[Contribution from the Department of Chemistry, Columbia University, No. 551]

SODIUM MONOMETAPHOSPHATE AND ITS ACID HYDRATION

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Received December 23, 1926 Published August 5, 1927

The hydration of metaphosphoric acid to orthophosphoric acid or a metaphosphate to the orthophosphate, as $NaPO_3 + H_2O \rightleftharpoons NaH_2PO_4$, has attracted the attention of chemists ever since the epochal work of Graham.[1] Much work has been done but the problem is not completely solved. Graham was aware of some of the difficulties to be encountered. In his work he states, "The problem is, therefore, environed with difficulties." These difficulties are twofold. First, metaphosphoric acids or their salts are not well understood. It is thought that polymers exist, the preparation of which has not been thoroughly investigated, and the decision as to their forms has been based mainly upon their methods of preparation or empirical formulas rather than upon experimental evidence. Second, the rate of hydration must be ascertained by the measurement, at intervals, of either the concentration of the metaphosphate left unchanged in the solution or the concentration of the orthophosphate formed during the progress of the reaction. On account of the widely differing solubilities of the so-called polymeric forms of the metaphosphates, the direct determination involving an actual separation of the ortho- from the metaphosphoric acid is by no means easy. This separation is actually necessary in order to study the factors influencing the hydration.

In order to understand this reaction better the two above-mentioned difficulties must be overcome as far as possible. This requires, as a basic consideration, that a salt of well-established identity be prepared and its hydration studied. Furthermore, the definite salt must be readily and quantitatively separable from the substances formed during the hydration.

Heretofore the methods employed in the study of the hydration of metaphosphoric acid have been to a great extent indirect, and the acid used was prepared by dissolving phosphorus pentoxide in cold water, by dehydrating orthophosphoric acid or by preparing a heavy metal salt from which a solution of the metaphosphoric acid was obtained by precipitating the metal with hydrogen sulfide. Acidimetry was used by Sabatier,[2] Montemartini and Egidi,[3] Berthelot and André[4] and Balareff;[5] thermochemistry by Giran;[6] gravimetric analysis by Holt and Meyers;[7]

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

[2] (a) Sabatier, *Compt. rend.*, **106**, 63 (1888); (b) **108**, 734, 804 (1889).

[3] Montemartini and Egidi, *Gazz. chim. ital.*, **31**, I, 394 (1901).

[4] Berthelot and André, *Compt. rend.*, **124**, 261 (1897).

[5] Balareff, *Z. anorg. Chem.*, **72**, 85 (1911).

[6] Giran, *Compt. rend.*, **135**, 1333 (1902).

[7] Holt and Meyers, *J. Chem. Soc.*, **99**, 384 (1911).

change of index of refraction by Blake and Blake;[8] change of conductivity by Prideaux;[9] and change of the lowering of the freezing point by Holt and Meyers.[10]

In their gravimetric method Holt and Meyers precipitated the unchanged meta- in the presence of ortho- and pyrophosphates as a barium metaphosphate bearing the empirical formula $Ba(PO_3)_2$. By repeated experiments with mixtures of ortho-, pyro- and metaphosphates, they claim very little variation in the composition of their precipitate. Judging from the irregularity of the curve they publish it seems that their method is open to question or fraught with a considerable error.

Other attempts to apply methods of precipitation were employed to show whether or not pyrophosphoric acid was formed during the process of hydration.[11] These methods are not applicable to the problem, for on the one hand, the method of Berthelot and André requires the heating of the solution to be analyzed, acidified with acetic acid, on a boiling water bath for three or four hours to secure the formation of an uncertain magnesium ammonium pyrophosphate, a treatment entirely out of the question in view of the marked effects of temperature and hydrogen ion upon the rate of hydration; on the other hand, the precipitation of pyrophosphate of copper or cadmium in an acetic acid solution, the method employed by Balareff, is not free from doubt because upon it he based his contention that no pyrophosphate as an intermediate product was formed during the hydration, a statement not in harmony with his later work.[12]

Moreover, there have been two different opinions as to whether pyrophosphoric acid was formed as an intermediate product during the hydration of meta- to orthophosphoric acid. One group of chemists maintained that the hydration was direct to ortho-, while another claimed pyrophosphoric acid as an intermediate product. The former was supported by Graham,[1] Sabatier,[13] Montemartini and Egidi[3] and Balareff,[14] while Berthelot and André,[15] Giran,[16] Holt and Meyers,[10] and Balareff[12] adhered to the latter.

Accordingly, a method has been devised and materials prepared for the attack of this problem whereby the conditions and factors influencing the reaction may be studied to a better advantage by direct, standard analytical methods. An account of the investigation follows.

[8] Blake and Blake, *Am. Chem. J.*, **27**, 68 (1902).

