them and probably represent the best values so far obtained. It is improbable that the value for the water solubility should be less than that obtained in this research. The water had a conductivity of 2×10^{-6} mhos and a *p*H of approximately 6.8. It was boiled to remove oxygen and carbon dioxide and stored under nitrogen. The chance for the presence of extraneous hydrogen ions in the samples was reduced to a minimum. On the other hand, the chance for the presence of hydroxyl ions was probably greater for the samples of manganese hydroxide were precipitated in alkaline solutions and washed with conductivity water. Of necessity the absence of chloride ions was used as an indirect test for the removal of the last traces of hydroxyl ions. A small amount of extraneous hydroxyl ions would, by common ion effect, greatly reduce the solubility of manganese hydroxide (see Fig. 2). The value of the water solubility obtained in this research seems to us to be the most probable one, not only due to the care observed in the preparation of the samples, but also to the fact that the water solubility values obtained from different preparations of manganese hydroxide are in good agreement (see Table I).

The Equilibrium in Alkaline Solutions.—If manganese hydroxide is a strong base then we may expect its hydrogen ion dissociation to be very slight, particularly the second dissociation. Unfortunately, the solubility is so slight in the range where it is possible to calculate these acid dissociation values that no data were obtained. However, the constant for Equation 4 has been evaluated through the range $m_{NaOH} = 1.0$ to 4.0 (see Table III). The variation in the value of K_4 through this range is from 3.8×10^{-5} to 6.6×10^{-5}. Using the value of $K_4 = 1 \times 10^{-5}$ as the most probable value (obtained by extrapolation of a plot of K_4 *vs.* m_{NaOH} to $m_{NaOH} = 0$) gives the value of $\Delta F^0_{298} = 7000$ cal. This makes possible the evaluation of the acid dissociation constant, K_7, for the reaction represented by Equation 7

$$Mn(OH)_2(s) = H^+ + HMnO_2^- \qquad (7)$$
$$K_7 = K_4 K_w / a_{H_2O} = 1 \times 10^{-19}$$

Acknowledgment.—We wish to thank Professors W. Brode and W. MacNevin for aid in the analyses of these solutions.

Summary

The solubility of manganese hydroxide has been determined in water, in dilute hydrochloric acid and in sodium hydroxide at 25 ± 0.02°. The data indicate that manganese hydroxide is a strong base. The main reaction taking place in acid solution is represented by Equation (3)

$$Mn(OH)_2(s) + 2H^+ = Mn^{++} + 2H_2O \qquad (3)$$

and in basic solution by Equation (4)

$$Mn(OH)_2(s) + OH^- = HMnO_2^- + H_2O \qquad (4)$$

The value of the solubility product calculated from Equation (3) is 1.6×10^{-13}; the value obtained from the water solubility data is 2.8×10^{-13}. The value of K_4 is 1×10^{-5} which gives the value for the ion product of the acidic dissociation, $Mn(OH)_2 = H^+ + HMnO_2^-$, of 1×10^{-19}.

COLUMBUS, OHIO RECEIVED MARCH 5, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

Phosphorus–Halogen Compounds from Phosphorus Pentoxide and Halides. Properties of Phosphorus Trifluoride and Phosphorus Oxyfluoride*

BY GRADY TARBUTTON, E. P. EGAN, JR., AND S. G. FRARY

The reaction of non-volatile halides with phosphorus pentoxide has been mentioned in the literature, but the conditions of the experiments and the properties of the products formed have not been thoroughly investigated. Schultze[1] prepared phosphoryl trifluoride by the action of phosphorus pentoxide on a fluoride, and Thorpe and Hambly[2] obtained the same compound from phosphorus pentoxide and cryolite. Lucas and Ewing,[3] however, reported that phosphorus pentafluoride, not phosphoryl trifluoride, was obtained by heating a mixture of phosphorus pentoxide and calcium fluoride. Curtis, Copson and Abrams[4] stated that the reaction between phosphorus pentoxide and sodium chloride yielded volatile phosphorus chlorides and that this type of reac-

