# FLUOROPHOSPHORIC ACIDS

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# INTRODUCTION

In carrying out this research two general aims were in view: to do research of some ultimate value to industry and research of definite scientific interest. The former aim defined the nature of the work, while the latter determined in how much detail the investigation was to be carried out.

The chemistry of fluorine is in many respects quite unlike that of the other halogens. Fluorine compounds are of considerable commercial, as well as scientific interest. Particularly during the past decade they have shown considerable industrial possibilities.

New industrial uses include the fields of insecticides, catalysts, refrigerants, and dye stuffs. In the field of insecticides organic fluorophosphates are of particular interest. For the commercial production of these compounds it is desirable to have anhydrous fluorophosphoric acids. These acids have not been available.

The initial purpose of this research was to find ways to prepare anhydrous monofluorophosphoric acid and to study its properties. The scope of the research was later enlarged to include the preparation and study of the properties of difluorophosphoric acid and the chem-

istry relating to pentavalent phosphorus fluorine compounds of this type.

# HISTORICAL REVIEW

A discussion of the fluorophosphoric acids resolves itself primarily into a discussion of a series of papers by W. Lange and coworkers which appeared over the years 1927 to 1935.

In the first of these papers[1] Lange described three ways of forming difluorophosphates. By passing phosphoryl trifluoride ($POF_3$) into cold water a solution containing hydrogen fluoride and difluorophosphoric acid ($HPO_2F_2$) was obtained as a result of partial hydrolysis of the phosphoryl trifluoride, one of the fluorine atoms being replaced by a hydroxyl group. By adding the acetate of nitron (diphenyl-endo-anilo-hydro-triazole), a base, nitron difluorophosphate precipitated.

Another method consisted of fusing phosphorus pentoxide with dry ammonium fluoride. An exothermic reaction resulted. The cooled, pulverized mass was extracted with ammoniacal methanol and the solution evaporated resulting in a small yield of ammonium difluorophosphate. The nitron salt could be obtained by adding nitron acetate solution to an aqueous solution of the fused mass.

The third procedure consisted of dissolving phosphorus pentoxide in aqueous hydrofluoric acid which gave

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[1] Lange, Ber. 60B, 962-70 (1927)

rise to difluorophosphate ions. The nitron salt could then be precipitated.

At this time it was observed that the nitron precipitates obtained either from the ammonium fluoride and phosphorus pentoxide melt or from the phosphorus pentoxide and aqueous hydrofluoric acid mixture contained a trace of another fluorophosphoric acid, the amount being insufficient for complete analyses.

In investigating this other fluorophosphoric acid Lange[1] observed that the nitron salts obtained in the manner discussed above did not consist of a single crystal type; there being present a small amount of a nitron salt other than nitron difluorophosphate. Moreover it was found that if the solution of the reactants was allowed to stand for some time before precipitating the nitron salts, the amount of difluorophosphate decreased, and the precipitate contained increasing percentages of the new nitron salt. After a certain time had elapsed, the quantity of the salt obtained by precipitation with nitron remained constant, and this material was then free from difluorophosphate. The final salt obtained in a very small yield was proved to be the nitron salt of hexafluorophosphoric acid ($HPF_6$).

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[1] Lange, Ber. 61B, 799-801 (1928)

Thus hydrolysis at room temperature had destroyed only difluorophosphoric acid. If, however, the solution of reactants was boiled for 15 minutes, both fluorophosphoric acids were hydrolyzed and no precipitate was obtained with nitron.

The above study led to a procedure for preparing nitron hexafluorophosphate. Phosphorus pentoxide was added to chilled aqueous hydrofluoric acid and the solution diluted with water and allowed to stand overnight at 18° C. This time was sufficient for the difluorophosphoric acid to hydrolyze completely. The addition of nitron acetate solution then precipitated fairly pure nitron hexafluorophosphate in a very small yield.

With this tedious procedure serving as a source for nitron hexafluorophosphate it was possible to study properties of the salt and synthesize other derivatives of the acid. The pure nitron salt was very stable toward hydrolysis. Recrystallizing from boiling water several times showed no signs of decomposition. This salt was also extremely stable toward alkali metal hydroxides; a sodium hydroxide fusion being necessary to quantitatively break up the complex.

The potassium salt was prepared by adding the calculated amount of potassium nitrate to a hot solution of the nitron salt. Upon cooling, nitron nitrate precipitated leaving a solution of potassium hexafluorophosphate. This solution was neutral to methyl orange

and phenolphthalein, and no precipitate was formed upon the addition of heavy metal or alkaline earth salts.

A solution of the barium salt could be prepared by allowing barium hydroxide and the phosphorus pentoxide-hydrofluoric acid solution to stand for a day and then filtering from the remaining solid material. By adding the calculated amount of sulfuric acid to this solution a solution of the free acid was obtained.

Another very interesting experiment was carried out at this time. It was found that if gaseous phosphorus pentafluoride was passed into cold water considerable amounts of hexafluorophosphate ions, as well as difluorophosphate, resulted.

Some time after this first work on hexafluorophosphates, a more satisfactory method was found for preparing salts from the nitron salt which was prepared in the above manner[1]. The nitron salt was shaken with a mixture of aqueous ammonia and chloroform. The liberated nitron went into the chloroform layer while the aqueous layer contained the ammonium hexafluorophosphate. After recovering the ammonium salt, other salts were synthesized from it. Even this method was far from satisfactory in that only a 0.4 percent yield of the ammonium salt was obtained on the basis of the original amount of phosphorus pentoxide used.

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[1] Lange and Müller, Ber. 63B, 1058-70 (1930)

A satisfactory method of preparing hexafluorophosphates was finally developed[1]. This consisted of heating phosphorus pentachloride with a metal fluoride. The following reaction took place:

$$PCl_5 + 6\ MF \longrightarrow MPF_6 + 5\ MCl$$

Potassium, ammonium and sodium hexafluorophosphates were prepared in this manner. It was postulated that phosphorus pentafluoride formed as an intermediate, since heating potassium fluoride to a dull, red heat in the presence of phosphorus pentafluoride gave rise to a very small amount of potassium hexafluorophosphate according to the reaction $KF + PF_5 \rightleftarrows KPF_6$.

A more detailed study of the hydrolysis of phosphoryl trifluoride was carried out by Lange[2]. The hydrolysis of phosphoryl trifluoride was shown to occur in separate steps according to the following reaction:

$$POF_3 \xrightarrow{H_2O} HPO_2F_2 \xrightarrow{H_2O} H_2PO_3F \xrightarrow{H_2O} H_3PO_4$$

By using a dilute base the hydrolysis could be stopped at the first step to give a difluorophosphate. By adding a nitron acetate solution, approximately the calculated amount of nitron difluorophosphate was obtained.

In a much later work Lange and Askitopoulos[3,4] synthesized thiophosphoryl trifluoride ($PSF_3$) from phosphorus

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[1] Lange and Kroeger, Ber. 65B, 1253-7 (1932)

[2] Lange, Ber. 62B, 786-92 (1929)

[3] Lange and Askitopoulos, Ber. 71B, 801-7 (1938)

[4] Lange (Henkel and Cie. G.M. b.H.). Ger. 669.384

pentasulfide ($P_2S_5$) and lead fluoride ($PbF_2$). By hydrolyzing this compound and then treating with nitron acetate, the nitron salt of thiodifluorophosphoric acid ($HPSOF_2$) was obtained. Other salts were also obtained.

The method for preparing salts of difluorophosphoric acid was found quite troublesome. The fusion of phosphorus pentoxide with ammonium fluoride, a previously studied method[1], was quite easy to carry out, but the procedure developed at that time gave low yields. Further research on developing this procedure was fruitful. A study of the yield of nitron difluorophosphate obtained from various ratios of phosphorus pentoxide and ammonium fluoride showed that the best ratio was 1 $P_2O_5$:3$NH_4F$. The final procedure consisted of fusing the reactants mixed in this ratio, extracting the ammonium difluorophosphate with boiling ethyl alcohol and recovering the crude salt by evaporating the alcohol. Pure ammonium difluorophosphate (m.p. 213°) was obtained by recrystallization from boiling water.

From solutions of this ammonium salt crystalline precipitates of tetramethylammonium, strychnine, brucine, morphine and cocaine in addition to nitron difluorophosphate were obtained. From concentrated solutions of the ammonium salt potassium and cesium difluorophosphate were prepared.

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[1] Lange, Ber. 60B, 962-70 (1927) see p. 3

In preparing these salts, the striking similarity of the difluorophosphates to the perchlorates was shown.

The above salts were stable in air and gave a neutral reaction in water. However, on long standing, especially at an elevated temperature, there was a progressive hydrolysis which gave the solution an acid reaction. By boiling a solution of a difluorophosphate with mineral acids, or with alkali, hydrolysis took place rapidly.

Attempts were made at this time to prepare free difluorophosphoric acid by distilling a difluorophosphate with concentrated sulfuric acid. These attempts were unsuccessful, resulting in complete decomposition of the difluorophosphate. However, a very dilute aqueous solution of the acid was prepared by reacting a solution of nitron difluorophosphate with the calculated amount of nitric acid. The nitron nitrate formed as a crystalline precipitate which was filtered off. Studies of such solutions showed that difluorophosphoric acid undergoes a slow hydrolysis.

The preparation of salts of monofluorophosphoric acid ($H_2PO_3F$) immediately followed[1]. By hydrolyzing a difluorophosphate in dilute potassium hydroxide solution, there remained a solution containing potassium

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[1] Lange, Ber. 62B, 793-801 (1929)

monofluorophosphate ($K_2PO_3F$). By adding a large excess of silver nitrate a crystalline precipitate of silver monofluorophosphate was obtained. Other salts could be obtained by metathesis.

A more satisfactory method was found by fusing phosphorus pentoxide and ammonium fluoride in a 1:3 ratio. The residue obtained after extracting the ammonium difluorophosphate with boiling ethyl alcohol was crude ammonium monofluorophosphate. Recrystallization from hot water gave the pure salt as the monohydrate ($(NH_4)_2PO_3F.H_2O$). Thus ammonium monofluorophosphate and difluorophosphate are synthesized according to the reaction $P_2O_5 + 3NH_4F \longrightarrow NH_4PO_2F_2 + (NH_4)_2PO_3F$.

Monofluorophosphates synthesized included the sodium, potassium, calcium, strontium, barium, mercurous, lead and benzidine salts.

The alkali monofluorophosphates were found to be very soluble in water, reacting neutral to phenolphthalein and basic to methyl orange. The second hydrogen of monofluorophosphoric acid was shown to have only weakly acid properties since titrating an alkali monofluorophosphate with acid to a methyl orange end point required one equivalent of acid per mole of salt used.

The alkali salts were surprisingly stable to hydrolysis even upon prolonged boiling in neutral or slightly alkaline solutions. They were, however, hydrolyzed almost immediately in hot acid solutions.

In preparing the salts of monofluorophosphoric acid a complete resemblence to the corresponding sulfates was noticed.

J. M. G. Marquina[1] described the preparation of a few mono- and difluorophosphates using Lange's phosphorus pentoxide-ammonium fluoride method.

Lange and G. V. Krueger[2] prepared esters of monofluorophosphoric acid by interacting the silver salt with an alkyl iodide in a sealed tube. The dimethyl and diethyl esters, which could be distilled at atmospheric pressure, were described in some detail. Mention was made that higher esters had been synthesized and purified by vacuum distillation. These esters had strong physiological effects. Thus, even in this respect, the similarity of the monofluorophosphates to the sulfates is shown.

