5. Adsorption and capillary condensation or surface liquefaction occurs with ethyl alcohol both at 52.3° and at 100°. A break at low pressures is obtained which is attributed to a specially active adsorbing area.

6. The specific surface is evaluated by adsorption of copper ions to be about 23 sq. meters per g. and the fraction of this surface strongly adsorbing and probably catalytically active is 1.3%.

7. The latent heat of capillary condensation is evaluated at some 9900 cal. per g. mole and that of surface adsorption at 14,000 cal. per g. mole.

CAMBRIDGE, ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 525]

AMMONIUM MONOMETAPHOSPHATE. PHOSPHATE III

BY SAMUEL J. KIEHL AND THOMAS M. HILL

RECEIVED OCTOBER 21, 1926 PUBLISHED JANUARY 11, 1927

The metaphosphates studied by Graham[1] were, in all probability, mixtures of various so-called polymers. Since his work, which outlined the possibilities in connection with the metaphosphates, the research in this field has been prolific but along rather restricted lines. In reviewing the literature we find that the investigations may be classed in one of the following groups. 1. Attempts to classify the metaphosphates in general. 2. Methods of determining the rate and products of hydration. 3. Methods of preparing various mixed salts or polymers, and the evidence pointing to their classification. 4. A disagreement of authors on methods of preparation and products formed.

Tammann,[2] in a general review of previous work along with his own, attempts a classification depending on conductivity measurements and freezing-point determinations. In his classification both isomerism and polymerism are assigned as properties of metaphosphoric acid. His salts were mostly prepared from the interaction of salts or bases with glacial metaphosphoric acid. Pascal[3] pointed out that the compounds and classifications considered by Tammann are open to doubt, due to methods of preparation and inaccuracies in analytical work as great as 8%.

Metaphosphoric acid, according to Holt and Myers[4] and Tilden and Barnett,[5] when prepared from phosphorus pentoxide and water, or by dehydration of orthophosphoric acid, is in an associated condition according to evidence obtained from freezing-point determinations.

---

[1] Graham, *Phil. Trans.*, **123**, 253 (1833).

[2] Tammann, *Z. physik. Chem.*, **6**, 122 (1890).

[3] Pascal, *Bull. soc. chim.*, **33**, 1611 (1923).

[4] Holt and Myers, (a) *J. Chem. Soc.*, **103**, 532 (1913); (b) **99**, 384 (1911).

[5] Tilden and Barnett, *ibid.*, **69**, 158 (1896).

Knorre[6] also gives a very complete review of the history of the metaphosphates along with some experimental work. His contributions follow the line of previous workers in that he deals almost entirely with the so-called associated forms of sodium metaphosphate, and their methods of preparation.

Pascal,[3,7] a more recent worker in the field of metaphosphates, states in connection with the literature, "There are few chapters of Inorganic Chemistry of which the confusion surpasses that of the history of the metaphosphates." From some experimental work he claims priority for the preparation of a sodium monometaphosphate. By the action of phosphorus pentoxide on ether he prepared the ethyl hexametaphosphate from which, on treatment with sodium ethoxide, his monometaphosphate was obtained. This product was freed from ether by distillation under reduced pressure. From his work he claims that only those salts prepared by the above procedure should be classified as monomolecular salts, and that association is not due to temperature and intramolecular reactions but rather to the presence of water.

Prior to Pascal's work, Beans and one of us[8] prepared sodium monometaphosphate by heating the monosodium orthophosphate to fusion and crystallizing at 450°. From the study of optical properties and the determination of molecular weight by freezing-point depression they drew the conclusion that it existed as a chemical individual in the crystalline state and in solution as any other non-associated salt.

Holt and Myers[9] obtained this same product by fusing sodium ammonium hydrogen phosphate and devitrifying the resulting viscous mass by heat until it crystallized, or by slow cooling from fusion. This method doubtless gives other forms besides sodium monometaphosphate.

