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

# The Partial Vapor Pressures of Water and Ammonia from the System Water–Phosphoric Acid–Ammonia

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## Introduction

This investigation of the ammonium orthophosphates was undertaken because of the growing importance of these salts commercially and the lack of precise information concerning their behavior.

Even such a fundamental property as the extent of hydrolysis of solutions of these salts has been investigated only partially previous to this work. Ball[1] measured the acidity of solutions of mono- and diammonium phosphates. Buchanan and Winner,[2] when studying the solubility of the above salts, found that only the latter was hydrolyzed. Ross, Merz and Jacob[3] discuss the dissociation of the three ammonium orthophosphates both in solution and in the solid form. The hydrolysis of solutions of the related compounds, disodium ammonium phosphate ($Na_2NH_4PO_4$) and sodium ammonium hydrogen phosphate ($NaNH_4HPO_4$), was investigated by Abbott and Bray.[4]

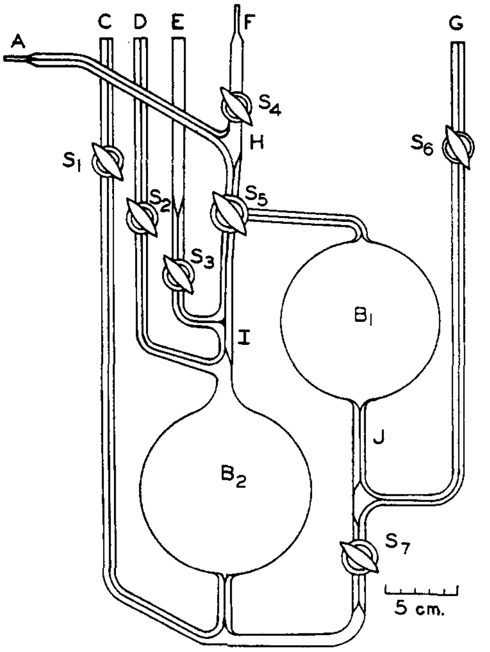

Fig. 1.—Sketch of the vapor pressure apparatus.

The dissociation pressures of some of the salts of this system have been studied by Warren[5] (mono-, di- and tri-ammonium phosphates), by Britzke and Dunaev[6] (diammonium phosphate) and by de Passille[7] (di- and tri-ammonium phosphates). The present work supplies the dissociation pressures of ammonia and water from triammonium phosphate trihydrate, $(NH_4)_3PO_4 \cdot 3H_2O$.

### Vapor Pressure Apparatus

A static method for measuring vapor pressure was devised which permitted the determination of the composition of the two phases in equilibrium. The principal part of the equipment was the Pyrex glass apparatus shown in Fig. 1. The bulbs $B_1$ and $B_2$ were of 500 and 700 ml. capacity, respectively. The apparatus was supported by a frame made of brass angle strips, the bulbs resting on brass rings covered with rubber tubing. The frame was fastened in the thermostat at two points only so that it could be rocked about an almost vertical axis through the center of $B_1$. Bulb $B_2$ could then be moved through an arc of approximately 1.3 cm. twice per second by an eccentric arm from an electric motor. The glass tubing H to A and the rubber tube connection at A were wrapped with auxiliary heating coils to maintain a temperature somewhat higher than that of the thermostat. The volume of $B_1$ from $S_5$ to a mark on J was determined carefully. A scale fastened to tube J was calibrated in terms of the volume of the tube.

The operation of the apparatus was typically as follows: $B_1$, from $S_5$ to G to $B_2$, was filled with mercury through G. Then $B_2$ was rinsed with carbon dioxide-free air. Next the desired solution was added through C and the apparatus submerged in the water-bath to bring the water level just above $S_5$. After reaching temperature equilibrium, $S_2$ was opened momentarily to reduce the inside pressure to atmospheric and the apparatus rocked to establish equilibrium between the liquid and vapor in $B_2$; this required from twelve hours to several days, the longer time being when solid phases were present. The temperature of the water-bath was maintained to $\pm 0.005°$ at 35° and below and to $\pm 0.015°$ above that range.

To remove the vapor sample for analysis, the mercury was allowed to flow (about 30 ml./min.) from $B_1$ to $B_2$, being displaced by the vapor from $B_2$ through $S_5$. The mercury was stopped in J to permit the determination of the volume of the sample, which was finally removed (by displacement to H with mercury from G) through the absorption train connected to A after the temperature of the water-bath was raised about 1° to prevent condensation.

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(1) Ball, THIS JOURNAL, **52**, 3901 (1930).

(2) Buchanan and Winner, *J. Ind. Eng. Chem.*, **12**, 448 (1920).

(3) Ross, Merz and Jacob, *ibid.*, **21**, 286 (1929).

