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THE BASIC PROPERTIES OF OXYGEN.

TWO-COMPONENT SYSTEMS OF THE HALOGEN HYDRIDES WITH ORGANIC SUBSTANCES CONTAINING OXYGEN.

[FIRST PAPER.]

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In a paper[1] on the basic properties of oxygen one of us has given the results of the investigation of several two-component systems, consisting of organic oxygen compounds and the halogen or halogen hydrides. These systems are of interest not from the standpoint of phase rule studies at low temperatures, but from the fact that various compounds are formed which may be ascribed to the oxygen assuming a higher valency than two. Indeed a number of complexes have been isolated, such as the combination of ethyl ether and dimethylpyrone[2] with hydrobromic acid, in which the oxygen may conveniently be viewed as a hexad. We have, then, investigated selected types of these two-component systems in order to collect, if possible, data for a systematic examination of the constitution of these compounds, with the hope of throwing some new light on the higher valences of oxygen, and of ascertaining whether these compounds may fairly be viewed as distinct from salts separating with water, alcohol or ether of crystallization.

In comparing the oxonium complexes with the so-called molecular compounds several distinctions stand out clearly:

(1) While salts with water or alcohol of crystallization[3] may form many combinations containing a large number of oxygen atoms—ferric chloride, for example gives four complexes, one containing 12 molecules of water—the oxonium compounds with hydrobromic or hydriodic acid

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[1] THIS JOURNAL, 33, 71 (1911).

[2] *Ibid.*, 32, 542 (1910).

[3] *Ibid.*, 30, 1101 (1908).

previously described[1] are remarkably simple. One molecule of the organic liquid unites with one, or at most, with two molecules of the acid; and even with the combinations containing the halogens[2] only one, two, or in a single case three atoms unite with one molecule.

(2) The melting points of the compounds are, in general, far above the melting points of the constituents. Thus hydrobromic acid (m. p. —86°) when mixed with methyl ether (m. p. —138°) yields a compound melting at —13°, while in the case of the molecular compounds with water, etc., the melting points are between or below the melting points of the components.

(3) When a "molecular" compound such as the hydrated copper sulfate is dissolved in water, its electrolytic behavior shows that the ions $Cu^{\cdot\cdot}$ and SO_4'' are present, *i. e.*, the salt undergoes dissociation, and one part of the salt proper moves to the cathode, the other to the anode. Quite a different behavior is shown by solutions of oxonium salts in the halogen hydrides. There the oxonium salt is the electrolyte, the liquefied acid the solvent. The ether or alcohol suffers no disruption but moves to the cathode under the electric stress. We shall, in the course of this paper, point out other distinctions between the two classes of oxonium salts—those with the halogen hydrides and halogens—and the molecular compounds.

It is well, however, to emphasize that the differences between the so-called molecular compounds and the admittedly real salts are not clearly drawn in chemical literature and seem to depend more on the predilections of the authors than on determined physical or chemical properties—thus the Grignard reagent is viewed as a simple oxonium salt of ether, although few chemical or physical facts are given to support this hypothesis.

Many accounts of investigations of the basic properties of oxygen have appeared. Friedel indicated the existence of a combination of methyl ether and hydrochloric acid as early as 1875; Collie and Tickle[3] in their study of the salts of dimethylpyrone drew the attention of chemists to this subject, while Baeyer and Villiger[4] in a series of papers showed that many of the stronger complex acids form combinations with alcohol, ether and acetone.

But the oxonium compounds with the halogens and halogen acids are simpler than those produced by Baeyer and Villiger, which may be solid solutions or combinations[5] quite analogous to salts with water of crystal-

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[1] Walker, McIntosh and Archibald, *Trans. Chem. Soc.*, (*London*) **85**, 1098 (1904); Archibald and McIntosh, *Trans. Chem. Soc.*, 85, 919 (1904); THIS JOURNAL, **27**, 26, 1013 (1905); **28**, 588 (1906); **32**, 542 (1910).

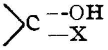
[2] *Trans. Chem. Soc.*, (*London*) **87**, 784 (1905).

[3] *Ibid.*, **75**, 710 (1899).

[4] *Ber.*, **34**, 2679, 3612 (1901); **35**, 1201 (1902).

[5] *Loc. cit.*

lization. Recently Baumé[1] has investigated some two-component systems of the halogen acid and methyl ether, etc., and has confirmed Friedel's views on the tetravalency of oxygen. On the other side Gomberg and Cone[2] conclude that in the salts of dimethylpyrone the acid is attached to the carbon atom and therefore infer that the compounds of the simple ketones with the halogen acids have the formula



$$>C\begin{matrix}-OH\\-X\end{matrix}$$

Against this view may be marshaled the many compounds of alcohols and ethers with acids which are quite as stable as the ketone combinations but can not be represented by any formula analogous to that given above. The hydrocarbons and saturated derivatives of the fatty series give, as far as we have studied this question, no compounds with acids. On the other hand toluene unites with both hydrobromic acid and chlorine and shows complexes in which the constituents are in simple molecular proportions. No appreciable amount of heat is evolved in these reactions, the compound is not ionized in acid solution, and the melting point is hardly above that of toluene itself. A distinction must be drawn between these combinations and the much more stable oxonium salts.

Materials.—The methyl and ethyl alcohol were dehydrated by lime and copper sulfate, the ethyl ether and toluene by sodium. The methyl ether was prepared from methyl alcohol and dried by means of phosphorus pentoxide. The ethyl acetate[3] was washed with water and dried with copper sulfate. The acetone was treated with calcium chloride and fractionally distilled. The halogen acids were prepared in the usual ways and when necessary were redistilled. The chlorine was made from hydrochloric acid and permanganate; the bromine was dried with calcium bromide and fractionated.

