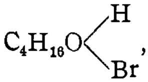
Benzophenone compound, melts —42°, showed 73.5, 72.7, 75.0 71.5 per cent. acid. $(C_6H_5)_2CO6HBr$ has 72.8 per cent.

Experiments with Hydrogen Chloride. Nitrobenzene, benzoin, anisole, phenol, phenetol, benzoic, phthalic and gallic acids are insoluble or sparingly soluble in liquefied hydrochloric acid. Thymol, salicylic acid, naphthol (α and β) benzyl alcohol, benzaldehyde and cresol are soluble and probably form compounds, but these were not obtained as solids. Resorcinol and benzophenone gave compounds melting below —85°. The resorcinol complex contained about 52 per cent. acid, which corresponds to three or four molecules of hydrogen chloride to one of resorcinol. The benzophenone hydrochloride contained 56.8 per cent. acid while $(C_6H_5)_2CO.7HCl$ has 58.4 per cent. The benzophenone compounds differ from the corresponding ones of the fatty series which contain a much smaller proportion of acid. There are, however, indications of simpler addition products.

Ethyl Ether and Hydrobromic Acid unite to form a compound containing one molecule of each substance and here the oxygen has been assumed to be tetravalent. Since on electrolysis in a hydrobromic acid solution the ether moves to the cathode, the ether hydrobromide has been given the constitution  $C_4H_{16}O\begin{smallmatrix} \diagup H \\ \diagdown Br \end{smallmatrix}$, its molecular weight, however, being unknown. A second compound, $C_4H_{10}O.2HBr$, probably exists (previous paper) in which, as in some acid salts of dimethyl pyrone, the oxygen may be taken as hexavalent. In the compounds of benzophenone and the halogen acids the latter are present in greater amounts than would be expected were the oxygen tetra- or even hexavalent. While the constitutions of such complexes might possibly be systematized by the assumption of the union of the acid with the carbon[1] it seems better, at present, to class them merely as substances with acid of crystallization.

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TWO-COMPONENT SYSTEMS.

PAPER I. ETHER-HYDROBROMIC ACID, ETHER-CHLORINE AND ETHER-BROMINE.

By D. McIntosh.

Received October 24, 1910.

While studying the compounds formed by organic substances containing oxygen with the halogens and with the halogen hydrides, I found it necessary to map out completely or in part several of these two-component systems. The results of three are given in the following pages.

The freezing-point determinations were made in a modified Beckmann apparatus with a platinum stirrer and a pentane thermometer, graduated

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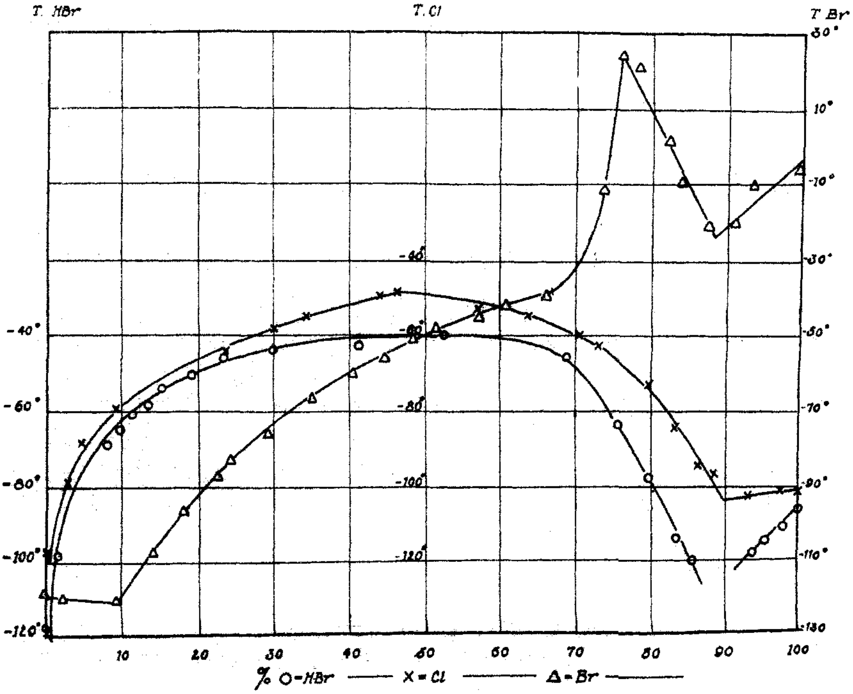
[1] Gomberg, *Ann.*, 370, 142 (1909).

in degrees and calibrated by means of a constant volume hydrogen thermometer. The temperatures were read to 0.5°, but owing to the sluggish way in which the pentane thermometer reaches equilibrium as well as to its other inherent disadvantages—drops of liquid adhering to the glass—the measurements are accurate only to one or two degrees.

