

would be one similar to that given by King. The first molecules entering will mostly be held at points of low energy, and at higher concentrations more and more water molecules will be held relatively loosely. This will result in an increase in the average mobility as the concentration increases.

Both the concentration and vapor pressure gradients, shown in Fig. 3e, drop very steeply near the dry surface of the film. Throughout the rest of the film, the concentration is high and the water molecules have high mobility.

Acknowledgment.—The author wishes to express his thanks to Dr. A. F. Smith of the Chemical Department for his continued guidance and interest in this work and to the Rayon Technical Division, E. I. du Pont de Nemours and Company, for generous support of this research.

Summary

1. A method is given for calculating the diffusion coefficient of a vapor within a film as a function of concentration. Data required are the permeation rates under several vapor pressure differences and the sorption isotherm. The method also furnishes a means for constructing the gradients of the effective vapor pressure and of the

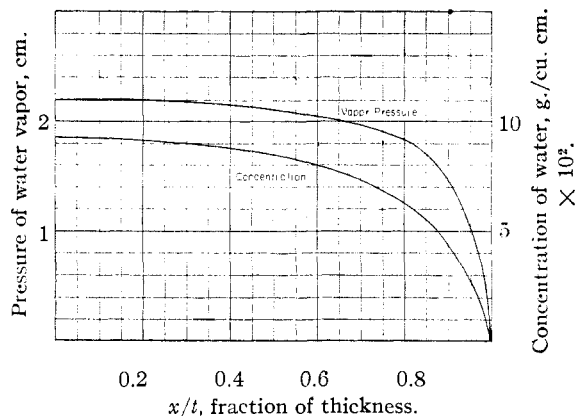


Fig. 3e.—Gradients of concentration and vapor pressure of water in nylon at the steady state at 25°.

concentration of the vapor within the film through which vapor is passing at a steady state.

2. Data are presented for water permeation and water sorption of polythene and nylon, and the diffusion coefficients of water vapor in these films at 25° are obtained as functions of concentration. Curves representing the vapor pressure and concentration gradients are also presented.

WILMINGTON, DELAWARE RECEIVED NOVEMBER 8, 1946

[CONTRIBUTION FROM THE APPLIED SCIENCE RESEARCH LABORATORY OF THE UNIVERSITY OF CINCINNATI]

Studies of Fluorophosphoric Acids and Their Derivatives. XIII. Preparation of Anhydrous Monofluorophosphoric Acid¹

BY WILLY LANGE² AND RALPH LIVINGSTON³

It has recently been shown that the esters of monofluorophosphoric acid, H_2PO_3F , which were previously known to be highly toxic,^{4,5} have a probable usefulness in the treatment of glaucoma and myasthenia gravis, the di-*i*-propyl ester being especially suited for this purpose.⁶ Unpublished observations by the present senior author have also shown that the esters possess insecticidal properties and may act as fumigants.

McCombie and Saunders have devised two convenient methods for the synthesis of these esters, but their prospective uses make a cheap, direct synthesis from monofluorophosphoric acid seem desirable. Although the salts of this acid have

been studied in considerable detail,⁷ the free acid has not been isolated previously and so the present study was undertaken to see whether the acid could be prepared in pure form.

In previous investigations 100% orthophosphoric acid had been allowed to react with hydrofluoric acid containing up to 41% hydrogen fluoride.⁸ In new studies started in 1941, the reaction with liquid anhydrous hydrogen fluoride was investigated. As expected, in reaction of the anhydrous components in 1:1 molar ratio, a substantial portion of the orthophosphoric acid, namely, 67%, was transformed into a fluorinated derivative. However, it was found that the monofluorophosphoric acid, formed in the reaction, entered into a new equilibrium reaction with unreacted hydrogen fluoride, resulting in the formation of difluorophosphoric acid, while some orthophosphoric acid was still present. These equilibrium reactions take place according to the following equations

(1) A portion of a thesis by R. Livingston, submitted to the Faculty of the Graduate Department of Applied Science, College of Engineering and Commerce, University of Cincinnati, in partial fulfillment of the requirements for the Degree of Doctor of Science, May, 1943.

