[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

THE ACIDITY OF MONO AND DIAMMONIUM PHOSPHATES

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It is well known that many samples of diammonium phosphate contain varying amounts of the mono salt. The only test bearing upon the ammonia–phosphate ratio in the diammonium salt which the writer has been able to find is that of the Committee on Analytical Reagents of the American Chemical Society.[1] According to this test, 1 g. of the salt in 10 ml. of water should give a pink color with 2 drops of phenolphthalein solution. This is in no sense a measurement of $P_{\rm H}$. The salt effect on the indicator is unknown and the intensity of the color is not specified. The present paper presents data upon the $P_{\rm H}$ of mono and diammonium phosphates. For both salts in dilute solutions this was obtained by titration of phosphoric acid with ammonia, and in addition the $P_{\rm H}$ of pure diammonium phosphate at various concentrations was measured with the hydrogen electrode. For higher concentrations, the colorimetric indicator method has been used.

Materials and Procedures

An approximately 0.10 N solution of phosphoric acid was made by dilution of a high grade analyzed sample, and its weight normality as a dibasic acid was determined by conversion to magnesium pyrophosphate.

49.915 g. of soln. yielded 0.2854 g. of $Mg_2P_2O_7$; wt. n. = 0.1027
49.943 g. of soln. yielded 0.2854 g. of $Mg_2P_2O_7$; wt. n. = 0.1026

A solution of freshly distilled ammonia was used in the titration of the phosphoric acid. It was standardized roughly against hydrochloric acid. In titrating phosphoric acid with ammonia, using a hydrogen–calomel electrode system, the first break in the curve, corresponding to the monoammonium salt, is so sharp as to make the accurate standardization of the ammonia unnecessary. Having determined the volume of reagent required to produce $NH_4H_2PO_4$, it is only necessary to double this to get the point on the curve corresponding to $(NH_4)_2HPO_4$. Because of the volatility of ammonia, this procedure seemed advisable. All e. m. f. measurements were made with a Leeds and Northrup students' potentiometer.

It is impossible to titrate in an open vessel in a stream of hydrogen because of the loss of ammonia in the more alkaline solutions. Consequently a rocking electrode vessel was designed consisting of a pyrex tube 13.5 cm. long and 4.3 cm. in diameter, having a capacity of 160 ml. This tube was sealed at both ends and had three tubulatures in the side for the insertion of a hydrogen electrode, a buret and a salt bridge. It was mounted horizontally on a small shelf attached to a vertical strip of wood 120 cm. long, which served as a pendulum, with its center of oscillation just below the shelf. A strip of sheet brass, with sharpened edges, ran through the wood to serve as a knife-edge which had bearing upon a metal arm clamped to the edge of the laboratory table. A heavy lead weight was attached to the lower end of the pendulum to lower the center of gravity. The buret was supported by clamps to that portion of the strip which projected above the electrode vessel. A hydrogen electrode of platinized platinum was inserted through a

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[1] *Ind. Eng. Chem.*, **19**, 645 (1927).

rubber stopper in tubulature No. 1 and a fine-tipped buret in No. 2. A potassium chloride bridge making contact with the calomel electrode, passed through one hole of a rubber stopper in No. 3. This bridge had a glass stopcock which was kept closed except while the e. m. f. measurement was being taken. A 30.5-cm. length of soft rubber tubing in the bridge and also in the hydrogen line gave sufficient flexibility to cause no interference with the rocking of the electrode. A hydrogen exit tube in the second hole of stopper No. 3 dipped about 1 mm. beneath the surface of mercury in a small vial standing upright on the shelf to prevent back-diffusion of air when the hydrogen stream was cut off. In operating, a weighed quantity of the phosphoric acid solution was placed in the vessel and a rapid stream of purified tank hydrogen was passed for about thirty minutes. By swinging the pendulum the vessel was rocked through an angle sufficiently large to cause complete submersion of the hydrogen electrode. Readings were taken at intervals until equilibrium was established and at this point the hydrogen stream was cut off and the titration started by running in ammonium hydroxide from the buret.

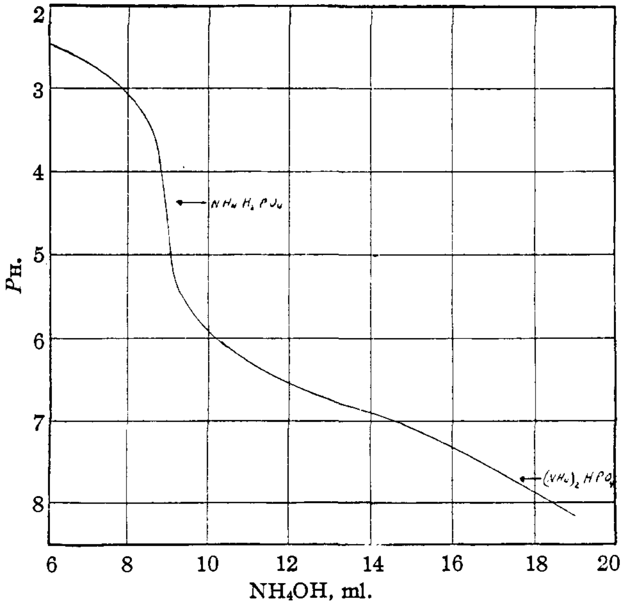

Fig. 1.—Titration curve of phosphoric acid with ammonia.