Apparatus.—A Beckmann apparatus with a glass stirrer was used in the freezing point determination. For temperatures above —78° carbon dioxide and ether served as the freezing mixture; and this refrigerant boiling under reduced pressure was used between —78° and —107°. For lower temperatures recourse was had to liquid air. Great care was taken to prevent the entrance of moisture into the apparatus. When a small amount of solid had separated the Beckmann apparatus was placed inside an unsilvered Dewar vessel, the liquid was vigorously stirred, and the temperature at which the last crystals melted was noted.

[1] *J. chim. phys.*, 9, 245 (1911).

[2] *Ann.*, 376, 183 (1910).

[3] Small amounts of water may be detected in ethyl acetate or ether by freezing the liquid and allowing it to melt. Less than 0.03% can be detected as ice crystals in the former liquid, and a smaller amount in ether if alcohol be absent. In fact, cooling an organic liquid is often an excellent test for impurities. Propyl bromide prepared most carefully and thought to be exceedingly pure showed the presence of water by this test.

Four thermometers were employed in this work. (1) A mercury thermometer graduated in 0.2° to —35°. (2) A thermometer containing an 8.5% thallium amalgam[1] (f. p. —62°) graduated in 0.5°. (3) A thermometer filled with pentane graduated in degrees to —130°. (4) A platinum resistance thermometer, the platinum wire being wound on a glass spiral. Its resistance was determined from time to time at the following points: The freezing and boiling temperatures of water, the boiling point of carbon dioxide (—78.2°) and of liquid air of known composition. The platinum thermometer could be read to 0.1°.

All these thermometers were calibrated by means of a constant volume hydrogen thermometer, and showed no change sufficient to affect the results during the course of the work. The platinum thermometer was used exclusively in the our systems, methyl ether–halogen hydrides and chlorine–hydrochloric acid. The freezing points of the other systems were determined by means of the direct reading thermometers, a number of points being confirmed with the platinum thermometer.

The various mixtures were in general made up by weight, so that the concentration of each component was known. However, on the addition of the organic liquid to the cooled hydride a large amount of heat is evolved, and this may vaporize the hydride and so change the concentration. In systems containing hydrobromic or hydriodic acid, it was found convenient to freeze the acid. Then the latent heat of fusion and the slowness of a reaction where a solid is involved were sufficient to prevent a too rapid rise in temperature. The actual weighing of the acid had, of course, to be performed quickly; but with a little practice this can be done to 0.25%. The organic substances, except methyl ether which boils at —23°, could be weighed to any desired degree of accuracy.

As a control on this method of determining concentrations analyses were made at different points in each system in the following manner: The material was allowed to stand at a temperature a few degrees above the melting point until a homogeneous solution was formed. A portion of this was placed in a tube previously weighed under identical conditions, surrounded by liquid air or carbon dioxide. It was stoppered, reweighed, the acid absorbed by water and finally analyzed by standard barium hydroxide.

It has previously been pointed out that ethyl ether probably unites with hydrobromic acid in two proportions yielding the compounds $C_4H_{10}O.HBr$ and $C_4H_{10}O.2HBr$. As hydrobromic acid itself is unassociated at low temperatures,[2] the second compound points to the existence of hexavalent oxygen. To study the question in detail and to analyze

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[1] McIntosh and Johnson, THIS JOURNAL, 34, 910 (1912).

[2] Steele, McIntosh and Archibald, *Z. physik. Chem.*, 55, 129 (1906).

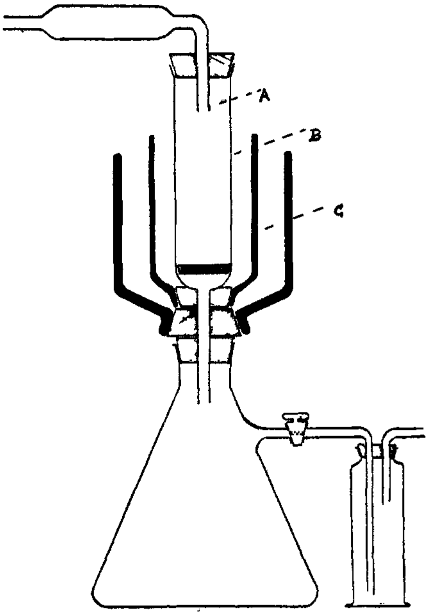


Fig. 1.

the compounds accurately we have used the apparatus shown in Fig. 1.

A is a filtering tube with a perforated plate and packed asbestos surrounded by the cooling bath *B*. Conduction of heat is prevented by *C* which is tightly packed with natural wool. The compound, crystallized from either an excess of acid or of ether, was placed in *A* and pressed down from time to time while dry air, at a temperature of —70°, was drawn through at a constant rate by a suction pump. By means of a cooled spoon portions of the solid were removed from time to time, weighed, and analyzed. Fig. 2 shows the results; the individual experiments are given in Table I.