Above —78° carbon dioxide was used as a refrigerant. Between —78° and —108° the solutions were kept at constant temperature by evaporating the carbon dioxide under reduced pressure, and portions were removed for analysis from time to time. The points on this part of the curve are probably much more nearly correct than at higher temperatures. Finally, the few points below —108° were obtained in a smaller Beckmann apparatus cooled by liquid air.



Ether–Hydrobromic acid.—The results of experiments with these substances are given in Table I and shown in the diagram. Ether freezes at —118°. The addition of hydrobromic acid lowers the freezing point slightly, then the compound $C_4H_{10}O.HBr$ separates out, and further addition of the acid raises the melting point giving the curve for the equilibrium between vapor, solution and solid ether hydrobromide. At —40° the ether hydrobromide melts. On adding more of the acid the freezing point falls until the eutectic point is reached, where solid hydrobromic acid and compound separate. This occurs at about —115° and the liquid contains 12 per cent. ether. The freezing point then rises with the addition of acid to —86°, the melting point of pure hydrobromic acid.

During these determinations two interesting facts were observed. When more ether than is required to form the compound $C_4H_{10}O.HBr$ is present, the liquid supercools and separates into two layers, the lower containing nearly all the hydrobromic acid. By adding a crystal of the solid compound supercooling may be prevented.

Analyses of the solid separating when over 70 per cent. of acid is present indicate that a compound containing two molecules of acid to one of ether is formed. The percentages are 70.7, 72.5, 67.0, 67.1 and 73.5 acid for compounds made at different times. $C_4H_{10}O.2HBr$ contains 68.7 per cent. acid. The substance obtained melts at —46° but the freezing-point curve shows no break at this temperature.

Hydrobromic acid and ether apparently give two compounds, $C_4H_{10}O$-HBr[1] and $C_4H_{10}O.2HBr$, and in the latter the oxygen may be regarded as hexavalent. An analogous combination was noticed in the case of dimethylpyrone.[2]

TABLE I.

Per cent. acid.	Freezing temperature.	Per cent. acid.	Freezing temperature.
0	—118°	41.3	— 43°
1.60	— 98°	52.5	— 40°
2.18	— 92°	68.7	— 46°
3.00	— 79°	75.8	— 64°
8.20	— 69°	79.8	— 78°
9.80	— 65°	83.5	— 94°
11.5	— 61°	85.7	—100°
13.5	— 58.5°	94.0	— 98°
15.4	— 54°	95.5	— 95°
19.4	— 50.5°	98.0	— 91°
23.4	— 46°	100.0	— 86°
29.9	— 44°		

Ether–Chlorine.—The results for this system are shown in Table II and in the diagram. Ether and chlorine form the compound $C_4H_{10}OCl_2$[3]. The first part of the curve shows the equilibrium of the ether-dichloride with solution and vapor. At —51° the compound melts. Further additions of chlorine lower the melting points to —103°, a quadruple point, where solid chlorine, $C_4H_{10}OCl_2$ solution, and vapor are in equilibrium. Pure chlorine melts at —101.5°.

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[1] Archibald and McIntosh, *J. Chem. Soc.*, **85**, 919 (1904).

[2] THIS JOURNAL, **32**, 542 (1910).

[3] *J. Chem. Soc.*, **87**, 784 (1905).

TABLE II.