After several unsuccessful attempts to prepare anhydrous monofluorophosphoric acid, Lange was first led to the conclusion that the acid was incapable of existence in the anhydrous condition. However the fact that stable esters of the acid could be formed indicated, by analogy, that the anhydrous acid should be capable of existence.

It was demonstrated[3] that the hydrolysis of

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[1] Marquina, Anal. Fis. Quim., 31, 516-23 (1933)

[2] Lange and Krueger, Ber. 65B, 1598-1601 (1932)

[3] Lange, Ber. 62B, 1084-8 (1929)

monofluorophosphoric acid went essentially to completion only in dilute aqueous solutions. In more concentrated solutions some monofluorophosphoric acid always remained. This indicated the possibility of an equilibrium. These suspicions were confirmed by reacting orthophosphoric acid with aqueous hydrofluoric acid and precipitating the resulting monofluorophosphoric acid as the silver salt. This established the equilibrium $H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$. The determination of the amount of unreacted orthophosphoric acid in a given case allowed the calculation of the equilibrium constant. The mass action "constant" was found to vary inversely as the water concentration. The observed deviations from the mass action law were explained on the grounds that fluorination of orthophosphoric acid takes place with only undissociated molecules. Hence in equilibrium mixtures containing small amounts of water there would be a relatively greater amount of undissociated orthophosphoric acid and hence a greater amount of fluorination.

This study was continued[1] and much more quantitative data was obtained. By carrying out a series of experiments using fixed quantities of 100 percent orthophosphoric acid and 41 percent aqueous hydrofluoric acid and then varying the amount of water from one run

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[1] Lange and Stein, Ber. 64B, 2772-83 (1931)

to the next, the effect of water on the equilibrium was determined. In dilute solutions the mass action law gave essentially constant values of K = .31, but in more concentrated solutions values of K as high as 3.17 were observed.

In one run, at measured intervals of time after mixing the orthophosphoric acid and aqueous hydrofluoric acid, samples were taken and analyzed. By determining the position of the equilibrium at known time intervals in this way, it was possible to compute the specific reaction rate constant for the formation of monofluorophosphoric acid. The reaction appeared to be bimolecular.

The investigators also showed that acid salts of phosphoric acid, such as monobasic potassium phosphate, gave rise to the same equilibrium upon adding hydrofluoric acid. Sodium pyrophosphate with hydrofluoric acid also formed the fluorophosphate ion.

Lange[1] also studied the affect of strong acids on the above equilibrium. Sulfuric, benzene sulfonic, nitric, and perchloric acids increased the amount of monofluorophosphoric acid formed; the first three showing progressively greater effects while perchloric acid exerted an abnormally large effect.

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[1] Lange, Z. anorg. allgem. Chem. 214, 44-54 (1933)

Of particular interest is a study made by G. Tarbutton and co-workers[1] on the reaction of calcium fluoride with phosphorus pentoxide at elevated temperatures. In most experiments the reactants were mixed according to the following equations:

$$3CaF_2 + 4P_2O_5 \longrightarrow 2POF_3 + 3\ Ca(PO_3)_2 \qquad (1)$$

$$3CaF_2 + 2P_2O_5 \longrightarrow 2POF_3 + Ca_3(PO_4)_2 \qquad (2)$$

The reactants were heated in a steel reaction chamber at temperatures ranging from 500° C. to 1000° C. In all experiments phosphoryl trifluoride formed in approximately an 80 percent yield. At temperatures above 500° C. small amounts of phosphorus trifluoride formed. This was believed to be due to the reaction of phosphoryl trifluoride with the iron of the reaction vessel. In addition hydrogen fluoride and difluorophosphoric acid formed. These products were explained on the basis of partial hydrolysis of the phosphoryl trifluoride due to a small amount of water present in the reactant charge. By fractionally distilling the products a small amount of difluorophosphoric acid was obtained. Its boiling point was reported as being between 108°-111° C. No phosphorus pentafluoride was found in the reaction products. In a previous short note H. J. Lucas and F. J. Ewing[2] reported that these reactants gave essentially

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[1] Tarbutton, Egan, and Frary, JACS, 63, 1782 (1941)

[2] Lucas and Ewing, JACS, 49, 1270 (1927)

phosphorus pentafluoride according to the reaction $5CaF_2 + 6P_2O_5 \longrightarrow 2PF_5 + 5Ca(PO_3)_2$. This work, however, lacked sufficient analytical data.

## DISCUSSION OF RESULTS

A method has been found for synthesizing anhydrous monofluorophosphoric acid ($H_2PO_3F$). This anhydrous acid is not reported in the literature as having been prepared previously. The synthesis is carried out according to reaction (1).

$$HF + HPO_3 \longrightarrow H_2PO_3F \qquad (1)$$

The method used for preparing a suitable metaphosphoric acid consists of thermally decomposing dibasic ammonium phosphate, first on a hot plate to affect initial decomposition and then at 500° C. for twelve or more hours. The metaphosphoric acid, while still hot, is placed in a platinum bottle. After cooling, slightly less than the stoiciometric amount of anhydrous hydrogen fluoride is added with the liberation of heat. The mixture is shaken in a machine. At first a white crystalline solid suspended in liquid forms. Upon continuing the shaking, usually for seven days, this solid material disappears and a clear oily liquid remains. The slight excess of metaphosphoric acid remains stuck to the bottom of the bottle. The clear, oily liquid is anhydrous monofluorophosphoric acid (confirmed by phosphorus, fluorine, and equivalent weight analyses). On the basis of hydrogen fluoride used, the yield is quantitative.

Since free monofluorophosphoric acid hydrolyzes in water[1], the equivalent weight cannot be determined by a direct titration with alkali. The method developed consists of dissolving the acid in at least a one hundred percent excess of standard alkali and back titrating with standard acid to a phenolphthalein end point.

Since alkali salts of monofluorophosphoric acid are stable in water solution[2], this procedure eliminates error due to hydrolysis. The end point of the titration corresponds to the formation of the acid salt. If larger sample sizes are used, erroneous results are obtained which are invariably higher than the true value. This indicates that the equivalence point in the titration of a pure alkali monofluorophosphate to the acid salt is not close enough to the phenolphthalein end point to be of use in a quantitative determination. The only suitable explanation found for the determination being quantitative is that under the conditions described above, considerable sodium chloride forms during the titration. The presence of this salt, i.e., sodium ions, causes the phenolphthalein end point to be close enough to the true equivalence point. Gerber and Mills[3] actually add sodium chloride or sodium nitrate to solutions of mixed phosphates which they determine volumetrically.

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[1] Lange, op. cit., p.9

[2] ibid.

[3] Gerber and Mills, Ind. and Eng. Chem., Anal. Ed. 10, 519-524 (1938)

Its presence changes the pH of the equivalence point which is a factor utilized in their scheme of analysis.

Monofluorophosphoric acid cannot be distilled, even under high vacuum. It is relatively stable thermally, heating to 185° C. under reduced pressure causing only moderate decomposition. The apparent decomposition is the reverse of equation (1). Since the acid cannot be distilled, it is now understood why an attempt made by Lange[1] for preparing the acid from a monofluorophosphate and sulfuric acid was unsuccessful. The anhydrous acid has practically no odor and does not attack glass. Upon cooling it becomes more viscous, at -30° C. hardly pouring, and finally sets to a solid glass at dry ice temperature. The value obtained for the density is $d_4^{25} = 1.818$.

The appearance and density of the acid are very similar to concentrated sulfuric acid. This is of interest in that Lange pointed out the striking similarity of the monofluorophosphates to the sulfates[2].

The acid may also be prepared by having the hydrogen fluoride in slight excess over the metaphosphoric acid, shaking to form a clear liquid, and then removing

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[1] Lange, op. cit., p.9

[2] ibid.

volatile constituents by a vacuum treatment. Experiments based on the reaction of 100% orthophosphoric acid with anhydrous hydrogen fluoride (reaction (2)).

$$H_3PO_4 + HF \rightleftarrows H_2PO_3F + H_2O \qquad (2)$$

indicate a possible, but difficult, method of synthesizing the acid. The reactants would be mixed using considerable excess hydrogen fluoride, vacuum treated until the liquid no longer decreased in fluorine content, then adding more hydrogen fluoride and repeating this treatment until an anhydrous monofluorophosphoric acid was obtained. A further discussion pertaining to this method will be presented later.

A method has been found for synthesizing anhydrous difluorophosphoric acid ($HPO_2F_2$). Tarbutton, Egan, and Frary[1] succeeded in isolating a small amount of the acid as a by-product in the preparation of phosphoryl trifluoride as previously discussed. Other than the analyses, the only data published on the free acid is that it boils at 108-111° C.

The method found for synthesizing the acid is according to reaction (3).

$$H_2PO_3F + POF_3 \longrightarrow 2HPO_2F_2 \qquad (3)$$

The monofluorophosphoric acid is prepared by the method previously discussed. Phosphoryl trifluoride (in this

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[1] Tarbutton, Egan, and Frary, op. cit., p. 14

case prepared by the method of Tarbutton, Egan and Frary) is bubbled through the monofluorophosphoric acid until absorption is complete. In one run over 90% of the stoiciometric amount was absorbed. In another run in which 78% absorption had taken place a yield of 77.5% difluorophosphoric acid was obtained on the basis of phosphoryl trifluoride absorbed. The acid is obtained by distilling the mixture at 10 mm. Hg. It is known that this yield can be increased materially by refining the technique. It is reasonable that the reaction is quantitative. In carrying out the reaction there was no noticeable heat affect. A slight amount of solid material formed. This is believed to be due to the slight amount of ammonia present in the monofluorophosphoric acid.

Difluorophosphoric acid is a clear liquid which gives off immediate, dense, white fumes on exposure to air. These fumes are very irritating. It does not attack glass when perfectly anhydrous. The presence of a small amount of moisture causes it to build up a slight pressure. The acid has a sharp melting point at -96.5 $\pm$ 1° C. The density ($d_4^{25}$) is 1.583. The vapor pressure over the temperature range 50° to 90° C. is given by $\log_{10} P = -\frac{1732.2}{T} + 7.3332$ where the pressure, p, is in mm. Hg and T is absolute temperature. The maximum deviation of

this equation from the experimental data is 0.23% . The extrapolated value of the boiling point is 115.9° C. (b.p. reported by Tarbutton and co-workers[1]: 108-111° C.). Distillation at atmospheric pressure results in partial decomposition. This is probably why the value of the boiling point reported in the literature is low. The calculated value of the heat of vaporization is 7,925 calories per mole. Trouton's constant, calculated from the above data, is 20.4.