Tammann,[2] by starting with glacial metaphosphoric acid, obtains an ammonium salt which he considers of doubtful formula but probably a trimetaphosphate.

Knorre,[6] in attempting to prepare the ammonium salt by heating ammonium dihydrogen phosphate to 250° or 300°, states that there is no evidence of the formation of an insoluble ammonium metaphosphate.

H. N. Stokes[10] prepared an amidophosphoric acid isomeric with ammonium metaphosphate which is considered by some as an ammonium metaphosphate. This compound, according to the author, is distinctly an amido compound and an acid.

---

[6] Knorre, *Z. anorg. Chem.*, **24**, 369 (1900).

[7] Pascal, *Compt. rend.*, **176**, 1712 (1923).

[8] Published and submitted as a dissertation in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science in Columbia University by Samuel J. Kiehl, February, 1921.

[9] Ref. 4, p. 535.

[10] Stokes, *Chem. Centr.*, **64**, 815 (1893).

Due to the limited scope of exact knowledge on the chemistry of the metaphosphates, it was considered possible that the preparation of the ammonium monometaphosphate would be of value in clearing some doubts in this field and in offering a means whereby the chemistry of monometaphosphoric acid might be more effectively studied. The preparation of monometaphosphate was undertaken and the results are given below.

Apparatus

The apparatus used to control temperature and measure the concentration of hydrogen ion has been described.[11]

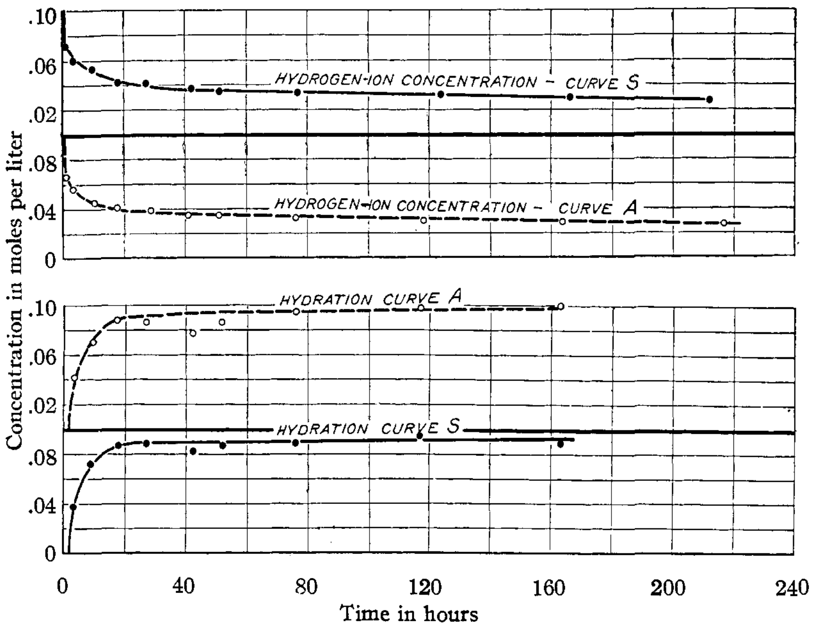

Fig. 1.—Hydration and hydrogen-ion concentration curves.
O — — O — — O A = 0.1 *M* NH_4PO_3 + 0.1 *M* HCl. ●——●——● S = 0.1 *M* $NaPO_3$ + 0.1 *M* HCl.

Conductivity measurements were made by means of Leeds and Northrup equipment. The source of current was a small Vreeland oscillator set to give frequencies of 1000 cycles per second. The bridge was a Kohlrausch circular slide-wire type with extension coils. Two variable rotary air condensers were used in parallel with the resistance boxes to balance the capacity of the cell. The point of minimum sound was taken with the aid of a double telephone receiver. Two cells were used. For conductivity water, the type of cell described by Beans and Eastlack[12] was em-

---

[11] Kiehl and Hansen, THIS JOURNAL, **48,** 2802 (1926).

