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THE HYDRATION OF SODIUM MONOMETAPHOSPHATE IN ALKALINE SOLUTION AT 75°. PHOSPHATE V

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Introduction

For almost a century it has been known through the work of Graham¹ that the phosphates, ortho-, pyro- and meta-, can be transformed from one to the other. His work at the time was an epoch-making contribution to the chemistry of phosphates, where even today it occupies a remarkably authoritative position.

During the intervening period attention has been directed more especially to the study of the orthophosphate and orthophosphoric acid, with a result of numerous, extensive and valuable researches. The chemistry of the meta- and pyrophosphates has not been as widely nor as satisfactorily developed. The nature of their inter-transformations and the conditions which influence them have been studied more particularly from the standpoint of the rate of hydration and the formulation of it.² To a limited extent the effects of concentration of acid and temperature upon the rate of hydration have been quantitatively investigated.³

No work, moreover, of a definite character has been done on the hydration of the metaphosphate in an alkaline solution. The lack of methods for determining the meta- and pyrophosphates has doubtless retarded the work in this range. The difficulty of obtaining containers which were unaffected by the alkaline solution has possibly contributed to the delay.

In the work which follows, a study of the alkaline hydration of sodium monometaphosphate to sodium pyrophosphate and sodium orthophosphate was undertaken. Pure silver flasks were used as containers. A method of separating and determining pyrophosphate in the presence of ortho- and metaphosphates was employed in following the progress of the hydration of metaphosphate to pyrophosphate. A method of separating

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

² (a) Sabatier, *Compt. rend.*, **106**, 63 (1888); (b) **108**, 734, 804 (1889); (c) Berthelot and André, *Compt. rend.*, **124**, 265 (1897); (d) **124**, 261 (1897); (e) Montemartini and Egidi, *Gazz. chim. ital.*, **31**, 394 (1903); (f) Balareff, *Z. anorg. Chem.*, **67**, 234 (1909); (g) **68**, 288 (1911); (h) **96**, 103 (1916); (i) **118**, 123 (1921); (j) Giran, *Ann. chim. phys.*, **30**, 203 (1903); (k) Holt and Meyers, *J. Chem. Soc.*, **99**, 385 (1911); (l) Aoyama, *J. Pharm. Soc. Japan*, **520**, 553 (1925); (m) Abbott, *THIS JOURNAL*, **31**, 763 (1909).

³ (a) Abbott, *THIS JOURNAL*, **31**, 763 (1909); (b) Beans and Kiehl, *THIS JOURNAL*, **49**, 1878 (1927); (c) Kiehl and Hansen, *THIS JOURNAL*, **48**, 2802 (1926); (d) Kiehl and Hill, *THIS JOURNAL*, **49**, 123 (1927).

and determining orthophosphate was employed in following the progress of the hydration of metaphosphate to orthophosphate. The results of the investigation are given below.

Apparatus

Bath.—An oil-bath, sensitive to ± 0.01 at 75° , was used. The regulator was a twelve-foot, quarter-inch steel tube, entirely filled with mercury, coiled within the bath. This made and broke in the usual manner an electrical circuit by which the heating current was supplied.

Flasks.—The hydrations were studied in a silver vessel whose capacity was a little over a liter, constructed somewhat after the style of an Erlenmeyer flask. The stopper, made of silver, was ground to fit. Two silver tubes, for the removal of samples, extended through the stopper—similar in the arrangement to an ordinary wash bottle. These tubes were closed with silver plugs ground to fit. As a further precaution against evaporation, the stopper was sealed to the flask with a wax made of one part paraffin and one part carnauba wax. A piece of rubber tubing, closed at one end, was placed over each of the plugs and tubes.

Preparation of Materials

Sodium Monometaphosphate.—Sodium monometaphosphate was prepared by the method previously described.⁴ The dihydrate was obtained when the salt was further purified by thrice crystallizing it from distilled water. By drying it overnight at 100° in a Freas oven the anhydrous salt was prepared. Analyses were made for any remaining water, whereby the necessary corrections were made when and where they were required.