(2) Present address: The Procter & Gamble Company, Ivorydale 17, Ohio.

(3) Present address: Monsanto Chemical Company, Clinton Laboratories, Oak Ridge, Tenn.

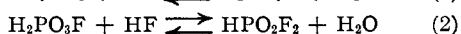
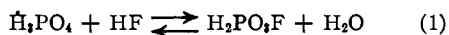
(4) W. Lange and G. v. Krueger, *Ber.*, **65**, 1598 (1932).

(5) H. McCombie and B. C. Saunders, *Nature*, **157**, 287 (1946).

(6) Honorable R. P. Patterson, *Chem. Eng. News*, **24**, 1029 (1946).

(7) (a) W. Lange, *Ber.*, **62**, 793 (1929); (b) W. Lange, *Nature*, **126**, 916 (1930).

(8) (a) W. Lange, *Ber.*, **62**, 1084 (1929); (b) W. Lange and G. Stein, *ibid.*, **64**, 2772 (1931).



Analyses of the equilibrium product showed that 33% of the orthophosphoric acid remained unchanged, 60% was transformed into monofluorophosphoric acid, and 7% into difluorophosphoric acid. Attempts to produce a pure monofluorophosphoric acid by bringing equilibrium (1) to completion without formation of difluorophosphoric acid, or by removing water and excess hydrogen fluoride from the equilibrium by means of distillation, or by removing the water of reaction with dehydrating agents, met with failure. One of the obstacles in these attempts was the fact that the equilibrium is shifted rapidly to the left by heating the reaction mixture.

After these attempts, a simple reaction was discovered which permits the preparation of anhydrous monofluorophosphoric acid in quantitative yields in practically pure form. It was observed that anhydrous metaphosphoric acid and liquid anhydrous hydrogen fluoride, mixed in stoichiometric quantities, react according to the equation



Because of the consistency of the metaphosphoric acid, the reaction is quite slow. Thus for a certain period of time, an excess of hydrogen fluoride is present together with small quantities of monofluorophosphoric acid, resulting in the formation of an intermediate product containing more than one atom of fluorine per atom of phosphorus. However, as the solid metaphosphoric acid goes into solution, this undesirable product of over-fluorination disappears, and pure monofluorophosphoric acid is finally obtained. To avoid the presence of traces of difluorophosphoric acid in the product, a slight excess of metaphosphoric acid may be used in the reaction. The unreacted metaphosphoric acid is insoluble in the liquid reaction product and may be removed by decanting at the end of the operation. The liquid product represents the practically pure monofluorophosphoric acid.

Thus far, monofluorophosphoric acid, an oily liquid, has not been distilled, even under high vacuum. It is relatively stable thermally, heating to 185° under reduced pressure causing only slight decomposition into metaphosphoric acid and hydrogen fluoride. The anhydrous acid has practically no odor and does not attack glass in the absence of moisture. Upon cooling, it becomes more viscous, will hardly pour at -30°, and finally sets to a rigid glass at Dry Ice temperature. The value obtained for density is $d_{25}^{25} 1.818$. The whole appearance of the acid is very similar to that of concentrated sulfuric acid, as might have been expected from the similarity of the salts of the two series.

