

samples of the two intermediates were sealed up with mercury in glass capillary tubes and heated to their approximate critical temperatures as estimated by the "three-halves" rule. The mercury

was badly attacked in both cases, so that the critical constants could not be determined.

### Summary

The fluorination of phosphoryl tribromide with antimony trifluoride yields three products, a gas, phosphoryl trifluoride, first described by Moissan, and two new, stable, volatile liquids, phosphoryl monobromodifluoride and phosphoryl dibromomonofluoride. All three have been isolated and purified. The boiling points, vapor pressure data, gaseous and liquid densities of the two phosphoryl bromofluorides have been determined and recorded along with some of their chemical properties.

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TABLE III  
PHYSICAL PROPERTIES

	POF <sub>2</sub> Br	POFBr <sub>2</sub>
Boiling point, <sup>a</sup> °C.	30.5 ± 0.1	110.1 ± 0.1
Freezing point, °C.	-84.8 ± .2	-117.2 ± .2
Liquid density (at 0°)	2.099	2.568
Gas density observed	166	
Theoretical	165	
Heat of vapn., <sup>b</sup> cal.	7093	7518
Trouton's constant	23.4	19.6

<sup>a</sup> From a plot of the vapor pressure data. <sup>b</sup> Calculated by the Clausius-Clapeyron equation.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF BROWN UNIVERSITY AND OF THE UNIVERSITY OF ILLINOIS]

## (I) The Reaction of Gallium with Perchloric Acid and (II) the Preparation and Properties of Gallium Perchlorate Hydrates

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### I. Reaction of Gallium with Perchloric Acid

Metallic gallium dissolves very slowly in the common mineral acids. Sebba and Pugh<sup>1</sup> reported recently that concentrated nitric acid was the most rapid reagent but, when it was kept near the boiling point, even it dissolved only 5 g. of the metal in ten hours. The rate was somewhat increased by alternately heating and cooling the mixture. They found, in addition, that because of the pronounced passivity of gallium, it was possible to free it from many metallic impurities with little loss of gallium by allowing it to remain in contact with concentrated nitric acid.

Perchloric acid and mixtures of perchloric acid with other acids have been used to dissolve many ordinarily very resistant alloys, particularly "stainless steels."<sup>2</sup> These same reagents have now been shown to dissolve gallium more rapidly than any used hitherto.

### Experimental

**Reaction of Gallium with Perchloric Acid.**—A small piece of gallium (0.5 g.) was heated with 20 ml. of per-

(1) Sebba and Pugh, *J. Chem. Soc.*, 1373 (1937). For a more complete survey of the literature concerning the reaction of gallium with various reagents, see Gmelin's "Handbuch der anorganischen Chemie," 8th ed., no. 36, 1936, pp. 42-45.

(2) Smith and Getz, *Ind. Eng. Chem., Anal. Ed.*, 9, 378 (1937); cf. G. F. Smith, "Mixed Perchloric, Sulfuric, and Phosphoric Acids and their Application in Analysis," G. F. Smith Chemical Co., Columbus, Ohio, 1935.

chloric acid (72%) in an Erlenmeyer flask (250 ml.) equipped with a Smith refluxing head.<sup>2</sup> A vigorous reaction took place and the metal was dissolved completely within fifteen minutes. In another experiment 5 g. of gallium was dissolved in 60 ml. of the acid within an hour. The gallium perchlorate formed is moderately soluble in the hot concentrated acid, but as soon as the mixture is cooled slightly, hexa-aquo gallium perchlorate separates in the form of coarse, white crystals. The remaining acid, recovered by filtration through a sintered-glass funnel, contains almost no gallium.