In order to determine if crystallization from water and subsequent heating at 100° would change the character of the salt heretofore described, qualitative tests were made and freezing-point depressions measured. Neither procedure indicated that the salt possessed properties different from those of the salt crystallized from fusion.

The water of hydration was determined by selecting a few large, quickly-dried crystals and finding the loss of weight by ignition. The following results were obtained.

TABLE I
ANALYSIS FOR WATER OF HYDRATION

Samples	No. 1	No. 2
Grams of crystals.....	1.8858	1.9217
Grams of anhydrous salt.....	1.3940	1.4189
Grams volatilized.....	0.4918	0.5028
Percentage of water of hydration.....	26.08	26.17
Percentage of water of hydration (theoretical).....		26.10

Calculations gave results which corresponded to the formula $\text{NaPO}_3 \cdot 2\text{H}_2\text{O}$.

The following crystallographic measurements were made by Professor Paul Kerr of the Geology Department in Columbia University. "The crystals are triclinic with the following angular measurements between faces:

⁴ Beans and Kiehl, *THIS JOURNAL*, 49, 1878 (1927).

TABLE II
CRYSTALLOGRAPHIC MEASUREMENTS

Faces		Angles measured	
001	100	64°	16'
100	010	73°	28'
010	110	42°	53'
100	110	62°	55'
001	010	82°	33'

"There is a perfect cleavage parallel to (001). On removal from the solution for measurement the crystals soon acquire a white powdery coating which darkens the reflection signals on the goniometer considerably and reduces the accuracy of measurement.

"The mean index of refraction is 1.400 and the double refraction is about 0.009. The material is biaxial with a large axial angle and one of the optic axes is nearly perpendicular to the cleavage (001). The acute bisectrix of the optic angle corresponds to γ , the slow ray, in dispersion $p > v$."

Sodium Pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$.—Normal sodium pyrophosphate was crystallized three times from distilled water and carefully dried.

Disodium Orthophosphate.—Disodium orthophosphate was prepared and the product standardized by the method described by Hansen and one of us.⁵

Sodium Hydroxide.—Solutions of sodium hydroxide used for hydration were made from a saturated solution of the purest available sodium hydroxide. This solution was filtered through a dry filter paper and diluted to a convenient concentration. It was then standardized by Bureau of Standards benzoic acid.

Zinc Acetate Reagent.—Zinc acetate of pure quality, free from phosphate, was used. Eighty grams of the zinc acetate was dissolved in distilled water and diluted to two liters. Two hundred and fifty cubic centimeters of glacial acetic acid were then added. This gave about a 0.2 *M* zinc acetate solution with a hydrogen-ion concentration of 5×10^{-4} moles per liter.

Method of Procedure

Separation of Pyrophosphate from Orthophosphate and the Determination of Pyrophosphate.—In order to determine the extent of hydration in alkaline solution, it was necessary to separate the pyrophosphate formed. After trying many other precipitants, the zinc acetate reagent was found to be the most satisfactory. Orthophosphate gives no precipitate under the conditions described below, except for concentrations greater than 0.1 mole per liter. It, therefore, was successfully used in the separation, even though it did not give a crystalline precipitate, provided the concentration of hydrogen ion was carefully controlled.