One source of error that was anticipated with this set-up was the diffusion of ammonia from the buret tip. A very slight upward drift in the potential was observed if the hydrogen electrode was left for some time without intermittent, complete submersion, but by rocking the vessel several times, the original reading could be obtained.

Two curves were run, one of which is shown in Fig. 1. The PH of monoammonium phosphate was found to be 4.35 in each case. It will be noted that there is no break at the equivalence point for diammonium phosphate, because of the hydrolysis of the salt.[2] By finding the point on the curve corresponding to twice the volume of ammonia required to produce the mono salt, the PH of the diammonium salt could be determined. Each curve showed a PH of 7.75 for this salt. The concentrations of the diammonium phosphate were 1.65 and 4.34 g. per liter, respectively, at the end-points

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

of the two titrations. These values will be referred to later in connection with the effect of concentration upon the acidity.

The test of the Committee on Analytical Reagents makes use of a solution containing 1 g. of diammonium phosphate in 10 ml. The above titration method could scarcely be applied to such high concentrations. Consequently, a high grade, analyzed, commercial sample of diammonium phosphate was carefully analyzed for ammonia and phosphorus in order to establish the ratio of these two constituents. Difficulty was encountered in getting check results, especially for ammonia, when small samples of the dry salt were taken. This was undoubtedly due to the fact that the salt was not uniform. Finally, a 25-g. sample was diluted to 250 ml. and the solution weighed. Weighed portions of this solution were analyzed for phosphorus by conversion to magnesium pyrophosphate, and for ammonia by distillation into standard acid. Five analyses which did not differ from the mean by more than 0.15% showed 0.007553 mole of phosphorus per gram of salt; calcd. for $(NH_4)_2HPO_4$, 0.007568 mole per gram. Two determinations of ammonia showed 0.01481 and 0.01481 mole per gram; calcd., 0.01514 mole per gram; ratio $NH_4:P = 1.96:1$. The salt, in addition to being deficient in ammonia, probably contained enough water to lower the percentage of phosphorus.

A solution was made from the original salt by taking a sample of sufficient size to yield exactly 50 g. of pure diammonium phosphate after fortification with the calculated amount of standard ammonia required to make up the deficiency. This solution was then diluted to 500 ml. to give a solution of the concentration used by the Committee. Four other solutions were made from this by successive dilution and the *P*H of each was determined by the hydrogen electrode in the rocking vessel already described. For these determinations, the apparatus was modified by inserting a two-holed stopper in tubulature No. 2. One hole carried the buret and the other a siphon tube with a pinchcock. This made it possible to remove the solutions through the siphon and replace them by others from the buret without admitting air. The vessel was flushed out with at least three 50-ml. portions of solution before the *P*H measurements were made. The *P*H of the most concentrated solution was also determined colorimetrically with cresol red and phenol red. The results are shown in Table I.

TABLE I

THE *P*H OF DIAMMONIUM PHOSPHATE AT VARIOUS CONCENTRATIONS

			*P*H		
Soln.	Concn., g. per liter	Concn., moles per liter	Hydrogen elect.	Cresol red	Phenol red
1	100	0.7568	8.01	8.3	8.1
2	40	.3027	7.89		
3	20	.1514	7.84		
3a	4.34	.0328	7.75[a]		
4	4.00	.0303	7.77		
4a	1.65	.01249	7.75[a]		
5	0.80	.00605	7.72		

[a] Solutions 3a and 4a were produced by titration.

The data of Table I are plotted in Fig. 2. The dots on the curve are points found by dilution of the pure salt and the crosses designate titration data. The maximum deviation from the smooth curve is 0.025 unit of *P*H. From 0.8 to 20 g. per liter the *P*H is almost a linear function of log $1/C$; above this concentration the *P*H increases rapidly to 8.01 at 100 g. per liter.

The salt error for cresol red is very marked in the concentrated solution

(100 g. per liter), being +0.29 unit of *P*H. Ramage and Miller[3] have noted an effect of +0.25 unit on this indicator in solutions of alkali chlorides of 2.5% concentration, and Wells'[4] data show errors of the same order. Phenol red shows a salt error of only 0.09 unit. Either of these indicators could be used empirically to test the ammonia–phosphate ratio, but neither gives the correct *P*H in solutions of the concentration used by the committee.