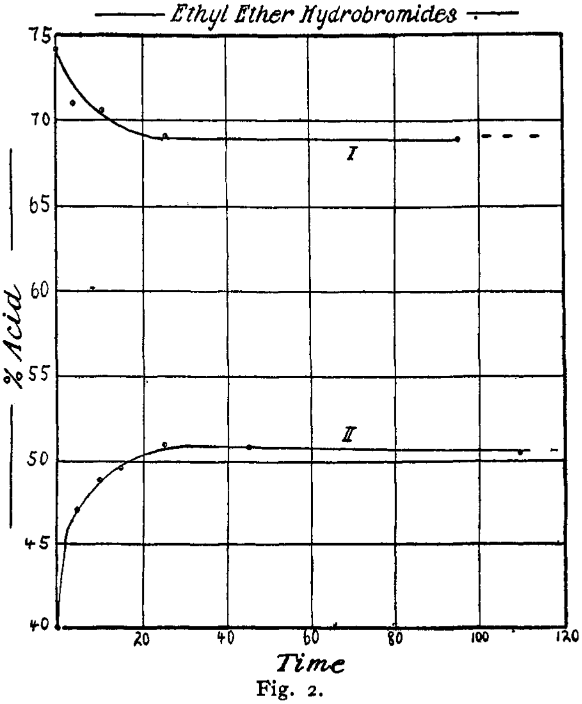


Fig. 2.

TABLE I.

Excess ether.		Excess acid.	
Time.	Per cent acid.	Time.	Per cent acid.
0	40.0	0	74.3
5	47.6	4	71.0
10	48.8	11	70.9
15	49.4	26	69.2
25	51.3	95	69.3
45	50.8	304	67.3
110	50.3	...	..

In the first experiment (Curve 2) the acid content of the compound rose to 50% in 20 minutes and remained practically constant. A similar experiment in which the material was crystallized from 78% acid by reducing the temperature showed that the acid had fallen to a value corresponding to the compound $C_4H_{10}O.2HB$ in about 20 minutes, and this value remained constant during 304 minutes.

These experiments show conclusively that two compounds of ether and hydrobromic acid exist—combinations quite analogous to phosphorus or iron with chlorine. An excess of ether promotes the formation of the monohydrobromide; an excess of acid the dihydrobromide. In the latter

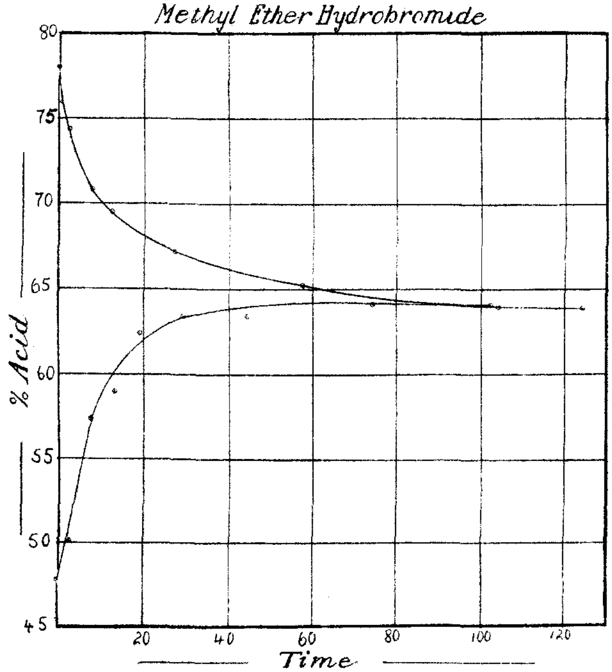
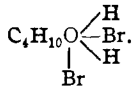


Fig. 3.

compound the oxygen probably functions as a hexad, and  $C_4H_{10}\underset{\displaystyle Br}{O}\begin{array}{l}H\\ Br.\\ H\end{array}$ may be given as the most probable formula.

Methyl ether and hydrobromic acid yield but one compound above —70°. This can be seen by reference to Fig. 3 and Table II. Analogous experiments to those described, in which the compound was crystallized from a large excess of acid or ether, showed but one compound, $C_2H_6O.HBr$. Curve 1 (Fig. 6) indicates that more than one compound is unlikely.

TABLE II.

Excess methyl ether.		Excess acid.	
Time.	Per cent acid.	Time.	Per cent acid.
0	47.8	0	78.0
2.5	50.1	2.5	74.6
7.5	57.5	7.5	70.8
13.5	59.0	12.5	69.5
19.5	62.4	27.5	67.2
29.5	63.4	57.5	65.2
44.5	63.4	103	64.1
74.5	64.2	...	..
104	64.1	...	..
124	63.8	...	..

For a comparison with the oxonium compounds we have examined the system chloroform-hydrobromic acid. The results are given in Table III and in Fig. 4. As anticipated no compounds were formed. The freezing point of each component is gradually lowered by the addition of the other until the eutectic is reached. A glance at any of the succeeding plates shows the difference in systems where oxonium compounds are produced.

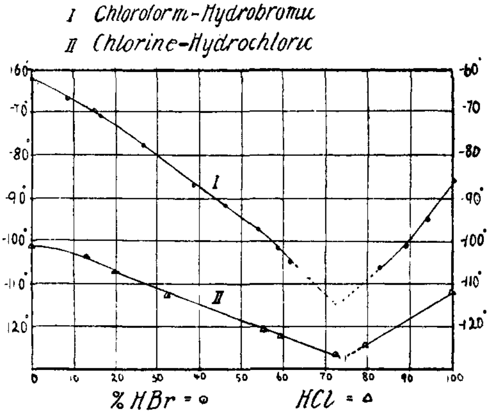


Fig. 4.

TABLE III.—CHLOROFORM–HYDROBROMIC ACID.

