Hückel expression for activity coefficient (equation 5).

Behavior of Cells

It was found that after the cells were filled and placed in the constant temperature bath, the time required to reach equilibrium (±0.03 mv. for at least two hours) was longer than most other reported work of this nature, especially in the higher *d*-glucose concentrations and in the higher hydrochloric acid concentrations. In the acid range of 0.01 to about 0.1 *m*, where most of the electromotive force readings were recorded, equilibrium times of 2 to 4, 4 to 6, 6 to 8 and 8 to 12 hours were required in the 5, 10, 20 and 30% *d*-glucose solutions, respectively. In the acid range above 0.1 *m* the electromotive force increased very rapidly for four to eight hours or longer until readings were suspended and the cells allowed to stand overnight. When readings were resumed next day the cells had stabilized and constant measurements could be obtained. This initial instability occurred even in solutions prepared several days prior to filling the cells and indicated some reaction occurred after the flow of hydrogen was begun. Scatchard[11] mentioned similar findings in sucrose solutions.

Acknowledgment is gratefully made to the National Bureau of Standards for the determination of the dielectric constants used in this investigation.

Summary

1. The values of the electromotive force at 25° of cells of the type H_2/HCl (*m*), *d*-Glucose (*x*), H_2O (*y*)/AgCl–Ag were determined for acid concentrations up to 0.5 *m* and for 5, 10, 20 and 30 weight per cent. *d*-glucose.

2. From the data obtained the standard potentials of the solutions were determined.

3. An ion size parameter for hydrochloric acid of 6.6 Å. is indicated in the solutions studied.

4. The mean activity coefficients of hydrochloric acid in these solvents are tabulated at rounded molalities to 0.5 *m*.

5. The activity coefficients may be calculated by a Debye–Hückel expression with a constant å and a linear or quadratic term added.

6. The behavior of the cells containing these solvents indicates possible reaction or rearrangement of the *d*-glucose molecule under conditions of the experiment.

CHAPEL HILL, NORTH CAROLINA RECEIVED JULY 8, 1949

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

Studies of Fluorophosphoric Acids and their Derivatives. XIV. Preparation of Anhydrous Difluorophosphoric Acid[1]

BY WILLY LANGE[2] AND RALPH LIVINGSTON[3]

Formation of difluorophosphoric acid was first observed during the hydrolysis of phosphorus oxytrifluoride.[4a,c,5] Formation of the acid in small

$$POF_3 \xrightarrow{H_2O} H[PO_2F_2] \underset{HF}{\overset{H_2O}{\rightleftharpoons}} H_2[PO_3F] \underset{HF}{\overset{H_2O}{\rightleftharpoons}} H_3[PO_4] \quad (I)$$

quantities, together with orthophosphoric, monofluorophosphoric and a trace of hexafluorophosphoric acids, was noted also when phosphorus pentoxide was dissolved in a 40% hydrofluoric acid solution. However, both the di- and the hexafluorophosphoric acids are unstable in this system and undergo slow but complete hydrolysis at room temperature.[4b] During the preparation of phosphorus oxytrifluoride by heating a mixture of calcium fluoride and phosphorus pentoxide in the presence of traces of moisture and fractionating carefully the volatile reaction products, Tarbutton, *et al.*,[6] isolated small quantities of anhydrous difluorophosphoric acid formed probably by hydrolysis of phosphorus oxytrifluoride in accord with (I).

Investigations confirmed, as anticipated from the equilibrium reactions indicated in (I), that neither hydrogen fluoride nor water should be present in appreciable quantities at the end of the reaction in any practical method of preparing pure difluorophosphoric acid. This objective was achieved by allowing phosphorus oxytrifluoride to react with anhydrous monofluorophosphoric acid, in accordance with the equation

$$POF_3 + POF(OH)_2 \longrightarrow 2POF_2(OH) \quad (II)$$

Purification of the liquid product by distillation at 75-mm. pressure results in good yields (calculated on the basis of phosphorus oxytrifluoride absorbed) of pure difluorophosphoric acid.

Experimental

Starting Materials.—Anhydrous monofluorophosphoric acid[5] contained 18.7% F and 30.95% P as compared with

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[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.

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[4] (a) W. Lange, *Ber.*, **60**, 965 (1927); (b) **61**, 799 (1928); (c) **62**, 786 (1929).

[5] W. Lange and R. Livingston, THIS JOURNAL, **69**, 1073 (1947).