The equilibrium given by reaction (4)

$$H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O \qquad (4)$$

was studied using essentially 100% orthophosphoric acid and anhydrous hydrogen fluoride. This was an extension of a study made in aqueous solution.[2] In the investigation carried out in aqueous solution essentially constant values for K (0.31), the equilibrium constant, were obtained in dilute solutions. However, the investigators found that increasing the concentrations to the use of 100% $H_3PO_4$ and 41% HF caused the value of K to increase abnormally, reaching a value of 3.17. In the present experiments the water free reactants were mixed in molecular ratios ($HF:H_3PO_4$) of 3.67 to 5.68 giving rise to values of K from 4.60 to 11.81. These extreme deviations from the mass

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[1] op. cit., p.14

[2] Lange and Stein, op. cit., p. 12

action law suggested that additional reactions might take place. Reaction (5) was considered likely.

$$H_2PO_3F + HF \rightleftharpoons HPO_2F_2 + H_2O \qquad (5)$$

It is written as an equilibrium since Lange[1] has shown the reverse reaction to be true. By mixing hydrogen fluoride and orthophosphoric acid (mole ratio of 1.4 HF; 1 $H_3PO_4$) and then adding a nitron acetate solution nitron difluorophosphate is formed. This confirms reaction (5) and explains, at least in part, the deviations of K observed experimentally. However, by mixing the reactants in a much higher ratio (5.4 and 5.9) essentially nitron hexafluorophosphate forms. The overall reaction would be (6).

$$H_3PO_4 + 6HF \longrightarrow HPF_6 + 4H_2O \qquad (6)$$

Since the present investigation has shown that difluorophosphoric acid does form with smaller amounts of hydrogen fluoride and a minimum of water, a more likely reaction would be (7).

$$HPO_2F_2 + 4HF \longrightarrow HPF_6 + 2H_2O \qquad (7)$$

However, there must be intermediates since (7) is written as a five particle reaction which is impossible on the basis of chemical kinetics. Supplying likely intermediates for (7) which are known compounds and rewriting (4) and (5) gives the complete picture.

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[1] op. cit., p. 7

$$H_3PO_4 + HF \rightleftarrows H_2PO_3F + H_2O \qquad (4)$$

$$H_2PO_3F + HF \rightleftarrows HPO_2F_2 + H_2O \qquad (5)$$

$$HPO_2F_2 + HF \rightleftarrows POF_3 + H_2O \qquad (8)$$

$$POF_3 + 2HF \rightleftarrows PF_5 + H_2O \qquad (9)$$

$$PF_5 + HF \rightleftarrows HPF_6 \qquad (10)$$

Equilibria (4) and (5) have been discussed above. It has been shown[1] that phosphoryl trifluoride hydrolyzes in water to give difluorophosphoric acid. This is (8) in the reverse direction. Moreover it has been shown[2] that phosphorus pentafluoride passed into water gives rise to hexafluorophosphoric acid and difluorophosphoric acid. This evidence proves the forward part of (10) and the combination of (8) and (9) in the reverse direction.

It was this system of equilibria that led to the synthesis of difluorophosphoric acid. By writing (5) and (8) in reverse, it is obvious that reacting mono-

$$H_2PO_3F + HF \rightleftarrows HPO_2F_2 + H_2O \qquad (5)$$

$$POF_3 + H_2O \rightleftarrows HPO_2F_2 + HF \qquad (-8)$$

fluorophosphoric acid with phosphoryl trifluoride should give a quantitative yield of difluorophosphoric acid. The presence of a small amount of water or hydrogen fluoride would catalyze the reaction. For if

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[1] Lange, op. cit., p. 7

[2] Lange, op. cit., p. 4

a small amount of water is added to $POF_3$ some $HPO_2F_2$ and HF will form. The HF in turn will react with the $H_2PO_3F$ present which will form more $HPO_2F_2$ and will regenerate the water. The case is similar where HF acts as the catalyst. It should be pointed out that the existence of these equilibria is a sufficient reason for the synthesis of difluorophosphoric acid but not a necessary one. For it is possible that difluorophosphoric acid might form by a different mechanism which has not been considered.

These equilibria not only explain many facts described in the literature, but they give a clearer insight with regard to phenomena observed in the present experimental work. No material has been found in the literature, nor were any experimental facts observed, which contradict this concept.

## EXPERIMENTAL

### A. The equilibrium $H_3PO_4 + HF \rightleftarrows H_2PO_3F + H_2O$

Before attempting the actual synthesis of anhydrous monofluorophosphoric acid, it was decided to extend the equilibrium study of Lange and Stein[1] to conditions as water free as possible. It was hoped that this study would throw some light on the feasibility of obtaining the free acid from such an equilibrium mixture.

The procedure used was essentially the same as that of the former investigators. One hundred percent orthophosphoric acid was prepared by heating Merck's reagent quality 85% orthophosphoric acid to 140-150° C. for several hours. A volumetric analysis of this material, titrating to a thymolphthalein end point, gave a value of 99.35% $H_3PO_4$. A gravimetric determination, precipitating as magnesium ammonium phosphate and weighing as the pyrophosphate, gave 99.25%. The value accepted for calculations was 99.3 % $H_3PO_4$. The source of hydrofluoric acid was a six pound cylinder of anhydrous hydrofluoric acid supplied by the Harshaw Chemical Company.

All reactions were carried out in a platinum bottle of about 100 ml. capacity. The desired amount of orthophosphoric acid was weighed into the tared bottle. Hydrogen fluoride, gaseous, was passed from the cylinder through an ice-jacketed, vertical, 1/4" copper tube. The condensed hydrogen fluoride ran into the platinum bottle

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[1] op. cit., p.12

which was connected, by means of a rubber stopper, to the bottom end of the tube. A small vent for relieving pressure in the system was provided. In most runs venting was through a drying tube packed with dry potassium fluoride. During all runs exposure to moisture of the air was kept at a minimum. The amount of hydrogen fluoride added was checked by periodically removing the bottle, stoppering it and weighing.

In all runs considerable heat was liberated upon mixing the reactants. For this reason the platinum bottle was always cooled in an ice bath during the hydrogen fluoride addition. After adding the desired amount of hydrogen fluoride, the reactants were thoroughly mixed by agitating the bottle. A clear liquid always resulted. Heat was often liberated in which case the bottle was cooled in an ice bath. In some cases the bottle with equilibrium mixture was stored for several hours in a refrigerator. Invariably a solid crystalline material formed which melted slightly below room temperature.

After allowing the reaction mixture in the tightly stoppered platinum bottle to stand at room temperature for at least one hour, the bottle was placed in an ice bath and enough chilled potassium hydroxide solution was added immediately to make the mixture basic. This mixture was transferred immediately to a beaker, neutralized with nitric acid, and a small excess of 0.5 N. silver nitrate

solution over that needed to precipitate the orthophosphate added. After adding the precipitant the solution was made slightly basic and allowed to stand for a short time. The silver phosphate precipitate was filtered off, washed, dissolved in hot dilute nitric acid and silver precipitated as the chloride by adding a slight excess of hydrochloric acid. The filtrate from this procedure was analyzed gravimetrically for phosphorus by precipitating magnesium ammonium phosphate and igniting to magnesium pyrophosphate. This analytical method determined the amount of unreacted orthophosphoric acid in the equilibrium mixture. The results are summarized in Table 1.

Table 1

The Equilibrium $H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$

| Run | Wt. $H_3PO_4$ (99.3%) used | Wt. HF used | Wt. Unreacted $H_3PO_4$ |
|---|---|---|---|
| 1 | 3.278 g. | 2.436 g. | .2326 g. |
| 2 | 3.391 | 3.902 | .0883 |
| 3 | 3.918 | 3.618 | .1685 |
| 4 | 3.710 | 4.175 | .0682 |
| 5 | 3.533 | 2.832 | .1895 |

In Run 2 the amount of reacted phosphoric acid as well as unreacted was determined. After precipitating the silver phosphate used for determining reacted phosphoric acid, the filtrate was freed of silver ions by adding hydrochloric acid and then analyzed for phosphorus

by precipitating as the phosphomolybdate followed by a double precipitation as magnesium ammonium phosphate and then an ignition to the pyrophosphate[1]. This analysis gave 3.242 g. of $H_3PO_4$ as having reacted, while 0.0883 g. was determined as being unreacted (Table 1) and a total of 3.391 g. of 99.3% $H_3PO_4$ was used. Thus of the 3.367 g. of $H_3PO_4$ actually used, 3.330 g. or 99% was accounted for. This was considered a satisfactory check on the analytical methods.

Table 2 gives the number of moles of reactants used, calculated on the basis of a 99.3% $H_3PO_4$.

Table 2

The Equilibrium $H_3PO_4 + HF \rightleftarrows H_2PO_3F + H_2O$

| Run | Moles $H_3PO_4$ Used | Moles HF Used | Moles $H_2O$ Used | Mole Ratio HF:$H_3PO_4$ |
|---|---|---|---|---|
| 1 | 0.03320 | 0.1218 | 0.001279 | 3.67 |
| 2 | 0.03435 | 0.1950 | 0.001333 | 5.68 |
| 3 | 0.03967 | 0.1808 | 0.001500 | 4.55 |
| 4 | 0.03758 | 0.2087 | 0.001445 | 5.56 |
| 5 | 0.03578 | 0.1415 | 0.001390 | 3.96 |

Table 3 gives the concentration conditions at equilibrium, calculated on the basis of $H_3PO_4 + HF \rightleftarrows H_2PO_3F + H_2O$

[1] Kolthoff and Sandell, Textbook of Inorganic Analysis, pp. 374-375, The Macmillan Company, New York, 1937

Table 3

Equilibrium Concentrations for $H_3PO_4 + HF \rightleftarrows H_2PO_3F + H_2O$

| Run | Moles $H_3PO_4$ | Moles HF | Moles $H_2PO_3F$ | Moles $H_2O$ | $H_3PO_4$ reacted | K |
|---|---|---|---|---|---|---|
| 1 | 0.002373 | 0.0910 | 0.03083 | 0.03211 | 93.0 | 4.60 |
| 2 | 0.0009007 | 0.1615 | 0.03345 | 0.03478 | 97.5 | 8.00 |
| 3 | 0.001719 | 0.1428 | 0.03795 | 0.03945 | 95.8 | 6.11 |
| 4 | 0.0006956 | 0.1718 | 0.03688 | 0.03833 | 98.0 | 11.81 |
| 5 | 0.001933 | 0.1076 | 0.03385 | 0.03524 | 94.5 | 5.74 |

$$K = \frac{[H_2PO_3F]\,[H_2O]}{[H_3PO_4]\,[HF]}$$

The percent $H_3PO_4$ reacted is calculated on the basis of 100% $H_3PO_4$.

The above data is presented in two ways. In Figure 1, the percent $H_3PO_4$ reacted is plotted against the mole ratio of initial HF to initial $H_3PO_4$. Figure 2 is plot of K, as determined above, against this same mole ratio of HF to $H_3PO_4$.

Fig. 1 $H_3PO_4 + HF \rightleftarrows H_2PO_3F + H_2O$

% $H_3PO_4$ Reacted

Mole Ratio $HF : H_3PO_4$

Fig. 2 $H_3PO_4 + HF \rightleftarrows H_2PO_3F + H_2O$

Y

Mole Ratio $HF : H_3PO_4$

## EXPERIMENTAL

### B. Anhydrous Monofluorophosphoric Acid

The early experiments for synthesizing anhydrous monofluorophosphoric acid consisted of submitting mixtures of anhydrous hydrofluoric acid and 100% orthophosphoric acid to vacuum treatments at various pressures and temperatures. The apparatus consisted of a steel cylinder with a cap which could be bolted down to give a tight seal. The platinum bottle just fit into the cavity in the cylinder. This cylinder could be connected with a vacuum system consisting of a copper dry-ice trap, a closed tube manometer and a final container of potassium hydroxide pellets to protect the mechanical vacuum pump. During runs, the steel cylinder with the enclosed platinum bottle could be heated in a water or oil bath.

In most runs equal weights of the two reactants were used. Pressures from 5 to 30 mm Hg and temperatures from 20° C. to 150° C. were maintained for periods up to more than twenty hours. After each experiment a fluorine analysis was made and compared with the 19.0% theoretical value for anhydrous monofluorophosphoric acid. The Rowley and Churchill[1] modification of the Willard and Winter[2] method was used for

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[1] Rowley and Churchill, Anal. Ed. 9, 551-2 (1939)

[2] Willard and Winter, Anal. Ed. 5, 7-10 (1933)

determining fluorine. In runs carried out under these conditions, the fluorine content of the final, clear, oily liquid was invariably low. Moreover higher temperatures gave samples of lower fluorine content. The following is a set of typical data obtained on a series of runs using essentially equal weights of reactants:

Run 1: Pressure of 10 mm. Hg with temperature slowly raised to 100° C. : 16.9% F.