Per cent acid.	Freezing temperature.	Per cent acid.	Freezing temperature.
100.0	—86.0	46.3	92.0
94.1	95.0	38.9	87.0
89.1	101.0	26.6	78.0
82.8	106.0	16.3	71.0
61.4	105.0	15.0	69.5
58.7	101.5	8.6	67.0
54.0	97.5	0.0	62.5

While the question of combination between the halogens and halogen hydrides is hardly within the scope of our present work, we have made a few determinations of the freezing points of these systems but find no indications of compounds. Bromine and iodine are extremely insoluble in the corresponding halogen acids at their freezing temperatures; but chlorine and hydrochloric acid are soluble in one another in all proportions. The freezing point curve is given in Fig. 4 (Curve 2) and the individual measurements in Table IV. The solution of chlorine in hydrochloric acid takes place without any marked temperature change.

TABLE IV.—CHLORINE–HYDROCHLORIC ACID.

Per cent acid.	Freezing temperature.	Per cent acid.	Freezing temperature.
100.0	—112.0	32.4	112.4
79.5	124.6	19.9	107.9
72.4	126.6	13.0	103.6
59.4	122.1	0.0	101.5
55.5	120.5		

Toluene Systems.

The systems toluene–hydrobromic acid and toluene–chlorine gave the results shown in Fig. 5. The systems show the formation of compounds[1] $C_7H_8.HBr$ and $C_7H_8.Cl_2$, with melting points a few degrees above that of toluene itself. Toluene then exhibits basic properties and it seems probable that carbonium compounds are formed, but they are very unstable compared with the oxonium complexes. It is interesting in this connection to note that substances such as benzophenone[2] containing but one oxygen atom add on more acid than can be explained on the assumption that oxygen is tetra- or hexavalent. Possibly here part of the acid is added to the benzene ring by means of the carbon valences.

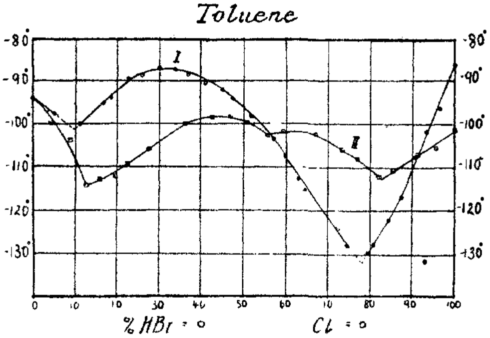


Fig. 5.

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[1] See Vorländer, *Ann.*, 341, 1 (1905).

[2] THIS JOURNAL, 33, 70 (1911).

TABLE V.—TOLUENE-HYDROBROMIC ACID.

Per cent acid.	Freezing temperature.	Per cent. acid.	Freezing temperature.
100.0	—86.0	51.1	98.0
96.7	96.0	47.3	94.0
93.5	101.5	44.9	92.0
90.6	107.5	40.9	90.5
87.6	116.0	36.9	88.5
84.7	122.0	34.1	87.0
80.9	128	29.8	87.0
79.3	130	26.5	88.5
74.6	128	22.6	89.5
72.2	124	19.0	94.0
64.7	115	16.3	95.0
63.0	112.5	11.2	100.0
59.8	107.5	4.9	98.0
56.7	103.5	0.0	94.0

TABLE VI.—TOLUENE-CHLORINE.

Per cent chlorine.	Freezing temperature.	Per cent chlorine.	Freezing temperature.
100.0	—101.5	46.9	98.0
95.3	105.5	42.1	98.5
91.0	107.0	35.9	100.0
85.3	110.5	27.3	106.0
82.1	112.0	22.5	109.0
77.1	108.0	19.7	112.0
73.1	106.0	15.8	112.5
67.2	102.0	12.6	114.0
59.7	101.5	9.3	103.5
55.7	102.5	4.0	100.0
50.8	99.5	0.0	94.0

Methyl Ether Systems.

The experiments with methyl ether are of peculiar interest since it is the substance from which Friedel attempted to prepare a compound with a tetravalent oxygen atom. He obtained a liquid with hydrochloric acid boiling at —2°, in which the ether and acid were in approximately molecular proportions. But a liquid boiling at a constant temperature is no proof of the formation of a compound, so that Friedel's experiment leaves the existence of tetravalent oxygen in doubt. A few years ago Archibald[1] and one of us predicted the existence of a compound, $C_2H_6O.5HCl$, from the heat evolved on mixing ether and acid, but were unable to isolate it. Recently Baumé[2] has examined the system methyl ether-hydrochloric acid completely and concludes that two compounds, $C_2H_6O.HCl$ and $C_2H_6O.4HCl$, are formed. The elaborate precautions

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[1] *Loc. cit.*

[2] *Loc. cit.* We are unable to procure Baumé's paper and so have depended on the abstract in the Zentralblatt and the abbreviated account, *Compt. rend.*, 148, 1322 (1909).

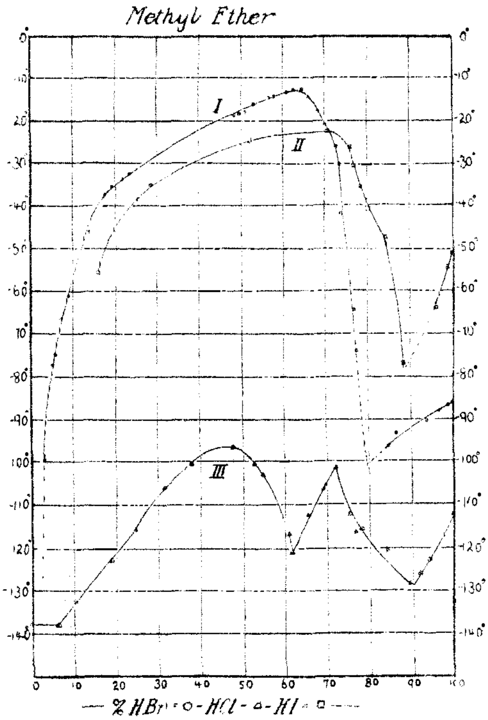


Fig. 6.

and large amount of materials employed make Baumé's results probably more accurate than the ones given here.