[9] Prideaux, *Chem. News*, **99**, 161 (1909).

[10] Ref. 7, p. 385; *ibid.*, **103**, 532 (1913).

[11] Balareff, *Z. anorg. Chem.*, **68**, 266 (1910); Ref. 4.

[12] Balareff, *Z. anorg. Chem.*, **96**, 103 (1916).

[13] Ref. 2 (a).

[14] Balareff, *Z. anorg. Chem.*, **67**, 234 (1909). Ref. 11, p. 288.

[15] Berthelot and André, *Compt. rend.*, **123**, 776 (1896); **124**, 265 (1897).

[16] Giran, *J. Russ. Phys.-Chem. Soc.*, **135**, 1333 (1902).

Apparatus

The apparatus used to measure the concentration of hydrogen ion has been described by Hansen and one of us.[17]

Preparation of Materials

Monosodium Phosphate, $NaH_2PO_4.2H_2O$.—A quantity of the purest monosodium phosphate obtainable was crystallized thrice from distilled water. The precipitation was accomplished each time by adding to the aqueous solution an equal volume of redistilled 95% alcohol and cooling in ice water. The final product was obtained quite free from moisture by washing by suction on a Büchner funnel thrice each with absolute alcohol and absolute ether. To remove the ether it was exposed to the air for a short time on a clean surface. The dihydrate was thus obtained. Its high dissociation pressure prevented other methods of drying and required hermetically sealed bottles as containers.

The following analyses were made for water of hydration:

Lot	Sample	Water of hydration plus water of constitution, %
1	1	34.47
1	2	34.52
2	1	34.73

The theoretical percentage for the hydrate $NaH_2PO_4.2H_2O$ is 34.63.

Sodium Monometaphosphate, $NaPO_3$.—Sodium monometaphosphate was prepared by dehydrating the $NaH_2PO_4.2H_2O$ as above prepared in a calibrated electric furnace. The hydrate in a large platinum crucible was held at a temperature of 200° for an hour. The temperature was then slowly raised during the next hour till the mass melted to a clear liquid. It was held at this temperature—approximately 600°—for ten minutes. Finally, the temperature was lowered to 450° and maintained at this point for two hours while the substance crystallized. At the end of this crystallization the metaphosphate was quickly cooled by dipping the bottom of the crucible in cold water.

The sodium metaphosphate above prepared was investigated by the freezing-point method with the following results.

Sodium metaphosphate, g.	Water, g.	F. p. depression	Mol. wt.
5.0472	100	0.916	102.5
2.8159	100	.546	95.9
1.3435	100	.351	86.9

These depressions indicate a sodium metaphosphate whose molecular weight corresponds to the formula $NaPO_3$ (Theoretical—102.04). The above sodium monometaphosphate was formerly prepared in a somewhat similar way[18] from sodium ammonium hydrogen phosphate by heating the resulting vitreous mass from fusion till it crystallized or by slow cooling from fusion. By taking 2.77 g. of their crystals in 100 cc. of water, Holt and Meyers obtained a depression of .51°, which corresponds to a molecular weight of 102 and a formula of $NaPO_3$.

An optical study of the sodium monometaphosphate made by Professor R. J. Colony of the Department of Geology of Columbia University confirms our belief that the sodium monometaphosphate prepared above is

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

[18] Tanatar, *J. Russ. Phys.-Chem. Soc.*, **30**, 99 (1898); Ref. 10 (b), p. 535.

a distinct chemical individual. Through the kindness of Professor Colony we are permitted to publish the following optical properties: "It has an index of refraction: $N_g = 1.486 \pm 0.005$, $N_p = 1.473 \pm 0.005$, birefringence $N_g - N_p = 0.013 \pm 0.005$. It is apparently monoclinic, optically negative and biaxial with a large optical angle. It shows uniformity in behavior, form and composition."

Sodium monometaphosphate is soluble in water. It reacts acid to litmus—a property described by Graham,[1] the explanation for which is not apparent. From a 0.3 *M* solution white, flocculent precipitates, which change to crystalline form on standing, may be obtained from solutions of the nitrates of silver, lead, mercury and bismuth. With solutions of the nitrates of zinc, cadmium, cobalt, nickel and copper, white amorphous precipitates are formed. It does not give a precipitate in a solution containing magnesium chloride, ammonium chloride and ammonium hydroxide in moderately high concentrations. This property was employed in the separation of monometaphosphoric acid from orthophosphoric acid.

Other Chemicals.—The hydrochloric acid, potassium chloride and mercurous chloride used were prepared according to the description given by Hansen and one of us.[17]

Method of Procedure

In planning a method of procedure the factors influencing the reaction have as far as possible been either measured or controlled. The temperature, the concentration of sodium monometaphosphate, the concentration of orthophosphate, the possible formation of pyrophosphate and the concentration of hydrogen ion are the variable factors which influence the hydration of sodium monometaphosphate.

