values for the electromotive force were obtainable. The extrapolated values of the transference number used in the calculation of the limiting slope are listed in the first row of the table.

Summary

1. Electromotive forces of the cells Ag–AgCl/HCl (m), dioxane (X), $H_2O(Y)$/HCl(r), dioxane (X), $H_2O(Y)$/AgCl–Ag have been obtained for 0, 20, 45, 70 and 82% dioxane solutions at 5° intervals from 0 to 50° and from 0.005 to 3.0 M acid concentration.

2. The cation transference number has been calculated over these ranges of temperature and concentration from these results and previous measurements of the cells without liquid junction.

3. The limiting transference number has been determined by extrapolation for all the solutions over the entire temperature range.

4. Agreement with the limiting law of the Onsager conductance theory was observed in the water, 20, 45 and 70% dioxane–water mixtures.

5. Results obtained with the mixtures containing 82% dioxane were less accurate. They have a value, however, since no transference number data in media of as low a dielectric constant ($D_{25} = 9.57$) are available.

NEW HAVEN, CONN.   RECEIVED AUGUST 31, 1939

Phosphoryl Bromofluorides

BY HAROLD SIMMONS BOOTH AND CHARLES GEORGE SEEGMILLER[1]

It has been found in this Laboratory that phosphoryl trichloride can be fluorinated stepwise to yield phosphoryl chlorofluorides[2a] by means of antimony trifluoride with antimony pentachloride as catalyst, and that phosphorus tribromide likewise can be fluorinated stepwise by means of antimony trifluoride but with bromine as the catalyst.[2b]

While the phosphoryl chlorofluorides were quite stable, the compounds $PBrF_2$ and PBr_2F decomposed on standing to PF_3 and PBr_3. Hence it was of interest to learn whether phosphoryl bromide could be similarly fluorinated stepwise and whether the fluorobromides so produced were stable.

Experimental

Phosphoryl tribromide[3] was prepared by the reaction between phosphorus pentabromide and phosphorus pentoxide: $P_2O_5 + 3PBr_5 = 5POBr_3$. The phosphoryl tribromide was fluorinated at a pressure of 25 to 50 mm. by the slow addition of sublimed antimony trifluoride[4] in the generator as described by Booth and Bozarth.[5] During the early stages, the reaction was vigorous at 60°,

but in its later stages it became quite slow, so that it was found advantageous to raise the temperature gradually to 100°. It was unnecessary to add a catalyst, perhaps due to traces of bromine left in the phosphoryl tribromide.

The product consisted of about 60% phosphoryl trifluoride, 10% phosphoryl monobromodifluoride, and 30% phosphoryl dibromomonofluoride. The products were separated and purified and their physical constants established, as described by Booth and Bozarth.[6] It was found in the case of the $POFBr_2$ and POF_2Br that an ice-salt mixture made a satisfactory refrigerant for the acetone which was circulated by an automatically actuated centrifugal pump through the fractionating column head.

Analysis.—The phosphoryl trifluoride was established by approximate boiling points obtained from a thermocouple in the fractionating column head, by molecular weight determinations by a gas density balance,[6] and by chemical analysis for phosphorus.

Samples of the phosphoryl bromofluorides were condensed in glass bulbs connected to the apparatus by conical joints as previously described[2a] and absorbed in an excess of potassium hydroxide. They reacted energetically with the solution on warming and were completely dissolved. The solution was then heated on a steam-bath for fifty hours to ensure completion of the reaction. Bromine was determined gravimetrically as silver bromide, and phosphorus

(1) From a portion of a thesis submitted by Charles George Seegmiller in partial fulfilment of the requirements of the degree of Doctor of Philosophy in Chemistry to the Graduate School of Western Reserve University, May, 1939.

(2) (a) Booth and Dutton, THIS JOURNAL, **61**, 2937 (1939); (b) Booth and Frary, *ibid.*, **61**, 2934 (1939).

(3) See "Inorganic Syntheses," Vol. II, for details of this preparation.

(4) Kindly furnished by the Harshaw Chemical Company, Cleveland, Ohio.

(5) Booth and Bozarth, THIS JOURNAL, **61**, 2927 (1939).

TABLE I

ANALYSES

| | Phosphorus | | Bromine | |
	Calcd.	Exptl.	Calcd.	Exptl.
POF_2Br	18.81	18.81	48.45	48.51
		18.67		48.45
$POFBr_2$	13.73	13.47	70.76	70.54
		13.70		70.85

(6) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

by precipitation as the phosphomolybdate and direct weighing as such. One set of samples was reprecipitated as magnesium ammonium phosphate and ignited to the pyrophosphate, and was found to be in good agreement with the above method.

Physical Properties.—The determination of the vapor pressure of phosphoryl monobromodifluoride was made by direct observation of the vapor pressure of the liquid held in a small glass bulb immersed in a thermostat, in the manner described by Booth and Bozarth.[6] Two separate samples, A and B, were run; as an extra check, a small portion was distilled out of each sample after a set of readings had been taken, at a pressure different from the pressure of the original distillation of the substance, and a few more points then determined. The temperature was observed with a Leeds and Northrup resistance thermometer calibrated by the United States Bureau of Standards.