Run 2: Same as above with final temperature of 123° C. : 13% F.

Run 3: Same as above with final temperature of 100° C. : 13.2% F. Continuing the run with a final temperature of 150° C. : 10.5% F.

Run 4: Same as above but at room temperature: 16.9% F.

In another experiment carried out at room temperature the mixture of equal weights of reactants after a three hour treatment at 5 mm. Hg gave a product containing 27.2% F. Continuing for 5-1/2 hours more, reduced the fluorine content to 17.9%. More hydrogen fluoride was added to the product, and after fourteen hours more at 10 mm. Hg a clear, oily liquid containing 19.1% F was obtained. Although this final sample contained the proper amount of fluorine, the general method was abandoned in search of a shorter and simpler technique.

Several experiments were carried out with phosphorus pentoxide and hydrogen fluoride with no greater success.

In the first of these experiments 21 g. of phosphorus pentoxide and 24.5 g. of hydrogen fluoride ($8.3HF;1P_2O_5$) were mixed with the evolution of considerable heat. The resulting clear liquid was placed in the vacuum system for several hours at room temperature. The mixture lost considerable weight, and a substance containing considerable phosphorus condensed in the trap. The product in the platinum bottle formed an immediate heavy precipitate with nitron acetate (m.p. 220.5-225° C.). The product from this run contained about 31% F. A duplicate run gave similar results with a product containing 30% F.

In a third experiment the reaction mixture was vacuum distilled. Less than a gram of a very hygroscopic liquid containing 65% F was obtained as the distillate. The residue formed a white silver salt when added to a concentrated silver nitrate solution.

In a fourth and final experiment the reactants were vacuum treated for eleven hours, the pressure at the end of the treatment being 3-4 mm. Hg. During this treatment the mixture was slowly heated to 100° C. and maintained at that temperature for 1-1/2 hours. The product was an oily, clear liquid possessing a faint odor of hydrogen fluoride. It contained 16.0% F and 27.13% P. (Theoretical phosphorus for $H_2PO_3F$ is 31.0%).

A successful method for the preparation of monofluorophosphoric acid was developed utilizing the reaction of anhydrous hydrogen fluoride with metaphosphoric acid according to the following equation:

$$HPO_3 + HF \longrightarrow H_2PO_3F$$

Preliminary experiments carried out with commercial metaphosphoric acid (glacial phosphoric acid) resulted in the formation of much solid material due to the presence of sodium metaphosphate in the commercial acid. It was necessary to synthesize the pure acid.

Pure metaphosphoric acid was prepared by thermally decomposing dibasic ammonium orthophosphate. Coleman and Bell's chemically pure and Mallinckrodt's reagent grade ammonium phosphate were used. The salt was placed in a platinum dish and heated on a hot plate until a clear liquid resulted. The dish was then heated to 600° C. in an electric furnace and kept at this temperature for several hours. The final, clear, viscous, metaphosphoric acid was poured into the tared platinum bottle while still hot. After cooling various reactions were tried.

In the first experiment 26.0 g. of hydrogen fluoride was added to 10.5 g. of metaphosphoric acid (an 890% excess of HF). The reaction mixture became quite warm. After thoroughly shaking, all of the metaphosphoric acid was brought into solution. This mixture was then submitted to a nine hour vacuum treatment at

room temperature and a pressure of about 10 mm. Hg. After this treatment the product weighed 8.5 g. It was a brownish white, solid sludge having a strong odor like hydrogen fluoride. A dilute solution of this product formed an immediate precipitate upon adding nitron acetate solution. This nitron salt was recrystallized from water. It was very slightly soluble, had a melting point of 227-230.5° C. and contained 24.06% fluorine. It was undoubtedly nitron hexafluorophosphate (24.88% F, m.p. 228-233° C., slightly soluble in water)[1].

In a second experiment using a 72% excess of hydrogen fluoride, the solid sludge formed as soon as the reaction mixture had cooled. In an extensive vacuum treatment at 5 mm. Hg. and 54° C. a clear, oily liquid containing 18.3% fluorine formed. Condensate from the dry-ice trap gave an immediate heavy nitron precipitate.

A shaking machine was constructed for carrying out further experimental work (see Figure 3). The rate at which the platinum bottle could be shaken was varied by a friction disk type variable speed drive.

Also a suitable analytical method was developed for determining phosphorus in samples containing appreciable percentages of fluorine. This method was similar to

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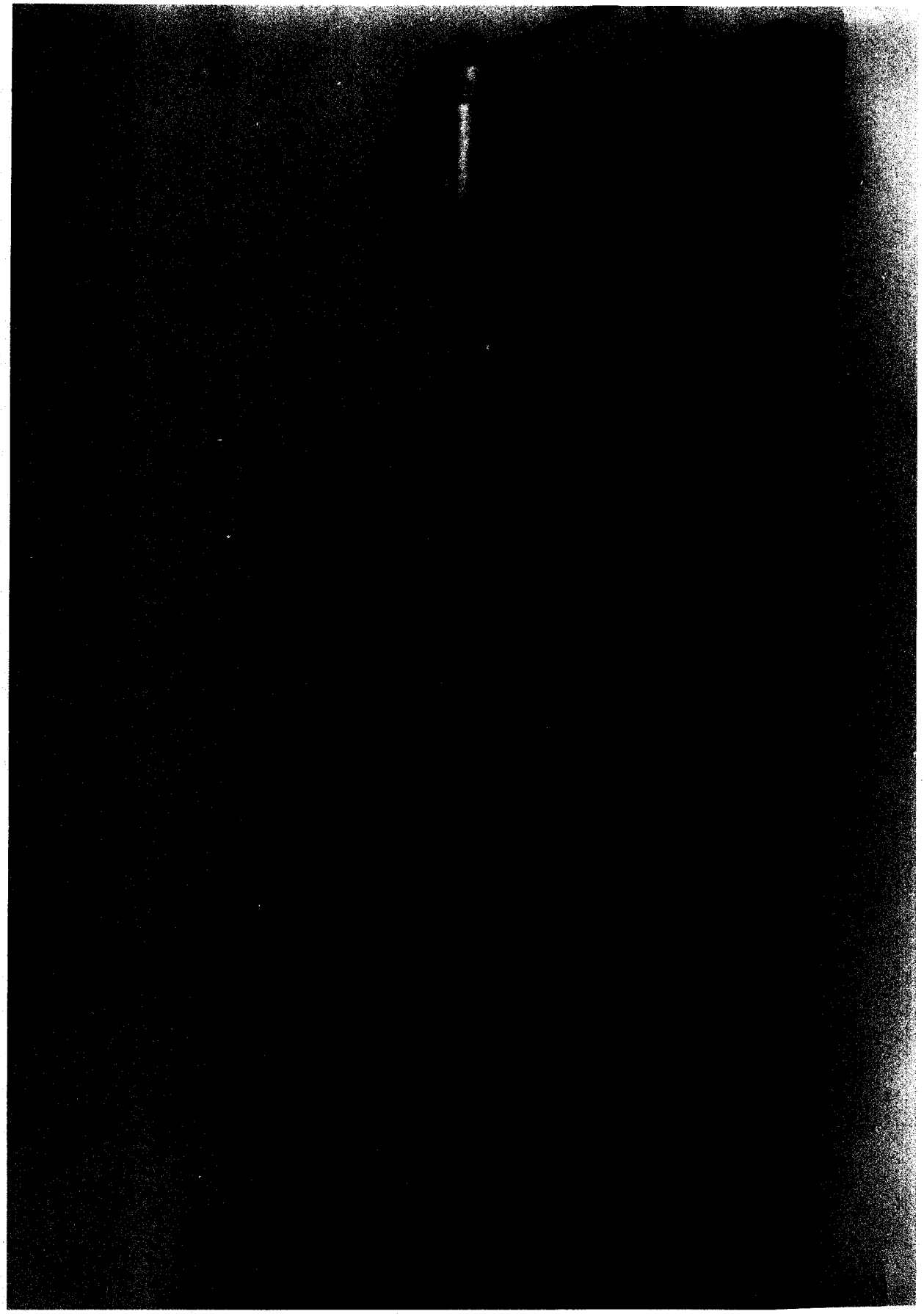
[1] Lange, op. cit., p.4

FIGURE 3

Shaking Machine with
Platinum Bottle in Place



that of previous workers[1,2]. A 5 to 7 g. sample, containing approximately 30% phosphorus, was made basic with potassium hydroxide solution and diluted to 500 ml. in a volumetric flask. An aliquot portion (10 ml.) was placed in a silver crucible containing 0.2 g. potassium hydroxide and carefully brought to complete dryness. The crucible was then heated to 500° C. in an electric furnace for 1/2 hour. After dissolving the fused mass in water, transferring to a beaker, and neutralizing with nitric acid, 10 ml. of 0.5 N. $AgNO_3$ solution was added and the solution made slightly basic. After at least four hours of aging, the silver phosphate precipitate was filtered off, washed, and dissolved in hot 2.5% nitric acid. Three ml. of concentrated hydrochloric acid were added to precipitate silver as the chloride. After four hours or more of aging, the silver chloride was filtered off. The filtrate contained the phosphorus as phosphoric acid free from fluorine. Two drops of methyl red indicator and 10 ml. of magnesia solution were added followed by slow addition of concentrated ammonium hydroxide to the indicator end-point. The solution was thoroughly stirred until most of the magnesium ammonium phosphate precipitated, then 5 ml. more of ammonium hydroxide were added. After four hours of aging, the precipitate was

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[1] Lange, op. cit., p.4

[2] Kolthoff and Sandell, op. cit., p.28

filtered off, washed with 1:20 ammonium hydroxide and ignited to magnesium pyrophosphate. All phosphorus analyses were carried out according to the above procedure. A check analysis was carried out on an accurately weighed sample of monobasic potassium phosphate containing an equal weight of potassium fluoride. A value of 22.87% P was found as compared to the theoretical value of 22.79%. Two samples were run on all analyses.

In another metaphosphoric acid experiment 16.573 g. of the acid and 4.425 g. of hydrogen fluoride (a 6.8% excess) were mixed and shaken in the machine for fifty-five hours. After the first twenty-four hours the reaction mixture was a clear, oily liquid with some unreacted metaphosphoric acid on the bottom of the bottle. At the end of the fifty-five hours the metaphosphoric acid had disappeared leaving just the oily liquid. A sample was taken for analyses and the remaining liquid submitted to a vacuum treatment at 50° C. until the material no longer lost weight. The 12.146 g. sample lost 0.460 g. during this vacuum treatment. This final product was also analyzed. The sample before vacuum treatment contained 19.9% F as compared to 20.0% on the basis of the weights of materials used. This was a satisfactory check. However, the phosphorus content was 31.2% as compared to the calculated value of 30.6%.