The temperature was regulated and controlled at 45° ± 0.01°. The ortho- was separated from the metaphosphoric acid and determined directly. By difference the unchanged meta- was obtained. No satisfactory quantitative method has as yet been found whereby pyrophosphoric acid may be determined in mixtures such as occur in this investigation. Therefore, an estimate by other means of the amount formed is all that is possible. The concentration of hydrogen ion was measured at intervals during the hydration.

Preparation of Solutions.—All solutions were prepared at 20°. The requisite amount of sodium monometaphosphate was dissolved in water in a volumetric flask. To this was added with constant rotation to avoid local excess the amount of hydrochloric acid necessary to furnish the desired hydrogen-ion concentration. The solution was then diluted to volume as quickly as possible. After thorough mixing, the solution was put in a "non-sol" bottle and placed in the bath. The whole operation, beginning with the addition of the acid, required not more than ten minutes.

The specific gravity of each solution was taken at 20° by means of a Westphal balance at the beginning of the reaction and again at the end. No change of volume was observed during the hydration greater than one part in one thousand. Hence one specific gravity measurement for each solution sufficed for calculating the amount of metaphosphate transformed to orthophosphate. The concentrations of the solutions were all expressed in moles per liter. Therefore, knowing the specific gravity and the concentration, the amount of sodium monometaphosphate in any weighed quantity of solution could be determined.

The Separation of Monometaphosphoric Acid from Orthophosphoric Acid.—Orthophosphoric acid was separated from monometaphosphoric acid by means of "magnesia mixture" in a cold solution. As previously stated, a solution of sodium monometaphosphate does not give a precipitate with "magnesia mixture" in concentrations used in this procedure—and in fact very much higher concentrations. This method of separation has been tested both qualitatively and quantitatively. Seven-tenths of a gram of sodium monometaphosphate together with 25 cc. of standard "magnesia mixture" in a total volume of 125 cc. was allowed to stand for 24 hours repeatedly and no precipitate appeared, while a precipitate of the orthophosphate appeared immediately in another solution similarly treated, excepting that 1 mg. of phosphorus in the form of orthophosphate was added. It remains now to be shown that monometaphosphoric acid is quantitatively separable from the orthophosphoric acid and that no appreciable hydration occurs during the time of standing required for the precipitation of the magnesium ammonium phosphate. Thirty determinations of orthophosphate according to the method outlined below, in the presence of varying quantities of sodium monometaphosphate from 900 mg. to 100 mg., have been made. The amount of orthophosphate used has varied and the times of standing have been 6, 12 and 18 hours, respectively. There was an increase in amount found over the amount added which was of the same order irrespective of the time of standing. This shows that hydration was not the cause of the increase; for if it had been, the amount of increase would have been a direct function of the time. This increase not due to hydration was inherent in the method and doubtless caused by adsorption and subsequent hydration by the acid used to dissolve the precipitate. The magnitude of the error from this source was found by the above determinations to be on the average not greater than ten parts per thousand for amounts of sodium monometaphosphate not exceeding 300 mg.

Determination of Orthophosphate.—Orthophosphate was determined by the standard gravimetric method. The samples of the solution were taken by means of Bailey weighing burets. Before precipitation each sample was diluted to 100 cc. Twenty-five cc. of "magnesia mixture" was then added, which made the final volume 125 cc. The separation of the magnesium ammonium phosphate precipitate from the unprecipitated meta- was made by filtration not more than 16 hours nor less than 6 hours after the first precipitation. After separating and washing with an ammonium hydroxide-ammonium nitrate solution, the orthophosphate precipitate was dissolved with hot hydrochloric acid and reprecipitated. Finally, after 12 hours' standing, the magnesium ammonium phosphate was filtered through a weighed Gooch crucible and weighed as magnesium pyrophosphate. By this method the amount of the monometaphosphate transformed to ortho- could be determined.

In the hydrations where the concentration of acid was high, the analytical results varied somewhat at the beginning of each hydration. The variation was due to the simultaneous precipitation of a gelatinous substance which contaminated the magnesium ammonium phosphate. This gelatinous precipitate was soluble in an excess of magnesium salts and from its behavior indicated that it was magnesium pyrophosphate. The pyrophosphate was formed during the hydration. The concentration of hydrogen ion showing abnormally low values for the high acid concentrations indicated further that pyrophosphate was probably formed. With no satisfactory quantitative method for separating pyro- from orthophosphate and determining it, the difficulty was met by preventing its precipitation by the addition of an excess of "magnesia mixture" a method which was on the whole quite successful.

Measurement of Concentration of Hydrogen Ion.—All hydrogen-ion concentration measurements were made at 45° by the apparatus and method described by Hansen and one of us.[17] The calculations were made by use of the formula $\log C_{H^+} = (0.2342 - E)/0.063$.