Upon mixing the anhydrous monofluorophosphoric acid with water, hydrolysis takes place slowly until, in accordance with the water concen-

tration, equilibrium has been established according to equation (1). Aqueous solutions of the acid, used immediately after preparation, may serve for producing the salts in good yields. Practically quantitative yields were obtained by pouring the ice-cold, anhydrous acid in a thin stream, with mechanical agitation, into strongly cooled aqueous solutions of ammonium, sodium or potassium hydroxides or into suspensions of the alkaline earth hydroxides in water, until stoichiometric quantities had reacted. The alkali salts were obtained by rapid evaporation of the solvent at low temperature, and the alkaline earth salts by simple filtration. The silver, lead and mercurous salts were prepared by mixing solutions of the alkali monofluorophosphates with solutions of the metal nitrates. The properties of the salts were identical with those described in the earlier report.^{7a}

Experimental

Anhydrous Monofluorophosphoric Acid

Starting Materials.—Commercial metaphosphoric acid contains sodium phosphates and thus is unsuitable for preparing a pure monofluorophosphoric acid. Pure metaphosphoric acid was prepared by thermally decomposing reagent grade dibasic ammonium orthophosphate. 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 500° in an electric furnace and kept at this temperature for twelve hours. Anhydrous hydrogen fluoride was used directly from a cylinder supplied by the Harshaw Chemical Company.

Reaction.—Hot, viscous metaphosphoric acid was poured into a tared 100-ml. platinum bottle, and its weight, after cooling, was found to be 49.467 g. Gaseous hydrogen fluoride was condensed in an ice-jacketed, vertical copper tube, and 11.734 g. of the liquid hydrogen fluoride was added to the metaphosphoric acid so that the meta acid was present in an excess of 5.4% over the stoichiometric quantity. The closed platinum bottle was shaken at room temperature in a specially constructed machine for a total of seven days. After this time there remained a clear oily liquid, representing anhydrous monofluorophosphoric acid, with unreacted meta acid sticking to the walls of the bottle.

Method of Analysis.—Phosphorus was determined in the monofluorophosphoric acid by a method similar to that of previous workers.⁹ A 5-7 g. sample was made alkaline 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. of potassium hydroxide and brought to complete dryness. The crucible was then heated to 500° in an electric furnace for half an hour. After dissolving the fused mass in water, transferring to a beaker, and neutralizing with nitric acid, 10 ml. of 0.5 N silver nitrate solution was added and the solution was made slightly basic. After at least four hours of aging, the silver orthophosphate precipitate was filtered off, washed and dissolved in hot 2.5% nitric acid. The solution contained the phosphorus as orthophosphoric acid free from fluorine. The Rowley and Churchill¹⁰ modification of the Willard and Winter¹¹ method was used for determining fluorine.

Since free monofluorophosphoric acid hydrolyzes in water due to the formation of an equilibrium, the equivalent weight could not be determined by a direct titration

(9) W. Lange, *Ber.*, **62**, 786 (1929).

(10) R. J. Rowley and H. V. Churchill, *Ind. Eng. Chem., Anal. Ed.*, **9**, 551 (1937).

(11) H. H. Willard and O. B. Winter, *ibid.*, **5**, 7 (1933).

with alkali. The determination was patterned after previous work on the monofluorophosphates in which it had been found that the dibasic salts react neutral against phenolphthalein and alkaline against methyl orange.^{7a} A sample of less than 1.6 g. of the acid was poured into 50 ml. of *N* sodium hydroxide solution, thus assuring an excess of at least one hundred per cent. alkali. The excess was back titrated with *N* hydrochloric acid to a phenolphthalein end-point. If sample weights of more than 1.6 g. were used, the end-points were poor, and duplicate samples gave inconsistent results. A suitable explanation for the fact that the determination is quantitative under the conditions specified is that a considerable concentration of sodium ions in the presence of monofluorophosphate ions causes the phenolphthalein end-point to be close enough to the true equivalent point. Gerber and Miles¹² actually added sodium chloride or nitrate to solutions of mixed phosphates which they determined volumetrically.

Densities were determined in a glass pycnometer of about 5 ml. capacity, using a constant temperature bath which could be regulated to within $\pm 0.06^\circ$. All weighings were corrected to vacuum.

Analytical Results.—Calcd. for $\text{H}_2\text{PO}_3\text{F}$: P, 30.98; F, 19.00; equiv. wt., 50.00. Found: P, 30.69; F, 19.15; equiv. wt., 49.74; d^{25} , 1.818. The value for the equivalent weight is the average of three determinations carried out with 1.5525, 1.0956 and 1.4414 g. of monofluorophosphoric acid, respectively, and resulting in values of 49.71, 49.81 and 49.70, respectively.