Thirty to forty cubic centimeters of zinc acetate reagent was added to the solution containing the pyrophosphate, whose hydrogen-ion concentration was adjusted to 5×10^{-4} moles per liter by the addition of acetic acid and water, thereby making a total of 120 cc. After standing

⁵ Kiehl and Hansen, *THIS JOURNAL*, **48**, 2802 (1926).

for three minutes it was centrifuged for three minutes. The clear liquid was then decanted through a weighed Gooch crucible. Fifty cubic centimeters of distilled water was added with stirring to the precipitate, which was again centrifuged and transferred to the Gooch crucible. Enough 2 *M* sodium hydroxide was added thereafter to dissolve the precipitate on the filter. After dilution to 75 cc. by washings from the filter and Gooch crucible, an equal volume of a solution, so prepared that it contained 4 *M* acetic acid and 0.5 *M* zinc acetate, was added to reprecipitate the pyrophosphate. This solution was centrifuged again and decanted through a weighed Gooch crucible. After decanting the clear solution and one washing with water, the precipitate was transferred to the Gooch crucible with repeated washing, filtered, dried and ignited with a Méker burner for half an hour.

Composition of Ignited Precipitate.—In order to determine whether the precipitated zinc pyrophosphate would give after ignition a product invariable in composition, several quantities of it were prepared and samples from each ignited lot were analyzed. The results of the zinc and phosphorus determinations from two such samples are given below.

Table III shows the amount of zinc found in the ignited precipitate by the potassium ferrocyanide method.

TABLE III
ZINC IN THE PYROPHOSPHATE PRECIPITATE

Sample	G. ppt. taken	G. Zn found
1	0.3026	0.1293
2	.2991	.1278

The phosphorus was determined by the standard gravimetric procedure after complete hydration by boiling with nitric acid. The following values were obtained.

TABLE IV
PHOSPHORUS IN PYROPHOSPHATE PRECIPITATE

Sample	G. ppt. taken	G. $Mg_2P_2O_7$	Equiv. to g. P
1	0.3853	0.2815	0.0784
2	.3286	.2408	.0670

The ratio of atoms of zinc to atoms of phosphorus in the first case is 1 to 0.997, in the second 1 to 0.993. From the percentage of both zinc and phosphorus in the ignited precipitate and from the ratio above, the empirical formula of the ignited zinc precipitate corresponds to $Zn_2P_2O_7$.

In order to determine if the acetic acid used would be sufficient to accelerate the hydration of metaphosphate at room temperature to interfere in the pyrophosphate determination, strong solutions of acetic acid were added to 0.2 *M* sodium monometaphosphate, which was allowed to stand for several days at room temperature. No precipitate with the zinc acetate reagent resulted. Mixtures of sodium acetate, acetic acid, zinc acetate,

0.2 *M* metaphosphate and 0.08 *M* orthophosphate, set aside at room temperature for several days, likewise gave no precipitate under the conditions of separation and determination of pyrophosphate.

Determination of Pyrophosphate.—To test the method the following were a few of the determinations which were made on aqueous solutions of sodium pyrophosphate of known value.

TABLE V
PYROPHOSPHATE BY ZINC ACETATE REAGENT

Mg. P taken as pyro-	31.04	31.04	31.04	31.04	31.04	31.04
Mg. P found as pyro-	31.05	31.09	31.05	31.08	30.82	30.74
Mg. P taken as pyro-	62.08	62.08	62.08	62.08	62.08	62.08
Mg. P found as pyro-	62.27	61.88	62.10	62.55	61.89	61.85
Mg. P taken as pyro-	153.0	153.0	153.0	153.0		
Mg. P found as pyro-	152.9	153.1	152.8	152.9		

The average deviation in parts per thousand by the above method for the analysis on 31.04 mg. of phosphorus as pyrophosphate is 2; for 62.08 mg. of phosphorus it is 3.

Determination of Orthophosphate in Filtrate.—In the actual hydration after separating pyrophosphate the filtrate contained zinc ion and metaphosphate ion which might offer the possibility of trouble. For assurance it was necessary, therefore, that this filtrate without orthophosphate present give no precipitate under conditions for determining orthophosphate, that metaphosphate be not hydrated in the alkaline solution during the process, and that no precipitate be formed with meta- and orthophosphates present and the magnesia mixture alone absent. Accordingly, no precipitate had formed after standing six days when a portion of plain filtrate without ortho- or metaphosphate present was made alkaline with NH_4OH and treated with the appropriate quantity of magnesia mixture. Likewise, when metaphosphate was added to the plain filtrate and treated as above no precipitate had occurred in fifteen days. Furthermore, with orthophosphate present without the magnesia mixture only, no precipitate had formed during four days.