Experimental Data

The following table gives the concentrations and the densities of the solutions selected for investigation.

TABLE I

	D	E	H	K	O	Z	S
Molar concn., $NaPO_3$	0.500	0.500	0.500	0.300	0.100	0.300	0.300
Molar concn., HCl	.483	.339	.192	.339	.339	.010	.000
d_{20}/d_{20}	1.044	1.042	1.041	1.025	1.011	1.025	1.025

All hydrations except the Z and S were made in duplicate. Duplicate samples of the two exceptions were taken. The mean deviation of the results in duplicate is not greater than five per cent. when the concentration of pyrophosphate is high at the beginning nor greater than one per cent. when the hydration nears completion.

TABLE II

SOLUTIONS D, C[a], E AND H

0.500 *M* $NaPO_3$

	Sample	Time, hours	Percentage hydrated	Voltage	(H^+)
Soln. D 0.483 *M* HCl	1	1.75	8.3	0.2716	2.55×10^{-1}
	2	4.67	47.1	.2785	1.98
	3	10.67	66.0	.2834	1.66
	4	24.17	81.6	.2881	1.39
	5	48.42	87.9	.2923	1.20
	6	72.92	92.7	.2946	1.10
	7	120.17	96.7	.2970	1.01
	8	168.70	98.4	.2979	0.95
Soln. C[a] 0.483 *M* HCl	1	3.17	45.9	0.2754	2.22×10^{-1}
	2	6.17	50.0	.2797	1.82
	3	10.17	67.8	.2830	1.68
	4	16.17	67.8	.2842	1.61
	5	25.17	81.6	.2888	1.42
	6	37.17	82.8	.2909	1.26
	7	49.17	88.2	.2922	1.20
	8	72.17	91.0	.2937	1.13
	9	121.17	98.0	.2963	1.03
	10	169.17	99.7	.2978	0.98

[a] The values for solution C, which is a duplicate of solution D, are given to show the reproducibility of measurements.

TABLE II (*Concluded*)

	Sample	Time, hours	Percentage hydrated	Voltage	(H^+)
Soln. E	1	2.17	7.6	0.2856	15.28×10^{-2}
0.339 *M* HCl	2	5.17	25.8	.2930	11.66
	3	11.17	50.3	.3005	8.86
	4	23.17	67.4	.3073	6.91
	5	48.58	75.1	.3144	5.30
	6	71.42	80.5	.3176	4.74
	7	119.05	84.3	.3214	4.13
	8	167.00	91.1	.3242	3.73
	9	239.42	95.7	.3262	3.47
	10	383.42	102.8	.3276	3.29
Soln. H	1	6.20	13.8	0.3150	5.22×10^{-2}
0.192 *M* HCl	2	13.37	24.5	.3224	3.98
	3	23.48	44.9	.3300	3.02
	4	47.30	63.4	.3383	2.28
	5	71.20	69.2	.3432	1.91
	6	119.31	73.4	.3486	1.53
	7	167.60	80.6	.3520	1.35
	8	192.53	78.1	.3533	1.29
	9	215.30	82.4	.3545	1.23
	10	263.70	85.1	.3562	1.16
	11	335.70	85.8	.3579	1.09
	12	457.10	92.3	.3596	1.02
	13	678.60	96.0	.3613	0.96
	14	875.30	98.4	.3625	.92

TABLE III

SOLUTION O

0.100 *M* $NaPO_3$, 0.339 *M* HCl

Sample	Time, hours	Percentage hydrated	Voltage	(H^+)
1	1.50	11.8	0.2715	2.56×10^{-1}
2	3.00	42.1	.2719	2.52
3	7.17	69.1	.2728	2.44
4	13.17	79.1	.2740	2.34
5	24.17	88.3	.2750	2.25
6	47.67	96.2	.2760	2.17
7	72.17	97.9	.2764	2.14

TABLE IV

SOLUTION K

0.300 *M* $NaPO_3$, 0.339 *M* HCl

Sample	Time, hours	Percentage hydrated	Voltage	(H^+)
1	1.50	9.2	0.2789	19.52×10^{-2}
2	3.00	36.1	.2805	18.41
3	7.00	58.8	.2842	16.08
4	15.00	65.2	.2889	13.54
5	27.00	73.5	.2932	11.63
6	51.00	86.2	.2973	9.96

TABLE IV (*Concluded*)

Sample	Time, hours	Percentage hydrated	Voltage	(H^+)
7	83.42	93.9	.2990	9.36
8	120.17	96.3	.2996	9.14
9	168.42	97.4	.3000	9.03
10	240.02	98.6	.3002	8.96