[12] Beans and Eastlack, *ibid.*, **37,** 2667 (1915).

ployed. The cell constant was 0.0095. The Freas type was used for salt solutions. The cell constant was 0.296.

Preparation and Purification of Materials

All chemicals were of the purest variety obtainable. They were further treated by recrystallization from water or by other means of purification when essential to the purity of the final product.

Sodium Monometaphosphate.—Due to the important position held by the sodium metaphosphate in this investigation, its method of preparation is outlined below.

The procedure followed was the same as used by Beans and one of us.[8] The metaphosphate was formed by the dehydration of the monosodium phosphate in the electric furnace so calibrated that the temperature could be controlled by the current. The hydrated salt in a platinum crucible was heated at approximately 200° until there was no longer evidence of the rapid loss of water. The temperature was then gradually raised until the mass melted to a clear liquid. It was held at this temperature, about 600°, for 15 minutes. The rheostat was then set so that a temperature of 450° was maintained for the next three hours while the salt crystallized. When the crystallization was complete, the salt was quickly cooled by placing the platinum dish in just sufficient cold water to wet the bottom and sides of the dish.

Method of Procedure

All solutions were prepared according to the accepted standard methods. Conductivity water was used when essential. The preparation of the ammonium metaphosphate may be represented by the following molecular equations.

$$NaH_2PO_4.x\ H_2O \rightleftharpoons NaPO_3 + (x + 1)\ H_2O \tag{1}$$

$$2\ NaPO_3 + Pb\ (NO_3)_2 \rightleftharpoons Pb\ (PO_3)_2 \downarrow + 2\ NaNO_3 \tag{2}$$

$$Pb(PO_3)_2 + (NH_4)_2S \rightleftharpoons PbS \downarrow + 2NH_4PO_3 \tag{3}$$

$$NH_4PO_3 \text{ dissolved} + \text{alcohol} \rightleftharpoons NH_4PO_3 \downarrow \tag{4}$$

Approximately two-gram molecular weights of the sodium salt, prepared as described above, was dissolved in cold distilled water. To this solution, cooled by ice, a solution containing roughly one gram molecular weight of lead nitrate was added and thoroughly stirred during the resulting precipitation.

The precipitated lead monometaphosphate was filtered on a Büchner funnel and washed with cold water until the filtrate gave no test for nitrate.

The treatment of the lead salt with sulfide was carried out in an evaporating dish surrounded by ice. The ammonium sulfide was added in small quantities to the lead monometaphosphate and well mixed with a pestle. The dissolved ammonium monometaphosphate was then separated from the mass of lead sulfide by pressing it through a folded towel and repeated filtration through double filters.

The ammonium monometaphosphate was precipitated from solution by the addition of five to six volumes of alcohol, filtered and washed free from water by absolute alcohol. The alcohol was removed by repeated washing with dry ether. The drying was completed over phosphorus pentoxide.

On the average, a little greater than 12% of the calculated yield was obtained on the first precipitation.

Discussion of the Procedure

The choice of the method previously outlined was made after many futile attempts to prepare the salt by a more direct method.

The outstanding points considered in choosing and carrying out this procedure were as follows.

(*a*) A substance of known monomolecular state was used, with the idea that unless polymerization took place in solution during the intermediate steps the final product should be obtained in the unassociated condition.

(*b*) The use of acid was avoided entirely.

(*c*) The concentration of hydroxyl ion was kept as low as possible and the salt did not remain in the alkaline solution for a greater length of time than was absolutely necessary.

(*d*) The reactions in solution were carried out at a low temperature; (*b*), (*c*) and (*d*) were considered with the view of preventing hydration of the salt.

(*e*) The lead salt was chosen to be the intermediate product because it forms both an insoluble sulfide and an insoluble metaphosphate, no soluble complexes with ammonia and, according to Holt and Myers,[4b] liberates the unimolecular metaphosphoric acid by double decomposition with hydrogen sulfide.