In the following paragraph the method is outlined for determining orthophosphate in the filtrate from analysis of pyrophosphate in the course of the hydrations.

Sufficient 15 *M* ammonium hydroxide was added to the pyrophosphate filtrate to re-dissolve the zinc precipitate at first formed. Twenty cubic centimeters of 5 *M* ammonium chloride was added. After standing for three hours it was filtered, dissolved and re-precipitated by the standard method in a total volume of 125 cc. After it stood at least three hours it was filtered, ignited and weighed as usual.

Table VI shows some of the determinations of orthophosphate made upon the pyrophosphate filtrate with and without metaphosphate present.

TABLE VI
ORTHOPHOSPHATE IN PYROPHOSPHATE FILTRATE

Mg. P taken as meta-	Mg. P taken as ortho-	Mg. P found as ortho-
388	31.49	33.19
388	31.49	32.45
155	31.49	31.60
155	59.92	60.97
139	14.98	15.42
77	38.80	39.00
77	38.80	38.90
None	31.49	31.48
None	31.49	31.49

Table VII contains a few of the determinations made directly upon orthophosphate solutions with meta- as indicated.

TABLE VII
ORTHOPHOSPHATE DIRECTLY

Mg. P taken as meta-	Mg. P taken as ortho-	Mg. P found as ortho-
217	14.98	15.42
217	59.92	61.03
139	59.92	60.89
77	38.80	38.95
None	59.92	59.47

The values in Tables VI and VII are representative of the many results obtained in testing the method, over the complete range of metaphosphate concentration in the filtrate from the pyrophosphate determination. The average deviation from the amount added is 25 parts per thousand. When tests were made in orthophosphate solutions directly the average deviation was of the order of that from the filtrate of the pyrophosphate with the same amount of metaphosphate present. Inasmuch as the amount of metaphosphate present at any one time did not exceed 140 mg., the average deviation was found from a number of determinations to be 15 parts per thousand.

Test of the Method under Conditions of Hydration.—Whether zinc acetate reagent would precipitate pyrophosphate quantitatively in the concentrations and under the conditions of the hydrations is yet to be demonstrated. Solutions of meta-, pyro- and orthophosphates and sodium hydroxide in concentrations to be found in the hydrations were made at 20° and taken from a buret. These were analyzed for pyro- and orthophosphates. Where 2 M sodium hydroxide was used enough glacial acetic acid was added to give a concentration of hydrogen ion of 5×10^{-4} moles per liter.

Table VIII which follows gives the milligrams of phosphorus taken as meta-, pyro- and orthophosphates and the milligrams of phosphorus found as pyro- and orthophosphates.

TABLE VIII
DETERMINATION OF PYRO- AND ORTHOPHOSPHATES

	Molar NaOH	P taken as meta-	P taken as pyro-	P found as pyro-	P taken as ortho-	P found as ortho-
1	2.0	217	15.42	14.90	14.98	15.02
2	2.0	139	15.42	14.93	None	None
3	1.0	124	6.21	6.16	None	None
4	1.5	124	108.64	108.78	93.12	92.82
5	2.0	108	46.30	46.17	14.98	15.06
6	2.0	108	30.85	30.85	None	None
7	0.5	93	45.56	47.05	31.04	31.24
8	2.0	46	61.70	61.27	99.86	101.01
9	2.0	45	61.70	61.66	44.94	46.40
10	2.0	31	77.12	78.28	44.94	46.40
11	2.0	15	77.12	77.34	59.92	60.97
12	2.0	15	77.12	76.85	5.99	5.90
13	None	None	77.60	77.70	31.04	None
14	None	None	77.60	77.24	31.04	None
15	None	None	77.60	76.97	None	None
16	None	None	31.04	30.92	77.60	78.64
17	None	None	31.04	30.41	31.04	31.02
18	None	None	31.04	31.06	62.08	62.13
19	None	None	77.60	77.30	77.60	76.39
20	None	None	None	None	31.04	31.49
21	None	None	None	None	31.04	31.21
22	None	None	None	None	59.92	59.47
23	2.0	None	92.60	92.55	59.92	60.00
24	None	None	63.00	63.18	None	None
25	None	None	315.00	318.50	None	None
26	None	None	315.00	318.80	None	None
27	None	None	31.00	31.21	None	None