**Reaction of Gallium with Mixed Perchloric-Sulfuric Acids.**—The reaction of gallium with a mixture containing two-thirds sulfuric acid (98%) and one-third perchloric acid (72%) was found to be more rapid than that with perchloric acid alone. Gas evolution started as soon as the cold acid mixture came in contact with the metal and proceeded very rapidly when it was warmed. Five grams of gallium was dissolved in 60 ml. of the mixture in about one-half hour. The reaction product was not so soluble in the mixed acids as in perchloric acid alone, however, and separated immediately as a finely divided, white precipitate. Its presence did not interfere with the progress of the reaction, and after the metal had disappeared the excess perchloric acid was removed by distillation with no "bumping" until sulfur trioxide fumes began to escape. At this point, "bumping" became severe. By dissolving the cooled mixture in water, a clear solution of gallium sulfate, containing excess sulfuric acid, was prepared. The entire process was accomplished in less than an hour.

**Reaction of Gallium (III) Oxide with Perchloric Acid.**—The soluble form of gallium oxide was found to dissolve readily in perchloric acid, but the insoluble form did not

react. The latter dissolves fairly rapidly in hot hydrochloric acid, however, and after the mixture has become clear, the excess hydrogen chloride may be removed by heating with perchloric acid. Hexa-aquo gallium perchlorate separates when the solution is cooled.

## II. Preparation of Gallium Perchlorate Hydrates

Aluminum perchlorate forms crystalline compounds containing 15, 12, 9 and 6 moles of water. It has been reported that a basic aluminum perchlorate,  $2\text{Al}(\text{ClO}_4)_3 \cdot \text{Al}_2\text{O}_3$ , is formed when the nonahydrate is heated rapidly.<sup>3</sup> With indium, the only perchlorate which has been prepared has the formula  $\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$ .<sup>4</sup> It has now been found that gallium perchlorate is stable only when extensively hydrated. The following hydrates have been identified:  $\text{Ga}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ga}(\text{ClO}_4)_3 \cdot 9\frac{1}{2}\text{H}_2\text{O}$ . Basic gallium perchlorates of indeterminate composition are formed when the hydrated crystals are heated.

### Experimental

**Preparation of Hexa-aquo Gallium Perchlorate.**—Ten grams of pure gallium, or an equivalent amount of the soluble form of gallium sesquioxide, is allowed to react with excess perchloric acid (72%) as described in a previous section. If the volume of acid used is larger than 150 ml., the product is entirely soluble at the boiling point of the mixture (200°) and the observation of the disappearance of the last small globules of the metal is facilitated. If less acid is used, the gallium perchlorate formed separates as a coarsely crystalline precipitate, but it does not interfere with the course of the reaction. Heating is continued after the metal has all reacted to remove water and the perchloric acid reduction products ( $\text{Cl}_2$ , etc.). The characteristic fumes of constant boiling perchloric acid soon appear, and heating is discontinued. When the mixture has cooled, the product may be collected by suction filtration on a sintered glass Büchner funnel and pressed dry with a glass or porcelain spatula. (The small amount of gallium in the filtrate is recovered separately.) The entire process does not require much more than an hour.

NOTE.—The moist crystals must not be allowed to come in contact with any organic material such as filter paper or a horn spatula. Because of the removal of water, due to the formation of hydrated crystals, the perchloric acid adhering to the product is more highly concentrated than 72%.

The remaining excess acid may be removed from the crystals by heating them *in vacuo* at 125° for about an hour in a glass tube, sealed at one end and large enough to hold the porcelain boat containing the product, and exhausted through a glass connection held in a rubber stopper. The tube may be heated conveniently in a

thermostated electric drying oven. It should be long enough (2 ft., 61 cm.) to afford an opportunity for the perchloric acid which is volatilized to condense and cool before it reaches the rubber stopper, and it is desirable to expand a section of the tube to provide a bulb into which the condensate may run. If a mechanical pump is used, it should be protected from the acid fumes by a trap containing solid sodium hydroxide.

The hexa-aquo gallium perchlorate thus prepared is a dry, free running powder. Large crystals of hexa-aquo gallium perchlorate may be prepared by slow evaporation, over concentrated sulfuric acid in a vacuum desiccator, of an aqueous solution of gallium perchlorate which contains excess perchloric acid.