The procedure up to the formation of the ammonium metaphosphate in solution goes smoothly. There is, however, considerable loss in separating the solution of the ammonium salt from lead sulfide because, as a rule, the lead sulfide, to keep the resulting solution concentrated was washed but once with about 75 cc. of water and pressed in a towel a second time.

It is apparent at this stage that the solution under the conditions of the experiment must be impure to the extent of having ammonium sulfide present, if the lead is to be removed completely as lead sulfide, or it must have lead metaphosphate to the limit of its solubility if we remove the sulfide ion by use of an excess of the lead salt.

The lead metaphosphate is classified as insoluble but no figures are obtainable. Therefore, at first the better plan appeared to be the use of ammonium sulfide in slight excess to reduce the lead ion to a minimum and then precipitate the ammonium metaphosphate by alcohol as a means for separating it from the ammonium sulfide. The result of this precipitation was a viscous oil which did not solidify except on long standing. It then contained pyrophosphate. Attempts to purify the oily substance by repeated solution and precipitation with a large excess of alcohol and then drying gave a product—crystals with occluded oil—which often gave strong tests for pyrophosphate, contained sulfur and ran high in ammonia content.

The excess of ammonium sulfide was thought to be a source of the difficulty, which might be obviated by oxidation of sulfide to sulfur. Therefore, the solution was packed in a freezing mixture of salt and ice, and air was bubbled through it. The test for sulfide by lead acetate paper was negative. Several filtrations apparently removed the sulfur. Solutions prepared in this manner were at times contaminated with pyrophosphate before all of the sulfide could be removed, if the excess of ammonium sulfide originally present was large. The product, obtained by repeated solution and precipitation as above, gave a mixture of very fine crystals cemented together with occluded oil. This mixture, nevertheless, could be washed with alcohol and dry ether, dried and ground to a powder. The product, moreover, ran high in ammonia and low in phosphorus content. It also gave a molecular weight much too high for the pure, unassociated salt. Immediate tests for a sulfate were negative, but the test was positive when the powder was fused with a mixture of sodium nitrate and sodium carbonate or boiled with hydrogen peroxide. Sulfide still persisted.

Attempts to substitute ammonia and ammonium hydroxide for alcohol proved ineffective as the results in either case gave crystals of ammonium pyrophosphate.

Due to the difficulties connected with the precipitation and purification of the metaphosphate in the presence of ammonium sulfide the procedure was changed to utilize the alternative scheme whereby the use of an excess of the lead salt would reduce the sulfide concentration to the solubility of lead sulfide. The method was to re-treat the filtered solution containing sulfide with fresh portions of the lead metaphosphate until there was no darkening due to the formation of lead sulfide.

The precipitation of the ammonium salt was then carried out as usual by the addition of alcohol to the cold solution. With the first portions of alcohol added, there was some tendency to form the oily layer but on slowly adding more alcohol, with stirring, the layer disappeared and a very finely divided white powder settled out which apparently at the time contained a slight amount of the oily material occluded.

To remove the lead metaphosphate known to be present, the first portion of the precipitate was discarded by filtration. The addition of alcohol was then continued but not in sufficient quantities to remove completely all the salt from solution. It was hoped that any substances more soluble than the ammonium salt would in this way pass into the filtrate. Approximately only the middle portion was accepted.

By the above procedure there was still a trace of lead, up to and including the fifth crystallization. The sixth crystallization, however, gave no test for lead by ammonium sulfide after the solution had stood for several hours. By replacing lead ion, by allowing pure magnesium to interact with the solution in the cold, a separation was attempted depending on the solubility of magnesium metaphosphate in alcohol. The results showed that this offered no special advantage, for there was a small quantity of magnesium retained in the precipitate which would offer ultimately the same difficulty as the lead.