Cooling of the Acid.—Freezing of the monofluorophosphoric acid was observed with an immersed thermometer. The consistency of the acid was observed as very viscous at -20° , semi-solid, non-flowing but readily deformable at -40° , very gummy and deformable only with difficulty at -50° , firm and somewhat deformable at -60° , and rigid without signs of crystallization at -70° .

Formation of Difluorophosphoric Acid in the Reaction of Orthophosphoric Acid with Hydrogen Fluoride

The procedure used was essentially the same as that in the earlier investigations.⁸ The orthophosphoric acid used, when precipitated as the silver salt and determined as magnesium pyrophosphate, gave a value of 99.83% phosphoric acid. The gaseous hydrogen fluoride from the cylinder was assumed to be 100% hydrofluoric acid.

All reactions were carried out in a 100-ml. platinum bottle. Orthophosphoric acid was weighed into the tared bottle, and condensed hydrogen fluoride was added to the phosphoric acid until a ratio as close as possible to 1 mole HF:1 mole H_3PO_4 had been attained. The platinum bottle was cooled in an ice-bath during the hydrogen fluoride addition. Exposure to moisture of the air was kept at a minimum. After adding the desired amount of hydrogen fluoride, the reactants were mixed thoroughly by shaking the bottle. After allowing the reaction mixture in the tightly stoppered platinum bottle to stand at 10° for two hours, the bottle was placed in an ice-bath, and a sample of about 2 g. was transferred to a tared silver crucible, covered with a closely fitting lid and weighed. Enough chilled potassium hydroxide solution to make the sample basic was added immediately, thus stabilizing the monofluorophosphate ions and preventing hydrolysis into orthophosphoric acid. This mixture was transferred to a Pyrex beaker, neutralized with nitric acid, and 0.5 *N* silver nitrate solution was added slightly in excess of the amount needed to precipitate the orthophosphate. 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, and analyzed for its phosphorus content. This analytical method provided an accurate determination of the amount of unreacted orthophosphoric acid in the equilibrium mixture.

In one of the runs, 52.6972 g. of the 99.83% orthophosphoric acid was mixed with 10.5910 g. anhydrous hydrogen fluoride. A sample of 2.1139 g. of the equilibrium mix-

ture was analyzed, and 0.6633 g. magnesium pyrophosphate was obtained, indicating that 0.5841 g. of orthophosphoric acid, or 33.24% of the initial quantity, had remained unfluorinated. Under the assumption that monofluorophosphoric acid alone had been formed, it may be calculated that the starting mixture with a composition corresponding to the ratio 1 mole H_3PO_4 :0.9861 mole HF:0.0093 mole H_2O had been transformed into an equilibrium product having a composition conforming to the ratio 0.3324 mole H_3PO_4 :0.3185 mole HF:0.6676 mole $\text{H}_2\text{PO}_3\text{F}$:0.6769 mole H_2O .

Analysis for Difluorophosphoric Acid.—However, investigation showed that the equilibrium product contained difluorophosphoric acid. The product gave a crystalline precipitate with nitron acetate solution, while orthophosphoric, monofluorophosphoric, and hydrofluoric acids form easily soluble salts with the organic base. A quantitative determination was attempted with the aid of this reaction. Results were probably low due to the noticeable solubility of nitron difluorophosphate in ice water (solubility in water of 18° is 1:300).¹³

