whose conductance has been determined. In general, the values obtained by the methods of Kohlrausch and of Noyes are greater than this upper limit.

5. An empirical graphic method is described by means of which an upper limit and a "probable" value for Λ_0 may be determined.

6. The limiting values and the "probable" values have been calculated for a number of the more common salts. These show good agreement. The "probable" values were adjusted by means of Kohlrausch's Law of the Independent Migration of Ions. The resulting Λ_0 values are smaller than those generally employed.

URBANA, ILLINOIS.

THE BASIC PROPERTIES OF OXYGEN. II.

BY O. MAASS AND D. MCINTOSH.

In a previous communication[1] we have shown that organic compounds containing oxygen unite readily with the halogens and halogen hydrides yielding compounds stable at low temperatures, which differ in many respects from molecular aggregates containing water or alcohol of crystallization. Following Friedel, these combinations are explained by ascribing to oxygen a higher valency than two, and, except in a few cases, the assumption of oxygen as a tetravalent element suffices. The constitutions of the compounds are not definitly fixed since their molecular weights have not as yet been determined with sufficient accuracy. In future papers we hope to discuss this problem and to determin not only the molecular weights but the ions present in solution.

While there is no doubt that compounds of the acids and ethers separate from their cooled solutions, the question of the existence of compounds in solution or in the molten state has not been investigated. We have endeavored to solve this problem by means of conductivity measurements, an account of which is given here with the freezing-point curves of several systems which we have determined for comparison with the conductivity results.

Few systems have had their resistances measured from pure solvent to pure solute and these only in aqueous solutions. Kohlrausch[2] and others have examined sulfuric acid in all concentrations; Veley and Manley[3] nitric acid, and Hill[4] hydrofluoric acid. Apart from the object we had in view, a comparison of water and other solvents over wide concentrations is not without interest. For this purpose only hydrochloric acid is available, since oxonium compounds separate from solutions of

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[1] THIS JOURNAL, 34, 1273 (1912).

[2] Wied. Ann., 17, 69 (1882); Pogg. Ann., 159, 233 (1876).

[3] Phil. Trans., (A) 191, 365 (1898).

[4] Proc. Roy. Soc. London, (A) 83, 130 (1909).

the other acids at temperatures far above their boiling points. It is indeed true that compounds with hydrochloric acid appear above the temperature at which the resistances were measured, but generally only on prolonged stirring. Avoiding too vigorous agitation it is quite possible to maintain the ethers and alcohols in liquefied hydrochloric acid as solutions many degrees below their real freezing points. The phenomenon of supercooling is particularly well seen in all these oxonium compounds.

The resistances of methyl and ethyl ethers and the corresponding alcohols in hydrochloric acid were measured at —89° by Kohlrausch's method. The bath consisted of a carbon dioxide-ether mixture in a Dewar flask boiling under reduced pressure, and did not vary in temperature more than a degree.[1] The conductivity cell was of the ordinary dip type with platinized electrodes, and all material was added by weight. Except with solutions of very high resistance the minimum in the telephone was most satisfactory. The investigation of the freezing points of the systems was carried out in the manner described in our former paper.

Fig. 1, Curve I, shows the temperatures at which solid separates in the system methyl ether-hydrochloric acid. Two compounds exist: $C_2H_6O.HCl$ and $C_2H_6O.4HCl(?)$ and of these the former is the more stable.
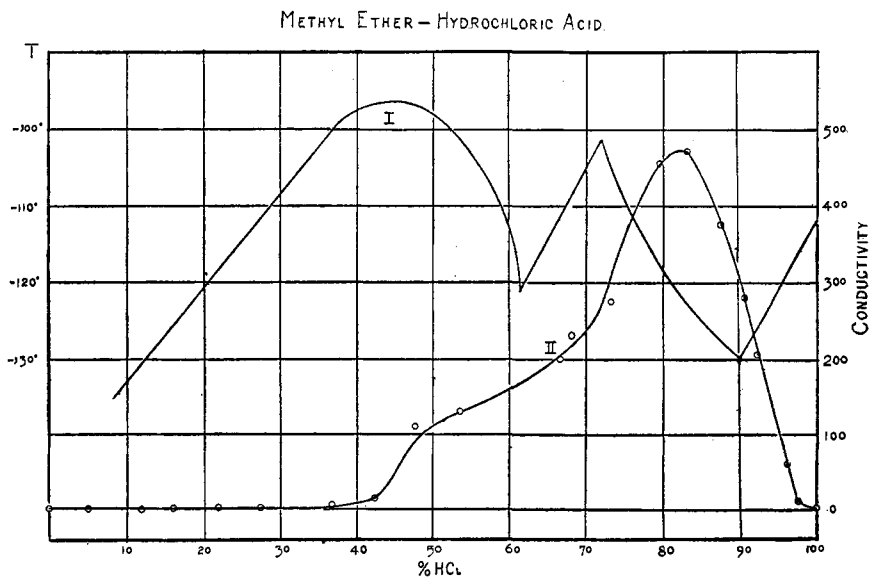