The conclusions drawn were: that the small quantity of lead carried into the precipitate was due to the physical state of the ammonium salt which in a saturated solution, from appearance, is partially colloidal; that the presence of lead or magnesium was preferable to an excess of ammonium sulfide. Throughout the procedure of this preparation, tests were made for the presence of pyrophosphate and orthophosphate after each re-solution of the salt. The usual test was used for orthophosphate. A 0.32 *M* zinc acetate solution in one-eighth of its total volume of glacial acetic acid, a method developed by Dr. H. P. Coats and one of us in this Laboratory, was used as a test for pyrophosphate. Concentrations of pyrophosphate to less than 0.0006 *M* in the presence of a 0.1 *M* metaphosphate solution may be detected. A 0.1 *M* solution of the ammonium salt as prepared gave no test for pyrophosphate unless it stood for some time. This was due to hydration, for the amount increased as it stood.

The crystalline product after the sixth precipitation was used in the experiments which follow.

Analysis and Some Properties of the Ammonium Metaphosphate

Phosphorus.—The metaphosphate was hydrated to orthophosphate and the analysis for phosphorus was carried out by the standard gravimetric procedure. It was precipitated as the magnesium ammonium phosphate and weighed as magnesium pyrophosphate.

The results were as follows.

TABLE I

Sample	NH_4PO_3, g.	$Mg_2P_2O_7$, g.	P, g.	P, %
1	0.2000	0.2282	0.0636	31.85
2	.2001	.2283	.0638	31.88
3	.2000	.2283	.0636	31.85
			Av.	31.86

The calculated percentage of phosphorus is 31.97.

Ammonia.—Determinations for ammonia were by the Kjeldahl method.

The calculated ammonia content is 17.54%.

TABLE II

Sample	NH_4PO_3, g.	NH_3, g.	NH_3, %
1	0.2000	0.0345	17.25
2	.2001	.0350	17.49
3	.2001	.0350	17.49
		Av.	17.41

From the above analysis the ratio of ammonia to phosphorus in this salt is as 1 to 1.003.

Molecular-Weight Determination.—From data obtained by the Beckmann freezing-point apparatus, the molecular weight was calculated by use of the standard formula: $M = K(W/dW)$.

The constant for water was taken as 1860.

TABLE III

Sample	G. of salt per 100 g. of water	Freezing point, °C.	F. p. depression, °C.	Mol. wt.
1	0	4.731	0	0
2	0.6870	4.560	0.171	74.7
3	2.9750	4.140	.591	93.5

The calculated molecular weight is 97.08.

Hydration.—The hydration of the ammonium monometaphosphate was compared to that of sodium monometaphosphate by the method

TABLE IV

CONDUCTIVITY DATA

Temperature = 25° ± 0.01°. Cell constant = 0.296

Concn. millimoles per liter	Resistance, ohms	Spec. cond., mhos	Mol. cond., mhos
AMMONIUM METAPHOSPHATE			
100.0	35.8	0.008300	83.0
50.0	69.4	.004265	85.3
25.0	136.5	.002169	86.7
10.0	274.5	.001077	107.8
5.0	498.5	.000593	118.6
1.0	2230.5	.000132	132.0
0.5	4000.5	.000073	146.0
SODIUM METAPHOSPHATE			
100.0	45.5	0.006505	65.1
50.0	80.5	.003677	73.6
10.0	344.5	.000859	85.9
AMMONIUM CHLORIDE			
100.0	31.5	0.009397	94.0
10.0	249.0	.001189	118.9
SODIUM CHLORIDE			
100.0	32.5	0.009108	91.1
10.0	290.5	.001019	101.9

employed by Beans and one of us.[8] Tenth molar solutions of the respective salts were made in 0.1 *M* hydrochloric acid and placed in a Freas thermostat at 55° ± 0.02°. All conditions were kept as nearly identical as possible for the two solutions.

The rate of hydration was followed by the change of hydrogen-ion concentration and gravimetric analysis with the same apparatus and by the same method used by Beans and one of us.