This indicated that the metaphosphoric acid might have a composition different from that given by the formula $HPO_3$. It has been shown[1] that preparing metaphosphoric acid at too high a temperature causes it to have a high phosphorus content. A 2.97 g. portion of this same sample gave 1.23 g. of nitron salt which was somewhat soluble in water, 0.24 g. of it dissolving when 100 ml. of water was rapidly passed through it in a filter crucible. This crude nitron salt contained 8.75% F. The final product after the vacuum treatment contained 18.8% F and 31.12% P which checks within the analytical limits for anhydrous monofluorophosphoric acid ( 18.99% F, 31.01% P). However, 5.00 g. of this material gave 2.47 g. of crude nitron salt, 0.34 g. of which dissolved when 100 ml. of water was passed through it in the filter crucible. The salt was recrystallized from 50 ml. boiling water and dried at 110° C. It contained 9.12% F, melted at 231.5-233.5° C. and had a solubility of 0.3436 g. per 100 ml. water at 20° C. It was undoubtedly nitron difluorophosphate (9.18% F, m.p. 230.5-232.5° C., sol. 0.3300 g. per 100 ml. water at 16.5° C.)[2].

A method was finally devised for synthesizing monofluorophosphoric acid. The metaphosphoric acid was

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[1] Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans, Green and Company, New York, V. 8, P.978 (1928)

[2] Lange, op. cit., p.4

prepared as previously described but at a maximum temperature of 500° C. for twelve hours. 11.734 g. of HF was added to 49.467 g. of this metaphosphoric acid (a 5.4% excess of $HPO_3$). The mixture was shaken in the machine for a total of seven days. During the first few days a solid crystalline material formed which remained suspended in the surrounding liquid. After six days this material had disappeared leaving a clear oily liquid with unreacted metaphosphoric acid on the bottom of the bottle. The analysis of this material is given in Table 4.

Table 4

Analysis of a Monofluorophosphoric Acid Sample

| Analysis | Experimental | Theoretical for $H_2PO_3F$ |
|---|---|---|
| Equiv. Wt. | 49.77 | 50.02 |
| %P | 30.69 | 31.01 |
| %F | 19.15 | 18.99 |

The method of determining equivalent weight was patterned after previous work on the monofluorophosphates[1]. A sample was poured into 50 ml. of 1 N. sodium hydroxide solution. The excess sodium hydroxide was back titrated with 1 N. hydrochloric acid to a phenolphthalein end-point. If sample weights over

[1] Lange, op. cit., pp.9,10

1.6 g. were used the end points were poor, and duplicate samples gave inconsistent results. In the above experiment, samples after six and seven days of shaking were analyzed for equivalent weight. The data is summarized in Table 5.

Table 5

Equivalent Weight Determination

| Sample No. | Days of Shaking | Wt. of Sample | Equiv. Wt. |
|---|---|---|---|
| 1 | 6 | 2.3433 G. | 52.82 |
| 2 | 6 | 1.5525 | 49.71 |
| 3 | 6 | 1.7715 | 49.99 |
| 4 | 7 | 2.5913 | 56.19 |
| 5 | 7 | 1.0956 | 49.81 |
| 6 | 7 | 1.4414 | 49.70 |

Sample sizes over 1.6 g. gave erroneous results. Sample numbers 2, 5, and 6 gave consistent results and their average was the value accepted (Table 4).

Monofluorophosphoric acid used in later work was prepared in the above manner, the essential features being to use a slight excess of metaphosphoric acid with shaking until a clear, oily product was obtained. The small excess of metaphosphoric acid always remained stuck to the bottom of the bottle.

## Properties of Monofluorophosphoric Acid

Some of the properties of the above monofluorophosphoric acid were determined. A distillation apparatus was constructed from glass in the form of an inverted U

tube. Appended to the top of the inverted U was a glass side arm to be used for filling and evacuating. After drying the apparatus, a sample of monofluorophosphoric acid was placed in one arm of the U (about 10 ml.) and evacuated to about 0.1 micron. At first, small bubbles of gas rose to the surface of the acid, but the rate quickly dropped off. There was no change in the volume of the acid. These bubbles were probably due to a small amount of dissolved gas. Upon slowly heating the acid, bubble formation increased considerably and at 60° the acid had the appearance of boiling or decomposing. The U tube was next sealed off from the vacuum system and heating continued to 185° C. over a two hour period. During this time the other arm of the U was cooled in a dry-ice-alcohol bath. A few drops of a clear liquid were obtained. There was very little change in the volume and viscosity of the acid. This acid residue contained 16.97% F and 31.17% P. The few drops of clear, distillate did not freeze at dry ice temperature, and, moreover, it built up little if any pressure upon warming to room temperature. Upon exposing the material to air heavy white fumes formed which gave an acid reaction to litmus paper. This distillate was probably hydrogen fluoride.

The monofluorophosphoric acid could not be frozen to a crystalline solid. The following was observed in

cooling a sample of the acid in which the bulb of a thermometer was immersed:

| | |
|---|---|
| -20° C. | Very viscous, would pour with difficulty. |
| -30° | Would not pour readily. |
| -40° | Semi-solid. Would not flow, but could be readily deformed. |
| -50° | Very gummy; could be deformed, but with difficulty. |
| -60° | Solid; could be deformed somewhat, but danger of breaking thermometer. |
| -70° | Solid; thermometer could not be moved; no crystals. |

The density of the acid was determined in an accurately calibrated glass pycnometer of about 5 ml. capacity. A constant temperature bath which regulated to $\pm$ .06° of the desired temperature was used. All weighings were corrected to weight in vacuo. Calibrated weights were used. The value obtained was $d_4^{25} = 1.818$.

## EXPERIMENTAL

### C. Difluorophosphoric Acid

Phosphoryl trifluoride was synthesized by a method patterned after that of Tarbutton, Egan and Frary[1]. Figures 4 and 5 show the apparatus used for synthesizing phosphoryl trifluoride and for difluorophosphoric acid. The reaction charge of phosphorus pentoxide and calcium fluoride was mixed in a ratio according to the reaction $3CaF_2 + 4P_2O_5 \rightarrow 2POF_3 + 3Ca(PO_3)_2$. Coleman and Bell's chemically pure and Mallinckrodt's phosphorus pentoxide and a technical grade of calcium fluoride were used. The reaction charge was thoroughly mixed and transferred to the reaction chamber after thoroughly drying the system by evacuation. Exposure to air was kept at a minimum. Usually a 275 gram reaction charge was used. The final reaction chamber was a 2" pipe 23" long. This pipe was capped at each end. A 3/4" pipe line led from the top pipe cap (see Figure 4) to the glass system. The connection was made with a large piece of vacuum tubing. The rubber connections were sealed with a vacuum wax. A cooling coil was provided for keeping the 3/4" pipe cool so the wax would not melt. With the exception of the top pipe cap, all metal connections were welded. The top cap was sealed with a cement made from water-glass and calcium fluoride. In earlier work

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[1] op. cit., p.14

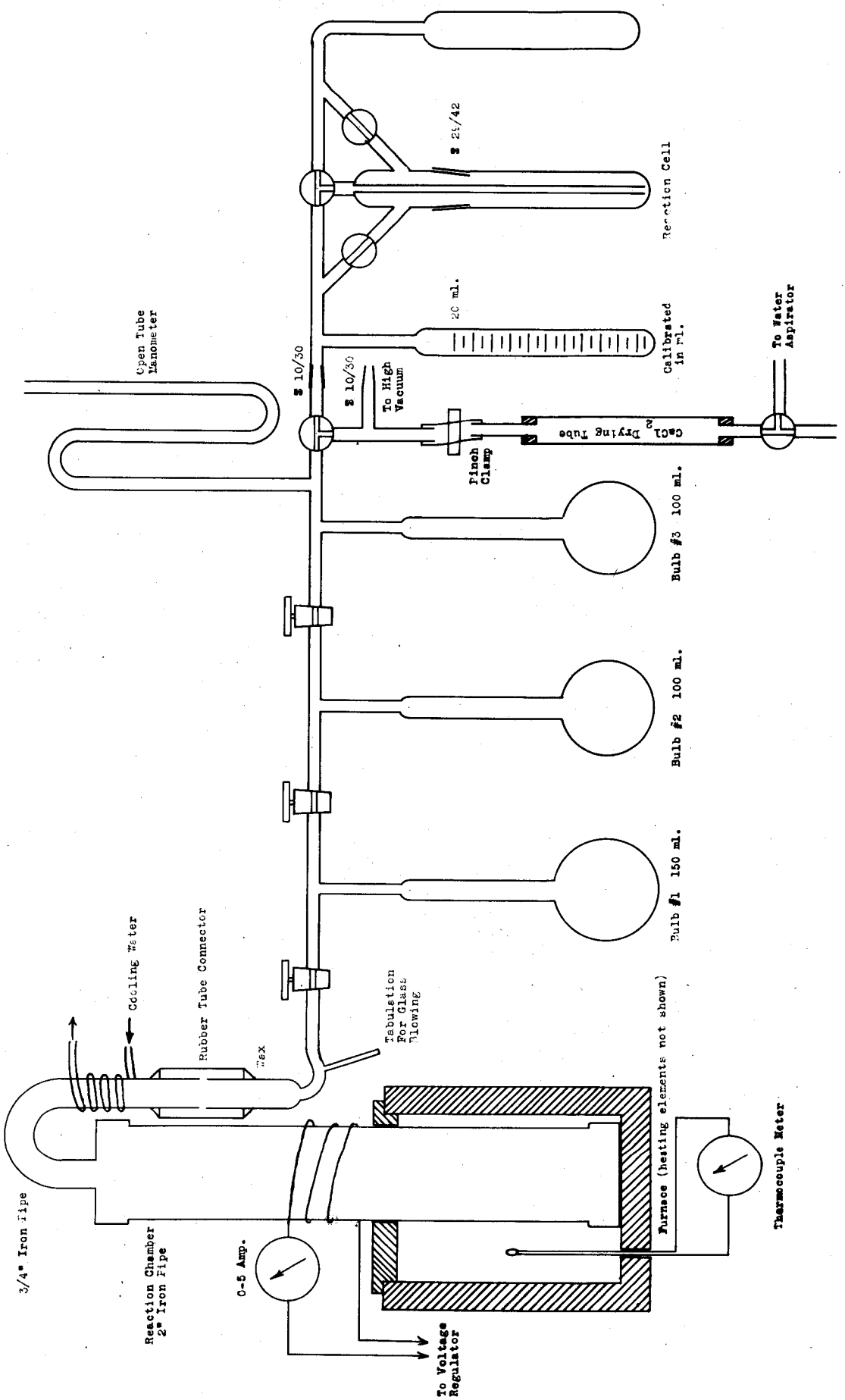
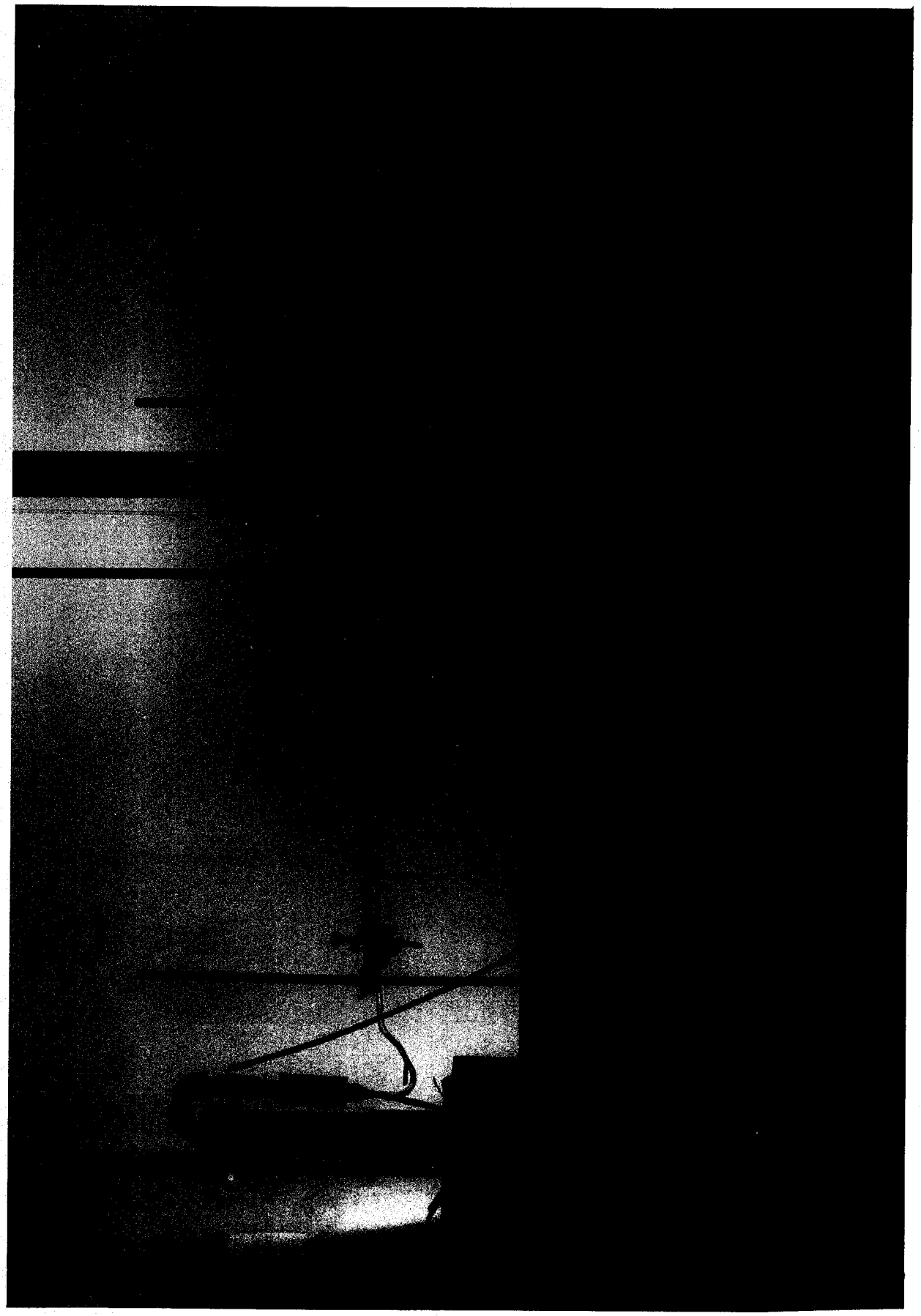



