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.

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SOME NEW REACTIONS WITH THIONYL CHLORIDE.

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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:

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

Sulfuryl chloride boils at about 70°. Considering the temperature at which the liquid contents of the tube distilled, the presence of hexavalent sulfur in the distillate, and the total absence of fumes of free sulfur trioxide when the tube was opened, there is little doubt that the liquid contents of the tube consisted in part of sulfuryl chloride. The solid portion of the contents was found upon analysis to consist of barium chloride and barium sulfate.

Other tubes were then prepared and tested in order to ascertain the relative amounts of chloride and sulfate formed. The results varied greatly. Further study led to the discovery that when a large excess of the reagent is employed, barium sulfate is not formed, the products of the reaction being only barium chloride, sulfuryl chloride and sulfur dioxide. The reaction proceeds according to the equation:

$$BaO_2 + 2SOCl_2 = BaCl_2 + SO_2 + SO_2Cl_2.$$

However, when molecular proportions of barium peroxide and thionyl chloride are used the reaction proceeds in a very different manner, barium sulfate always being formed. This reaction can be represented by the equation:

$$2BaO_2 + 2SOCl_2 = BaCl_2 + BaSO_4 + SO_2Cl_2.$$

By varying the amounts of the reagent, the reaction appears to be a combination of the two, the products obtained being barium chloride, barium sulfate, sulfur dioxide and sulfuryl chloride, with the relative amounts of barium chloride and barium sulfate varying widely.

Barium Oxide.—The lower oxide of barium, BaO, closely resembles the oxides of glucinum, calcium and strontium[1] in its deportment with thionyl chloride, being entirely unattacked by the reagent at 150°. The authors have been unable to obtain a specimen of barium oxide free from peroxide and as a result reaction was found to proceed slightly, but to stop as soon as all barium peroxide had been used. Inasmuch as a large excess of reagent was employed, the products of the reaction with the barium peroxide were barium chloride, sulfuryl chloride and sulfur dioxide, as shown by the equation previously given. A relatively large amount of barium oxide remained unattacked. No trace of barium sulfate was found.

Duplicate tubes were prepared and heated for many hours at temperatures up to 200° but in every case the results were the same—reaction proceeded only until all barium peroxide had been used and upon examination the tubes were found to contain relatively large quantities of barium oxide and thionyl chloride together with small amounts of barium chloride, sulfur dioxide and sulfuryl chloride.

Lead Dioxide.—Lead dioxide was found to react in a manner similar to barium peroxide at a temperature of about 150°. The brown color

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[1] This Journal, April, 1913.

of the oxide soon disappeared with the simultaneous formation of a white powder. When an excess of reagent is employed, the reaction proceeds according to the following equation:

$$PbO_2 + 2SOCl_2 = PbCl_2 + SO_2Cl_2 + SO_2,$$

but when a slight excess of the oxide is used, lead sulfate is also produced, reaction following the equation:

$$2PbO_2 + 2SOCl_2 = PbCl_2 + PbSO_4 + SO_2Cl_2.$$

As in the case of barium peroxide, by varying the amounts of oxide and reagent used, a combination of the two reactions is obtained.

Lead Tetroxide.—Lead tetroxide reacts in much the same manner as lead dioxide, though the proportions of oxide and reagent differ slightly. The reactions proceed according to the equations:

$$Pb_3O_4 + 4SOCl_2 = 3PbCl_2 + 3SO_2 + SO_2Cl_2;$$
$$2Pb_3O_4 + 6SOCl_2 = 5PbCl_2 + PbSO_4 + 4SO_2 + SO_2Cl_2,$$

depending entirely upon the relative amounts of oxide and reagent employed.

Sulfur dioxide is always one of the products of the reaction of thionyl chloride on lead tetroxide, the reaction proceeding as with a mixture of lead dioxide and lead monoxide.

Manganese Dioxide.—Manganese dioxide reacts with thionyl chloride at 150° in a manner similar to lead dioxide, reaction taking place according to one or the other of the following equations, depending upon the relative amounts of material used:

$$MnO_2 + 2SOCl_2 = MnCl_2 + SO_2 + SO_2Cl_2,$$
$$2MnO_2 + 2SOCl_2 = MnCl_2 + MnSO_4 + SO_2Cl_2.$$

As in the previously described cases, a combination of the two reactions may be obtained by varying the amounts of oxide and reagent.

Sodium Peroxide.—Sodium peroxide, in contrast to the other higher oxides studied, reacts with thionyl chloride at the ordinary temperature with considerable violence. Much heat is liberated and flame is produced when the two substances are brought together. The reaction was carried out by adding the peroxide in very small quantities to the thionyl chloride contained in a long glass tube. When sufficient peroxide had been added, the supernatant liquid was distilled off, decomposed by water and tested with barium chloride. An insoluble precipitate of barium sulfate showed that sulfuryl chloride is produced by the reaction. The solid matter in the tube was found to consist of a mixture of sodium chloride and sodium sulfate. Reaction proceeds according to the equation:

$$2Na_2O_2 + 2SOCl_2 = 2NaCl + Na_2SO_4 + SO_2Cl_2,$$

or, when a very small amount of peroxide is employed, according to the equation:

$$Na_2O_2 + 2SOCl_2 = 2NaCl + SO_2 + SO_2Cl_2.$$

From these experiments the authors conclude that sulfuryl chloride is always one of the products of the action of thionyl chloride on a peroxide, and that a sulfate of the metal is always formed when the reagent is not present in decided excess.

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CONTRIBUTION TO THE CHEMISTRY OF GOLD.

BY VICTOR LENHER.

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The general methods by which derivatives of the aurous type of gold may be prepared are limited. Through the work of Krüss,[1] Thomsen,[2] Lengfeld[3] and Diemer, it has been established that when auric chloride is submitted to a temperature of 190°–200° it loses chlorine and the yellow-white aurous salt is formed. Aurous chloride thus prepared is unstable in character, the action of light or elevation of temperature causes it to pass to metallic gold, while the action of water causes hydrolysis with the production of metallic gold along with the trichloride. Aurous bromide is formed by the same general method of procedure as the chloride, and its properties are naturally quite similar. Aurous iodide is formed as a yellow-green precipitate when a soluble iodide is added to a solution of auric chloride, iodine being liberated at the same time. This simultaneous liberation of iodine with the formation of aurous iodide has been made available by Gooch and Moseley[4] as a volumetric method for the determination of gold, the liberated iodine being titrated with sodium thiosulfate.

One of the more general characteristics of the aurous type of derivatives is their instability. Their general tendency is to undergo with ease further reduction to metallic gold.

It has appeared obvious that should auric chloride be capable of losing two atoms of chlorine through the agency of heat and be capable of passing to the aurous state, surely some of the many available reducing agents should be capable of forming a definit aurous chloride. Repeated experiments have been made with gold trichloride and its behavior toward heat, and the best that can be said is that gold monochloride owes its existence to-day to a temperature control which gives a yellow-white solid whose analysis shows approximately the ratio of one atom of chlorine to one of gold and to the characteristic hydrolysis by water into gold and auric chloride.

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[1] *Ann.*, 237, 274 (1887).

[2] *J. prakt. Chem.*, [2] 13, 341 (1876).

[3] *Amer. Chem. J.*, 26, 324 (1901).

[4] *Amer. J. Sci.*, [4] 8, 261 (1899).