The data shown in Table IV and Fig. 1 were obtained. Curves marked *A* are for the ammonium salt while *S* represents the sodium salt. The similarity of the curves indicates that the hydration in each case is the same in character. The two ions which are reacting are the same.

Conductivity.—The conductivity of the salt in dilute solution was compared to other uni-univalent salts. All determinations were carried out under comparable conditions.

Correction for the conductivity of the water was made for dilutions of ten millimoles to a liter or greater. The water used had a specific conductivity of 1×10^{-6} mhos.

The results indicate that the ionization of the sodium and ammonium metaphosphates are of the same order and are comparable to other uni-univalent salts.

Other Properties, Physical and Chemical.—For the following report of an optical study on a sample of the ammonium salt the authors wish to express their appreciation to Professor R. J. Colony, Department of Geology, Columbia University.

"The sample consists of groups of monoclinic crystals and single individuals, all more or less platy, some irregular.

"The crystals are biaxial and optically positive.

"The optic angle is large—not determined. Index of refraction, lower limit = 1.490 (N_x); upper limit = 1.505 (N_y). Bi-refringence, $N_y - N_x$ = 0.015."

The salt as prepared is white and to the naked eye appears as a fine powder. Its density determined in xylene is 2.2084. It is soluble in water up to 25 to 30 g. per hundred cc. at room temperature. More highly concentrated solutions are not entirely clear. The cloudy appearance beyond 50 or 60 g. per hundred cc. increases rapidly but no solid appears in the bottom of the container until it has been allowed to stand for some time at the higher concentrations.

The cloudiness is only partially removed by filtration, but it disappears when a few drops of a strong acid or base are added. A solution of the salt reacts neutrally to litmus paper. It is, moreover, slightly on the acid side to methyl red or phenolphthalein. There is no indication of its being a hydrate. On heating, it apparently is stable to a temperature slightly above 100°, when there is dissociation and ammonia is given off.

By heating to a higher temperature for some time, a viscous, glassy fluid is formed. On cooling, it appears as a hard, brittle glass which is strongly acid in solution resembling the glacial metaphosphoric acid.

Finally, the solution of ammonium monometaphosphate similar to sodium precipitates the insoluble monometaphosphates of the heavy metals such as iron, copper, lead, etc. No precipitate, however, is produced on the addition of barium chloride to a solution acidified with a little nitric acid. An acidified solution coagulates albumin.

Summary

1. A new salt, ammonium monometaphosphate, has been prepared and some of its properties have been determined and compared to those of sodium monometaphosphate.

2. The monomolecular metaphosphates may enter into reactions of double decomposition when dissolved in water without undergoing polymerization.

3. The ammonium salt is the ammonium monometaphosphate.

The above conclusions are justified on the basis of: (*a*) quantitative analysis, (*b*) molecular-weight determinations, (*c*) analogous results from conductivity and hydration measurements to a known salt, (*d*) reactions attributed to the metaphosphate ion and metaphosphoric acid.

New York, N. Y.

[Contribution from the Chemical Laboratories of the University of New Hampshire]

SOLUBILITIES OF RARE-EARTH SALTS. II

By C. James, H. C. Fogg, B. W. McIntire, R. H. Evans and J. E. Donovan

Received October 23, 1926 Published January 11, 1927

This work was undertaken as mentioned in a separate publication,[1] in order to obtain full information in regard to the solubility curves of the bromates of those elements near to the element of atomic number 61 in solubility.

Preparation of the Bromates.—These salts, with the exception of that of praseodymium, were prepared by stirring the pure sulfates with an excess of pure barium bromate suspended in water. The praseodymium salt was obtained directly by the fractionation of praseodymium-neodymium bromates very rich in praseodymium. This method was found to be much superior to those usually employed for the separation of these elements.

The solubilities of the bromates of lanthanum, praseodymium, neodymium, samarium, gadolinium and terbium of the type $M(BrO_3)_3.9H_2O$

---

[1] Cook, James and Fogg, *Proc. Nat. Acad. Sci.*, December, 1926.