Per cent. chlorine.	Freezing temperature.	Per cent. chlorine.	Freezing temperature.
0	—118°	57.3	— 53°
3	— 99°	64.1	— 55°
5	— 89°	71.3	— 60°
9.5	— 80°	73.2	— 63°
18.3	— 71°	80.0	— 74°
19.2	— 70°	83.6	— 85°
23.8	— 65°	86.6	— 95°
30.0	— 58°	88.6	— 97°
34.8	— 55°	93.2	—103°
44.3	— 50°	97.8	—101.5°
46.5	— 49	100.0	—101.5°

Ether–Bromine.—These substances unite to form $C_4H_{10}OBr_2$.[1] The addition of bromine to ether depresses the freezing point of the latter and at —119.5° solid ether and ether-dibromide separate. The ether-dibromide melts at —38° and the addition of bromine raises the melting point, the compound $C_4H_{10}OBr_3$[2] being formed. This substance melts at +23°. On adding more bromine the freezing point falls and at —20°, bromine and the tribromide separate. These results are shown in Table III and in the diagram.

TABLE III.

Per cent. bromine.	Freezing temperature.	Per cent. bromine.	Freezing temperature.
0	—118°	57.3	—45°
2.6	—119°	60.8	—42°
9.6	—119.5°	66.4	—40°
14.4	—107°	68.4	—38°
18.4	— 96°	74.1	—12°
23.0	— 87°	76.4	+23°
24.6	— 82.5	78.6	+20°
29.5	— 75.0°	82.7	+ 0.5°
35.6	— 66°	84.6	—10°
40.8	— 59.5°	87.8	—21°
44.9	— 56°	91.5	—20°
48.6	— 51°	94.0	—11°
51.8	— 48°	100.0	— 7°

Above —40° the measurements are difficult to make with any degree of accuracy. Substitution of the bromine in the ether may begin and I have never succeeded in obtaining the tribromide without several per cent. of hydrobromic acid. The dibromide can be made with less than 1/20 per cent. acid. It may be pointed out that the phenomena[3] observed by Plotnikov and others—conduction of the ether-bromine mix-

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[1] *J. Chem. Soc.*, **87**, 784 (1905).

[2] Schützenberger, *Ann.*, **129**, 50 (1864).

[3] Johnson and McIntosh, THIS JOURNAL, **31**, 1138 (1909).

ture and its action on metals, etc.—are probably due to the hydrobromic acid formed rather than to the ether-bromine compounds.[1]

Further work on similar systems at low temperatures is being done in this laboratory.

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[Contribution from the Laboratory of Soil Fertility Investigations.]

METHOXYL IN SOIL ORGANIC MATTER.[2]

By Edmund C. Shorey and Elbert C. Lathrop.

Received October 13, 1910.

The fact that the quantity of organic matter in different soils varies has been so well established that it is common knowledge. On the other hand the fact that the organic matter of soils varies widely in kind, that two soils may contain the same quantity of organic matter and this material be made up of quite different organic compounds in each case, while quite easily demonstrated, has not received general recognition.

The prevailing ideas regarding humus and humus formation seem to be based on the assumption that the multitude of organic compounds of many types present in the dead vegetation that contributes to the formation of the organic matter of soils is in some mysterious way reduced in the process of decay to a few compounds of the same type. The first step toward showing that this assumption is unwarranted is taken when it can be shown that soil organic matter varies greatly in the kind or types of organic chemical compounds comprising it. This can be shown in a number of ways, but the methods used can be classed under two general heads: first, the isolation of a number of definit· organic compounds of different types; second, the application of group or class reactions that disclose the presence or absence of certain groups of organic compounds.

Under the first head much work has been done and has already been reported.[3] In this work the demonstration of the variability in kind of organic matter has been incidental to the broader investigation of the chemical nature of this material.

In the use of type or group reactions the application may be simply a qualitative one, or where the reaction is of a character to permit it, may be quantitative. A reaction that may be used in this way is the formation of methyl iodide when compounds in which there is a methoxyl group, CH_3O, are treated with concentrated hydriodic acid. The method

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[1] Note.—Carefully dried ether and bromine (75 per cent. Br) had at —30° a resistivity of 1000 ohms; then chemical action commencing the temperature rose and in a few seconds the resistance had fallen to 7 ohms.

[2] Published by permission of the Secretary of Agriculture.

[3] *Bulls.* **53** and **74**, Bureau of Soils, U. S. Dept. Agr. This Journal, **30**, 1295, 1599 (1908); **31**, 116 (1909); **32**, 1674 (1910). *J. Biol. Chem.*, **8**, 381 (1910).