Fig. 1.

[1] With good vacuum flasks the maintenance of constant temperatures at any point between —80° and 0° is simple. It is only necessary to stir the liquid (ether) by a vigorous but adjustable air current and to drop in a small piece of carbon dioxide from time to time. The carbon dioxide driven out by the air cools the liquid so that with a pentane thermometer the apparent variation need not be greater than 0.1°.

The pure acid has an extremely low conductivity but this increases very rapidly on the addition of ether and reaches a maximum at about the proportion $C_2H_6O : 5HCl$. Further addition of ether lessens the conducting power of the liquid, which falls to a very low value when the compounds are in molecular proportion (Curve II). The actual results obtained for the freezing points were given in a former paper; the conductivities in Table I.

TABLE I.—METHYL ETHER.

Per cent. acid.	Conductivity × 10⁴.	Per cent. acid.	Conductivity × 10⁴.
97.7	9.93	42.8	12.7
96.2	59.5	36.7	6.12
92.2	206.0	32.1	5.40
90.5	281.0	27.6	3.84
87.3	377.0	22.6	2.64
83.0	470.0	19.0	1.56
79.5	455.0	16.1	0.99
73.1	274.0	11.9	0.40
67.9	234.0	5.2	0.12
60.6	200.0	2.1	0.02
53.3	129.0	0.5	0.004
47.6	110.0		

The freezing-point curve for the system, hydrochloric acid–ethyl ether (Fig. 2, Table II) is more complex than would be expected from a study of the former case. Three compounds, $C_4H_{10}O.HCl$, $C_4H_{10}O.2HCl$ and $C_4H_{10}O.5HCl$, melting at —92°, —88° and —89°, respectively, are formed. On adding ether to hydrochloric acid a large amount of heat is
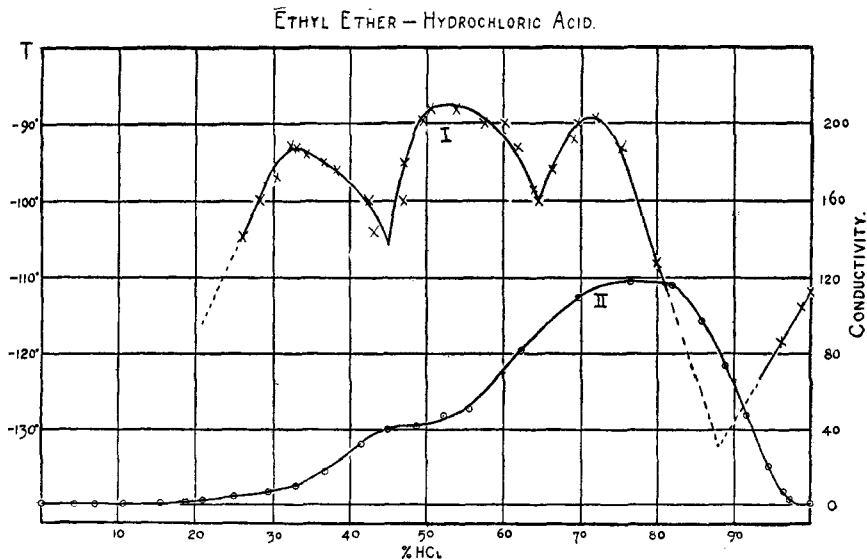

Fig. 2.

evolved, until the liquid has the composition $C_4H_{10}O.5HCl$.[1] Further addition of ether causes no marked heat development.