(4) Abbott and Bray, THIS JOURNAL, **31**, 729 (1909).

(5) Warren, *ibid.*, **49**, 1904 (1927).

(6) Britzke and Dunaev, *J. Chem. Ind. U. S. S. R.*, **5**, 161 (1928).

(7) De Passille, *Compt. rend.*, **199**, 356 (1934).

Tube A was finally washed with a stream of purified air admitted at $S_4$.

The absorption train consisted of a small tube filled with barium oxide desiccant, for absorbing water, and the ammonia absorber which was made of two 125-ml. Erlenmeyer flasks fitted with glass tubes so that the gas stream bubbled through the liquid. Following this was a Mariotte flask adjusted to maintain the pressure at A a little below atmospheric. The rubber connections at F, A and between the water and ammonia absorbers were treated as suggested by Pregl.[8]

After absorption of the vapor sample, the temperature of the water-bath was lowered to its original value and a portion of liquid removed from $B_2$, by displacement with mercury, through $S_2$ into a weighed sampling bulb attached at D. Any liquid in the capillary tube outside the stopcock on the sampling bulb was removed and the bulb wiped and weighed. The long tube on the sampling bulb was broken under an excess of sulfuric acid, the liquid then diluted to volume in a volumetric flask and suitable aliquots taken for the determination of ammonia and phosphate content.

### Reagents

The preparation and purification of the materials used in this research which are not specified elsewhere were as follows.

**Phosphoric Acid.**—A "reagent" grade phosphoric acid (85% $H_3PO_4$) was concentrated to near 97% and crystallized by seeding with a few crystals of the acid. The crystals were separated by centrifuging in porcelain cups, and dissolved in water to make a stock solution which contained approximately 45% phosphoric acid. This solution was diluted to the desired strength, as needed. A check on the purity of this acid solution was obtained by analyzing three of the diluted solutions both gravimetrically for phosphate content and acidimetrically, the two methods agreeing within the limits of experimental error. The stock solution was also found to be free of reducing substances.[9]

**Diammonium Phosphate.**—A "C. P." grade of diammonium phosphate was recrystallized twice, and dissolved in water to give an approximately saturated solution. Since there was loss of ammonia from the solutions during recrystallization, the stock solution was analyzed for both ammonia and phosphate content, and ammonia added until the analyses showed a value of two for the molar ratio of ammonia to phosphate ion. This solution was diluted suitably for use in the experiments on the hydrolysis of diammonium phosphate.

**Ammonia.**—The gas from a tank of liquid ammonia was led through a barium oxide tube before use to remove any water which might have been present.

**Water.**—The water used was distilled through a block tin condenser and stored in a tin tank. Its specific resistance was approximately $10^6$ ohms, without removal of the carbon dioxide.

**Ammonium Chloride.**—This salt was purified by recrystallization.

**Mercury.**—The mercury was cleaned by allowing it to drop through a column of dilute nitric acid, in the conventional apparatus.

### Analytical Methods, Calculation and Accuracy of Vapor Pressure Determinations

**Determination of Water in the Vapor Phase.**—A microtechnique was employed. A Kuhlmann balance and microabsorption tubes of the type described by Kemmerer and Hallett[10] were used. The method of weighing was essentially that described by Pregl,[11] except that only a single wiping with a slightly damp chamois was made.

The final choice of barium oxide as a desiccant in the absorption tube was reached after aluminum oxide, calcium oxide and potassium hydroxide had been found unsatisfactory. The barium oxide was pulverized and packed in the absorption tubes in layers separated by Pyrex fiber. The flow of the gas stream through the absorption train was 5 ml. per min., the maximum rate that could be used safely.

The increase in weight of the barium oxide was taken as the weight of water in the sample except at temperatures above 25°. In these cases, a correction was made for the vapor pressure of mercury; at 50° this correction was 0.057 mg.

**Determination of Ammonia in the Vapor Phase.**—Slightly acidulated water or 4% boric acid solution was used as an absorbent for ammonia. Forty ml. of the former was used and the ammonia content determined directly by Nesslerization[12] when the ammonia pressure was less than 0.3 mm. The lowest pressure that could be measured by this method was about 0.002 mm.

Twenty-five or 50 ml. of the boric acid solution was used for the higher pressures of ammonia, and the quantity determined by titrating with standard hydrochloric acid, using brom phenol blue indicator. The end-point of this titration was determined in such a manner as to obviate the effect of the salts and water on the indicator. This was accomplished through the use of a solution of ammonium chloride of the same normality as the hydrochloric acid. For each titration a similar amount of the boric acid solution was treated in just the same way as the portion with the sample, except that ammonium chloride solution was added in place of the acid, until the sample showed approximately the color of the end-point. Then standard acid was added to the duplicate until the colors matched, and this volume subtracted from the volume of acid added to the sample. This corrected volume represented the acid equivalent to the ammonia in the sample. The end-point was checked by adding more acid to one solution, and matching the color again by adding to the other. Usually the correction amounted to a few tenths of a ml. of 0.015 $N$ acid. Under these conditions the color change caused by 0.01 ml. of the standard acid could be seen.