**Analysis.**—Since the hydrates of gallium perchlorate were found to be very soluble in alcohol, it was possible to carry out analyses on a single sample for both the perchlorate ion and the gallium, and by difference to compute the percentage of water. Potassium perchlorate, precipitated by the addition of an excess of an alcohol solution of potassium thiocyanate, was weighed in a sintered glass filtering crucible, after having been dried for an hour at 120°. Water was added to the filtrate and after the alcohol had been removed by distillation, the gallium was precipitated by means of tannin.<sup>5</sup>

**Anal.** Calcd. for  $\text{Ga}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ : Ga, 14.64;  $\text{ClO}_4$ , 62.65. Found: (A. Crystals heated *in vacuo* for six hours at 120°), Ga, 14.8 (av.);  $\text{ClO}_4$ , 62.5 (av.). (B. Large crystals from perchloric acid solution, dried quickly on filter paper), Ga, 14.24;  $\text{ClO}_4$ , 61.8, 61.7.

**Properties of Hexa-aquo Gallium Perchlorate.**—After it has been freed of excess perchloric acid, the hexa-aquo complex is a dry crystalline meal. It is very deliquescent, extremely soluble in water, forming a clear solution, and very soluble in alcohol and glacial acetic acid. The crystals which are deposited by slow evaporation from a perchloric acid solution are large, regular octahedra. In polarized light they are seen to be isotropic and may be classified as *cubic*. At atmospheric pressure, the hexa-aquo complex decomposes at 175° and *in vacuo* at 155°, yielding gaseous products and basic gallium perchlorate residues of indefinite composition. At still higher temperatures, it is finally converted to the insoluble form of gallium oxide.

Since hexa-aquo gallium perchlorate is readily prepared from either the metal or the oxide and readily freed from the excess acid, it serves admirably as the starting material for the synthesis of other gallium compounds. Conversely, Willard and Fogg<sup>6</sup> electrolyzed a solution of gallium perchlorate for the preparation of the pure metal.

**Preparation and Properties of Gallium Perchlorate,  $9\frac{1}{2}$  Hydrate.**—A concentrated aqueous solution of hexa-aquo gallium perchlorate, containing only a slight contamination of free perchloric acid, was allowed to evaporate in a vacuum desiccator over concentrated sulfuric acid. The very large crystals, 3 cm.  $\times$  5 mm.  $\times$  2 mm., which formed were shown to contain 9.5 moles of water by the analytical method previously described.

(3) Gmelin's "Handbuch der anorganischen Chemie," 8th ed., no. 35, Part B, 1934, p. 217.

(4) Mathers and Schuederberg, *THIS JOURNAL*, **30**, 212 (1908).

(5) Moser and Brukl, *Monatsh.*, **51**, 325 (1929); Sebba and Pugh, *Trans. Roy. Soc. S. Africa*, **25**, 392 (1938).

(6) Fogg, *Trans. Electrochem. Soc.*, **66**, 107 (1934); Willard and Fogg, *THIS JOURNAL*, **59**, 1197 (1937).

*Anal.* Calcd. for  $\text{Ga}(\text{ClO}_4)_3 \cdot 9\frac{1}{2}\text{H}_2\text{O}$ : Ga, 12.93;  $\text{ClO}_4$ , 55.33. Found: Ga, 12.92 (av.);  $\text{ClO}_4$ , 55.63 (av.).

A known weight of the  $9\frac{1}{2}$ -hydrate, in the form of a single, large, clear crystal still slightly moist with mother liquor and contained in an uncovered wide-form weighing bottle, was heated at  $120^\circ$  at atmospheric pressure. After thirty-six hours, the loss in weight corresponded to the loss of about one mole of water, and although the crystal had become translucent and somewhat deformed, it had not lost completely its original contours. The sample continued to lose water only very slowly. After a few days, the weighing bottle was transferred to a vacuum desiccator and at the end of six weeks the loss in weight indicated a conversion of the original material to the hexa-aquo derivative. The composition of the product was confirmed by analysis.

*Anal.* Calcd. for  $\text{Ga}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ : Ga, 14.64;  $\text{ClO}_4$ , 62.65. Found: Ga, 14.80;  $\text{ClO}_4$ , 62.32.

