THE SYSTEMS HYDROGEN CHLORIDE—ETHYL ETHER AND HYDROGEN CHLORIDE—ACETONE.

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In 1904, Archibald and McIntosh(1) published the results of an investigation of the compounds produced by the addition of the halogen hydrides to organic substances containing oxygen. They isolated a compound of hydrogen chloride and ether, melting at $-92°$, which had the composition $C_4H_{10}O$–5HCl. This ratio was fixed by two methods. The liquefied acid was "titrated" with ether at the same temperature, and a point was found, corresponding to the ratio of five molecules to one, where the further addition of ether developed very little heat, while before that amount of ether was added, any addition occasioned a considerable heat evolution. By a second method, in which a serious error could hardly be made, the compound was separated, dried at low temperature and analysed. The results showed that the compound corresponded closely to the formula $C_4H_{10}O$–5HCl.

Maass and McIntosh(2) investigated the system ether—hydrogen chloride. They found that the three compounds $C_4H_{10}O$–HCl, 2HCl and 5HCl

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(1) *J. Chem. Soc.*, 85 (1904), 919.

(2) *J. Am. Chem. Soc.*, 35 (1913), 535.

existed, so that this system was more complicated than that of the methyl ether and acid, examined by them and by Baume(1). In 1926 Hirai(2) repeated this work, and concluded that but one compound, $C_4H_{10}O–2HCl$, was formed. As these oxonium compounds have a new interest on account of the development of the electron theory of valence, I have re-examined certain parts of this system. The results show the formation of three compounds mentioned above.

Materials and Apparatus. The ether and acetone were purified and dried by sodium and calcium chloride, respectively. The hydrogen chloride was made by the action of strong sulphuric acid on hydrochloric acid. It was dried by sulphuric acid and phosphoric anhydride.

The apparatus is shown in the sketch. It consisted of a double-walled freezing-point tube, closed by a rubber stopper. This contained a magnetic stirrer and a resistance thermometer. Two glass tubes passed through the stopper; one reaching to the bottom served to introduce the gaseous acid. The solutions were made by weight, all weighings being made at low temperature. We have shown in previous papers that this can be done to 0.1 per cent.

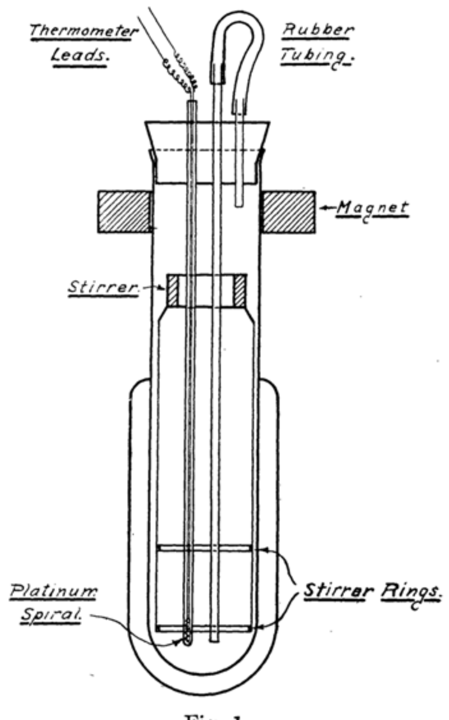

Fig. 1.

A Heraeus platinum-quartz thermometer with a resistance of 25.031 ohms and a Leeds and Northrup bridge were used. The thermometer was tested at the carbon dioxide temperature, at the freezing temperature of acetone (−94.6°), and at the temperature of boiling oxygen. Immediately before or after each series of measurements its resistance at −94.6° or −78.5° was determined.

The solutions were cooled by a bath of carbon dioxide and ether boiling under reduced pressure. It was an easy matter to keep the temperature of the bath within a few degrees of the freezing-point of the solution.

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(1) *Arch. Science physiques*, 33 (1912), 415.