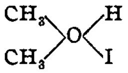
The results of our experiments are given in Tables VII, VIII and IX, and shown graphically in Fig. 6. Curve I is for the system methyl ether and hydrogen bromide. The acid freezes at —86.0. Addition of methyl ether lowers the freezing temperature to the eutectic point at —100° where ether, hydrobromic acid, compound and vapor are in equilibrium. Further additions of ether raise the melting point until finally a maximum of —13° is reached. Here the mixture consists of 64% acid, which corresponds exactly to the compound $C_2H_6O.HBr$.

TABLE VII.—METHYL ETHER-HYDROBROMIC ACID.

Per cent acid.	Freezing point.	Per cent acid.	Freezing point.
100.0	—86.0	56.3	—14.9
98.7	86.8	52.8	16.6
97.0	88.0	50.4	18.4
93.9	90.2	49.4	18.7
86.4	93.3	48.4	19.7
84.8	95.2	25.4	26.3
77.0	74.3	23.1	32.5
76.4	64.7	21.4	33.8
73.8	42.0	19.0	35.5
73.2	30.4	17.2	37.2
72.3	26.3	13.5	46.3
70.0	21.1	12.7	48.2
68.4	18.0	8.0	61.0
65.9	14.4	6.9	66.2
64.3	12.3	5.7	75.0
62.4	13.0	5.0	77.3
60.6	13.5	3.0	99.8
57.8	14.3	0.0	138.0

As we have said before there is but one compound of methyl ether and hydrobromic acid, $C_2H_6O.HBr$. Its formation is accompanied by a heat evolution as large, probably, as when ethyl ether is employed (90 × 10^{10} ergs per gram molecule formed).[1]

Analogous results were obtained with hydriodic acid (Curve 2, Table VII). The eutectic point is about —78°, and the mixture contains 12% of ether. The melting point of the compound is —22° C. and its formula is



$$\begin{matrix} CH_3 & & H \\ & O & \\ CH_3 & & I \end{matrix}$$

TABLE VIII.—METHYL ETHER–HYDRIODIC ACID.

Per cent acid.	Freezing temperature.	Per cent acid.	Freezing temperature.
100.0	—50.9	76.4	30.8
98.8	53.4	76.2	26.3
96.0	64.1	70.1	22.0
88.3	77.0	51.8	25.0
84.1	47.5	28.2	35.0
79.8	40.7	25.5	28.5
78.1	35.7	15.3	56.0

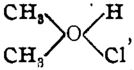
Methyl ether and hydrochloric acid (Curve 3, Table IX) show two maximums at about —96° and —102°, where the composition of the solution indicates that the compounds $C_2H_6O.HCl$ and $C_2H_6O.3HCl$ or $4HCl$ are formed. Baumé[1] finds the more complex compound to consist of 4 molecules of acid but as the liquid is viscous in the neighborhood of this point accurate determinations are difficult to make. The constitution of the first compound is probably  $\begin{matrix} CH_3 & & H \\ & O & \\ CH_3 & & Cl \end{matrix}$, the oxygen acting as a tetrad. Since hydrochloric acid is largely associated at low temperatures,[2] we believe it unnecessary to assume a higher valency than four for oxygen to explain the formation of the second salt. The combination may well take place by means of trivalent chlorine atoms.

TABLE IX.—METHYL ETHER–HYDROCHLORIC ACID.

Per cent acid.	Freezing temperature.	Per cent. acid.	Freezing temperature.
100.0	—112.0	61.3	121.2
94.5	122.7	60.7	117.0
92.0	126.0	54.6	103.0
89.6	128.7	52.2	100.4
84.1	120.6	47.2	96.8
78.2	115.8	37.2	100.4
76.5	116.8	31.2	106.0
75.3	117.2	24.4	116.0
72.1	101.2	18.6	123.0
69.6	105.7	9.8	132.4
69.1	106.1	0.0	138.0
65.5	112.4		

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[1] *J. Physic. Chem.*, 12, 167 (1908).

[2] *Loc. cit.*

Methyl Alcohol Systems.

Two systems only were examined, *i. e.*, those with hydrobromic acid and bromine. The first (Fig. 7, Curve 1, and Table X) shows only one compound, $CH_3HO{<}^{H}_{Br}$, melting at —12°, while alcohol and acid melt at —95° and —86°, respectively. Large amounts of heat are given out on the formation of this compound, about 57 J being liberated for each gram molecule formed.

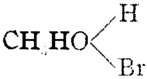

Table X.—Methyl Alcohol–Hydrobromic Acid.