**Determination of Ammonia in Solution.**—The method of distillation from an alkaline solution into 4% boric acid solution, as used by Markley and Hann,[13] was employed.

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[8] Roth, "Quantitative Organic Microanalysis of Fritz Pregl," 3rd English Edition, P. Blakiston's Son and Co., Inc., Philadelphia, Penna., 1937, p. 26.

[9] Collins, Farr, Rofin, Spencer and Wichers, *Ind. Eng. Chem.*, **19**, 1369 (1927).

[10] Kemmerer and Hallett, *Ind. Eng. Chem.*, **19**, 173 (1927).

[11] Roth, *loc. cit.*, p. 43.

[12] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 642.

[13] Markley and Hann, *J. Assoc. Off. Agr. Chem.*, **8**, 455 (1925).

The same principle of color matching, as applied in the previous determination, was utilized here.

**Determination of Phosphoric Acid.**—The phosphate analyses were performed by a double precipitation of magnesium ammonium phosphate and final ignition to magnesium pyrophosphate ($Mg_2P_2O_7$).[14] The phosphoric acid was titrated as a dibasic acid using phenolphthalein indicator.[15]

**Standardization of Hydrochloric Acid.**—This reagent was standardized using phenolphthalein indicator with carbonate-free sodium hydroxide, using recrystallized potassium biphthalate[16] as the primary standard.

**Calculations and Constants Used.**—Use was made of the perfect gas law to calculate partial pressures from the number of moles, analytically determined, of ammonia or water vapor. The value of the gas constant $R$ was taken to be 1.9864 cal. The weighings were corrected to values *in vacuo* except in the case of solutions whose densities were unknown.

**Accuracy of the Vapor Pressure Determinations.**—Numerous determinations of the vapor pressure of water were made at 25° to develop the details of the procedure. The average of nine determinations was 23.778 mm.; average deviation was 0.018 mm.; the deviation of the mean from the accepted value[17] was −0.001 mm.

The partial pressures of ammonia and water from several aqueous solutions of ammonia were determined at 25° in an early part of this research to test the method. While the results were not as consistent as those obtained after the technique of the various operations had been improved, the data are shown in Table I, to indicate the accuracy at this stage of development.

TABLE I

A COMPARISON OF THE PARTIAL PRESSURES OF AMMONIA AND WATER FROM AQUEOUS SOLUTIONS OF AMMONIA AT 25° WITH THOSE PUBLISHED PREVIOUSLY

| Ammonia in soln., % | Found, partial press. of ammonia, mm. | Found, partial press. of water, mm. | Calculated, partial pressure, mm. Ammonia de Wijs[a] | Calculated, partial pressure, mm. Ammonia Perman[b] | Calculated, partial pressure, mm. Water Wilson[c] | Calculated, partial pressure, mm. Water Perman[b] |
|---|---|---|---|---|---|---|
| 3.959 | 32.77 | 22.80 | 32.6[d] | | 22.68 | |
| 2.016 | 16.13 | | 15.91 | 15.8 | 23.22 | 23.0 |
| 2.012 | 15.78 | 22.78 | 15.88 | 15.7 | 23.22 | 23.0 |
| 1.997 | 16.01 | 23.57 | 15.76 | 15.6 | 23.22 | 23.0 |
| 2.008 | 16.11 | 22.98 | 15.85 | 15.7 | 23.22 | 23.0 |
| 2.008 | 16.06 | 23.07 | 15.85 | 15.7 | 23.22 | 23.0 |

[a] De Wijs, Thesis, Delft, 1923; "International Critical Tables," Vol. III, p. 259. [b] Perman, *J. Chem. Soc.*, **83**, 1168 (1903). [c] Wilson, *Univ. Ill. Exp. Sta., Bull.* 146 (1925). [d] This value was obtained by extrapolating de Wijs' curve with the aid of data from Morgan and Maass.[18]

To ascertain whether or not ammonia was absorbed by the barium oxide in the water absorption tube, the following experiment was performed. The barium oxide from one of these tubes, which had been used for six determinations and through which approximately 0.4 millimole of ammonia had passed, was divided into two parts, and each analyzed for ammonia. The part of the barium oxide which had absorbed the water in those six determinations, *i. e.* the front end, showed no ammonia, and the rest of it showed $6.5 \times 10^{-3}$ millimole. The molar ratio of ammonia to barium oxide in the latter portion of the tube was calculated and found to be $1.9 \times 10^{-4}$. Hence absorption of ammonia by the barium oxide was considered to be negligible. The small residues of ammonia left in the barium oxide from each determination would introduce a very small error, since successive determinations were made on solutions with the same, or nearly the same, pressures of ammonia, and were made under similar conditions, thus making the residues approximately the same each time.