TABLE II.—ETHYL ETHER-HYDROCHLORIC ACID.

Per cent. acid.	Freezing temperature.	Per cent. acid.	Freezing temperature.
100.0	112.0	50.2	88.0
98.7	114.0	49.5	89.0
76.2	116.5	47.0	95.0
79.9	108.0	46.9	100.0
75.2	93.0	43.0	104.0
72.0	89.0	42.3	100.0
71.5	90.0	38.1	96.0
69.6	90.0	36.5	95.0
69.0	92.0	34.2	94.0
66.3	96.0	33.0	93.0
64.5	100.0	32.2	92.5
63.7	98.5	30.3	97.0
61.7	93.0	28.2	100.0
60.2	90.0	25.9	105.0
57.5	90.0		
53.8	88.0		

The conductivity curve, II (Table III), is quite analogous to that with methyl ether. Two breaks occur in both cases: One, the more distinct, where the acid and ether are nearly in molecular proportions; the other in the neighborhood of the ratio $C_4H_{10}O:2HCl$.

TABLE III.—ETHYL ETHER.

Per cent. acid.	Conductivity $\times 10^4$.	Per cent. acid.	Conductivity $\times 10^4$.
97.5	2.75	48.9	41.9
96.5	6.88	41.4	32.4
94.4	20.0	36.7	17.8
91.8	47.0	33.0	10.0
88.9	73.6	29.0	6.68
85.7	97.0	25.0	4.42
82.0	117.0	21.0	2.42
76.6	112.0	18.7	1.83
69.7	109.0	15.5	1.13
62.4	82.3	10.6	0.37
55.5	53.7	6.1	0.12
52.2	47.8	4.2	0.025

In conductors of the second class, excluding molten salts, the view that chemical compounds conduct badly has been so firmly held since Faraday's time that the resistance is usually taken as a measure of purity (see Walden). Nearly all pure liquids conduct badly and the views held of the ions present in many cases show considerable divergence. The change in the direction of conductivity-concentration curves and in particular

[1] This method of "titrating" was used to determin the proportions of the constituents in the compound formed. See Archibald and McIntosh, *J. Chem. Soc. London*, **85**, 919 (1904).

minima in conductivity point to the presence of pure substance, *i. e.*, chemical individuals.

The ethers are known to be poor ionizing solvents even at ordinary temperatures while the halogen acids at low temperatures yield conducting solutions with many substances. On the addition of ethyl ether to liquid hydrochloric acid a compound, $(C_4H_{10}O)x(HCl)y$, is probably formed and this dissolves and in the excess acid yields ions. The maximum conductivity gives no hint as to the complexity of the compound, but as a minimum occurs where the composition of the solution is $C_4H_{10}O.$-$2HCl$ it seems probable that this compound is present. When the two liquids are present in molecular proportions a second and more pronounced change in the direction of the curve is observed. It is probable that $C_4H_{10}O.HCl$ is present, but, as in ether, little ionization takes place, the conductivity values do not rise.