TABLE V

SOLUTION Z

0.300 *M* $NaPO_3$, 0.010 *M* HCl

Sample	Time, days	Percentage hydrated	Voltage	(H^+)
1	0.03	..	0.3637	87.99×10^{-4}
2	.32	..	.3777	52.75
3	.82	..	.3829	43.64
4	1.83	..	.3896	34.15
5	3.01	..	.3960	27.02
6	5.01	..	.4039	20.25
7	6.93	12.2	.4088	20.26
8	13.88	25.3	.4200	11.24
9	20.88	42.0	.4271	8.67
10	27.71	48.7	.4325	7.12
11	39.67	58.2	.4393	5.55
12	57.75	72.9	.4451	4.49
13	93.67	87.3	.4488	3.92
14	122.70	93.3	.4507	3.66
15	144.56	97.1	.4521	3.48

TABLE VI

SOLUTION S

0.300 *M* $NaPO_3$, 0.000 *M* HCl

Sample	Time, days	Percentage hydrated	Voltage	(H^+)
1	0	..	0.6267	0.59×10^{-6}
2	1.00	..	.6037	1.37
3	2.00	..	.5894	2.30
4	4.00	..	.5776	3.54
5	5.00	..	.5739	4.05
6	7.00	..	.5678	5.07
7	10.00	..	.5608	6.54
8	15.00	..	.5522	8.96
9	20.00	..	.5460	11.41
10	25.00	1.8	.5412	13.39
11	45.00	5.2	.5292	20.55
12	60.00	7.5	.5258	23.52
13	74.00	10.4	.5231	25.96
14	88.00	13.2	.5212	27.82
15	109.00	19.6	.5191	30.06
16	149.00	32.3	.5157	34.02
17	177.00	41.4	.5132	37.28
18	200.00	49.1	.5109	40.64

Discussion

The Change of Concentration of Hydrogen Ion.—The data in the foregoing tables and the curves in the accompanying figures given as examples show that there was a considerable decrease in the concentration of hydrogen ion in all cases when hydrochloric acid was added to the solutions in the beginning. This decrease was progressive and became less pronounced as the transformation of the meta- to orthophosphate became more nearly completed. The explanation is obvious. Monometaphosphoric acid is a stronger acid than orthophosphoric acid. When, however,

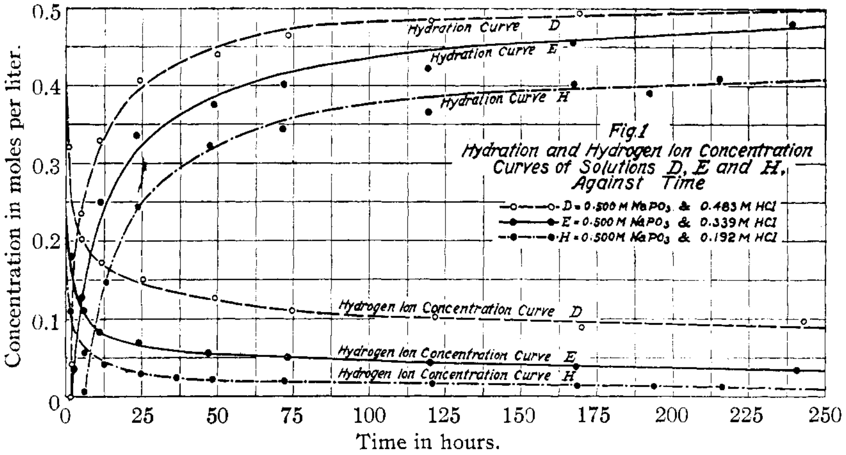


Fig. 1 Hydration and Hydrogen Ion Concentration Curves of Solutions D, E and H, Against Time