The behavior of crystal fragments when heated in small melting point tubes was quite different. Under these circumstances the  $9\frac{1}{2}$ -hydrate underwent a transition, at about  $80^\circ$ , to a mixture of the hexa-aquo complex in equilibrium with a small amount of saturated solution. Evidently, when it is heated in an open vessel, water evaporates rapidly enough to coat the surface with an adherent film sufficiently strong to permit the entire mass to retain substantially its original shape.

The  $9\frac{1}{2}$ -hydrate usually crystallized in large, colorless, transparent, pseudo-hexagonal prisms terminated in clinodomes, but occasionally it appears as a mass of fine needles. Both forms are monoclinic and exhibit parallel extinction in the prismatic region, and seem to be identical except for size. The substance is very soluble in water, alcohol and glacial acetic acid and is very deliquescent.

**Thermal Decomposition of Hexa-aquo Gallium Perchlorate.**—When hexa-aquo gallium perchlorate is heated in an evacuated Pyrex tube in an electric furnace, it begins to undergo decomposition at about  $155^\circ$ . Above that temperature it crumbles and some particles are swept out of the container in the stream of evolved gases, giving the appearance of sublimation. This product, however, is not volatile and upon analysis is seen to be a basic gallium perchlorate. Analyses of the residues in the container show the composition to be variable and dependent upon the duration of heating and the temperature attained. Some of the products corresponded fairly closely to the formulas  $2\text{Ga}(\text{ClO}_4)_3 \cdot 3\text{Ga}_2\text{O}_3$ , and  $3\text{Ga}_2\text{O}_3 \cdot \text{Ga}(\text{ClO}_4)_3$ . Others showed intermediate compositions. Only once, when the heating was not prolonged, did the analysis of the residual material correspond at all closely to that of anhydrous gallium perchlorate,  $\text{Ga}(\text{ClO}_4)_3$ .

Due to the insolubility of the basic perchlorates in alcohol, the method of analysis used with the hydrated perchlorates could not be followed. Attempts were made to determine the amount of perchlorate ion by precipitating methylene blue perchlorate<sup>7</sup> from a solution of the basic salt in dilute acids, but the results were unreliable. The precipitate was hard to filter and analyses of aliquot parts of a solution differed by as much as 50% due to incomplete precipitation. It was found practicable, however, to prepare an alcoholic solution of the sample by moistening it with glacial acetic acid and allowing it to stand for two hours or more to convert it to a soluble acetate. When alcohol was then added, a clear solution usually resulted. Potassium perchlorate was precipitated and weighed, and the gallium was determined as gallium oxide after precipitation by means of tannin as before.

A sample of a basic perchlorate, the formula of which corresponded fairly closely to  $3\text{Ga}_2\text{O}_3 \cdot \text{Ga}(\text{ClO}_4)_3$ , was heated in a covered porcelain crucible over a Meker burner. The product was the insoluble form of gallium oxide.

*Anal.* Calcd. for  $2[3\text{Ga}_2\text{O}_3 \cdot \text{Ga}(\text{ClO}_4)_3] \rightarrow 7\text{Ga}_2\text{O}_3$ ; loss, 29.5%. Found: 32.7%.

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### Summary

1. Gallium has been found to dissolve rapidly in hot concentrated perchloric acid and in perchloric-sulfuric acid mixtures.
2. Two hydrates of gallium perchlorate, containing 6 and 9.5 molecules of water of crystallization, have been prepared and characterized.
3. The conditions of stability of the hydrates have been investigated and their conversion at elevated temperatures to basic perchlorates of indefinite composition and finally to the insoluble form of gallium oxide has been established.

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(7) Atack, *J. Soc. Dyers and Col.*, Jan., Sept. and Oct., 1913; *Can. Chem. Metallurgy*, 9, 201 (1925); Hofmann, Hartmann and Hofmann, *Ber.*, 58, 2748 (1925); *Z. anal. Chem.*, 69, 305 (1926); Bolliger, *ibid.*, 94, 403 (1933).