Per cent acid.	Freezing temperature.	Per cent acid.	Freezing temperature.
100.0	—86.0	75.0	13.5
98.4	87.5	71.3	12.8
95.3	94.0	65.0	33.9
94.3	97.0	63.5	44.4
89.2	85.0	57.2	54.5
87.9	72.4	54.5	64.0
86.0	58.0		

All compounds obtained with the halogen hydrides dissolved in excess of either constituent—preferably the acid—conduct the electric current and are consequently dissociated. On the other hand the halogens unite with the organic liquids with only a trifling heat evolution, giving compounds which do not conduct the current when dissolved in either constituent, and which are therefore undissociated. Ether, alcohol, etc., when dissolved in bromine are to some extent acted on with the formation of hydrobromic acid even when the greatest care is taken, so the part of the curves containing an excess of bromine, *i. e.*, from 100% to the eutectic is a little lower than its true value. The remainder of the curve can be realized without substitution taking place and is therefore more nearly correct. Curve 2 points to the existence of a compound, $CH_3HO.Br$, melting at —66°. This substance[1] was isolated and examined a number of years ago.

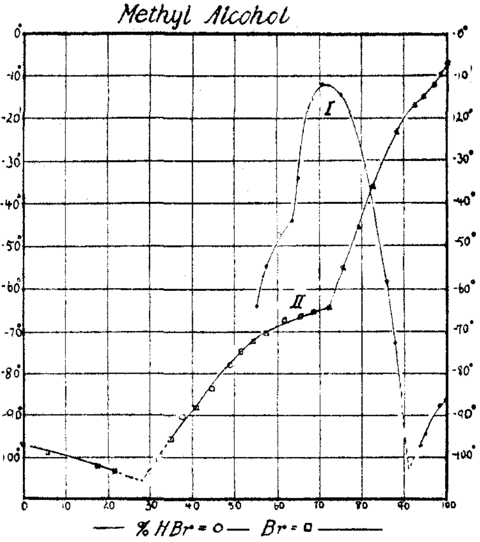

Fig. 7.

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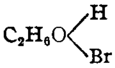
[1] *Loc. cit.*

TABLE XI.—METHYL ALCOHOL-BROMINE.

Per cent bromine.	Freezing temperature.	Per cent bromine.	Freezing temperature.
100.0	—7.3	57.7	70.0
98.5	9.7	54.6	72.0
95.9	12.0	51.6	74.5
94.2	14.8	49.1	77.5
92.3	16.5	44.7	83.5
88.6	23.0	40.9	88.0
82.4	36.0	37.7	90.0
79.3	45.5	35.0	95.5
75.2	55.0	21.3	103.5
71.9	64.0	17.7	102.0
67.9	65.0	5.9	99.0
65.3	66.0	0.0	97.0
61.9	67.5		

Ethyl Alcohol Systems.

The results are given in Tables XII and XIII and shown in Fig. 8. Curve 1 is the freezing temperature of mixtures of alcohol and hydrobromic acid. The eutectic point is at —104°, and there the mixture contains 91% acid. The maximum temperature of —12° was observed, and the composition at this point corresponds almost exactly to the compound $C_2H_6O.HBr$. The formula of this substance is probably



$C_2H_6O\langle^{H}_{Br}$

The parts of the curves where an excess of the alcohol was present could not be obtained in the hydrobromic acid system. The very viscous liquid prevented the compounds from crystallizing.

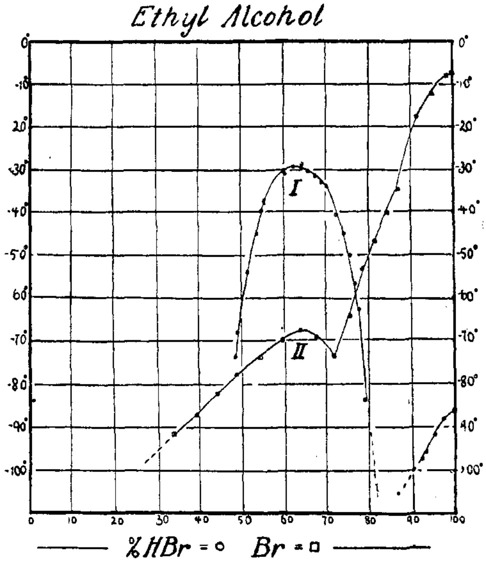


Fig. 8.

With mixtures of alcohol and bromine the highest freezing temperature is —56° and the curve shows that a complex, $C_2H_6O.Br$, exists. To explain its constitution the formula must be doubled and the compound written $C_2H_6O = Br — Br = OC_2H_6$.

The eutectic points are at —106 and —64° and the solid phases contain 28% and 72% of bromine, respectively.

TABLE XII.—ETHYL ALCOHOL-HYDROBROMIC ACID.

Per cent acid.	Freezing temperature.	Per cent acid.	Freezing temperature.
100.0	—86.0	67.6	31.4
97.9	88.0	66.2	30.3
95.4	91.5	64.6	29.6
93.3	95.5	64.0	28.5
92.3	97.0	62.3	29.5
78.9	83.5	60.2	31.0
77.8	62.5	60.0	30.0
76.8	56.5	55.3	37.5
75.4	50.1	55.0	40.0
74.1	45.2	53.8	45.0
72.4	40.5	51.3	54.0
70.4	34.8	49.2	68.1
68.8	33.3	48.9	73.4

TABLE XIII.—ETHYL ALCOHOL-BROMINE.

Per cent bromine.	Freezing temperature.	Per cent bromine.	Freezing temperature.
100.0	—7.3	71.6	73.5
98.7	7.8	67.6	69.0
94.9	12.0	64.1	67.5
91.5	17.5	59.9	70.0
87.6	34.5	54.7	73.5
84.5	40.0	48.8	77.5
81.7	46.5	44.6	82.0
78.7	53.0	39.4	87.0
75.8	64.0	34.2	91.0

Acetone Systems.