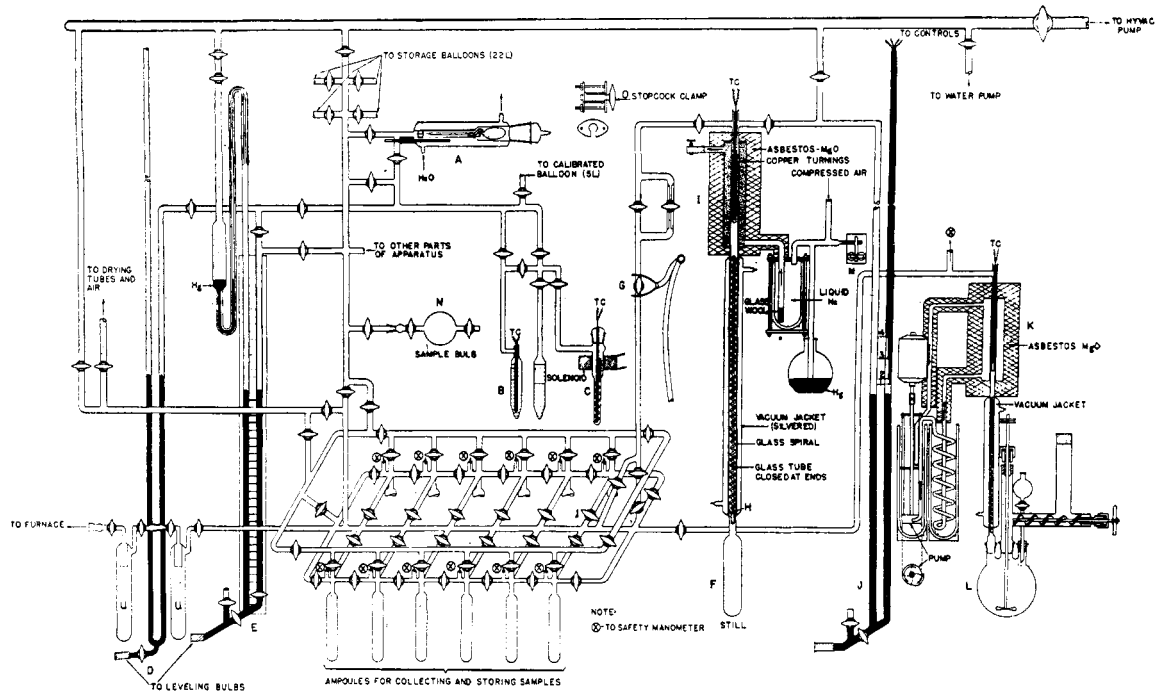
* Original manuscript received April 22, 1940.

(1) H. Schultze, *J. prakt. Chem.*, (2) **21**, 443 (1880).

(2) T. E. Thorpe and J. F. Hambly, *J. Chem. Soc.*, **55**, 759 (1889).

(3) H. J. Lucas and F. J. Ewing, THIS JOURNAL, **49**, 1270 (1927).

(4) H. A. Curtis, R. L. Copson and A. J. Abrams, *Chem. and Met. Eng.*, **44**, No. 3, 140–142 (1937).



Gas generation and purification apparatus.

Fig. 1.—A, gas density balance; B, graduated ampoule for measuring liquid volume; C, melting point-vapor pressure cell; D, control and indicating manometer; E, absolute manometer; G, automatic stopcock; H, dropper for return of refluxed liquid; I, liquid air-cooled still head; J, control manometer; K, CO_2–acetone-cooled still head or generator head; L, gas generator; M, magnetic valve; TC, thermocouples; U, condensation traps.

tion should be a general one. They also pointed out that most of the fluorine in rock phosphate is liberated in the process of making crude calcium metaphosphate (metaphos) by treating rock phosphate with phosphorus pentoxide at a high temperature.

In the present paper are reported studies of the reaction of phosphorus pentoxide with the following substances: (1) calcium fluoride, (2) rock phosphate, (3) fluorapatite, (4) calcium chloride, (5) sodium chloride. The reaction of phosphorus pentoxide with mixtures of sodium chloride and calcium fluoride also was studied, to determine whether mixed fluorochlorine compounds of phosphorus can be prepared in this way.

The properties of the phosphorus–fluorine and phosphorus–fluorine–chlorine compounds had not been studied extensively prior to this investigation, although Booth and his co-workers were studying their preparation.[5,6] Therefore, this work included studies of their physical properties, so that uses for them might be discovered and means of identifying them would be available in case they should be obtained as by-products in the processing of rock phosphate.

Materials and Apparatus

Materials.—The rock phosphate was native brown Tennessee; the fluorapatite was from Quebec. The native fluorspar contained 51.6% CaO, 46.2% F, 0.7% R_2O_3, and 0.0% SiO_2. The other materials were of C. P. grade except the sodium chloride and calcium chloride which were of technical grade. The phosphorus pentoxide contained less than 1% reducing agents, calculated as P_2O_3, and possibly 1 or 2% water. In some cases it was sublimed in an atmosphere of dry oxygen before use.

Apparatus.—The reactions were carried out in a three-inch iron or stainless steel closed-end tube inserted into a 40-inch refractory tube furnace. Heat was supplied in three units which were controlled independently.

The apparatus, comprising the gas collecting and handling system, shown in Fig. 1, was set upon a specially hooded bench, since some of the gases were known to be toxic, and was patterned to an extent after that of Booth and his co-workers[7,8,9]. It was, of course, necessary to make some modifications to fit the conditions encountered. It was necessary, for instance, to devise a more positive

(5) H. S. Booth and C. F. Swinehart, THIS JOURNAL, **54**, 4751–4753 (1932).

(6) H. S. Booth and A. R. Bozarth, *ibid.*, **55**, 3890 (1933).

(7) H. S. Booth and W. C. Morris, *ibid.*, **58**, 90–93 (1936).

(8) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470–475 (1937).