FIG. 4 APPARATUS FOR PREPARING PHOSPHORYL TRIFLUORIDE AND DIFLUOROPHOSPHORIC ACID

FIGURE 5

Apparatus for Preparing Phosphoryl Trifluoride and Difluorophosphoric Acid



a smaller reaction chamber and connecting tubes were used. The combination of sublimation of a portion of the phosphorus pentoxide, swelling of the reaction charge and sublimation of zinc from the pipe fittings caused the system to become plugged. In the final reaction chamber described above these objections were eliminated.

After adding the reaction charge the entire system was evacuated to 5 microns or lower. The pumping system consisted of a two-stage mercury diffusion pump backed by a mechanical pump. The high vacuum was read on a McLeod gauge. The reaction chamber was heated in an electric furnace provided with a thermocouple. Additional heating, enough to allow the furnace to come up to temperature, was provided by wrapping nichrome wire around the upper portion of the reaction chamber. A "varitrans" voltage regulator controlled the current in this coil. An ammeter was provided in the circuit. At 300° C. the high vacuum was cut out and the first 150 ml. bulb cooled in a Dewar flask of dry ice and alcohol. The reaction chamber was heated to 500° C. and maintained at this temperature as long as material condensed in the cooled bulb. This condensed material was a white crystalline solid.

The product was purified by cooling the second bulb in dry ice and alcohol and allowing the first bulb to warm. After the phosphoryl trifluoride had distilled

over, the stopcock separating these bulbs was closed. The residue was a white solid at 0° C. which melted upon warming to room temperature. The phosphoryl trifluoride was then distilled into the third bulb which was maintained at about -40° C. in an alcohol bath cooled with dry ice. Under these conditions the phosphoryl trifluoride (m.p. -39.1, b.p. -39.7) was a liquid during the distillation. This distillation was carried out at a little over atmospheric pressure. Only a very small amount of residue was obtained. The phosphoryl trifluoride was finally distilled into the apparatus for preparing difluorophosphoric acid. After this final distillation no residue remained. Although this method of purification was not a highly refined procedure such as that used by Tarbutton and co-workers, it gave a product of sufficient purity for synthesizing difluorophosphoric acid since the other compounds formed as by-products have boiling points at room temperature or higher[1]. As Tarbutton and co-workers showed, only a trace of phosphorus trifluoride is formed in carrying the synthesis out at 500° C. Phosphorus trifluoride is difficult to separate from phosphoryl trifluoride.

Three runs were carried out. In the first run only a few grams of product were obtained. The reaction

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[1] Tarbutton, Egan and Frary, op. cit., p.14

chamber, which was of old design, became plugged. In the other two runs using a reaction chamber of new design as previously described, yields of about 20 g. of purified phosphoryl trifluoride were obtained.

A preliminary reaction was carried out with the product from the first run. The phosphoryl trifluoride was condensed into one arm of an inverted U tube which contained an excess, about 1.5 ml. (2.7 g.) of monofluorophosphoric acid. After sealing the U tube off from the system it was allowed to warm very slowly (caution!) and the reactants mixed by shaking. The reaction mixture became cloudy. By cooling the other arm of the U tube, unreacted phosphoryl trifluoride, as needle crystals, and a small amount of a clear liquid condensed out. These were distilled back into the first arm and the system allowed to stand at room temperature overnight. The U tube was then opened and the material distilled at atmospheric pressure. The distillate started to come over at 111° C., but the temperature slowly rose to over 130° C. accompanied by decomposition of the residue. The residue was a very viscous liquid. The distillate was a clear liquid giving immediate, dense, white fumes on contact with air and giving a precipitate with a nitron acetate solution. About 1.5 g. of product were obtained which proved to be difluorophosphoric acid. The analyses are given in Table 6.

A special apparatus for absorbing phosphoryl trifluoride in monofluorophosphoric acid, having features similar to an apparatus constructed by Kharasch, Lewis, and Reynolds[1], is shown in Figures 4 and 5 and in detail in Figure 6. The desired weight of monofluorophosphoric acid was placed in the reaction cell and the system evacuated. An equimolar quantity of phosphoryl trifluoride (d. 1.7) was distilled into the calibrated tube at the left of the reaction cell. By properly setting the stopcocks above the reaction cell, cooling the container to the right in dry ice and alcohol, and allowing the calibrated tube containing the phosphoryl trifluoride to warm, the phosphoryl trifluoride bubbled through the monofluorophosphoric acid. The decrease in volume could then be read on the calibrated tube. When reading volumes the phosphoryl trifluoride was maintained just above its melting point. Upon completion of the absorption the reaction cell was transferred to a distillation apparatus and difluorophosphoric acid distilled. Contact with moisture from the air was kept at a minimum.

In the second run 16.7 g. of monofluorophosphoric acid was placed in the reaction cell and 17.4 g. (10.2 ml.) of phosphoryl trifluoride condensed in the calibrated tube. After the first pass (over and back), 46% of the

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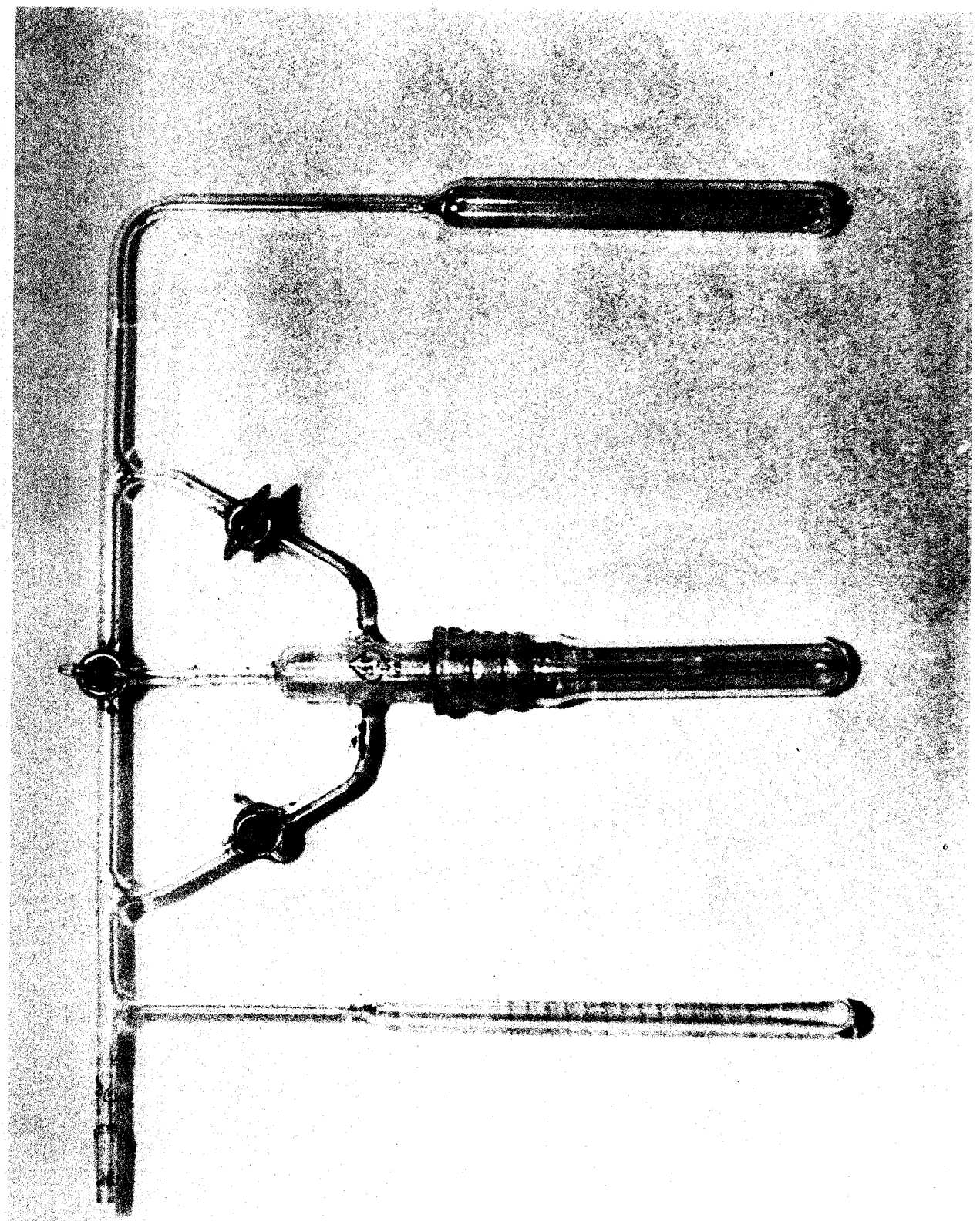
[1] Kharasch, Lewis, and Reynolds, JACS 65, 493, (1943)

FIGURE 6

Absorption Apparatus for Preparing
Difluorophosphoric Acid



phosphoryl trifluoride was absorbed. The percent absorbed after each subsequent pass decreased until after twenty passes over 90% of the original phosphoryl trifluoride had been absorbed. Some difluorophosphoric acid distilled from the reaction cell into the two tubes. It was distilled back into the reaction cell by warming the tubes and cooling the cell. The material was then distilled at atmospheric pressure in glass equipment. Distillation started at 110-112° C., but the temperature soon dropped with considerable fluctuation. A great deal of decomposition resulted giving a semi-solid residue. A trap which was connected to the system and cooled in dry-ice and alcohol contained considerable phosphoryl trifluoride and another less volatile material, possibly hydrogen fluoride. The clear, liquid product was vacuum distilled at about 75 mm Hg at which pressure it distilled at 43.0-43.3° C. A few grams of difluorophosphoric acid were obtained. This material was not analyzed, but the boiling point at 75 mm Hg checked with the correct value determined later.