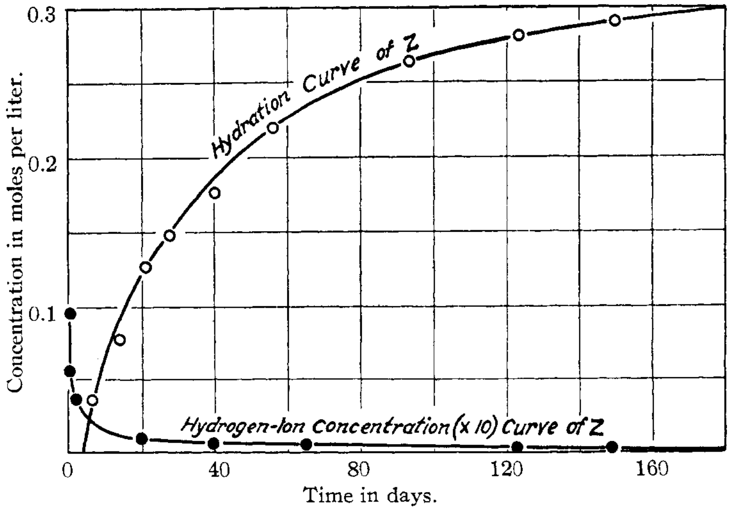
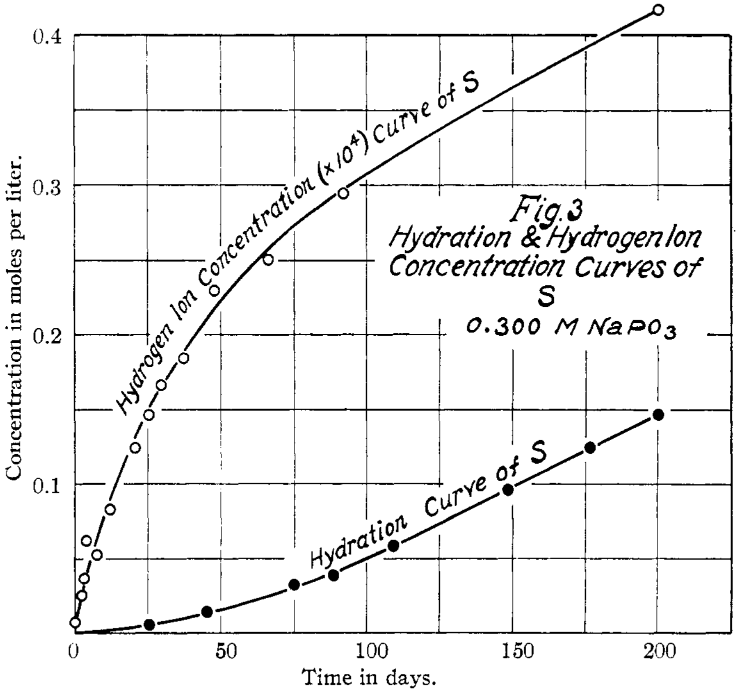


Fig. 2.—Hydration and hydrogen-ion concentration curves of solution Z, 0.300 M $NaPO_3$, 0.010 M HCl.

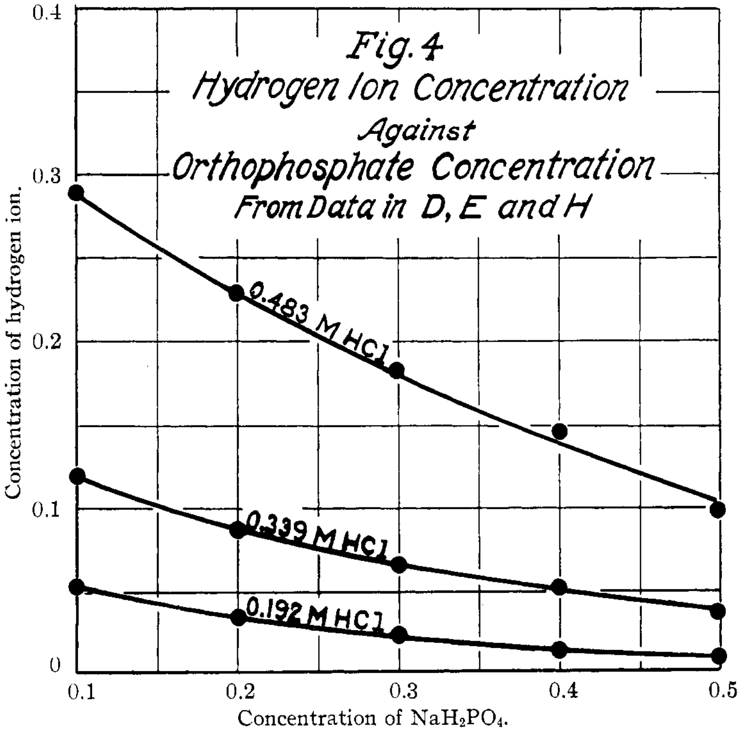
there was no acid added to the solution, as in solution S, an actual increase in the concentration of hydrogen ion occurred. This increase was due to the formation of hydrogen ions during the reaction to pyrophosphate and orthophosphate in a region where the concentration of hydrogen was below that given by the solution of the end-product, monosodium orthophosphate.

Abnormal Decrease of Hydrogen Ions in the First Part of Hydration.—In Figs. 1, 2, and 3, all the hydration curves show periods at the beginning where apparently very little orthophosphate was present in the solutions.