(9) By courtesy of Professor Booth, the authors were privileged to visit the laboratory at Western Reserve University and study the apparatus in operation.

acting automatic stopcock control to operate at supra-atmospheric pressure. This control consisted of a motor-driven arm which was operated through a series of relays by contacts in the control manometer (J, Fig. 1). The melting-point cell stirring mechanism (Fig. 2) is considered to be a novel development.

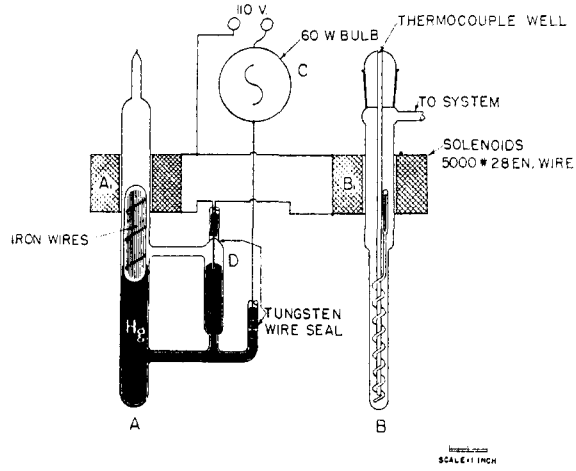


Fig. 2.—Stirring mechanism for melting point cell.

Vapor pressures were determined in the melting point cell (see Fig. 3), since stirring of the liquid helped to establish equilibrium with the vapor. The temperature of the surrounding bath was maintained constant at each point of measurement, either by means of a thermocouple which actuated the heater control mechanism of the potentiometer; or when the pressure was high, the pressure of the liquid itself was used as the controlling element. While the latter method is not inherently accurate, it gave such control that variations in temperature (<0.1 °C.) could not be distinguished on the special recording potentiometer.

Experimental

The reacting materials were mixed in a closed vessel, then transferred to the reaction vessel as rapidly as possible to avoid absorption of moisture, and the vessel was closed and connected with the collecting system. The pipe joints were made gas tight with a cement composed of calcium fluoride and water glass. The entire system was rinsed with dry air and evacuated before reaction began. The volatile products resulting from the reactions were passed into traps U, Fig. 1, where they were condensed by means of carbon dioxide snow and liquid nitrogen.

Reaction of Phosphorus Pentoxide with Calcium Fluoride.—Since the data reported by Schultze[1] indicated that the reaction between phosphorus pentoxide and a fluoride yielded phosphoryl trifluoride, the reactions illustrated by the following equations were believed to be possible:

$$3CaF_2 + 4P_2O_5 \longrightarrow 2POF_3 + 3Ca(PO_3)_2 \quad (1)$$
$$6CaF_2 + 5P_2O_5 \longrightarrow 4POF_3 + 3Ca_2P_2O_7 \quad (2)$$
$$3CaF_2 + 2P_2O_5 \longrightarrow 2POF_3 + Ca_3(PO_4)_2 \quad (3)$$

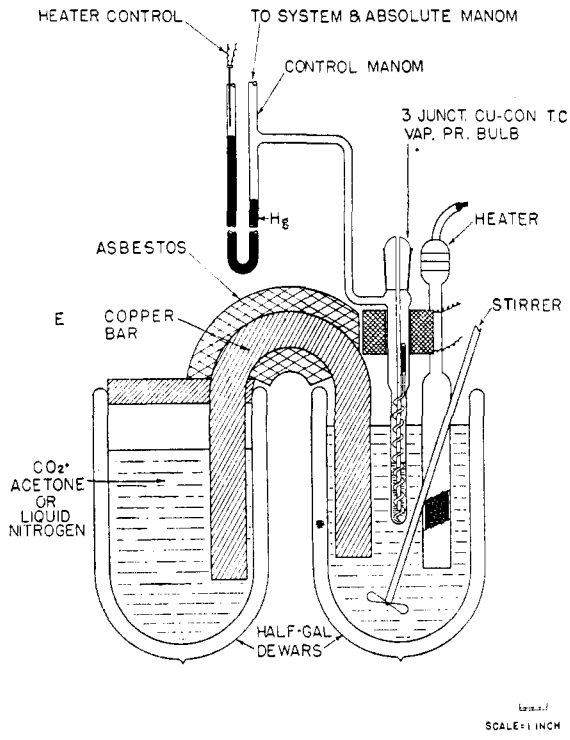


Fig. 3.—Vapor pressure apparatus.