In the third run 20.7 g. of monofluorophosphoric acid and 21.5 g. (12.7 ml.) of phosphoryl trifluoride were used. After twenty passes 78% of the phosphoryl trifluoride was absorbed. The material was distilled at about 75 mm Hg (42-43° C.). The yield was 26.9 g. This material built up a slight pressure upon standing so it

was submitted to a short vacuum treatment to remove any gases such as phosphoryl trifluoride or hydrogen fluoride that might have been present. This procedure was probably unnecessary as later experience showed that the absorption of only a small amount of moisture caused difluorophosphoric acid to build up a slight pressure. The final yield was 25.6 g. or 77.5% on the basis of $POF_3$ absorbed. The analytical data is given in Table 6. In this run a few grams of material were left in the absorption system. This material would have materially increased the yield.

Table 6

Analysis of Difluorophosphoric Acid

| Analysis | Run 1 | Run 2 | Theoret. of $HPO_2F_2$ |
|---|---|---|---|
| % P | 30.03 | 30.67 | 30.40 |
| % F | 37.16 | 37.17 | 37.24 |

The monofluorophosphoric acid used in all runs contained 18.7% F and 30.95% P. It also contained a small amount of ammonia which was present in the metaphosphoric acid from which it was synthesized.

A very small amount of solid material formed in each run during the absorption procedure. This probably was an ammonium salt.

## PHYSICAL PROPERTIES OF DIFLUOROPHOSPHORIC ACID

The density of difluorophosphoric acid at 25° C. was determined in a 5 ml. specific gravity bottle. Two determinations were made. Although the bottle lost a few milligrams due to attack of the acid which had absorbed a little moisture, the values 1.5824 and 1.5835 were considered suitable. Thus for difluorophosphoric acid $d_4^{25} = 1.583$.

The melting point of the acid was determined by cooling a few grams in a test tube which in turn was cooled in a large test tube containing ethanol. The large test tube was cooled in a Dewar flask containing liquid nitrogen. The small test tube with sample was sealed with a one hole stopper through which a low temperature thermometer fitted. By cooling to about -100° C. and working the thermometer in the sample, the acid froze to a white crystalline solid. Upon warming, the temperature rose to -96.5 $\pm$ 1° C. and then stopped at this value until most of the acid had melted. Repeating several times always gave a sharp melting point at this temperature. The specified limit of accuracy is due to the calibration of the thermometer and not the temperature reading.

The vapor pressure-temperature relation for the acid was determined by distillation at various pressures. An eleven inch, asbestos insulated, Vigreaux column was

used. The bottom of the column terminated in a 19/38 standard taper to which a 100 ml. flask could be connected. The receiver was a flask of the same type. A thermometer-well was provided at the top of the column and the take-off tube was placed as high as possible so that the entire thermometer-well would be surrounded with hot vapors. The thermometer used was calibrated against a National Bureau of Standards certified thermometer. Constant pressure was maintained with an electrically controlled manostat. Two 12 liter bottles were placed in the system for ballast. No pressure fluctuation was observed during the entire course of each run. Pressures were determined with a closed tube manometer which was read with a cathetometer. Atmospheric pressure determined on the manometer checked satisfactorily with the pressure read on a mercurial barometer.

During the distillation a few boiling chips were added to the distillation flask. In all cases, except the distillation at the lowest pressure used, (see later) the material distilled at a constant temperature. The pressure was read two times or more during each distillation and the average value used. The differences in the readings during a given distillation were due to the accuracy of setting the cathetometer. The data is given in Table 7.

Table 7

The Vapor-Pressure of Difluorophosphoric Acid

| Run | Pressure in mm. Hg | Corrected Temperature | Temp. of Heating Bath |
|---|---|---|---|
| 1 | 100.5 | 51.7°C | 65 - 70°C |
| 2 | 201.4 | 71.2 | 85 - 95 |
| 3 | 147.7 | 62.3 | 75 - 85 |
| 4 | 251.4 | 77.9 | 95 - 105 |
| 5 | 301.4 | 83.7 | 110 - 120 |
| 6 | 47.0 | 33.8 | 50 - 60 |
| 7 | 72.0 | 43.5 | 55 - 65 |
| 8 | 399.9 | 92.9 | 140 - 155 |
| 9 | 502.6 | 101.5 | 150 - 160 |
| 10 | 70.3 | 43.7 | 60 - 70 |
| 11 | 71.2 | 43.8 | 60 |

The data are given in the order taken. After each run the distillation flask and receiver were interchanged and the next run carried out. In Run 9 there was evidence of decomposition, for in the next run most of the distillate came over by heating the distillation flask from 60° to 70°, but it was necessary to go to a much higher temperature to distill the last part of the acid. A non-distillable residue remained. Thus difluorophosphoric acid shows definite signs of decomposition upon heating to 160° C. (See Table 7.) Run 6 is known to be in error. The temperature of the vapor was 33.8° C. while the room temperature was about 30° C. Under these conditions there was no reflux, and the temperature did not stay constant due to superheating of the vapor. Also in Runs 7, 10, and 11 there was very little or no reflux, but in these cases the distillation temperature remained

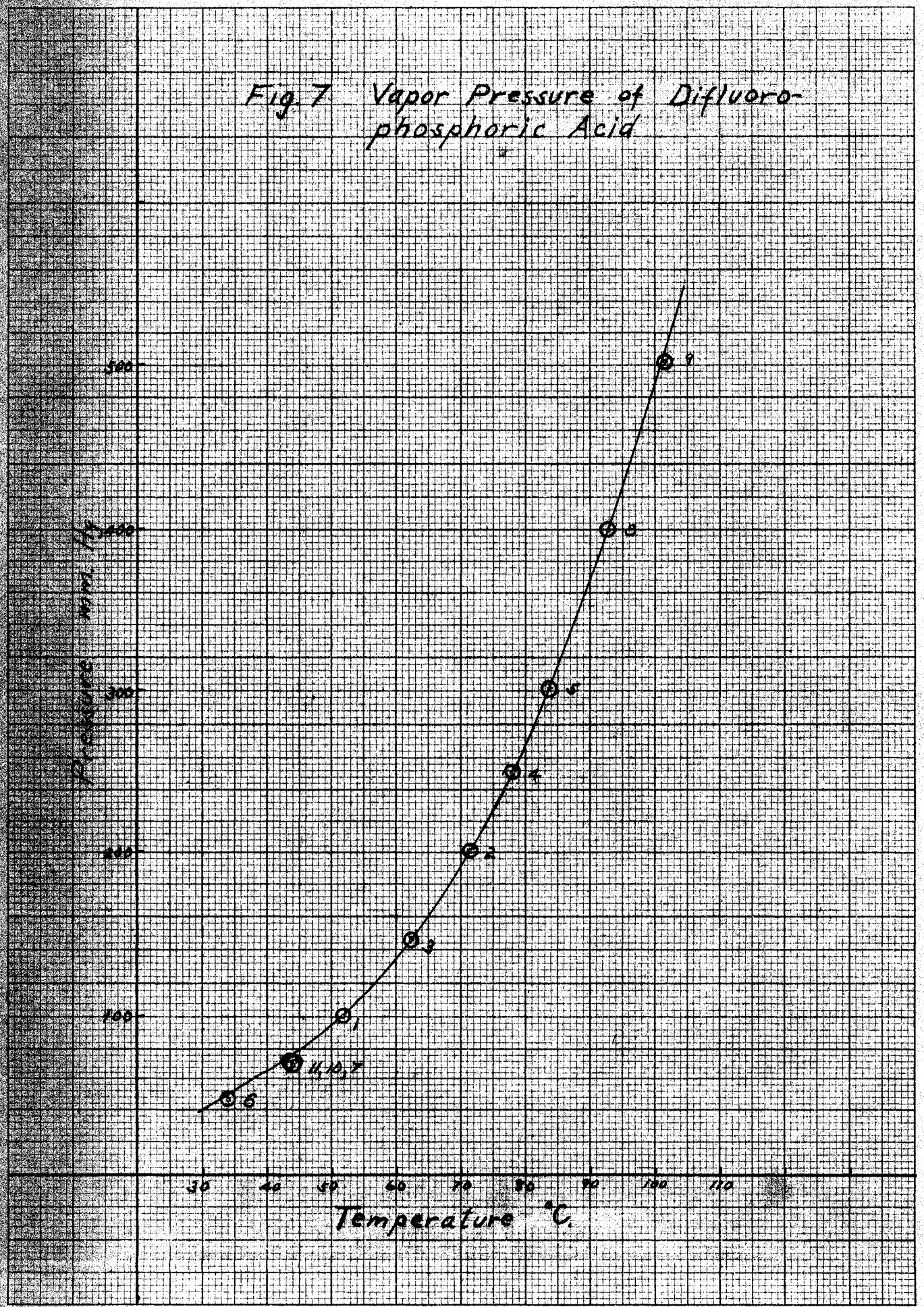
constant. In Table 8 the data are rearranged in order of increasing temperatures, and calculated values of absolute temperature, reciprocal of absolute temperature and log of pressure are included.

Table 8

Vapor Pressure of Difluorophosphoric Acid

| Run | T°C. | T°A. | $\frac{1}{T°A}$ | P mm Hg | $\log_{10}$ P mm Hg |
|---|---|---|---|---|---|
| 6 | 33.8 | 307.0 | .0032573 | 47.0 | 1.6721 |
| 7 | 43.5 | 316.7 | .0031576 | 72.0 | 1.8573 |
| 10 | 43.7 | 316.9 | .0031556 | 70.3 | 1.8470 |
| 11 | 43.8 | 317.0 | .0031546 | 71.2 | 1.8524 |
| 1 | 51.7 | 324.9 | .0030779 | 100.5 | 2.00217 |
| 3 | 62.3 | 335.5 | .0029806 | 147.7 | 2.16938 |
| 2 | 71.2 | 344.4 | .0029036 | 201.4 | 2.30406 |
| 4 | 77.9 | 351.1 | .0028482 | 251.4 | 2.40037 |
| 5 | 83.7 | 356.9 | .0028019 | 301.4 | 2.47914 |
| 8 | 92.9 | 366.1 | .0027315 | 399.9 | 2.60195 |
| 9 | 101.5 | 374.7 | .0026688 | 502.6 | 2.70122 |

The value used for absolute zero was -273.2° C. Figure 7 is a plot of pressure in mm. Hg against temperature (Centigrade). Figure 8 is a plot of $\log_{10}$ of pressure in mm. Hg against reciprocal of temperature (absolute). From Figure 8 it is evident that the data from Runs 1, 2, 3, 4, 5, and 8 are in excellent agreement. Run 9, in which there was evidence of decomposition, deviates slightly. Run 6, which is known to be in error due to superheating, deviates considerably in the expected direction. Runs 7, 10, and 11, in which superheating was suspected, also deviate somewhat in the expected direction.