These conclusions are more clearly deduced from the experiments with methyl and ethyl alcohols. The results obtained with the former are shown in Fig. 3, and in Tables IV and V. Only one compound, $CH_4O.$-HCl^1 (m. p. —62°) was isolated. The portion of the curve between ₍8
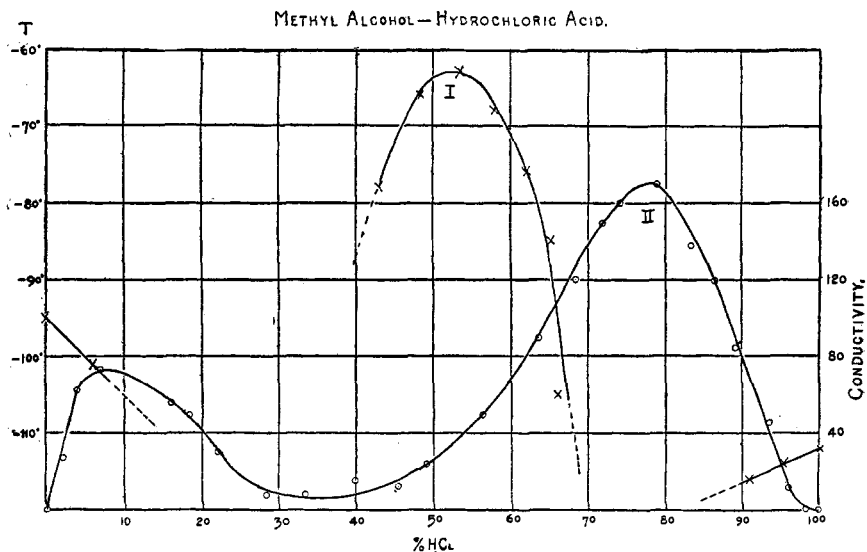

METHYL ALCOHOL—HYDROCHLORIC ACID.

Fig. 3.

and 40 per cent. was not examined for complexes since the viscous liquid, when cooled, gave a glassy mass. Alcohol is a better ionizing medium than the ethers, as hydrochloric acid dissolved in it gave a good conducting solution, a maximum occurring with 8% acid. Alcohol dissolved in the acid conducts well, a maximum being obtained at 78%.

¹ G. Baumé, *Compt. rend.*, 155, 426 (1912).

TABLE IV.—METHYL ALCOHOL–HYDROCHLORIC ACID.

Per cent. acid.	Freezing temperature.	Per cent. acid.	Freezing temperature.
100.0	112.0	57.8	68.0
95.4	114.0	53.3	63.0
91.2	116.0	48.3	66.0
65.9	105.0	42.9	78.0
65.0	85.0	6.1	101.0
62.0	76.0	0	95.0

TABLE V.—METHYL ALCOHOL.

Per cent. acid.	Conductivity × 10⁴.	Per cent. acid.	Conductivity × 10⁴.
98.3	0.67	49.0	24.4
96.0	12.5	45.4	12.2
93.5	46.2	40.0	16.6
89.2	85.1	33.5	8.0
86.4	121.2	28.5	8.0
83.1	137.8	21.9	30.5
78.8	172.5	18.5	49.8
73.8	161.4	16.1	56.1
71.7	149.3	7.0	74.0
68.3	122.1	4.5	63.5
63.5	91.4	2.2	26.9
56.8	51.8		

The ethyl alcohol curves (Fig. 4, Tables VI and VII) show similar results. There is but one compound, $C_2H_6O.HCl$, melting at —65°; and that part of the system containing an excess of alcohol is viscous. The
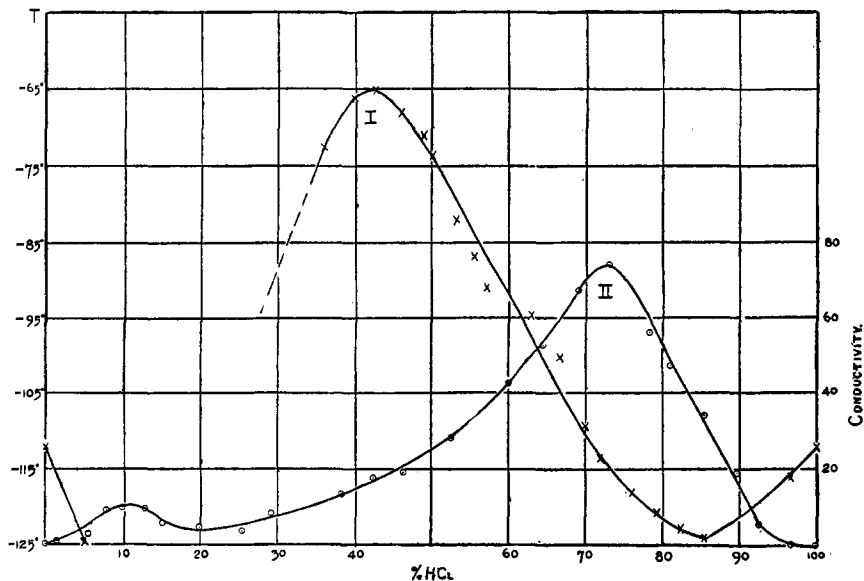

Fig. 4.

conductivity curve shows two maxima at 78 and 10% acid, and a minimum at about 30%. No deductions can be made regarding the relative dissociating powers of acid and alcohol on account of the viscosity of the solution where the alcohol is in excess. There is no doubt that this factor brings the minimum point further to the left than its correct position.