An estimate of the reliability and accuracy of the method was obtained from the last data taken, namely, those recorded in Table IV. The average deviation of the thirteen individual points from the straight line determined by the method of least squares was found to be 0.09 mm. for the water pressure and 0.03 mm. for the ammonia pressure, with about 60% of the variation due to four values in the first case, and two in the latter.

**Partial Pressures of Ammonia and Water from Solutions of the Ammonium Orthophosphates at 25°.**—Owing to hydrolysis, solutions of the secondary and tertiary ammonium phosphates would be expected to exhibit a pressure of ammonia. To study the extent of this reaction, solutions of phosphoric acid were titrated with anhydrous ammonia, and the partial pressures of both ammonia and water above the solutions determined at 25° as a function of the composition of the solution. The results of these experiments are shown in Table II, and graphically in Fig. 2.

Kabulkov and Zagwosdkin[19] have published the only available data with which these may be compared. Their values for the partial pressure of water from the 1.0 and 0.25 $M$ solutions are 23.2 and 23.6 mm., respectively; the corresponding results reported herein are 23.16 and 23.55 mm.

A noteworthy point in Fig. 2 is on Curve E, where $R$ equals 3. The fact that no break in the value of the ammonia pressure occurs here shows that triammonium phosphate is practically completely hydrolyzed in this solution.

**Hydrolysis of Diammonium Hydrogen Phosphate at 25°.**—Diammonium phosphate undergoes the following hydrolytic reaction

$$(NH_4)_2HPO_4 + H_2O \rightleftarrows NH_4OH + NH_4H_2PO_4 \quad (1)$$

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[14] Hillebrand and Lundell, *loc. cit.*, p. 563.

[15] Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1936, p. 533.

[16] Kolthoff and Sandell, *loc. cit.*, p. 524.

[17] "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 212.

[18] Morgan and Maass, *Can. J. Research*, **5**, 162 (1931).

[19] Kabulkov and Zagwosdkin, *Z. anorg. allgem. Chem.*, **224**, 315 (1935).

TABLE II

PARTIAL PRESSURES OF AMMONIA AND WATER FROM SOLUTIONS OF THE AMMONIUM ORTHOPHOSPHATES AT 25°

| Phosphate ion, molality | $R^a$ | Partial pressures in mm. Water | Partial pressures in mm. Ammonia |
|---|---|---|---|
| 0.9971 | 0 | 23.16 | 0 |
| | 0 | 23.15 | 0 |
| | 0.4860 | | <0.002 |
| | 0.4860 | | < .002 |
| | 1.067 | 23.10 | < .002 |
| | 1.239 | 23.11 | < .002 |
| | 1.469 | | .002 |
| | 1.469 | | .002 |
| | 1.469 | | .002 |
| | 1.605 | | .003 |
| | 1.762 | 23.09 | .003 |
| | 1.854 | 23.14 | .037 |
| | 2.086 | | 1.81 |
| | 2.091 | 23.10 | |
| | 2.278 | | 4.70 |
| | 2.530 | | 8.77 |
| | 2.879 | 22.78 | 14.73 |
| 0.5010 | 1.274 | | 0.002 |
| | 1.532 | 23.49 | .003 |
| | 1.689 | 23.36 | .003 |
| | 1.940 | | .089 |
| | 2.052 | 23.30 | .53 |
| | 2.401 | 23.19 | 3.27 |
| | 2.719 | 23.10 | 5.74 |
| | 2.719 | 23.12 | 5.75 |
| | 3.299 | 23.03 | 9.92 |
| | 3.593 | 22.96 | 12.36 |
| 0.2501 | 0 | 23.53 | 0 |
| | 0 | 23.57 | 0 |
| | 1.281 | | <0.002 |
| | 1.444 | | < .002 |
| | 1.617 | 23.55 | < .002 |
| | 1.886 | | .039 |
| | 2.030 | 23.49 | .22 |
| | 2.076 | 23.54 | .36 |
| | 2.225 | 23.37 | .80 |
| | 2.388 | 23.38 | 1.42 |
| | 2.627 | 23.24 | 2.22 |
| | 2.832 | 23.24 | 2.91 |
| | 2.994 | 23.33 | 3.46 |
| | 2.994 | 23.36 | 3.47 |

[a] $R$ represents the molar ratio of ammonia to phosphate ion.