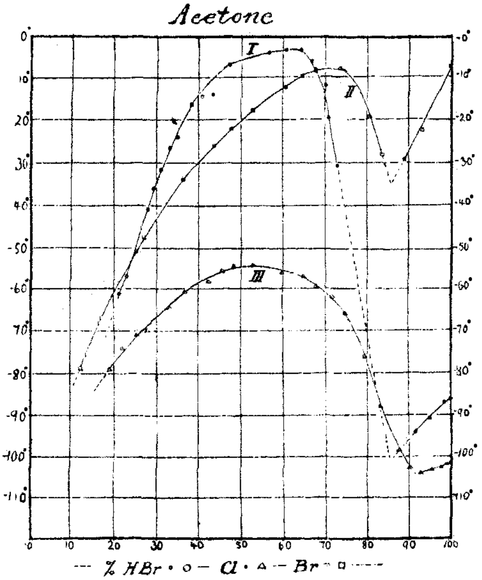
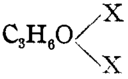


Fig. 9.

The results obtained in a study of the systems acetone-hydrobromic acid, acetone-bromine and acetone-chlorine are given in Tables XIV, XV and XVI and the curves in Fig. 9. With hydrobromic acid one compound, $C_3H_6O.HBr$, melting at —4°, is formed. Bromine or chlorine yields one compound containing two atoms of the halogens to one of acetone. The constitution may be represented by



$$C_3H_6O\begin{matrix}\diagup X\\ \diagdown X\end{matrix}$$

or

$C_3H_6O=X—X=X—X=OC_3H_6$. We believe the second formula to be the correct one,

TABLE XIV.—ACETONE-HYDROBROMIC ACID.

Per cent acid.	Freezing temperature.	Per cent acid.	Freezing temperature.
100.0	—86.0	43.6	14.0
98.7	86.8	40.3	14.0
95.0	90.5	38.2	16.0
91.3	94.0	35.1	24.2
73.0	30.6	33.1	26.6
71.8	19.3	31.3	31.4
70.0	11.7	29.6	36.
66.8	6.0	28.0	41.2
64.6	3.2	25.1	50.5
60.4	3.0	22.8	57.0
56.3	4.1	21.4	61.0
47.1	5.8		

TABLE XV.—ACETONE-BROMINE.

Per cent bromine.	Freezing temperature.	Per cent bromine.	Freezing temperature.
100.0	—7.3	60.3	12.0
93.2	22.0	52.7	17.5
89.0	29.0	47.8	22.0
83.7	28.0	43.8	26.0
80.5	19.0	36.4	34.0
73.8	7.5	26.5	48.0
67.4	8.0	11.7	79.0
64.3	9.5		

TABLE XVI.—ACETONE-CHLORINE.

Per cent chlorine.	Freezing temperature.	Per cent chlorine.	Freezing temperature.
100.0	—101.5	59.4	56.0
99.1	101.5	52.9	54.5
97.6	102.5	49.2	55.5
95.8	103.0	45.2	55.5
93.1	103.5	42.3	58.5
90.1	102.5	37.1	60.3
87.3	98.5	33.2	64.5
79.3	76.0	28.1	70.0
74.7	66.0	25.3	71.0
71.6	62.0	22.0	75.0
68.0	59.5	19.0	79.0
65.0	57.0		

Ethyl acetate unites with hydrobromic acid, bromine and chlorine (Fig. 9, Tables XVII, XVIII and XIX). The compounds are more complex than those previously described and in the case of the halogens contain 3 atoms to a molecule of the acetate. This is not unexpected, since one hydroxyl oxygen atom is balanced by one halogen atom and a carbonyl oxygen atom by two. These compounds when dissolved in excess of the acetate or halogen do not conduct the electric current and so a constitution essentially different from combinations with the halogen hydrides must be ascribed to them. The simplest way of expressing these complexes we believe to be

$$CH_3.CO{=}X{-}X{=}X{-}X{=}OC.CH_3$$

$$C_2H_5O{=\!=}X{-\!-\!-}X{=\!=}OC_2H_5$$

The system ethyl acetate-hydrobromic acid shows three maxima:

(1) 48% acid, m. p. .... —36°
(2) 70% acid, m. p. .... —52°
(3) 78% acid, m. p. .... —60°

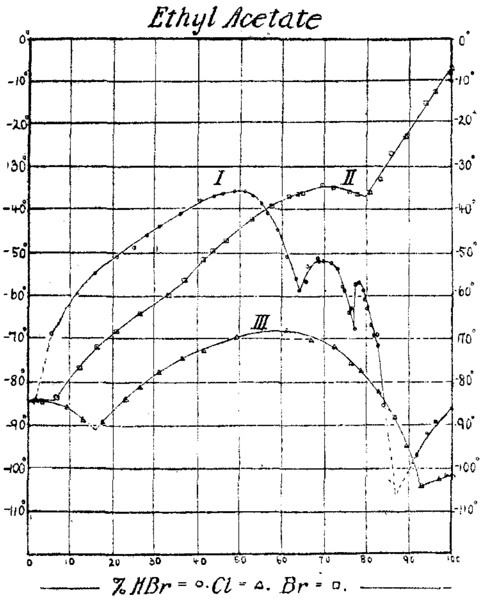


Fig. 10.

corresponding to the compounds $CH_3COOC_2H_5 . HBr$, $(CH_3COOC_2H_5)_2(HBr)_5$ and $CH_3COOC_2H_5(HBr)_4$ which contain 48, 70 and 78.5% acid. Since the quantivalence of oxygen increases with decreasing temperature, we may account for the first by assuming that at —36° only one, probably the carbonyl oxygen atom, functions as a tetrad. The constitution of the last compound may be explained by assuming both oxygen atoms to be hexavalent. But the compound containing two molecules of ester to five of acid is so unexpected that any speculation about its formula would be worthless.

