...	...	...	...	...	...
2000.	58.0	59.8	...	...	...	...	...	...	...	...	...
1500.	50.2	52.0	...	...	...	...	...	...	...	...	...
1250.	46.2	48.1	90.0	...	...	...	...	...	...	...	...
1000.	41.5	43.4	81.5	...	...	...	...	...	...	...	...
750.	36.8	38.2	71.8	...	...	...	...	...	...	...	...
500.	31.2	31.4	60.0	...	...	...	...	56.9	...	...	...
250.	22.7	22.5	44.5	...	...	...	...	...	...	...	51.1
125.	18.0	17.1	31.9	...	...	...	...	76.4	...	160.6	56.0
100.	...	...	...	...	...	...	...	88.5	243.3	156.2	58.2
50.0	...	...	...	...	...	...	...	132.5	222.7	142.0	70.0
40.0	9.2	8.9	...	...	...	2.794	...	164.8	217.5	138.3	76.1
25.0	...	...	...	...	...	...	...	278.6	211.5	135.0	94.0
20.0	7.3	7.0	...	...	...	4.12	...	394.4	208.6	134.3	105.8
12.50	5.3	4.9	...	5.68	...	5.80	0.486	717.	216.1	138.8	139.6
10.00	4.8	4.5	...	6.80	5.80	7.15	0.485	974.	236.4	146.3	162.0
5.00	3.4	3.0	...	18.4	15.1	19.75	0.502	...	387.5	205.0	230.0
4.00	3.1	2.7	...	29.8	23.9	31.7	...	...	454.	246.2	...
3.33	...	...	...	44.8	34.3	44.2	0.605	...	525.	285.0	...
2.00	2.12	1.8	...	123.5	98.5	127.8	1.002	...	769.	433.	...

the corresponding solutions of the acids, in conducting power.

The form of the dilution—molecular conductivity curve, for solutions of these acids in the several solvents, are shown in Plate V, where the



ordinates represent the dilutions, and the abscissae the molecular conductivities. The curves for the halogen hydride solutions all differ in form from those for the water solutions, with the exception of salicylic acid for its more dilute solutions, that being the only part represented here. It seems likely, however, that if the acetic acid curve could be drawn for much more dilute solutions, that it, too, would have the shape of the water solution curves at its upper extremity.

Attention was drawn above to the fact that, for the more dilute solutions of isovaleric and of acetic acid in hydrogen bromide, the former

acid exceeded the latter in conductivity, while in the more concentrated solutions the acetic acid is the better conductor. The same variations for the water solutions of acetic and butyric acids is shown here by the curves crossing at a dilution of about 350.0 liters; the butyric acid being the better conductor in the dilute and the acetic the better in the concentrated solutions.

As pointed out above, Steele, McIntosh and Archibald have shown, that, where a substance dissolves and combines with the solvent to give an addition compound which contains  $n$  molecules of the dissolved substance, and which subsequently undergoes ionic dissociation, the concentration of the electrolytic compound would be proportional to the  $n$ th power of the concentration of the dissolved substance, and the molecular conductivity would be given by the expression  $\kappa V^n$ . McIntosh<sup>1</sup> has shown that such addition compounds of the organic acids and the halogen hydrides may be prepared. For instance, in the case of acetic acid and hydrogen chloride, the compound which separates out has the composition  $(\text{CH}_3\text{COOH})_2 \cdot (\text{HCl})_3$ . In the case of acetic acid and hydrogen bromide, Tschitschibabin<sup>2</sup> obtains a compound  $(\text{CH}_3\text{COOH})_2 \cdot \text{HBr}$ . If then, we calculate the molecular conductivity from the expression  $\kappa V^n$ , we may expect to obtain a series of values which vary with dilution as the molecular conductivity varies in the case of water solutions.

Such values have been calculated in a few instances for solutions in both the halogen hydrides, where there was a marked decrease in the molecular conductivity with dilution, and the results obtained are shown in Table 7, together with the dilutions to which these values apply.