Fifty ml. of a 10% ammonia solution in a beaker was cooled with an ice-salt mixture. Ten grams of the ice-cold equilibrium product was poured with mechanical stirring into the solution as quickly as removal of heat of neutralization permitted. Immediately after the addition of the acid, the mechanical stirrer was removed, the solution was neutralized with acetic acid, and 40 ml. of solution containing 4 g. of nitron in 5% acetic acid was added. The beaker was placed in ice, and the walls were rubbed with a glass rod to induce crystallization. After three hours, the precipitate was filtered off in a sintered glass Gooch crucible and washed with 5 ml. of water and 25 ml. of an aqueous solution of nitron difluorophosphate saturated at 0° , both wash liquids having a temperature of 0° . The precipitate was dried at 110° . A yield of 2.5398 g. of the nitron salt was obtained, containing 8.73% fluorine as compared to the value of 9.17% F calculated for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{HPO}_2\text{F}_2$. From the yield it was calculated that at least 7.23% of the original orthophosphoric acid had been transformed into difluorophosphoric acid.

A combination of the analytical data indicates an approximate composition of the equilibrium product corresponding to the ratio 0.3324 mole H_3PO_4 :0.2462 mole HF:0.5953 mole $\text{H}_2\text{PO}_3\text{F}$:0.0723 mole HPO_2F_2 :0.7492 mole H_2O .

Isolation of Monofluorophosphoric Acid as the Silver Salt.—The presence of monofluorophosphoric acid in the equilibrium was shown directly by the isolation of its characteristic silver salt which is present to the extent of 1.862 g. in 100 ml. of an aqueous solution saturated at 20° . This silver salt is isomorphous with silver sulfate.^{7a}

A sample of 3.2587 g. of the equilibrium mixture was chilled in a platinum dish with a salt-ice mixture, and 25 ml. of a 20% potassium hydroxide solution, chilled in the same manner, was stirred rapidly into the acid. A cold, saturated aqueous solution of 5 g. of silver nitrate was run into the neutralized reaction product at ice temperature. During this addition, alkali was added as needed to keep the reaction nearly neutral or slightly alkaline. The solution was rapidly filtered from the yellow silver orthophosphate precipitate, and to the filtrate was added 10 g. of crystallized silver nitrate. Upon dissolution of the crystals, white, crystalline silver monofluorophosphate precipitated. The solution was kept nearly neutral, never on the acid side. After standing for half an hour in ice, with frequent stirring, the crystal precipitate was dried on a porous plate. A yield of 3.42 g. silver monofluorophosphate was obtained, corresponding roughly to 66% of the monofluorophosphoric acid present in the equilibrium mixture. The precipitation of the silver salt could not be used for a quantitative determination since its solubility is too high and it tends to form strongly supersaturated solutions upon precipitation.

Acknowledgment.—This work was done under a graduate cooperative fellowship (R. L.)

(12) A. B. Gerber and F. T. Miles, *ibid.*, 10, 519 (1938).

(13) W. Lange, *Ber.*, 61, 799 (1928).

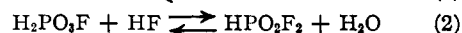
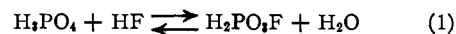
sponsored by the Ozark Chemical Company, Tulsa, Oklahoma.

Summary

1. Anhydrous monofluorophosphoric acid was prepared by reaction of anhydrous metaphosphoric acid with liquid anhydrous hydrogen fluoride according to the equation $\text{HPO}_3 + \text{HF} = \text{H}_2\text{PO}_3\text{F}$. The reaction was complete.

2. In the reaction of a 100% orthophosphoric acid with anhydrous hydrogen fluoride in a 1:1 molar ratio, mono- and difluorophosphoric acids

were formed in equilibrium according to the equations



In the reaction product, 33% of the orthophosphoric acid had remained unchanged, 60% was transformed into mono- and 7% into difluorophosphoric acids. The first of the above equilibrium reactions has been described earlier.