In most of the experiments the proportion of the reactants corresponded to that required either by (1) or (3). The temperature was varied from 500 to 1000°. The weights of volatile products obtained corresponded closely to (1) on the basis of the P_2O_5 added, even though sufficient fluoride was present to satisfy (3). Small amounts of compounds other than phosphoryl trifluoride were among the volatile products (Table I). Contrary to the results reported by Lucas and Ewing,[3] no phosphorus pentafluoride was found. The presence of phosphorus trifluoride was probably due to the reduction of some phosphoryl trifluoride by the iron or stainless steel reaction vessels. Data from experiments on the stability of phosphoryl trifluoride (discussed in a later section) support this view. The presence of di-

TABLE I

DISTRIBUTION OF VOLATILE PRODUCTS FROM THE REACTION $P_2O_5 + CaF_2$

Temp., °C.	Volatile products, g.	POF_3 Wt. % of volat.	PF_3 Wt. % of volat.	Other compds.[a] Wt. % of volat.
500	21.6	77.8	trace	22.2
600	83.6	84.2	4.3	11.5
750[b]	27.5	65.4	7.3	27.3
750	108.7	81.9	7.6	10.8
1000	82.7	82.1	4.1	13.5

[a] Including HPO_2F_2 and HF. [b] Charge was quite moist.

TABLE II

THE REACTION OF PHOSPHORUS PENTOXIDE WITH MIXTURES OF CALCIUM FLUORIDE AND SODIUM CHLORIDE. DISTRIBUTION OF VOLATILE PRODUCTS

Expt.	Temp., °C.	Charge, atomic ratios[a] P/Hal.	F/Cl	Volatile products, g.	Wt. % of volatile POF_3	PF_3	$POCl_3$	P-Cl-F Compounds Compound	Wt. % of volat.	Compound	Wt. % of volat.	HCl Wt. % of volat.
6	600	2:3	1:1	177.4	50.8	26.1	..	Unidentified	3.9			19.0
19	600	5:3	1:1	157.7	29.9	1.3	22.4	$POFCl_2$	19.5	POF_2Cl	20.0	6.9
18	500	4:3	1:1	244.6	26.8	3.7	13.5	$POFCl_2$	21.0	POF_2Cl	22.4	9.4
20	500	4:3	2:3	175	28.6	0.9	26.5	$POFCl_2$	16.8	POF_2Cl	14.0	13.2
22	425	4:3	1:1	86.3	16.4	0.0	52.8	$POFCl_2$	7.7	POF_2Cl	4.9	18.2
21	350	4:3	1:1	60.2	2.3	0.7	50.5	$POFCl_2$	5.3	POF_2Cl	..	41.2

[a] Refer to Equation 5.

fluophosphoric acid, HPO_2F_2, is explained by assuming partial hydrolysis of phosphoryl trifluoride, by the small amount of water present in the charge, according to the equation

$$POF_3 + H_2O \longrightarrow HPO_2F_2 + HF^{10} \quad (4)$$

The reaction appeared to begin at about 400° and usually was complete below 600°. These temperatures were indicated by means of thermocouples mounted in contact with the outside of the reaction vessel. No direct relationship was noted between the temperature and the nature or relative proportions of the volatile products.

The Reaction of Phosphorus Pentoxide with Rock Phosphate and Fluorapatite.—A few exploratory experiments were made in which mixtures of phosphorus pentoxide with rock phosphate and with fluorapatite were heated to about 700°. The results indicated that most of the fluorine was volatilized as silicon tetrafluoride although phosphorus trifluoride and phosphoryl trifluoride, as well as carbon dioxide, were identified. The mixture of products was not fractionated completely because the pressure necessary for obtaining the carbon dioxide in liquid form exceeded the limit of safety in the glass apparatus.

The Reaction of Phosphorus Pentoxide with Metal Chlorides.—The reaction of phosphorus pentoxide with calcium chloride and with sodium chloride in an iron or stainless steel vessel produced a mixture of phosphoryl trichloride, phosphorus trichloride and hydrogen chloride. The weight of the first compound was from three to ten times that of the second and the weight of hydrogen chloride formed was proportional to the water in the charge. The phosphorus trichloride could have resulted from the reduction of phosphoryl trichloride by the metal reaction vessel. A trace of elemental chlorine was detected among the volatile products, but no phosphorus pentachloride was obtained. The reaction between phosphorus pentoxide and sodium chloride began at about 250° and the analogous reaction between phosphorus pentoxide and calcium chloride at about 400°.

(10) W. Lange, *Ber.*, **62**, 786–792 (1929).

Reaction between Phosphorus Pentoxide and a Mixture of Sodium Chloride and Calcium Fluoride.—In mixing the charges for these experiments, the theoretical reaction illustrated by the following equation was assumed.

$$3CaF_2 + 6NaCl + 8P_2O_5 \longrightarrow 2POF_2Cl + 2POFCl_2 + 3Ca(PO_3)_2 + 6NaPO_3 \quad (5)$$

However, the atomic ratio of phosphorus (in P_2O_5) to halogen was varied between 2:3 and 5:3, and that of chlorine to fluorine between 1:1 and 3:2. The temperature was varied between 350 and 600°. The distribution of the volatile products obtained is shown in Table II. When a charge containing a deficiency of phosphorus pentoxide was heated to 600° with a mixture of calcium fluoride and sodium chloride (Expt. 6) the phosphorus pentoxide reacted preferentially with the fluoride. However, when the phosphorus pentoxide was sufficient to react with both halides, according to (5), a mixture of phosphorus trifluoride, phosphoryl trifluoride, phosphoryl difluoromonochloride, phosphoryl monofluorodichloride, phosphoryl trichloride, and hydrogen chloride was produced. Phosphoryl trifluoride was the major single constituent of the volatilized products from every experiment made at or above 500°, but much smaller proportions of this and other fluorine compounds were obtained in experiments made at temperatures of 350 or 425°. The percentages of the two mixed halogen compounds (POF_2Cl and $POFCl_2$) were largest when the temperature was 500° and the ratios of the reactants satisfied (5). However, no great changes in the percentages of these compounds were noted with temperature variations between 500 and 600° and with the variations of atomic

ratios of phosphorus, chlorine and fluorine indicated in Expts. 18 to 20.