TABLE VI.—ETHYL ALCOHOL–HYDROCHLORIC ACID.

Per cent. acid.	Freezing temperature.	Per cent. acid.	Freezing temperature.
100.0	112.0	55.3	87.0
96.9	116.0	53.1	82.0
85.4	124.0	50.3	73.5
82.6	123.0	48.9	71.0
79.3	120.5	45.7	68.0
76.2	118.0	42.6	65.0
72.1	113.0	40.0	66.0
70.2	108.0	36.2	72.5
66.9	100.0	5.0	125.0
62.9	94.5	0.0	112.0
57.1	91.0		

TABLE VII.—ETHYL ALCOHOL.

Per cent. acid.	Conductivity $\times 10^4$.	Per cent. acid.	Conductivity $\times 10^4$.
97.3	0.14	42.5	18.8
92.4	5.53	38.5	13.9
89.7	19.2	29.3	9.21
85.4	34.5	25.2	3.51
81.2	47.7	20.0	4.62
78.4	58.4	15.4	5.78
73.6	74.7	13.0	9.60
69.1	67.6	10.1	9.60
64.5	53.2	7.8	9.51
59.9	43.2	6.3	2.15
52.5	28.3	1.4	0.86
46.4	19.1	0.7	0.41

The reaction in solution may be represented as

$$C_2H_6O + HCl \rightleftharpoons C_2H_6O.HCl.$$
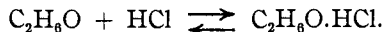
On increasing the concentration of alcohol the amount of free acid is decreased and the oxonium salt increased. If the acid when dissolved in alcohol conducts better than the oxonium salt, any dissociation would bring the point of minimum conductivity toward the part of the curve where alcohol is in excess.

These two reasons, the increased viscosity and the dissociation, appear to us quite sufficient to explain why the minima are not at the points where the liquids are in molecular proportions. These minima represent the existence of chemical compounds; and the presence of compounds in solution in which the acid and alcohol are in molecular proportion is, we believe, proved by these measurements. Doubtless some free alcohol

and acid are present, but the amount of this dissociation cannot be ascertained, as any deductions made from the heat of formation and the change of conductivity would be further complicated by viscosity and ionization changes. The amounts of uncombined acid and alcohol at —80° are probably not large.

Of the four solutions examined, the best conductor was one consisting of 17% methyl ether, which had at —89° about the same resistance as a 3% potassium chloride solution at 18°. Our measurements show that the conductivity of the ether solutions increases by about 2% per degree; so if it were possible to realize a temperature of 18° the conductivity of this liquid would equal that of a 9 or 10% solution of sulfuric acid.