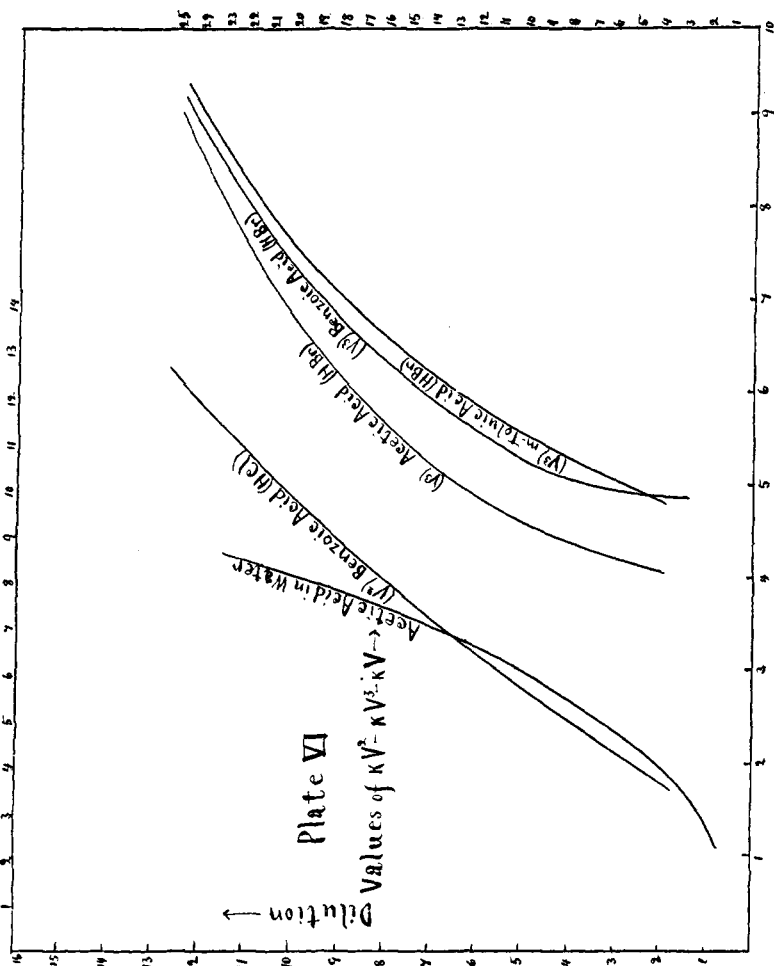
TABLE 7.  
VALUES OF  $\kappa V^n$

Dilutions	Hydrogen Bromide Solutions				Hydrogen Chloride Solutions			
	Acetic Acid		Benzoic Acid		<i>m</i> -Toluic Acid		<i>m</i> -Toluic Acid	
	$\kappa V^2$	$\kappa V^3$	$\kappa V^3$	$\kappa V^3$	$\kappa V^2$	$\kappa V^3$	$\kappa V^2$	$\kappa V^2$
250.0	....	....	....	....	....	....	12.78	9.01
200.0	....	....	....	....	....	....	10.36	7.50
125.0	....	....	....	....	....	....	7.00	4.42
100.0	....	....	....	....	....	....	5.82	3.78
50.0	....	....	....	....	....	....	3.50	2.87
40.0	....	....	....	....	....	....	3.04	2.57
25.0	....	....	....	....	....	....	2.35	2.21
20.0	....	....	....	....	....	....	2.11	2.07
12.50	0.071	0.88	0.073	0.91	0.073	0.91	1.74	....
10.00	0.068	0.68	0.072	0.72	0.073	0.73	1.62	....
6.66	0.075	0.50	0.087	0.58	0.111	0.74	....	....
5.00	0.092	0.46	0.099	0.49	0.109	0.55	....	....
4.00	0.119	0.48	0.126	0.51	0.128	0.51	....	....
3.33	0.149	0.50	0.147	0.49	0.161	0.54	....	....
2.50	0.204	0.51	0.195	0.49	0.211	0.53	....	....
2.00	0.247	0.49	0.256	0.51	0.266	0.53	....	....
1.25	0.32	0.39	....	....	0.367	0.46	....	....
1.00	0.33	0.33	....	....	0.435	0.44	....	....

<sup>1</sup> This Journal, 28, 588 (1906).

<sup>2</sup> J. Russ. Phys. Chem. Soc., 7, 1058 (1906).

It will be seen that by making  $n = 2$  in the case of the hydrogen chloride solutions, and  $n = 3$  for the hydrogen bromide solutions, we obtain a series of values which increase as the dilution increases. However, if we represent these results graphically, as we have done in plate VI,



plotting the dilutions as ordinates and the values of  $\kappa V^n$  as abscissae, we obtain a different form of curve from that for water solutions.

It is obvious that it would be of considerable interest to determine to what extent these organic substances, as well as some inorganic ones, form conducting solutions with liquid hydrogen fluoride. Experiments with this end in view are being started, and it is hoped, that before long, some results worth communicating may be obtained.