Separation of Volatile Products.—The various mixtures of volatile products obtained were separated by a series of fractional distillations. Two stills were employed and distillation below 0° was carried out as described by Booth and Bozarth.[8] For distillation below −50° a still with a liquid nitrogen-cooled head (I, Fig. 1) was used, and for distillations between −50 and 0° the still used (not shown in Fig. 1) was provided with a carbon dioxide–acetone cooled head, like that shown at K, Fig. 1, in connection with the gas generator. Compounds which boiled above 0° were fractionated in a small still, similar in construction to that used for lower temperatures, which could be cooled with refrigerated brine, tap water, or air.

The volatile products were separated roughly into two fractions, one boiling below and the other above 0°. The final distillation of the higher boiling fractions was simple. On the other hand, fractionating the lower boiling mixtures presented problems which were not covered by Booth and Bozarth.[8] Despite the fact that the boiling points of phosphorus trifluoride and phosphoryl trifluoride (−101.8 and −39.7°, respectively) as well as their vapor pressure curves (Fig. 4) lie far apart, it is difficult to separate them by fractional distillation in glass stills. The reasons for this difficulty are: (a) the vapor pressure of phosphoryl trifluoride is 785 mm. at its melting point (−39.1°), and even at −90° it has a measurable vapor pressure. (b) The two compounds are not very soluble in one another, thus the melting point of phosphoryl trifluoride is not lowered very much by the presence of phosphorus trifluoride. (c) The vapor pressure of phosphorus trifluoride rises rapidly above its boiling point and amounts to about 23 atmospheres at the melting point of phosphoryl trifluoride.

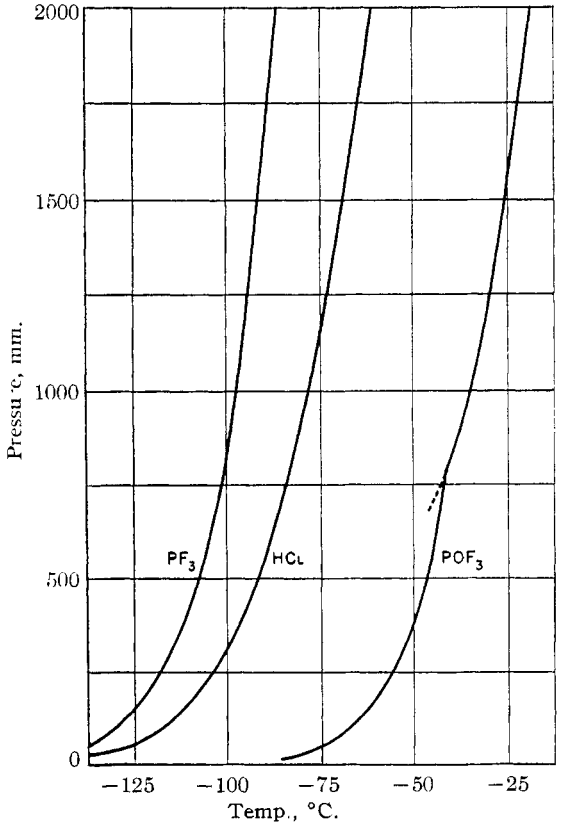


Fig. 4.—Vapor pressure curves.

Germann and Booth[11] pointed out that pure compounds cannot be obtained from mixtures of volatile solids by fractional sublimation, since each solid exerts its own vapor pressure independently of the other substance present. This principle applies also to other systems composed of two or more volatile phases. Thus, when mixtures of phosphorus trifluoride and phosphoryl trifluoride are distilled at temperatures below the melting point of phosphoryl trifluoride, a part of the latter compound sublimes along with the more volatile one. Also, a part of the phosphoryl trifluoride is deposited in the distilling column and cooling head, and is not washed back into the still pot since it is not soluble in phosphorus trifluoride. This results in plugging of the column and the operation must be stopped. On the other hand, ordinary glass stills will not withstand the high pressure required to convert the mixture of the two compounds into a single liquid phase.

Pure phosphorus trifluoride and pure phosphoryl trifluoride were obtained from mixtures of the two compounds by first slowly distilling phosphorus trifluoride from an ampoule at −100°, or below, into an ampoule cooled with liquid nitrogen, which gave two fractions, one rich in phosphorus trifluoride and the other rich in phosphoryl trifluoride. Then each fraction was subjected to a careful distillation in the fractionating column, and by discarding the proper fractions, pure compounds were obtained. However, a quantitative separation would require a large number of time-consuming fractionations. The distillation of phosphorus trifluoride was carried out at about −90° and 1450 mm. pressure, and that of phosphoryl trifluoride at −25.6° and 1500 mm. pressure.