(2) This journal, 1 (1926), 123.

TABLE 1.

Experiment	Mols. per cent. Acid.	Freezing-point.	Experiment	Mols. per cent. Acid.	Freezing-point.
1.	42.5	−102.9°	5.	67.6	−83.2°
	47.3	−100.0		70.0	−84.8
	56.5	−100.4			
			6.	80.5	−99.6
2.	53.2	− 98.9		83.6	−92.9
				85.0	−94.2
3.	50.0	− 98.6			
	68.6	− 83.2	7.	81.5	−96.2
				85.0	−94.2
4.	46.7	−101.3			
	54.2	− 97.9	8.	53.7	−99.5
	65.9	− 82.0		67.6	−82.8
	68.6	− 83.2			
	71.6	− 97.6	9.	66.4	−82.0
5.	50.6	− 99.7	10	84.5	−92.6

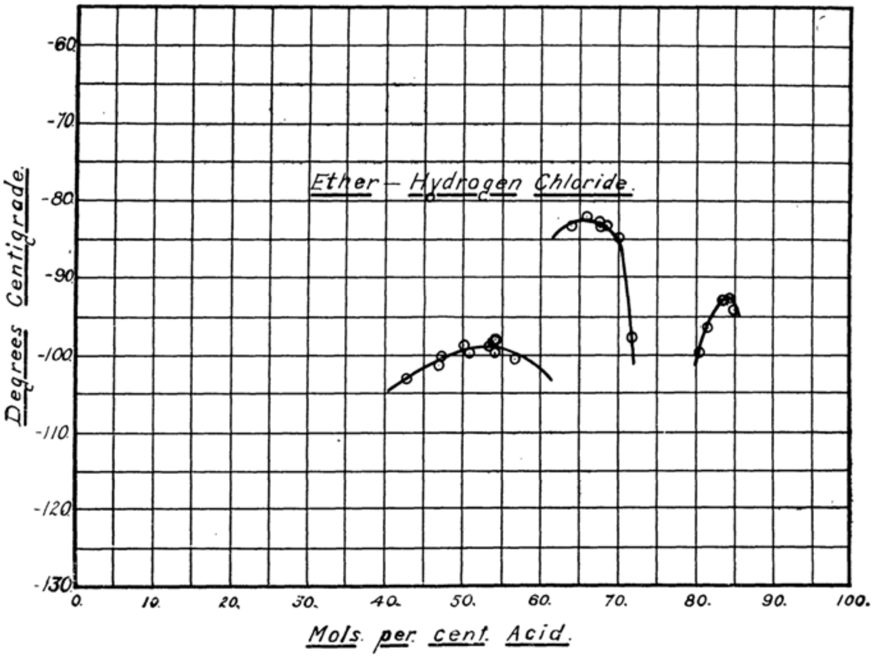

Fig. 2.

The results are shown in Table 1 and on the curve, and indicate the formation of the three compounds found by Maass and McIntosh. The general form of the curves is the same in the two investigations, but the individual points differ rather widely. From the irregularities in my results an experimental error of about two degrees may be assumed.

The difference in our results is due, I think, to Hirai's failure to realize the difficulty of precipitating compounds from the supercooled liquids. Maass and McIntosh(1) say: "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"; and I have repeatedly kept these mixtures at ten degrees below their true freezing-points for five hours at a time, agitating meanwhile with the magnetic stirrer, without precipitation taking place.

It is possible, however, to bring about crystallisation at any temperature below the freezing-point by "inoculating" the solution with a minute amount of the ether-hydrogen chloride or bromide complex introduced by means of a capillary tube. The crystals of the latter are made up of a mixture of $C_4H_{10}O$–HBr and $C_4H_{10}O$–2HBr,(2) and bring about a separation of the one and two hydrogen chloride salts, with a consequent rise in temperature, so that determinations can be made with any desired degree of accuracy. These salts have no influence on the precipitation of the 5HCl compound; that must be brought about by vigorous stirring and low temperature.