The vapor pressure data for phosphoryl dibromomonofluoride, which is a liquid at room temperature, were determined in an isoteniscope,[7] as was that small portion of the curve for phosphoryl monobromodifluoride which was run above room temperatures (Sample C). Here again, for the phosphoryl dibromomonofluoride, two separate samples A and B were run, and small portions were pumped off and more points run as a further check of purity.

The freezing points of phosphoryl dibromomonofluoride and phosphoryl monobromodifluoride were observed in the glass melting point apparatus which is standard in this Laboratory. The rate of cooling was observed on the Micromax recording potentiometer actuated by a three-junction thermocouple which had been calibrated against a platinum resistance thermometer standardized by the United States Bureau of Standards. The freezing points obtained were sharp and easily reproducible. Both compounds showed supercooling under favorable experimental conditions, sometimes as much as 15°.

The liquid density of the phosphoryl bromofluorides at 0° was determined using a pycnometer as described by Booth and Herrmann.[8]

Discussion

Phosphoryl tribromide was found to yield the expected intermediate fluorination products as well as phosphoryl trifluoride. No catalyst was found to be necessary, possibly due to traces of bromine in the phosphoryl tribromide, although Schumb and Gamble[9] found a catalyst was unnecessary in the fluorination of SiBr$_4$ by SbF$_3$. No tendency toward decomposition of the intermediate compounds to the completely brominated and completely fluorinated end-products was observed at any temperature used, in which the phosphoryl bromofluorides resemble the phosphoryl chlorofluorides and not the fluorobromophosphines.

(7) Booth, Elsey and Burchfield, THIS JOURNAL, **57**, 2064 (1935).
(8) Booth and Herrmann, ibid., **58**, 63 (1936).
(9) Schumb and Gamble, THIS JOURNAL, **58**, 994 (1936).

TABLE II

VAPOR PRESSURE OF POFBr$_2$

$$\log p = (-1642.9/T) + 7.1687$$

	Temp., °C.	Obsd.[b]	Calcd.[c]	Deviation, mm. Hg
A	27.0	51.8	49.2	− 2.6
A[a]	40.0	78.7	83.2	4.5
B	43.6	96.6	99.9	3.3
A	47.3	107.6	109.3	1.7
A	59.6	165.4	169.4	4.0
B	62.8	191.3	188.9	− 2.4
A[a]	66.6	212.2	214.4	2.2
B	73.1	261.0	263.8	2.8
A[a]	75.1	285.9	280.9	− 5.0
B	81.0	338.8	337.3	− 1.5
A	85.4	372.5	384.5	12.0
B[a]	90.7	453.4	447.8	− 5.6
A	96.8	527.7	532.0	4.3
A	102.4	612.3	619.5	7.2
B	103.8	653.6	643.1	−10.5
B[a]	107.0	715.4	714.7	1.5
A	109.1	736.8	739.5	2.7
B	110.2	769.2	760.7	− 8.5
A	111.5	787.6	786.5	− 1.1

VAPOR PRESSURE OF POF$_2$Br

$$\log p = \frac{-1550.0}{T} + 7.9662$$

A	−53.1	8	8.3	0.3
B	−36.5	25	25.8	0.8
A	−34.6	29	29.2	− 0.2
A	−30.3	40	38.0	− 2.0
B[a]	−26.7	47	47.6	0.6
A	−22.1	63	61.3	− 1.7
B	−16.4	87	84.3	− 2.7
B[a]	−12.1	107	105.9	− 1.1
B	− 9.3	125	122.3	− 2.7
A	0.7	206	201.0	− 5.0
B[a]	3.6	233	230.3	− 2.7
A	6.5	270	263.1	− 6.9
B[a]	10.2	314	311.5	− 2.5
A	12.6	353	346.3	− 6.7
B	16.4	414	408.6	− 5.4
C	26.4	626	616.5	− 9.5
C	30.7	717	729.0	12.0
C[a]	31.7	751	758.0	7.0
C	33.2	791	802.5	11.5

[a] Indicates check run after part was distilled out.
[b] Observed pressures have been corrected to 0° and standard gravity according to the "International Critical Tables." [c] Calculated values were determined by the use of the above equations.

The properties of the phosphoryl bromofluorides lie between those of the tribromide and the trifluoride. When pure, both phosphoryl bromofluorides are colorless in all states. They hydrolyze and fume in moist air, and react violently with water. They attack nichrome wire only slightly or not at all. In order to investigate the possibility of determining critical constants,

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

TABLE III

PHYSICAL PROPERTIES

	POF₂Br	POFBr₂
Boiling point,[a] °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.,[b] cal.	7093	7518
Trouton's constant	23.4	19.6

[a] From a plot of the vapor pressure data.   [b] Calculated by the Clausius–Clapeyron equation.

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.

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

BY LAURENCE S. FOSTER

I. Reaction of Gallium with Perchloric Acid

Metallic gallium dissolves very slowly in the common mineral acids. Sebba and Pugh[1] 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."[2] 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.[2] 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