The hydrolysis constant is defined by the equation

$$K_h = k_w/K_aK_b \qquad (2)$$

and can be formulated in terms of the experimental values as follows. We have

$$K_w = a_{H^+}a_{OH^-}/a_{H_2O}$$
$$K_a = a_{H^+}a_{HPO_4^{--}}/a_{H_2PO_4^-}$$
$$K_b = a_{NH_4^+}a_{OH^-}/a_{NH_4OH}$$

and substituting in equation (2) we obtain

$$K_h = \frac{a_{H_2PO_4^-}a_{NH_4OH}}{a_{HPO_4^{--}}a_{NH_4^+}a_{H_2O}}$$

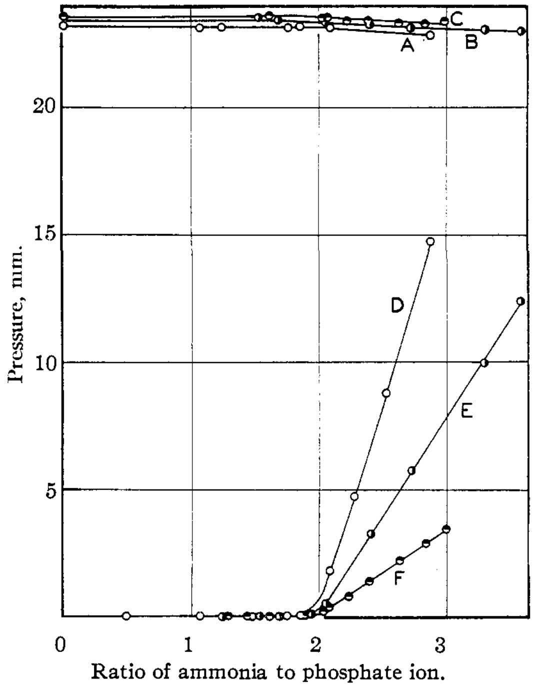

Fig. 2.—Partial pressures of ammonia and water from solutions of the ammonium orthophosphates at 25°. Curves A, B and C represent the partial pressure of water from solutions whose phosphate ion molalities are 1.0, 0.5 and 0.25, respectively. Curves D, E and F show the partial pressures of ammonia from the same solutions, respectively.

Consider a solution of diammonium hydrogen phosphate, of molality $M_2$, of which $X$ is the fraction hydrolyzed. Then at equilibrium the molality of the $H_2PO_4^-$ ion and also that of the ammonium hydroxide is $XM_2$; also the molalities of the $HPO_4^-$ and $NH_4^+$ ions are $(1 - X)M_2$ and $(2 - X)M_2$, respectively, assuming no appreciable ionization of the ammonium hydroxide. Then

$$K_h = \frac{X^2}{(1-X)(2-X)} \frac{\gamma_{H_2PO_4^-}\gamma_{NH_4OH}}{\gamma_{HPO_4^{--}}\gamma_{NH_4^+}a_{H_2O}}$$

Letting

$$K_h' = \frac{X^2}{(1-X)(2-X)} \qquad (3)$$

and expressing in logarithmic form

$$\log K_h = \log K_h' + \log \frac{\gamma_{H_2PO_4^-}\gamma_{NH_4OH}}{\gamma_{HPO_4^{--}}\gamma_{NH_4^+}a_{H_2O}}$$

Use was made of a correction factor similar to the Debye and Hückel expression for the activities of ions for evaluating the last term of the preceding equation. Doing this we obtain

$$\log \frac{\gamma_{H_2PO_4^-}}{\gamma_{HPO_4^{--}}\gamma_{NH_4^+}} = \frac{4A\sqrt{\mu}}{1 + B\sqrt{\mu}}$$

$A$ has the value 0.506 at 25° and $B$ is a semi-

TABLE III

HYDROLYSIS OF DIAMMONIUM HYDROGEN PHOSPHATE AT 25°

| Diammonium hydrogen phosphate molality, ($M_2$) | Partial press., mm. Water | Partial press., mm. Ammonia | $M_0$ | $X$ | $-\log K_h'$ | $\mu$ | $-\log K_h^*$ |
|---|---|---|---|---|---|---|---|
| 5.007 | 21.13 | 1.019 | 0.07784 | 0.01555 | 3.9076 | 14.86 | 2.067 |
| 5.007 | 21.24 | 0.959 | .07328 | .01463 | 3.9607 | 14.87 | 2.119 |
| 2.745 | | .667 | .05089 | .01854 | 3.7528 | 8.133 | 2.053 |
| 2.219 | 22.32 | .618 | .04705 | .02120 | 3.6342 | 6.564 | 1.989 |
| 1.662 | | .474 | .03600 | .02166 | 3.6153 | 4.919 | 2.045 |
| 1.662 | 22.32 | | | | | | |
| 1.104 | 22.74 | .352 | .02664 | .02413 | 3.5200 | 3.259 | 2.068 |
| 0.9211 | | .325 | .02468 | .02673 | 3.4294 | 2.714 | 2.030 |
| .4011 | | .144 | .01077 | .02685 | 3.4257 | 1.182 | 2.276 |

empirical constant related to the ionic radius, $a$, by the relation $B = 0.327 \times 10^8 a$, when the difference between the molality and normality is negligible.