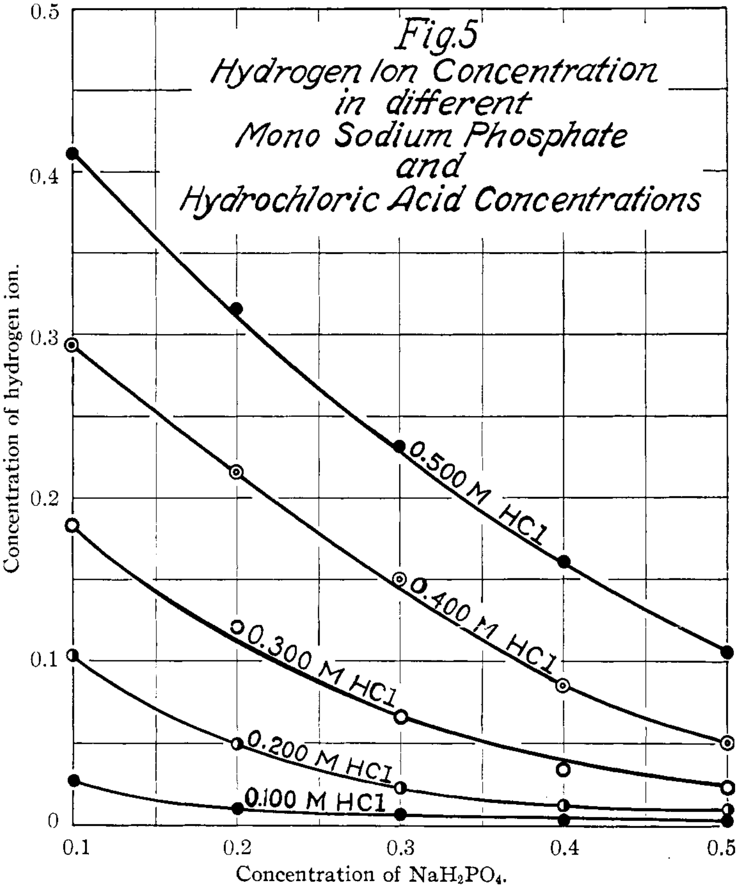


There was, however, at this point a reaction of a very pronounced character taking place. The hydrogen-ion concentration decreased more rapidly at this stage than at any other stage of its course. The change of hydrogen-ion concentration could not be explained by the very little orthophosphate which was undoubtedly present but not determinable. Even after the orthophosphate had acquired a comparatively high concentration it was insufficient to cause the change in concentration which occurred. For example, in Curve H, Fig. 1, there was a decrease of 0.14 mole of hydrogen ion when 0.10 mole of orthophosphate had been formed; in E, 0.13 mole, with the formation of 0.10 mole of orthophosphate; and in C, 0.16 mole of hydrogen ion disappeared when 0.10 mole of orthophosphate had been formed.

Furthermore, in studying these hydrations it was thought, at first, that the orthophosphate was produced directly from the metaphosphate. We therefore plotted the hydrogen-ion concentrations found against the orthophosphate concentration. These curves were compared with curves secured from the measurement of synthetic solutions of monosodium orthophosphate and hydrochloric acid in concentrations calculated to be identical with the experimental solutions, assuming that the orthophosphate was produced directly from the metaphosphate. It was thought proper to omit the metaphosphate from these synthetic solutions since its effect on the hydrogen-ion concentration was slight. The curves in Fig. 4 represent the results from solutions D, E and H. Fig. 5 represents values from the corresponding synthetic solutions just described. When Fig. 5 is superimposed on Fig. 4 the result is shown in Fig. 6. The curves are not coincident. The hydrogen-ion values from the actual hydrations near the beginning are much lower than those from the seemingly comparable synthetic solutions. The differences, however, decrease as the reactions proceed, until finally, near completion, the concentrations of hydrogen ion in both cases become identical.



From the above consideration it is evident that synthetic solutions are not entirely comparable to the solutions produced by hydrations. The actual solutions produced under conditions of hydration have a substance capable of diminishing the concentration of hydrogen ion beyond that which would be present if orthophosphate alone were formed. Therefore, inasmuch as pyrophosphate was detected during the analysis of samples and inasmuch as there was a decrease of hydrogen-ion concentration in hydrochloric acid solutions when pyrophosphate is added, it seemed reasonably certain that the large decrease of hydrogen-ion concentration at the beginning was due to the pyrophosphate formed. During the reaction, however, it finally was hydrated to orthophosphate in the acid solution, thus tending to eliminate the difference of corresponding hydrogen-ion concentration values as the reaction approached more nearly complete transformation to orthophosphate.



In the hydration of solution S, where no acid was added, there was a further indication of the formation of pyrophosphate. The concentration of hydrogen ion constantly increased. At the end of 200 days its value was 4.06 × 10^{-5}, while the concentration of 0.3 *M* monosodium phosphate, the natural end-product, gave a value of 3.81 × 10^{-5}. Then, too, the reaction was but 50 per cent. complete, with the hydrogen-ion concentration still showing a marked tendency to increase when judged from the slope of its curve in Fig. 3. The final value it could ultimately attain would be about 1.5 × 10^{-4} *M*, the value for a 0.15 *M* disodium dihydrogen pyrophosphate solution with no orthophosphate present. This concentration, moreover, could not be reached as orthophosphate was present. But the final value with no pyrophosphate present at complete transformation would be that for 0.300 *M* orthophosphate. Hence, a maximum in the hydrogen-ion concentration should be expected before complete hydration.