The distillation of mixtures of phosphorus trifluoride, phosphoryl trifluoride and hydrogen chloride presented an interesting problem. The third component, hydrogen chloride, whose vapor pressure curve lies between those of the phosphorus–fluorine compounds (Fig. 4), dissolved the other two compounds and yielded a single liquid phase at or below −90°. Thus the mixture was distilled at −90° under a convenient pressure of 1450 mm. Under these conditions all of the phosphorus trifluoride was separated in practically pure form. But the separation of hydrogen chloride and phosphoryl trifluoride was found to be difficult. If the proportion of hydrogen chloride was high, a large part of it distilled in pure form at −72° and 1450 mm. Then distillation became erratic. The temperature fluctuated between the boiling points of hydrogen chloride (−72°) and phosphoryl trifluoride (−26.5°) at 1450 mm. until the hydrogen chloride had been distilled. The distillate contained both the compounds. The final portion of phosphoryl trifluoride was distilled off in fairly pure form although its melting point was low, indicating an impurity. It was found also that the mixtures which distilled erratically under 1450 mm. pressure distilled quite smoothly at about −41° and 760 mm. pressure. The latter distillate was found, by analysis, to be composed of

(11) A. F. O. Germann and H. S. Booth, *J. Phys. Chem.*, **21**, 81 (1917).

TABLE III

PROPERTIES OF VOLATILE PRODUCTS OBTAINED

Compd.	Mol. Wt. Found	Mol. Wt. Theor.	M. p., °C. Found	M. p., °C. Publ.	B. p., °C. Found	B. p., °C. Publ.	Compn., Weight % P Found	P Theor.	F Found	F Theor.	Cl Found	Cl Theor.
PF_3	84–90	88	−151.5	−151.5[12]	−101.8	−101.15[12]	35.2	35.2	64.5	64.8	..	..
POF_3	102–104.5	104	− 39.1	− 39.4[13]	− 39.7	− 39.8[13]	29.8	29.8	54.8	54.8	..	..
HPO_2F_2	102.3[a]	102	....	....	108–111	.....	29.6	30.2	38.0	37.4	..	..
POF_2Cl	120.7	120.5	....	− 96.4[13]	2.5	3.1[13]	23.3–25.2	25.8	30.7	31.6	24.3	29.4
$POFCl_2$	..	136.9	− 84.5	− 80.1[13]	54.0	52.9[13]	22.4	22.7	16.0	13.9	50.4	51.8
PCl_3	..	137.4	....	− 91[14]	75–76	76[14]	..	22.5	..	..	..	77.4
$POCl_3$	..	153.4	0.6–0.8	1.25	106.4–106.8	107.2	20.5	20.2	..	..	67.4	69.4
HCl	35.4–36.9	36.46	−111	−111[15]	1450 mm. − 71.4 760 mm. − 85[16]	− 70.8[16]	..	..	..	..	96.4	97.2

[a] Calculated formula weight from analysis.

hydrogen chloride and phosphoryl trifluoride in a mole ratio of approximately 1:1.2. This indicated that this fraction may have been a constant boiling mixture, or a compound formed between hydrogen chloride and phosphoryl trifluoride, which was stable at −41° but unstable at −26.5°.

Identification of Volatile Compounds.—The various volatile compounds were identified from their physical properties and chemical analyses. The data on which identifications were made are summarized in Table III.

Analytical Procedures.—The main problem involved in the analysis of the phosphorus–halogen compounds, particularly those containing fluorine, was that of decomposing and converting them into compounds in which the phosphorus could be determined by standard analytical procedures. The determination of fluorine and chlorine presented no great difficulty.

Weighed samples of the phosphorus–halogen compounds were dissolved in dilute ammonium hydroxide solution. The chlorine was determined by the Volhard method and the fluorine by a modification of the Willard and Winter method,[17] which involved distilling with perchloric acid and titrating the fluorine with thorium nitrate in a buffered water solution, using alizarin as the indicator.[18]

The best method found for determining total phosphorus in both phosphoryl trifluoride and phosphorus trifluoride was to treat alkaline solutions of the materials with an excess of 60% perchloric acid, heat until the acid had fumed for an hour, cool and dilute with water, and determine the phosphate by the ammonium molybdate or magnesium pyrophosphate method. The effectiveness of perchloric acid for this purpose was suggested by the fact that both phosphoryl trifluoride and phosphorus trifluoride were decomposed satisfactorily by this acid in the determination of fluorine. When samples of the phosphorus fluorides (PF_3 and POF_3) were digested with nitric acid and other equally strong oxidizing agents before precipitating the phosphate with ammonium molybdate, the phosphorus values were usually low. According to Lange,[10] phosphoryl trifluoride hydrolyzes by a stepwise process to give the intermediate products, mono-, di- and hexafluophosphoric acids. Hexafluophosphoric acid, HPF_6, is difficult to convert into orthophosphoric and hydrofluoric acids.[19] The method proposed by Lange[19] for the determination of phosphorus in hexafluophosphoric acid gave equally satisfactory results with phosphoryl trichloride, but was found to be more tedious.