Next, a quantity $K_h^*$ was defined by the equation

$$\log K_h^* = \log K_h' + \frac{4A\sqrt{\mu}}{1 + B\sqrt{\mu}} \qquad (4)$$

If $\log K_h^*$ is plotted against $\mu$, the ionic strength, the intercept at zero ionic strength is the logarithm of the hydrolysis constant.

The following procedure was employed to evaluate $K_h'$. Suppose that a membrane were available which would permit the passage of ammonia but which would be impermeable to water vapor. If this membrane were placed between a solution of diammonium phosphate and water, ammonia would distil from the former to the latter until the activity of the ammonia would become the same in all three phases. Let $a_0$ represent the activity and $M_0$ the molality of un-ionized ammonia in the ammonia solution. Let $P_0$ represent the partial pressure of ammonia. The ammonia solution would exhibit the equilibria

$$NH_{3(g)} \rightleftarrows NH_{3(soln.)}$$

$$NH_{3(soln.)} + H_2O \rightleftarrows NH_4OH$$

$$K_0 = \frac{(a_{NH_4OH})}{(a_{NH_3(soln.)})(a_{H_2O})}$$

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

Then

$$a_0 = M_0\gamma_0 = (a_{NH_3(soln.)}) + (a_{NH_4OH}) = (a_{NH_3(soln.)})(1 + K_0 a_{H_2O})$$

and since the activity of ammonia in solution is proportional to its partial pressure above the solution

$$a_0 = M_0\gamma_0 = P_0K_2(1 + K_0 a_{H_2O})$$

Therefore, the activity of the un-ionized ammonia in both solutions would be directly proportional to the pressure of ammonia, if the activity of water were the same in the two cases.

The value of $M_0$, the molality of un-ionized ammonia in the water solution, was calculated by using $P_0$, the ionization constant of ammonium hydroxide, and the pressure–composition curve for ammonia in water.[20] Since the activity of the un-ionized ammonia was essentially the same in the two solutions, $M_0$ was also taken as equal to $XM_2$, the molality of the un-ionized ammonia in the diammonium phosphate solution. This was based on two approximations: first, that the activity coefficients of the un-ionized ammonia in the two solutions were the same, and, second, that the activities of water in the two solutions were the same. $X$ was calculated from this value of $M_0$ and the analytically determined $M_2$. These values were introduced into equation (3) and $K_h'$ computed.

The molality of diammonium phosphate was varied approximately from 5.0 to 0.4 and the measured values of $P_0$ plotted against $M_2$. These values are shown in Table III, and graphically in Fig. 3, Curve A. Curve B gives the corresponding values of the partial pressure of water, with the addition of three values in the dilute solution from Fig. 2.

Table III also includes the calculated values for $-\log K_h^*$, arbitrarily taking $B$ in equation (4) to be 0.84. No trend is apparent in the values of $-\log K_h^*$; the best value is probably 2.053 ($K_h^* = 8.86 \times 10^{-3}$), the average of the values given omitting the last one for the most dilute solution because of its evident inconsistency. $K_h$ was found to be $8.87 \times 10^{-3}$, using the values $10^{-14}$ for $K_w$, $6.226 \times 10^{-8}$ for $K_a$[21] and $1.81 \times 10^{-5}$ for $K_b$.[22] Since the arbitrarily chosen value of $B$ influenced the magnitude of $K_h$, the agree-

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[20] The values for the partial pressures of ammonia from the ammonia–water solutions were those of de Wijs (see Note *a*, Table I).

[21] Nims, THIS JOURNAL, **55**, 1946 (1933).

[22] "International Crit. Tables," Vol. VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 240.

ment of the two values for this constant is not a complete check on the validity of the present work. Using the value 0.84 for $B$, however, the average ionic radius was calculated to be $2.56 \times 10^{-8}$ cm., slightly lower than similarly obtained values[23] yet nevertheless quite reasonable. Hence the agreement of the value of $K_h$ obtained from our experimental data with that calculated from the defining equation (2) is deemed to be satisfactory.