In the above table the average deviation from amount added is 9 parts per 1000 for pyrophosphate and 11 parts per 1000 for orthophosphate.

Experimental Part

The temperature selected for conducting the hydrations was 75°. Solutions were made in a two-liter, calibrated flask with as little contact with air as possible. A sample of each solution was then taken for analysis and for a pycnometric density determination. The remainder was placed in two silver flasks and hydrated in duplicate. The density of each solu-

TABLE IX
SOLUTIONS STUDIED

Soln.	Concn. NaPO ₃ moles per l.	Concn. NaOH moles per l.	Sp. gr.	
			15.5°/15.5° at beginning	15.5°/15.5° at end
A ₁	0.100	0.500	1.031	1.032
B ₁	.200	.500	1.039	1.040
D ₁	.100	2.000	1.093	1.093
E ₁	.200	2.000	1.101	1.101

tion was again determined at the end of each experiment and no change in any case greater than one part in one thousand was observed.

In the beginning from time to time small samples were taken through the silver tubes and tested for pyrophosphate and orthophosphate. When they were found a sample was drawn into a small flask which was quickly stoppered and cooled to 20°. By means of a calibrated pipet 25 cc. was taken and analyzed as described above. The following tables give the percentages of pyrophosphate and orthophosphate found in the solutions at the stated intervals.

In the heading for each table the weight of $Zn_2P_2O_7$ equivalent to the total phosphorus in 25 cc. of solution is given. This we shall call **M**. Similarly the weight of $Mg_2P_2O_7$ will be designated **N**. The calculation of the percentage of phosphorus transformed to pyrophosphate and orthophosphate, respectively, becomes simple when the amounts of $Zn_2P_2O_7$ and $Mg_2P_2O_7$ are actually known for each 25cc. portion.

TABLE X
SOLUTION A

$NaPO_3 = 0.099 M$; $NaOH = 0.500 M$; **M** = 0.3777 g. $Zn_2P_2O_7$; **N** = 0.2759 g. $Mg_2P_2O_7$.

Sample	Hours	$Zn_2P_2O_7$, g.	% hydrated to pyro-	$Mg_2P_2O_7$, g.	% hydrated to ortho-	% meta-by diff.
1	18.5	0.0189	5.0
2	23.5	.0267	7.1
3	29.5	.0443	11.6	0.0151	5.5	82.9
4	41.5	.0603	15.9	.0223	8.1	76.0
5	65.5	.0872	23.0	.0339	12.3	64.7
6	89.5	.1151	30.5	.0460	16.7	52.8
7	113.5	.1384	36.6	.0561	20.4	43.0
8	137.5	.1549	41.0
9	185.5	.1880	49.8	.0756	27.4	22.8
10	275.5	.2231	59.1	.0864	31.3	9.6
11	353.50926	33.6	..
12	449.5	.2357	62.4	.0958	34.7	2.9
13	545.5	.2375	62.9	.0958	34.7	2.4
14	713.5	.2416	64.0	.0946	34.3	1.7
15	881.5	.2454	65.0	.0933	33.9	1.8
16	915.5	.2456	65.0
17	1002.5	.2409	63.8	.0949	34.4	1.8
18	1123.0	.2430	64.4	.0957	34.7	0.9