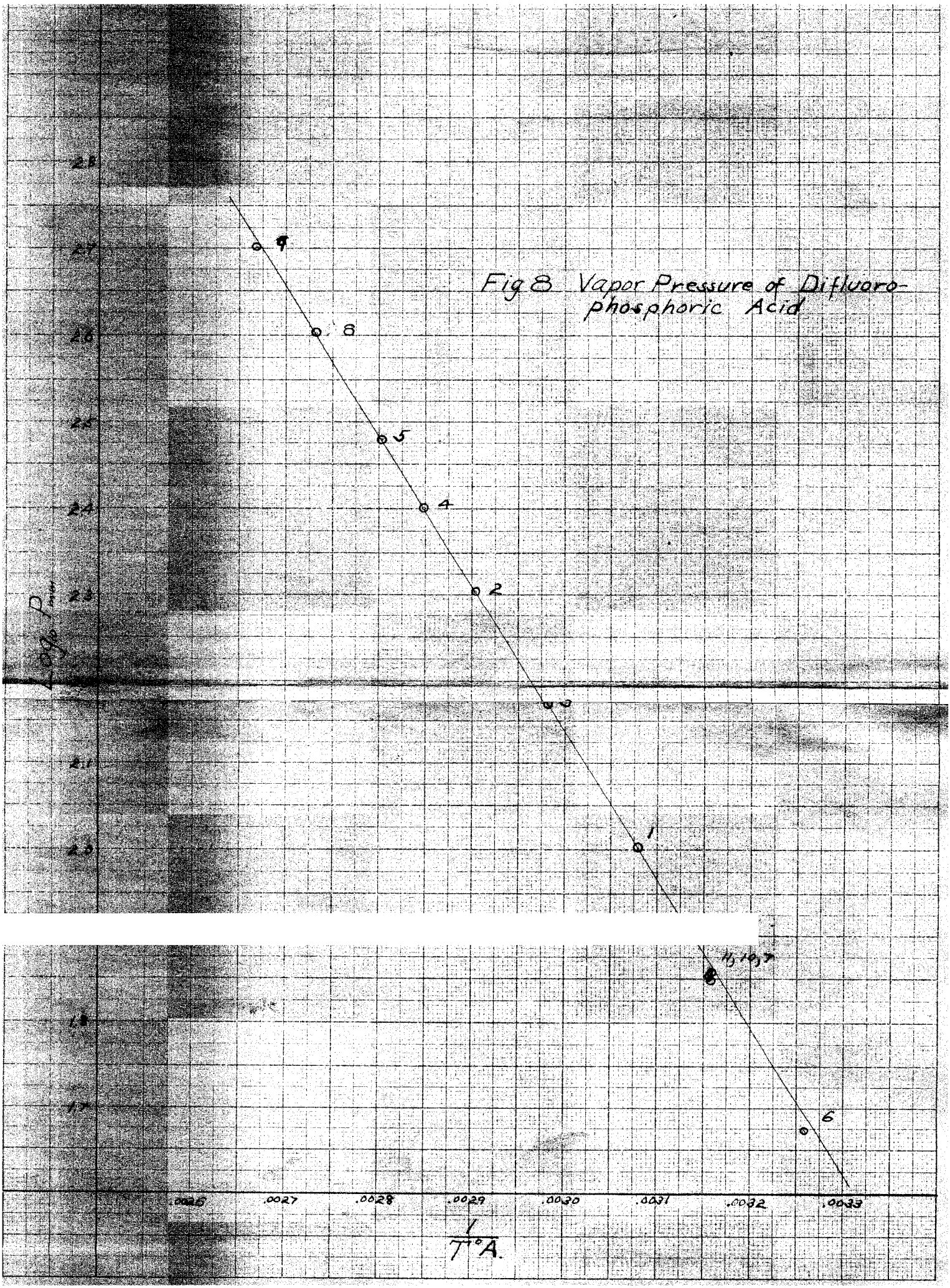



Fig 8 Vapor Pressure of Difluoro-phosphoric Acid

The constants of the equation $\log_{10} p = -\frac{a}{T} + b$ were evaluated with the data from the six runs which were in good agreement. The theory of least squares was used[1]. The data was applied to the following equations:

$$\sum \log p + a \sum \frac{1}{T} - nb = o$$

$$\sum (\log p)\left(\frac{1}{T}\right) + a \sum \left(\frac{1}{T}\right)^2 - b \sum \frac{1}{T} = 0$$

The equations obtained were the following:

$$13.95707 + .0173437a - 6b = 0$$

$$.0402088642 + .0000502133168a - .0173437b = 0$$

A simultaneous solution gave a = 1732.16 and b = 7.33320. Hence the final equation for the vapor pressure of difluorophosphoric acid over the temperature range 50° to 90° C. is

$$\log_{10} p = -\frac{1732.2}{T} + 7.3332$$

Table 9 shows the agreement of the data with the values calculated from the above equation.

Table 9

Measured and Calculated Vapor Pressures of Difluorophosphoric Acid

| T°A | Measured Pressure | Calculated Pressure | Deviation | Percent Deviation |
|---|---|---|---|---|
| 324.8 | 100.5 mm. | 100.4 mm. | -0.1 mm. | -0.10 |
| 335.4 | 147.7 | 148.0 | +0.3 | +0.23 |
| 344.3 | 201.4 | 201.2 | -0.2 | -0.10 |
| 351.0 | 251.4 | 251.0 | -0.4 | -0.16 |
| 356.8 | 301.4 | 301.9 | +0.5 | +0.17 |
| 366.0 | 399.9 | 399.7 | -0.2 | -0.05 |

The maximum deviation is 0.23%.

[1] Dr. E. F. Farnau of the Chemical Engineering Department, University of Cincinnati, kindly assisted in applying this theory.

The boiling point of difluorophosphoric acid, obtained by extrapolating with the above equation, is 115.9° C. Tarbutton, Egan, and Frary[1] reported a value of 108-111° C.

Since the constant a = 1732.2 is equal to $\frac{\Delta H}{2.3026R}$, where $\Delta H$ is the heat of vaporization and R the gas constant, (1.987 cals. per degree) the value of $\Delta H$ can be computed. This gives a value for the heat of vaporization of difluorophosphoric acid equal to 7,925 calories per mole.

Trouton's constant is $\frac{\Delta H}{T}$, where T is the boiling point of the acid (389.1°A). Thus the calculated value for difluorophosphoric acid is 20.4.

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[1] op. cit., p.14

## EXPERIMENTAL

### D. Additional Experiments with Hydrogen Fluoride

A series of short experiments were carried out with essentially 100% orthophosphoric acid and hydrogen fluoride. In the first experiment 3.0 g. of hydrogen fluoride was added to 2.886 g. of orthophosphoric acid in an open platinum dish (mole ratio of 5.4 HF: $1H_3PO_4$). After standing thirty minutes, 25 ml. of water and 60 ml. of 10% nitron in 5% acetic acid were added. A large amount of precipitate formed in big lumps with much occluded liquid. Upon stirring, these lumps broke up and a crystalline slurry remained. The precipitate was filtered off, washed with two 10 ml. portions of water and dried at 110° C. Yield of crude salt: 7.920 g. The precipitate was recrystallized from 4 liters of boiling water. Yield: 5.06 g. The fact that the salt was so slightly soluble was an indication of nitron hexafluorophosphate. A fluorine analysis confirmed this (found: 25.24% F, theoretical: 24.88% F). This yield of recrystallized salt alone represents a 38% transfer of orthophosphate to hexafluorophosphate. The above experiment was carried out with an orthophosphoric acid synthesized by oxidizing white phosphorus with nitric acid and then concentrating by heating to 150° C. for several hours[1].

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[1] Vanino, Handbuch der präparativen Chemie, Encke, Stuttgart, Vol. I, pp.189-191 (1921)

A similar experiment was carried out with an orthophosphoric acid made by heating Merck's 85%, reagent grade orthophosphoric acid to 150° C. for several hours. The results were identical in principle. Four grams of orthophosphoric acid and 4.6 g. of hydrogen fluoride (a mole ratio of 5.9 HF: $1H_3PO_4$) gave 10.9 g. of crude nitron salt. An attempt to recrystallize from 100 ml. of boiling water gave essentially no product. Thus there was very little, if any, nitron difluorophosphate present. The bulk of the remaining product was recrystallized from 3 liters of water giving 4.5 g. of nitron hexafluorophosphate.

In a third experiment using the acid synthesized from phosphorus, 1.1 g. of hydrogen fluoride was added to 4.048 g. of orthophosphoric acid (a mole ratio of 1.4 HF:$1H_3PO_4$). Upon adding the nitron acetate solution, a precipitate slowly formed. After cooling in a refrigerator for a short time, it was filtered off and washed with 5 ml. of water. It was noticeably soluble in this amount of water. The yield of crude salt was 1.627 g. It contained 8.4% F. Recrystallizing from 50 ml. of water gave 0.76 g. of product. All of the crude salt was soluble in this amount of water. This indicated that the salt was nitron difluorophosphate. A fluorine analysis confirmed this (found: 9.03% F, theoretical: 9.18% F). Moreover it is evident from the above data

that essentially no hexafluorophosphate was present.

In another experiment 60 g. of hydrogen fluoride was added to 49 g. of orthophosphoric acid (6.3 HF:1$H_3PO_4$). Upon cooling in an ice bath considerable white, solid, crystalline material formed. This was filtered off in a silver filter crucible and pressed as dry as possible. Yield: 45 g. This material slowly melted upon warming to room temperature. The melting point was not sharp. An attempt to distil it at 100 mm. Hg in a glass still resulted in so much attack of the glass that the material had to be discarded.

In another similar run 20 g. of hydrogen fluoride was added to 44 g. of orthophosphoric acid (2.3 HF:1$H_3PO_4$). No solid phase formed upon cooling to 0° C. However, by adding 30 g. more of hydrogen fluoride (giving 5.8 HF: 1$H_3PO_4$) considerable solid phase formed upon chilling. This white, solid material was filtered and pressed as dry as possible. A small portion of it dissolved in water gave an immediate heavy precipitate with nitron acetate solution. The remaining product was placed in a vacuum desiccator. After a few hours a damp slurry remained. After several more hours a clear liquid with considerable corrosive fumes remained. This final liquid gave no precipitate with a nitron acetate solution.

Monofluorophosphoric acid with anhydrous hydrogen fluoride also, upon cooling, gave large amounts of this white, solid phase.

## SUMMARY

Anhydrous monofluorophosphoric acid ($H_2PO_3F$) has been synthesized in quantitative yields by reacting anhydrous metaphosphoric acid with anhydrous hydrogen fluoride according to the equation $HPO_3 + HF \longrightarrow H_2PO_3F$. This anhydrous acid has not been reported in the literature. Properties of the acid have been determined.

Anhydrous difluorophosphoric acid ($HPO_2F_2$) has been synthesized in high yield by reacting phosphoryl trifluoride with monofluorophosphoric acid according to the equation $POF_3 + H_2PO_3F \longrightarrow 2HPO_2F_2$. This acid had been obtained in a very small yield and its approximate boiling point determined in a previous investigation reported in the literature. Properties of this acid, including accurate vapor pressure data, have been determined.

A series of five equilibria which relate all fluorophosphoric acids and associated compounds has been presented. Much experimental evidence, both from the present research and from the literature, has been given to verify the equilibria.