**Dissociation Pressures of Triammonium Phosphate Trihydrate from 25 to 50°.**—The measurement of the dissociation pressures corresponding to the reaction

$$(NH_4)_3PO_4{\cdot}3H_2O(s) \rightleftharpoons (NH_4)_2HPO_4(s) + 3H_2O(g) + NH_3(g) \quad (5)$$

was accomplished by preparing a solution saturated with respect to both solids and measuring the partial pressures of ammonia and water exerted by this solution over the temperature range 25 to 50°. This solution was prepared by adding gaseous ammonia to the 45% phosphoric acid solution until the above solids were present.

The phase rule shows that during the addition of ammonia the composition of the solution and the partial pressures of ammonia and water will not change as long as both triammonium phosphate trihydrate and diammonium phosphate are in equilibrium with the solution. This constancy of the partial pressures with changing total composition was taken as the chief criterion for determining when the two solid phases were present. The solubility curves of the system, known approximately at these temperatures[24,2] served to locate the approximate composition of the solution at this equilibrium. When nearly enough ammonia had been added to give the above equilibrium mixture, a vapor pressure determination was made, more ammonia or 45% phosphoric acid added, and the determination repeated, until at least two successive experiments gave the same values for the partial pressures. Proceeding in this manner, four determinations at 50° gave essentially the same partial pressures when the ammonia content of the mixture was varied about 3.2%. This variation was calculated from the weight of solution added and the time during which ammonia was added through a calibrated Venturi meter.

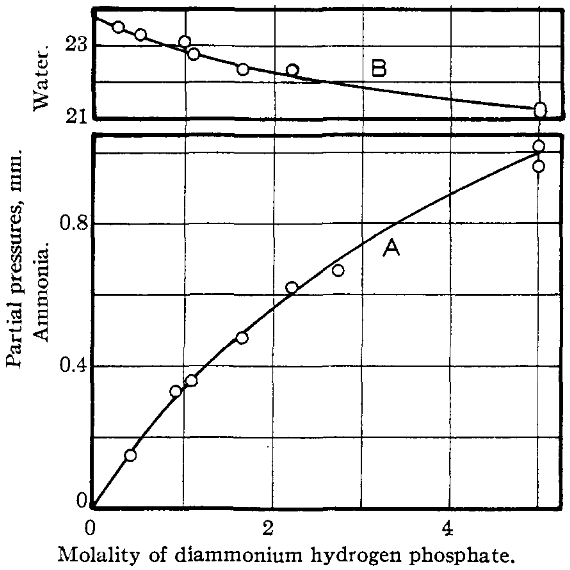

Fig. 3.—The hydrolysis of diammonium phosphate at 25°.

Then the temperature variations of the partial pressures were determined by changing the temperature of the apparatus to the values 40, 45, 35, 30, 25, 20 and 25°, respectively. The data obtained are given in Table IV. Figure 4 shows a graph of the logarithm of the pressure against the reciprocal of the absolute temperature.

Table IV

Dissociation Pressures of Triammonium Phosphate Trihydrate from 25 to 50°

| Temp., °A. | Partial press., mm. Water | Partial press., mm. Ammonia | $\Delta R$[a] % | $-\log K_p$ | $K_p \cdot 10^7$ | $\Delta F°$ calcd. | $\Delta S$ calcd. |
|---|---|---|---|---|---|---|---|
| 298.14 | 21.26 | 3.995 | | | | | |
| 298.14 | 21.11 | 3.995 | | | | | |
| 298.14 | 21.14 | 4.012 | +1.0 | 6.9440 | 1.138 | 9469 | 151.5 |
| 303.16 | 28.10 | 5.958 | | 6.4017 | 3.966 | 8877 | 149.0 |
| 308.14 | 37.04 | 8.825 | | 5.8714 | 13.45 | 8275 | 146.6 |
| 313.14 | 48.34 | 12.84 | | | | | |
| 313.14 | 48.39 | 12.82 | | | | | |
| 313.14 | 48.48 | 12.85 | +0.5 | 5.3600 | 43.65 | 7677 | 144.3 |
| 318.14 | 62.89 | 18.55 | | 4.8591 | 138.3 | 7071 | 142.0 |
| 323.14 | 80.51 | 26.39 | | | | | |
| 323.14 | 80.50 | 26.27 | −0.1 | | | | |
| 323.14 | 80.33 | 26.39 | −3.0 | | | | |
| 323.14 | 80.45 | 26.50 | −0.1 | 4.3853 | 411.8 | 6482 | 139.8 |

[a] $\Delta R$ represents the increase in the value of the ratio of ammonia to phosphoric acid in the mixture from the value in the experiment immediately preceding the one for which the value is tabulated.

From the average values at each temperature the following equations were calculated by the method of least squares, where the pressures are

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[23] Dole, "Principles of Experimental and Theoretical Electrochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 302.