[6] G. Tarbutton, E. P. Egan, Jr., and S. G. Frary, *ibid.*, **63**, 1782 (1941).

the theoretical values 19.00% F and 30.98% P. **Phosphorus oxytrifluoride** (b. p. −39.7° (760 mm.), m. p. −39.1° (785 mm.)[6]) was synthesized by a modification of the method of Tarbutton, *et al.* Usually a mixture of 80 g. of calcium fluoride (1.03 moles) and 195 g. of phosphorus pentoxide (1.37 moles) was placed in a vertical reaction tube made of a capped 23-inch length of 2-inch steel pipe. A metal exit tube welded to the top cap of the reactor led to the glass receiver and purification system. This arrangement provided sufficient volume for the swelling of the reaction charge. During the evacuation of the system, the bottom half of the reactor was heated in a furnace to 300°. The connection to the pump was then closed and the reactor heated to 500°. The gaseous products were condensed in a 125-ml. glass bulb cooled in a Dry Ice-bath, which served as the first part of the receiver and purification system. Adequate purification was obtained by distilling the crude product into a second glass bulb, cooled with a Dry Ice-bath, and by discarding a white residue which was solid at 0° and liquid at room temperature. This step was followed by a distillation into a third bulb maintained at about −40°. The phosphorus oxytrifluoride was liquid during the entire distillation which was performed at slightly above atmospheric pressure. The fluoride was given a final distillation during transfer to the apparatus used in the preparation of the difluorophosphoric acid.

Reaction.—The apparatus depicted in Fig. 1 was similar to one used by Kharasch, *et al.*[7] In one experiment 20.7 g. of anhydrous monofluorophosphoric acid was placed in cell B and an equimolar quantity of phosphorus oxytrifluoride, 12.7 ml. corresponding to 21.5 g., was distilled into A which was calibrated in ml.; volume readings were taken with the phosphorus oxytrifluoride just above its melting point. By properly setting the stopcocks, cooling the tube C in a Dry Ice-bath, and allowing the temperature of tube A to rise, the gaseous fluoride bubbled through the monofluorophosphoric acid and the unabsorbed gas condensed in C. By reversing the process, the fluoride was passed again through the acid and the unabsorbed material condensed back in A. The decrease in volume of unreacted phosphorus oxytrifluoride was then read; 46% had been absorbed in the first two passes. Twenty passes in all were made with the result that 78% of the original phosphorus oxytrifluoride was absorbed. A small quantity of difluorophosphoric acid was found to have distilled into tubes A and C. It was returned to B by warming tubes A and C and chilling cell B. Cell B was then disconnected from the system at the standard taper joint and made part of an all-glass distillation apparatus. The product was distilled at about 75 mm. (b. p. 42–43°) to yield 26.9 g. of pure difluorophosphoric acid (81.5% based on absorbed phosphorus oxytrifluoride).

Anal.[5] Calcd. for HPO_2F_2: P, 30.38; F, 37.26. Found: P, 30.67; F, 37.17.

Properties.—Difluorophosphoric acid is a thin, clear liquid which on exposure to moist air forms very irritating, dense fumes resembling those of anhydrous fluorosulfonic and perchloric acids of the same isosteric type. The dry acid does not attack glass noticeably at room temperature. It has an average density of d^{25}_4 1.583, m. p. −96.5 ± 1°. The vapor pressure-temperature relationship is given by the equation

$$\log_{10}p = -1732/T + 7.333 \quad (\text{for } T = 324.8 \text{ to } 366.0°)$$

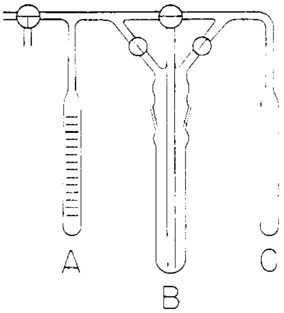

Fig. 1.—All-glass apparatus for reaction of phosphorus oxytrifluoride and monofluorophosphoric acid: A, calibrated tube; B, reaction cell.

Measured and calculated vapor pressures are listed in Table I.

TABLE I

MEASURED AND CALCULATED VAPOR PRESSURES OF DIFLUOROPHOSPHORIC ACID

T, °K.	Measured pressure, mm.	Calcd. pressure, mm.	% Deviation
324.8	100.5	100.4	−0.10
335.4	147.7	148.0	+ .23
344.3	201.4	201.2	− .10
351.0	251.4	251.0	− .16
356.8	301.4	301.9	+ .17
366.0	399.9	399.7	− .05

Decomposition was noted when efforts were made to distil the acid at temperatures above 100°, where the vapor pressure is about 500 mm.; hence difluorophosphoric acid should not be distilled at atmospheric pressure. The products of thermal decomposition were not investigated. Extrapolation indicates that the normal boiling point is 115.9° as compared with 108–111° found by Tarbutton, *et al.*[6] The heat of vaporization was calculated as 7,925 cal. per mole and the Trouton constant is 20.4.

On mixing difluorophosphoric acid with water, slow hydrolysis takes place in accordance with equation I until an equilibrium is reached. Neutralization of a freshly prepared solution of the acid with an aqueous solution of an alkali hydroxide yields the difluorophosphate; however, the $PO_2F_2^-$ ion is unstable even in neutral solution, so that the preparation of the pure alkali difluorophosphates by this method is quite difficult.

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Summary

Anhydrous difluorophosphoric acid, HPO_2F_2, was prepared in good yield by the reaction of anhydrous monofluorophosphoric acid with gaseous phosphorus oxytrifluoride in accord with the equation $POF(OH)_2 + POF_3 = 2\ POF_2(OH)$.

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[7] M. S. Kharasch, D. W. Lewis and W. B. Reynolds, THIS JOURNAL, **65**, 493 (1943).