The System Acetone—Hydrogen Chloride. Archibald and McIntosh made and analysed a compound containing two molecules of acetone to five of acid. The examination of this system by Hirai yielded only one compound, C_3H_6O–HCl. I have therefore determined a few points on the freezing-point curve, and these show that both compounds are formed. The results are given in Table 2 and are shown on the curve. They are in fair agreement with Hirai's up to sixty mols. per cent. acid.

TABLE 2.

Mols. per cent. Acid.	Freezing-point.	Mols. per cent. Acid.	Freezing-point.
36.5	−91.5°	69.7	−81.2°
47.1	−76.9	71.7	−80.8
54.0	−78.0	74.3	−85.3
57.7	−84.6	53.8	−78.0
63.2	−94.6		

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(1) *J. Am. Chem. Soc.*, loc. cit.

(2) McIntosh, ibid., 33 (1911), 71; Maass and McIntosh. ibid., 34 (1912), 1273.

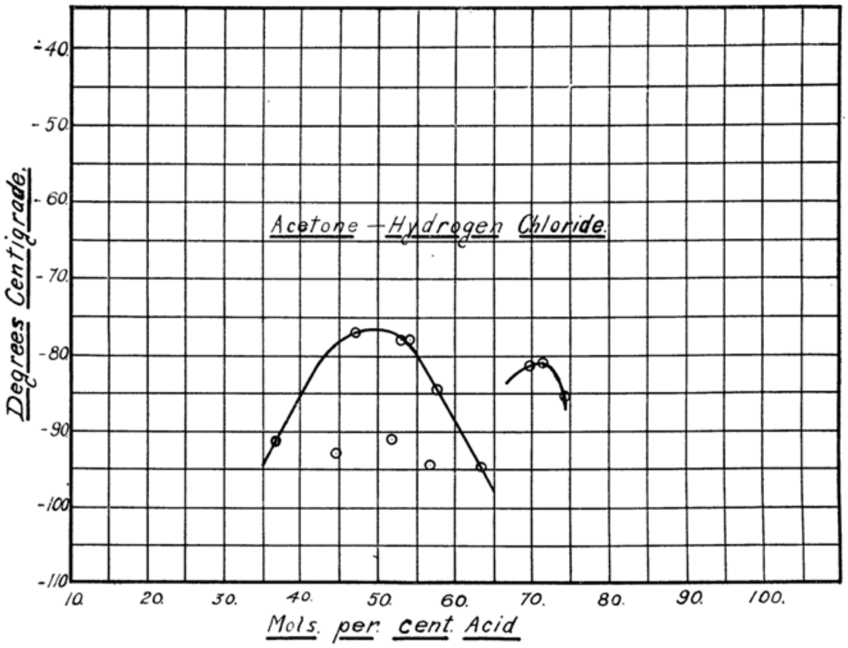

Fig. 3.

What has been said of the ether-hydrogen chloride system applies with equal force to the acetone one. The separation of the first compound takes place on the addition of the acetone-hydrochloric or acetone-hydrobromic complex; the other compound is not precipitated in this way; it is formed by cooling the solution and stirring.

The freezing-point (−79°) given by Hirai for his compound is too low. I have kept the solid crystallized from 50.1 mols. per cent. acid at −78.5° for 20 hours without melting taking place.

On the diagram three points inside the curve are shown. These points were obtained when a chalky precipitate, quite different in appearance from either of the two compounds, separated. On re-melting and repeating the observation the result fell on the curve. This may mean a new compound which separates from the solution as does the heptahydrate of sodium sulphate from a supersaturated solution of the decahydrate when the system is cooled to a fairly low temperature.

Finally, an acetone-hydrogen chloride solution containing for more than sixty mols. per cent. acid does not become viscous if kept only a degree or two below its true freezing-point. If cooled to a low temperature it naturally forms a glass.

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