[24] D'Ans and Schreiner, *Z. physik. Chem.*, **75**, 95 (1911); Parker, *J. Phys. Chem.*, **18**, 653 (1914); Jänecke, *Z. physik. Chem.*, **127**, 71 (1927); **A177**, 7 (1936).

in mm. of mercury and $T$ is the absolute temperature.

$$\log_{10} P_{NH_3} = (-3161.3/T) + 11.2045 \quad (25 \text{ to } 50°)$$
$$\log_{10} P_{H_2O} = (-2239.0/T) + 8.8353 \quad (25 \text{ to } 50°)$$

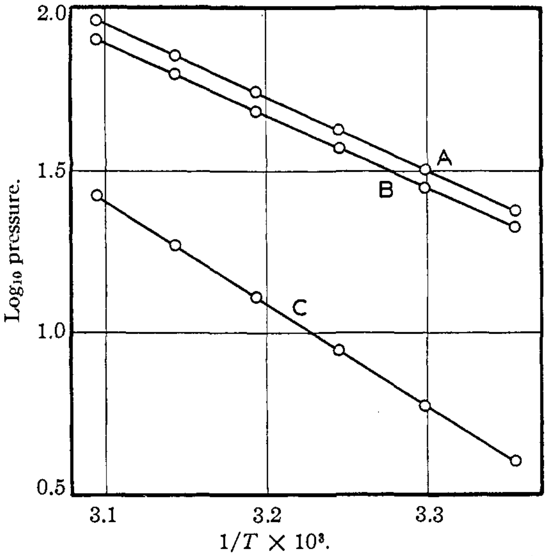

Fig. 4.—The dissociation pressures of triammonium phosphate trihydrate from 25 to 50°. Curve A shows the vapor pressure of pure water. Curves B and C represent the partial pressures of water and ammonia, respectively.

For equation (5) the following well-known thermodynamic quantities were evaluated

$$K_p = (P_{H_2O})^3(P_{NH_3})$$
$$\log_{10} K_p = (-\Delta H/2.3026RT) + C$$
$$\Delta F° = -RT \log_e K_p$$
$$\Delta S = \Delta H/T$$

The following equations were derived from the above after converting the unit of pressure to the atmosphere

$$\log_{10} K_p = (-9878.4/T) + 26.1870$$
$$\Delta F° = 45{,}183 - 119.78\ T \text{ cal.}$$
$$\Delta H = 4.518 \cdot 10^4 \text{ cal.}$$

The values of $\log_{10} K_p$, $K_p$, $\Delta F°$ and $\Delta S$, which were computed directly from the experimental values, are listed in the last four columns of Table IV.

Samples of the solution were removed at both 25 and 50° and subsequently analyzed. The results of these analyses are given in Table V.

TABLE V

COMPARISON OF THE ANALYSIS OF THE SOLUTIONS SATURATED WITH DIAMMONIUM PHOSPHATE AND TRIAMMONIUM PHOSPHATE TRIHYDRATE AT 25 AND 50°

| | Found, % | | Calcd., % | | |
|---|---|---|---|---|---|
| Temp., °C. | Ammonia in soln. | Phosphoric acid in soln. | Ammonia in soln. | Phosphoric acid in soln. | Source |
| 25 | 10.79 | 30.08 | 11.03 | 31.0 | D'Ans and Schreiner[25] |
| 25 | 10.79 | 30.38 | | | |
| 50 | 12.08 | 34.10 | 12.7 | 34.7 | Jänecke[26] |

It is believed that the discrepancies in Table V are not due to lack of attainment of equilibrium conditions, because of the constancy of the ammonia pressure found. Whether or not the analytical values were in error due to a mistake in sampling is difficult to judge. On the other hand, the values of Jänecke are the result of an interpolation and can only be considered as approximate.

Parker's[24] investigation at 25° throws no light on this particular point and apparently is in error in this region. At least his data for this range are at variance with those of other investigations,[25,2] which are in fair agreement. None of these, however, except that of D'Ans and Schreiner, has included this point.

## Summary

1. A method for determining the partial pressures of ammonia and water from solutions has been developed.

2. The partial pressures of these gases were measured at 25° from solutions of orthophosphoric acid containing varying amounts of ammonia.

3. These partial pressures were determined at 25° for solutions of diammonium phosphate of varying molality, and the hydrolysis constant of this salt was calculated.

4. The dissociation pressures of ammonia and water for the reaction: $(NH_4)_3PO_4 \cdot 3H_2O(s) \rightleftarrows (NH_4)_2HPO_4(s) + 3H_2O(g) + NH_3(g)$ were measured over the temperature range from 25 to 50°. From these measurements $K_p$, $\Delta F°$, $\Delta S$ and $\Delta H$ were computed for this reaction.

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(25) D'Ans and Schreiner, *Z. physik. Chem.*, **75**, 95 (1911).

(26) Jänecke, *ibid.*, **A177**, 7 (1936).