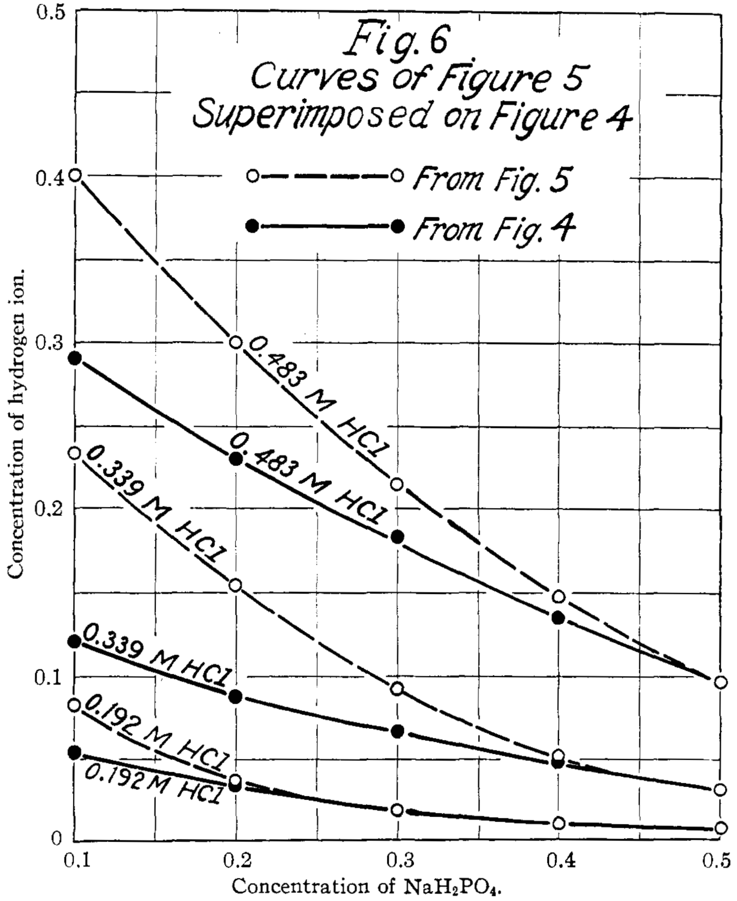


Fig. 6
Curves of Figure 5 Superimposed on Figure 4

Comparison of Effects of Changes in Concentrations.—The results of the various hydrations indicate the comparative effects of the concentrations of metaphosphate and hydrochloric acid. The times required for the attainment of the same percentage transformation depended more upon the concentration of hydrogen ion in solution than upon the metaphosphate concentration. The data in Tables II, III, IV, V and VI, exemplified in Figs. 1, 2 and 3, confirm this assertion. Where the concentration of metaphosphate in solutions C, E and H initially was 0.500 *M*, with the hydrochloric acid 0.483 *M*, 0.339 *M* and 0.192 *M*, respectively, the times for the attainment of the same percentage hydration increased greatly with decrease of hydrogen-ion concentration. Likewise in solutions E, K and O, of 0.339 *M* hydrochloric acid and 0.500 *M*, 0.300 *M* and 0.100 *M* sodium metaphosphate, respectively, the concentration of hydrogen ion rather than the concentration of sodium monometaphosphate affects the rate of the reaction to the greatest extent. The influence of the concentration of hydrogen ion is most strikingly shown in solutions K, Z and S, of 0.300 *M* monometaphosphate with 0.339 *M*, 0.010 *M* and 0.000 *M* hydrochloric acid, respectively.

Summary

1. $NaH_2PO_4.2H_2O$ was prepared, a hydrate not hitherto described.
2. Sodium monometaphosphate was prepared and its hydration studied by direct methods.
3. The hydrogen-ion concentration decreased as the reaction proceeded in regions of initial concentration above that given by the end-product, monosodium orthophosphate, but increased when the initial hydrogen-ion concentration was below that of the end-product.
4. Pyrophosphate was formed as an intermediate product. Its presence was detected during the separation and determination of orthophosphate. The abnormally low values for the hydrogen-ion concentrations at the beginning with high hydrochloric acid concentrations and the increasing of the hydrogen-ion concentration above that of the final end-product indicated that an acid stronger than orthophosphoric but weaker than hydrochloric was formed.
5. The hydration was much more affected by a change of concentration of hydrogen ions than by a change of the concentration of sodium monometaphosphate.
6. The presence of an intermediate product makes the reaction somewhat complex.

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