The work described in the preceding pages shows :

(1) That in the case of the monobasic organic acids, the members of the benzene series, and the lower members of the paraffin series, dissolve in the liquid hydrogen chloride and bromide to give conducting solutions; the only exception to this being formic acid, which does not give conducting solutions with hydrogen bromide.

(2) That the polybasic acids do not, in general, give conducting solutions with either solvent, the exceptions here being the dibasic acids of the ethylene group, racemic and fumaric, which give conducting solutions with hydrogen chloride. The fact that the polybasic acids did not give conducting solutions with the halogen hydrides was explained, by assuming that the free bonds of one oxygen atom were satisfied by the free bonds of another, there being here a great many ways in which such a combination could take place.

(3) That for the hydrogen bromide solutions, the molecular conductivity decreases rapidly with increasing dilution; the one exception being salicylic acid, which in the case of a few of the more dilute solutions, shows an increase in the molecular conductivity with dilution.

(4) That, in the case of the greater number of the hydrogen chloride solutions, the molecular conductivities for the more dilute solutions increases with the conductivity, this increase being the more marked the higher the conductivity of the acid. For all the concentrated solutions, however, the molecular conductivity increases rapidly as the dilution decreases.

(5) That for the hydrogen chloride solutions of the paraffin series of monobasic acids, the conductivity increases from butyric acid down, until we reach formic acid, which has a much lower conductivity than the acids which stand next above it in the series.

(6) That the temperature coefficients of conductivity are in all cases positive, although they vary greatly in magnitude on passing from one acid to another. It was shown, too, that the more concentrated the solution the larger the temperature coefficient.

(7) That in the case of acetic, butyric and benzoic acids, the halogen hydride solutions have a higher conductivity than the water solutions, at least for those dilutions for which we have measurements in common.

(8) That, if we take cases where the molecular conductivities, as calculated from the expression  $\kappa V$ , decrease with dilution, and calculate them anew from the expression,  $\kappa V^n$ , where  $n$  is the number of molecules of dissolved substance associated with the solvent to form the electrolyte, we obtain a series of values which vary in the same manner as the molecular conductivities for water solutions of inorganic electrolytes.

In conclusion, I wish to record my appreciation of a grant from the trustees of the Elizabeth Thompson Science Research Fund, which helped to defray the expenses incurred in carrying on this work.

CHEMICAL LABORATORY,  
SYRACUSE UNIVERSITY,  
SYRACUSE, N. Y.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY. NO. 142].

## MOLTEN HYDRATED SALTS AS SOLVENTS FOR THE FREEZING POINT METHOD II.

BY J. LIVINGSTON R. MORGAN AND F. T. OWEN.

In a recent paper<sup>1</sup> Morgan and Benson have shown that the molten hydrated salts  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , and  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ , when used as solvents for the freezing point method, lead to molecular weights for the dissolved substances which are similar to those obtained when water is the solvent, except that when the substance added has an ion in common with the molten hydrated salt, its ionization is prevented either wholly or in part. And when the ions of the dissolved substance are different from those of the solvent, its ionization is apparently unaffected, the molecular weights calculated, not differing materially from those observed in water solutions. In this investigation three other molten hydrated salts,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Mn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , have been studied as solvents.

The apparatus employed was the one already described by Morgan and Benson, except that a Beckmann thermometer, reading to  $0^\circ.01$ , and set by aid of a normal thermometer, reading to  $0^\circ.02$ , was used throughout. The depressions recorded are each the average of three determinations, agreeing among themselves to  $0^\circ.02$ . Just as with the other salts the separation of the solid phase was induced by infection with a crystal of the pure solvent; and the overcooling was kept below  $1^\circ$  to avoid the necessity of correcting for the fraction of solvent separating as a solid phase.

### Determination of the Constants.

For  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  the latent heat of fusion is 33.49 gram-calories per gram, according to Pickering<sup>2</sup>, so that the freezing point constant can be calculated directly from the relation  $K = \frac{0.02T^2}{w}$ , where  $T$  is the absolute freezing point of the pure solvent,  $w$  its latent heat of fusion for 1 g. at that temperature, and  $K$  the depression of the freezing point in degrees, caused by the presence of 1 mol. of dissolved substance in 100 g. of the solvent. Since the freezing point of molten  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , as determined by us, is  $42^\circ.31$ , we have

<sup>1</sup> This Journal, 29, 1168-75, 1907.

<sup>2</sup> See Landolt-Börnstein-Meyerhoffer. Tabellen. Third ed., p. 470.