TABLE XVII.—ETHYL ACETATE-HYDROBROMIC ACID.

Per cent acid.	Freezing temperature.	Per cent acid.	Freezing temperature.
100.0	—86.0	—77.0	68.1
96.0	89.0	75.9	63.0
94.0	92.0	75.7	64.0
91.8	97.0	74.3	59.0
83.7	85.2	74.1	58.3
82.5	71.3	72.7	54.0
82.4	69.2	72.4	54.0
81.4	69.2	71.2	52.5
80.8	67.1	69.6	52.0
79.8	63.0	68.3	52.0
79.1	61.0	68.2	51.5
78.8	59.3	66.0	53.0
77.8	56.5	65.3	57.0
77.2	56.0	64.0	59.0

TABLE XVII (*continued*).

Per cent acid.	Freezing temperature.	Per cent acid.	Freezing temperature.
63.0	56.0	40.3	38.0
60.7	51.0	35.9	41.0
58.7	45.0	30.4	44.0
56.2	41.0	28.1	46.0
55.2	39.0	25.2	49.0
53.0	37.0	20.7	51.0
51.1	36.1	15.6	54.5
48.7	36.0	11.1	58.0
45.9	36.3	5.4	69.1
43.3	37.0	0.0	83.0

TABLE XVIII.—ETHYL ACETATE-BROMINE.

Per cent bromine.	Freezing temperature.	Per cent bromine.	Freezing temperature.
100.0	—7.3	57.2	39.5
99.6	8.0	52.3	42.5
95.8	12.5	46.8	47.5
93.6	15.0	43.7	50.0
89.2	23.0	41.1	52.0
85.2	27.0	36.7	56.5
83.0	33.0	33.1	60.0
80.1	36.0	21.6	64.5
77.4	36.5	20.6	68.5
75.5	36.0	15.9	72.0
71.7	35.0	10.9	77.0
69.4	34.5	6.6	84.0
64.3	36.5	3.0	84.5
63.6	36.5	2.0	84.0
61.1	37.0	0.0	83.0

TABLE XIX.—ETHYL ACETATE-CHLORINE.

Per cent. chlorine.	Freezing temperature.	Per cent chlorine.	Freezing temperature.
100.0	—101.5	60.9	68.2
99.0	101.5	49.2	70.0
97.3	102.5	41.4	73.0
92.8	104.0	36.2	74.3
89.4	95.0	30.7	78.0
86.3	88.5	26.4	81.0
82.5	82.3	22.8	84.5
78.4	78.0	17.3	89.5
76.0	76.0	12.7	89.0
72.2	72.0	9.2	86.0
66.8	70.0	0.0	83.0

Summary.

In this article we have given the results of the freezing points of certain two-component systems consisting of organic substances containing oxygen with the halogens or halogen hydrides. As several of these compounds have not been isolated before, and as their melting points were determined with a fair degree of accuracy we have collected the results in Table XX.

Table XX.

Compound.	M. P.
$(CH_3)_2O.HBr$	— 13°
$(CH_3)_2O.HI$	— 22°
$(CH_3)_2O.HCl$	— 96°
$(CH_3)_2O(HCl)_3$?	—102°
$CH_3HO.HBr$	— 12°
$CH_3HO.Br$	— 66°
$C_2H_5HO.HBr$	— 30°
$C_2H_5HO.Br$	— 58°
$C_3H_6O.HBr$	— 4°
$C_3H_6O.Br_2$	— 8°
$C_3H_6O.Cl_2$	— 54°
$CH_3COOC_2H_5.HBr$	— 36°
$(CH_3COOC_2H_5)_2(HBr)_5$	— 52°
$(CH_3COOC_2H_5)(HBr)_4$	— 57°
$CH_3COOC_2H_5.Br_3$	— 35°
$CH_3COOC_2H_5.Cl_3$	— 68°

In these compounds we believe that the union is brought about by the increase in valency of the oxygen at the low temperatures employed. The halogen hydride complexes, it will be noticed, melt far above the melting points of either constituent. The combinations are formed with the evolution of an amount of heat equal to or greater than that given out when a halogen acid is neutralized by potassium hydroxide. These compounds whether molten or in a solution of either constituent conduct the electric current readily.

The chlorine and bromine compounds evolve only a small amount of heat on their formation, and are non-conductors when free from the corresponding halogen acids. Their constitutional formulas are doubtful, but they must differ radically from the compounds ionized in solution. We are now attempting to solve the question of their structure and that of other oxonium and carbonium complexes by means of molecular weight determinations at low temperature.

McGill University, July, 1912.

A METHOD FOR DETERMINING THE MOLECULAR WEIGHTS OF VOLATIL LIQUIDS.

By C. W. Porter.

Received July 20, 1912.

All vapor density methods for determining molecular weights are based upon the gas law as expressed in the equation $PV = RT$. The numerical value of the constant (R) is usually calculated by allowing P to represent atmospheric pressure at sea level, T, 0° C. (273° Abs.) and V the volume occupied by a gram molecule of a gas under the above conditions of temper-