The trivalent phosphorus of PF_3 is not oxidized and hydrolyzed easily to the orthophosphate ion, and at this time no satisfactory analytical method for the determination of phosphorus trifluoride and phosphoryl trifluoride in mixtures of the two has been found. In searching for a method, samples of phosphorus trifluoride in water solution were titrated as phosphorous acid with both iodine and permanganate. Permanganate gave the more consistent results, but neither method gave the theoretical value for phosphorous acid.

Properties and Physical Constants.—The samples of phosphorus trifluoride and phosphoryl trifluoride used in these tests were highly purified by fractional distillation and the values of their physical constants are believed to be quite accurate. The other compounds studied were obtained in relatively pure form by distillation, and the chemical analysis was considered adequate for the purpose of identification.

Phosphorus trifluoride was prepared by fluorinating phosphorus trichloride with antimony trifluoride and by the reaction between phosphorus pentoxide and calcium fluoride in an iron vessel. Both products gave the same melting and boiling points which were −151.5° and −101.8°, respectively. The measured vapor pressures for liquid

(12) H. S. Booth and A. R. Bozarth, THIS JOURNAL, **61**, 2927–2934 (1939).

(13) H. S. Booth and F. B. Dutton, *ibid.*, **61**, 2937–2940 (1939).

(14) A. J. Zvoruikin, *Chem. and Ind.*, **35**, 1034–1039 (1936).

(15) N. A. Lange, "Handbook of Chemistry," Handbook Publishing Co., Sandusky, Ohio, 1934, p. 149.

(16) *Ibid.*, p. 967.

(17) H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7–10 (1933).

(18) The details of this procedure as practised in this Laboratory are to be published later.

(19) W. Lange, *Ber.*, **61**, 799–801 (1928).

PF_3 can be represented by the equation: log $P_{mm.} = -861.9/T + 7.9269$, with an accuracy of $\pm 5\%$ up to about two atmospheres. The heat of vaporization and Trouton's constant were calculated to be 3950 cal./mole and 23.1, respectively. These measurements were made before the data of Booth and Bozarth[12] were published. The two sets of data check very well. The authors were acquainted with the work being done by Professor Booth and had been warned about the toxicity of phosphorus trifluoride.[20]

Phosphorus trifluoride dissolves slowly in water and rapidly in alkaline solutions. The dry gas is stable in contact with glass at room temperature, but reacts with silica at 500°, yielding silicon tetrafluoride.[12] The presence of water vapor accelerates the reaction with silica at elevated temperatures.

Although phosphoryl trifluoride was prepared by treating phosphorus pentoxide with calcium fluoride at or above 500°, and by fluorinating phosphoryl trichloride with antimony trifluoride,[5,13] that prepared by the first method was used for making the physical measurements. The difficulties encountered in purifying phosphoryl trifluoride have been discussed already. However, it should be pointed out further that when prepared from phosphoryl trichloride it is not easily freed of traces of impurities, probably chlorine compounds, which lower its melting point appreciably. This may account for the difference between the melting point reported by Booth and Dutton,[13] −39.4°, and the authors' value of −39.1°.

The boiling point, melting point, and sublimation point found for POF_3 were −39.7°, $-39.1°_{785}$, and $-39.5°_{760}$, respectively. The measured values for the vapor pressure of solid POF_3 can be represented by the equation: log $P_{mm.} = -1984.7/T + 11.3755$ with an accuracy of $\pm 5\%$; and for liquid POF_3 by: log $P_{mm.} = -1207/T + 8.0524$ with an accuracy of $\pm 1\%$. The heats of sublimation, vaporization, and fusion were calculated to be 9150, 5550, and 3600 cal./mole, respectively. Trouton's constant was found to be 23.8. The data which can be compared with those of Booth and Dutton[13] are in fairly good agreement.

At room temperature, phosphoryl trifluoride dissolves rapidly in water, ethyl alcohol and acetone; fairly rapidly in trichloroethylene and carbon tetrachloride; and slowly in benzene and mineral oil. It is quite stable toward glass at room temperature. However, a sample of the liquefied compound which has been kept in a sealed glass tube for four years appears to have reacted slightly with the glass. The dry gas was found to be decomposed only slightly when passed over glass, copper and carbon at 600° and silicates at 900°. Iron reduced it slowly at 600°, yielding phosphorus trifluoride. This result explains the presence of phosphorus trifluoride among the volatile products obtained when mixtures of phosphorus pentoxide and calcium fluoride were heated in an iron or a stainless steel vessel. At 950°, steel wool completely absorbed phosphoryl trifluoride, yielding solid products. At the same temperature, carbon decomposed 50% of the gas within fifty-three seconds, yielding phosphorus trifluoride and carbon monoxide. A small amount of elemental phosphorus and an unidentified gas, probably carbon tetrafluoride, were also formed.