We have attempted to apply this conductivity method to a study of the hydrates possibly present in aqueous solutions of sulfuric and nitric acid but without success. Nitric acid undoubtedly yields hydrates which separate out on cooling; but no minimum point coinciding in composition with a definit hydrate was observed even at low temperatures (—40°). Fig. 5 shows the freezing-point curve for the system SO_3–H_2O (Curve I) and Kohlrausch's conductivity curve (Curve II). The compound $H_2SO_4.4H_2O$, melting at 8°, corresponds exactly with the composition of the liquid having minimum conductivity. But at lower tempera-
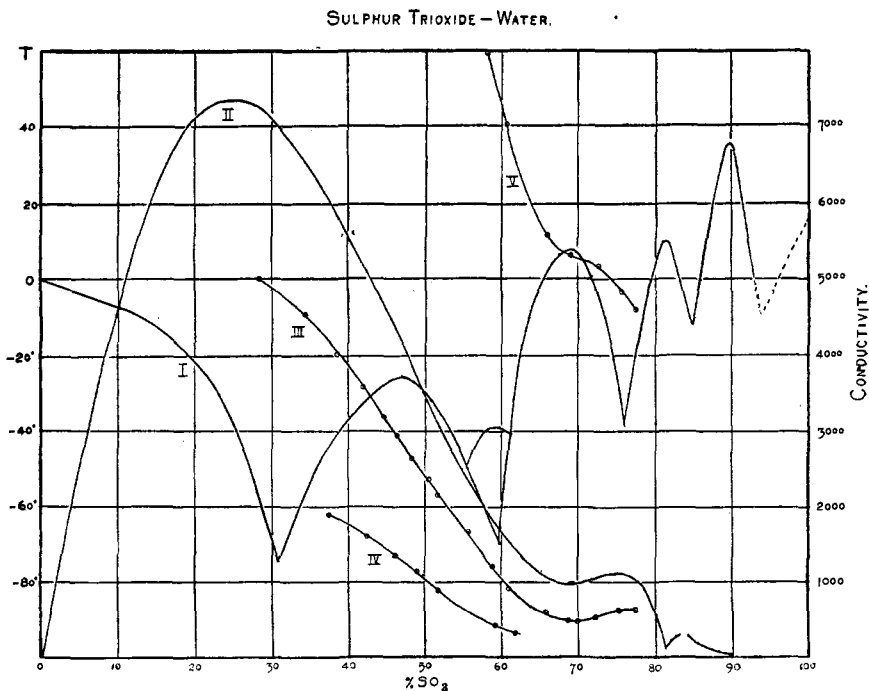
SULPHUR TRIOXIDE — WATER.

Fig. 5.

tures (0°, Curve III, —25° Curve IV) where the more complex hydrates might be thought to exist in solution no indication of their presence was given by the conductivity measurements. As the temperature rises, the minimum point ($H_2SO_4H_2O$) appears less clear, and at 100° (Curve V), due possibly to the decomposition of the hydrate, disappears.

In this paper we have given the results of a study of the two component systems of hydrochloric acid with ethyl and methyl ethers and with ethyl and methyl alcohols. Conductivity measurements were made over their complete concentration range at —89°, and the probability of the existence of compounds in solution shown.
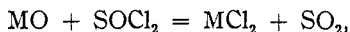
McGILL UNIVERSITY, MONTREAL.

SOME NEW REACTIONS WITH THIONYL CHLORIDE.

By H. B. NORTH AND A. M. HAGBMAN.

In a previous number of THIS JOURNAL (April, 1913) the authors described the action of thionyl chloride on the more ordinary oxides of certain metals and metalloids. Reaction was found to proceed according to the general equation:

$$MO + SOCl_2 = MCl_2 + SO_2,$$

except in cases in which oxidation as well as chlorination takes place.

During the investigation of the action of thionyl chloride on oxides, a number of reactions were studied with the higher oxides or peroxides. These compounds were found to react readily with thionyl chloride at elevated temperatures and the products always include sulfuryl chloride, SO_2Cl_2. Furthermore, a certain amount of sulfate of the metal is usually produced. With one exception the reactions described below were carried out in sealed glass tubes, the temperature employed being about 150°.

Barium Peroxide.—In the first experiment with barium peroxide, no particular attention was paid to the relative amounts of oxide and reagent employed. The tube was heated at 150° for some time, and when opened was found to be under slight pressure due to sulfur dioxide. The supernatant liquid was distilled, all passing over between the temperatures of 65° and 85°. The distillate was decomposed in water and the solution tested and found to contain considerable sulfuric acid. Thionyl chloride, which boils at about 78°, when decomposed by water, gives sulfur dioxide and hydrochloric acid according to the equation:

$$SOCl_2 + H_2O = 2HCl + SO_2.$$
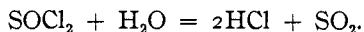
Sulfuryl chloride, on the other hand, reacts with water according to the equation:

$$SO_2Cl_2 + 2H_2O = 2HCl + H_2SO_4.$$