Ten ml. of the pure diammonium phosphate solution (1 g. in 10 ml.) gave a pink color with 2 drops of phenolphthalein, (10 g. in 1 liter of 95% alcohol) which was removed by 0.30 ml. of 0.10 *N* sulfuric acid. The solution contained a total of 0.007568 mole of the diammonium salt. Only 0.00003 mole, or 0.38%, would be converted into the mono salt by the acid required to decolorize the solution. The test of the Committee, therefore, appears to be sufficiently accurate for all practical uses.

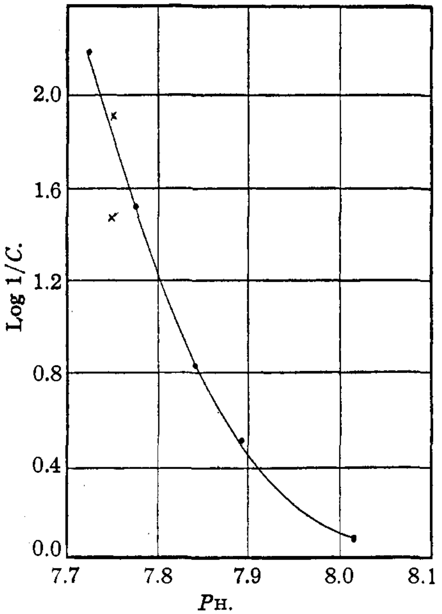

Fig. 2.—The effect of concentration upon the *P*H of $(NH_4)_2$ HPO_4 solutions.

A word might be in order regarding the use of diammonium phosphate as a precipitant for zinc. Ball and Agruss[5] have shown that zinc is best precipitated at a *P*H between 6.5 and 6.9. The titration curve of Fig. 1 shows that in this range of acidity from 30 to 50% of the excess phosphate would exist as the monoammonium salt. Obviously the usual precaution of applying the phenolphthalein test is not necessary.

Summary

The *P*H values of diammonium phosphate solutions, ranging in concentration from 0.8 to 100 g. per liter, have been determined.

At concentrations up to 20 g. per liter, the *P*H is almost a linear function of log 1/*C* and increases with the concentration. Above 20 g. per liter the *P*H increases rapidly.

The test of the Committee on Analytical Reagents of the American Chemical Society is accurate, within about 0.4%.

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[3] Ramage and Miller, This Journal, **47**, 1230 (1925).

[4] Wells, *ibid.*, **42**, 2160 (1920).

[5] Ball and Agruss, *ibid.*, **52**, 120 (1930).

Cresol red shows a salt error of +0.29 unit when applied to the solution used by the Committee. Phenol red shows an error of 0.09 P_{H} unit.

In dilute solution, monoammonium phosphate has a P_{H} of 4.35.

A simple, inexpensive type of rocking electrode has been described.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

EXPLOSIONS IN DETONATING GAS MIXTURES. I. CALCULATION OF RATES OF EXPLOSIONS IN MIXTURES OF HYDROGEN AND OXYGEN AND THE INFLUENCE OF RARE GASES[1]

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Historical

In the year 1881, Berthelot and Vieille[4] and independently Mallard and Le Chatelier[5] announced the discovery of the propagation of explosions in gas mixtures with speeds enormously greater than had been measured previously. These investigators were able to measure the speeds in a number of different mixtures by means of chronoelectric[6] and photographic[7] methods, respectively. Since then, Dixon and others[8] have continued these studies and have measured the velocity of propagation of the detonation wave in a large number of gas mixtures.

Properties of the Detonation Wave.—When certain inflammable gas mixtures are ignited at one end of a uniform tube, the initial slow movement of the flame is rapidly accelerated to a high speed, which remains constant, regardless of the length of the tube. The term "detonation wave" is applied to the propagation of a disturbance at this constant

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Read before American Chemical Society at Atlanta, Georgia, April, 1930.

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[4] Berthelot and Vieille, *Compt. rend.*, **93**, 18 (1881).

[5] Mallard and Le Chatelier, *ibid.*, **93**, 145 (1881).

[6] Berthelot and Vieille, *ibid.*, **94**, 101, 149, 822 (1882); **95**, 151, 199 (1882); *Ann. chim. phys.*, **28**, 289 (1883).

[7] Mallard and Le Chatelier, *Ann. des Mines*, [8] **4**, 274, 335 (1883); *Compt. rend.*, **130**, 1755 (1900); **131**, 30 (1900).

[8] H. B. Dixon, *Phil. Trans. Roy. Soc.*, **184A**, 97 (1893); **200A**, 315 (1903). See Bone and Townend, "Flame and Combustion in Gases," **1927**, pp. 511–518, for more complete list of references.