CINCINNATI, OHIO

RECEIVED SEPTEMBER 6, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Molal Electrode Potentials of the Silver-Silver Chloride Electrode in *i*-Propyl Alcohol-Water Mixtures from 0 to 40°¹

BY ROBERT LEE MOORE² WITH W. A. FELSING

Object of the Investigation.—The purpose of this investigation was the continuation of the study of the effect of changes in solvent media upon the thermodynamic properties of strong electrolytes. Such studies were initiated by Harned and co-workers³ at Yale University and some work has been reported from this Laboratory by Patterson and Felsing.⁴ These latter determined the molal electrode potential of the silver-silver chloride electrode in 10 and 20% ethyl alcohol-water mixtures and the ionization constants of propionic acid in the same solvents as well as in 10 and 20% methyl alcohol-water mixtures. It was intended to extend such measurements to propyl and *i*-propyl alcohol solutions in order to determine the effect of the lengthening of the aliphatic carbon chain on these quantities. In such determinations, the value of the molal potential of the reference silver-silver chloride electrode is needed for the calculation of the ionization constant of the weak acid. This was determined by the use of cells of the type



The only report found in the literature on cells containing propyl or *i*-propyl alcohol was that of Harned and Calmon,⁵ who determined the molal potential in 10% *i*-propyl alcohol at a single temperature, 25°. No work, apparently, has been done in *n*-propyl alcohol-water mixtures. This is readily understandable in view of our inability to obtain reversible or reproducible behavior with the hydrogen electrode in this solvent.

(1) Constructed from a portion of the thesis to be presented to the graduate faculty of the University of Texas by Robert Lee Moore in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1947.

(2) du Pont Fellow, 1945-1946, 1946-1947.

(3) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Co., New York, N. Y., 1942.

(4) Patterson with Felsing, *THIS JOURNAL*, **64**, 1478 (1942).

(5) Harned and Calmon, *ibid.*, **61**, 1491 (1939).

Experimental Procedures

The preparation and purification of the materials used as well as the techniques employed are presented under appropriate headings following

Hydrochloric Acid.—Constant boiling hydrochloric acid was prepared by the method of Foulk and Hollingsworth⁶ and the concentrations corresponding to the prevailing barometric pressures were obtained from their tables. In preparing solutions from this material, the molecular weight was taken to be 36.465.

***n*-Propyl Alcohol.**—Eastman Kodak Company "White Label" *n*-propyl alcohol was dried by the method of Lund and Bjerrum⁷ and was then distilled through a one-meter, packed column.

***i*-Propyl Alcohol.**—A commercial 99% material was dried by refluxing over unslaked lime for five hours and was subsequently fractionated through a column packed with glass helices. The middle portion of the distillation was reserved for use.

Hydrogen.—Commercial electrolytic tank hydrogen was washed by passage through a purifying train consisting of sulfuric acid-dichromate solution, sodium hydroxide solution, and water. It was then passed through a drying tube packed with "Drierite" into a heated tube containing copper turnings to remove any traces of oxygen. Upon entering the thermostat, the hydrogen was passed through a twenty-foot coil of copper tubing in order to attain the bath temperature before reaching the pre-saturators.

Electrodes.—The hydrogen electrodes were constructed from platinum foil ($1 \times 1\frac{1}{2}$ cm.) sealed into soft glass tubes; they were platinized in the usual manner. The silver-silver chloride electrodes were of two types. Those employed in the majority of the measurements were of the type described by Patterson and Felsing,⁴ in which a silver oxide-silver chlorate paste was thermally decomposed. In one series of measurements the Harned Type-2 electrode⁸ was also employed. Apparently, the two types were equally satisfactory, the observed cell voltages agreeing to within the precision of measurement. The electrodes were always allowed to age several days in small portions of the solutions on which determinations were made prior to the actual voltage measurements.

Solutions.—Stock solutions somewhat less than one-half molal in hydrochloric acid were prepared in the desired solvent mixtures by weighing out suitable quanti-

(6) Foulk and Hollingsworth, *ibid.*, **45**, 1229 (1923).

(7) Lund and Bjerrum, *Ber.*, **64B**, 210 (1931).

(8) Harned, *THIS JOURNAL*, **51**, 416 (1929).