A small amount of difluophosphoric acid, HPO_2F_2, was isolated. Its boiling point was between 108 and 111°. No record could be found of this compound having been isolated before. However, the analytical data (Table III) seem to be sufficient proof of the existence of the free acid.

In making material balances, it was necessary to know the weights of the various compounds obtained. The weights were obtained by measuring the volumes and densities of the liquefied compounds. Liquid densities of volatile compounds were determined by evaporating a measured volume of the liquid from B, Fig. 1, into a calibrated balloon, measuring the pressure developed, noting the temperature, and then calculating the density from the known density or molecular weight of the gas. The liquid densities of phosphorus trifluoride, at its boiling point; phosphoryl trifluoride, at its melting point; and difluophosphoric acid, at room temperature were found to be 1.6, 1.7, and 1.6, respectively.

Booth and Dutton[13] found the melting points of phosphoryl difluoromonochloride and phosphoryl monofluorodichloride to be −96.4° and −80.1°, and their boiling points to be 3.1° and 52.9°, respectively. The corresponding preliminary values (Table III) found in this Laboratory agreed fairly well, and the analytical data obtained correspond approximately to theory also.

The physical properties of phosphoryl trichlo-

(20) H. S. Booth and A. R. Bozarth, private communication, 1936.

ride, phosphorus trichloride, and hydrogen chloride are well established and the data obtained for these compounds prepared in the present study (Table III) checked very well with those reported in the literature.

Summary

When heated to about 500°, mixtures of P_2O_5 with simple fluorides or chlorides yielded POX_3 (X = F or Cl) as the major volatile compound. PX_5 was not found in any case. In iron reaction vessels some PX_3 was formed due to reduction of POX_3 by the iron vessel. Mixtures of CaF_2 and NaCl with P_2O_5 yielded a mixture of PF_3, POF_3, POF_2Cl, $POFCl_2$, and $POCl_3$ upon heating to 350° or above. The reaction of P_2O_5 with rock phosphate and with fluorapatite at about 700° yielded some PF_3 and POF_3.

The melting and boiling points for POF_3 and PF_3 were determined, and vapor pressure equations calculated. The heats of sublimation, fusion and vaporization of POF_3, the heat of vaporization of PF_3, and Trouton's constant for both POF_3 and PF_3 were calculated. Difluophosphoric acid, HPO_2F_2, a new compound, was isolated. Carbon was found to reduce POF_3 to PF_3 at elevated temperatures.

The digestion of samples of PF_3 and POF_3 with concentrated $HClO_4$ was found to be convenient and satisfactory for converting the phosphorus to the orthophosphate ion for analysis. An analytical method was not found for determining the quantities of PF_3 and POF_3 in mixtures of the two compounds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LINGNAN UNIVERSITY*]

Local Dielectric Constant and Solute Activity. A Hydration-Association Model for Strong Electrolytes

BY HENRY S. FRANK

Introduction

It has been shown recently[1] that the entropies of dilution of a number of strong electrolytes in aqueous solution show a general type of concentration dependence which can be plausibly interpreted on the basis of a few simple assumptions. One of these is that the ions affect the entropy of the solution in part through breaking down the structure of the water, and that the individual differences among the curves for different solutes are related chiefly to the different ways in which the ions exert this structure-breaking influence.

There seems to be no straight-forward general way to formulate the influence of the structure of a solution upon its thermodynamic properties. Since, however, a change in structure may be expected to have an effect on the dielectric constant, the influence through the dielectric constant on, say, the activity coefficient of a solute salt, will be one sort of contribution to the more general phenomenon. Since the local dielectric constant in the neighborhood of an ion is the quantity directly influenced by the structure effect of the ion, we shall want, in the first instance, to discuss the way in which a change in this local dielectric constant affects the activity coefficient of the solute ions.

A basis for this discussion has been given by Debye and Pauling.[2] For the purpose of showing that the validity of the limiting law of Debye and Hückel[3] is not impaired by changes in the dielectric constant around the central ion, they set up equations (see below) for the potential in two separate regions of different dielectric constant, with appropriate boundary conditions, and obtained a complicated expression for the potential of the central ion in its ion cloud. By expanding this expression in powers of concentration they showed that the leading term is exactly that given by the limiting law. They did not examine further the functional form of their expression, nor did they form any estimate of the magnitude of the deviations from the limiting law which their theory predicts. It is in these questions that we are at present interested. Before taking them up, however, we wish to consider an alternative derivation of the Debye-Pauling equation.

* The Lingnan University is in Canton, China. It is at present operating partly in Canton and partly in Hong Kong at the University of Hong Kong. The trustees wish to state that the University's plant is undamaged and that its valuable work is being continued.

(1) H. S. Frank and A. L. Robinson, *J. Chem. Phys.*, **8**, 933 (1940).

(2) P. Debye and L. Pauling, THIS JOURNAL, **47**, 2129 (1925).

(3) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).