Discussion of Results

In the alkaline hydration of sodium monometaphosphate, and under the conditions of our experiments, both orthophosphate and pyrophosphate are formed. This was shown by the analyses of the solutions. It was further shown by crystals that separated from the completely hydrated solutions. When these completely hydrated solutions were allowed to stand for several days at room temperature, sodium pyrophosphate

crystallized. The large crystals could be separated easily and washed free of mother liquor and analyzed. If, however, some of the completely

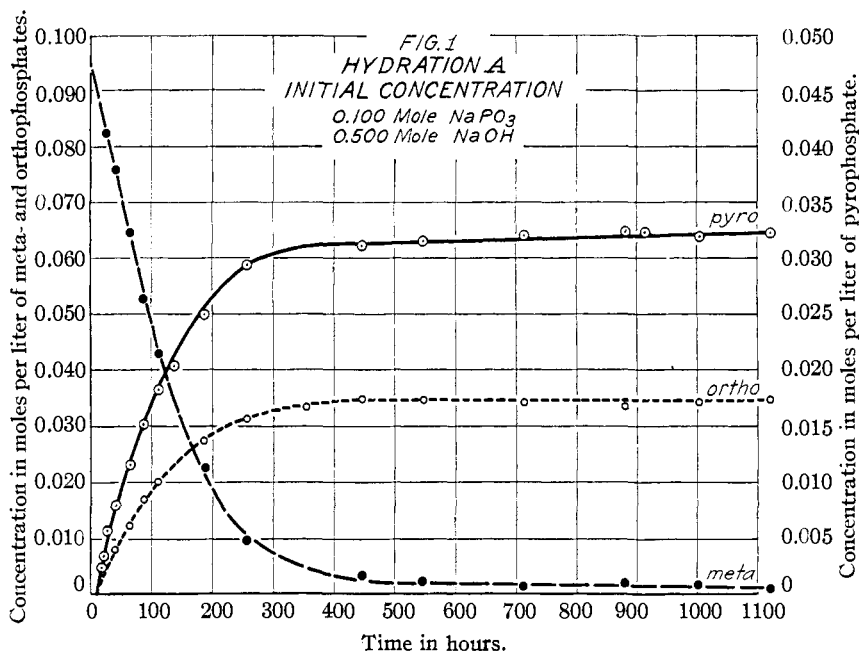


TABLE XI
SOLUTION A₂^a

$\text{NaPO}_3 = 0.099 \text{ M}$; $\text{NaOH} = 0.500 \text{ M}$; $\mathbf{M} = 0.3777 \text{ g. Zn}_2\text{P}_2\text{O}_7$; $\mathbf{N} = 0.2759 \text{ g. Mg}_2\text{P}_2\text{O}_7$.

Sample	Hours	$\text{Zn}_2\text{P}_2\text{O}_7$, g.	% hydrated to pyro-	$\text{Mg}_2\text{P}_2\text{O}_7$, g.	% hydrated to ortho-	% meta-by diff.
1	18.5	0.0190	3.1
2	23.5	.0267	7.1
3	29.5	.0446	11.8	0.0151	5.5	82.7
4	41.5	.0610	16.1	.0217	7.9	76.0
5	65.5	.0865	22.0	.0334	12.1	65.0
6	89.5	.1146	30.3	.0473	17.1	52.6
7	113.5	.1380	36.5	.0555	20.1	43.4
8	137.5	.1540	40.8
9	185.5	.1880	49.8	.0750	27.2	23.0
10	257.5	.2220	58.8	.0864	31.3	9.9
11	353.50926	33.2	..
12	449.5	.2338	61.9	.0960	34.8	3.3
13	545.5	.2398	63.4	.0955	34.5	2.1
14	713.5	.2460	65.1	.0936	33.0	2.0
15	881.5	.2457	65.1	.0940	34.1	0.8

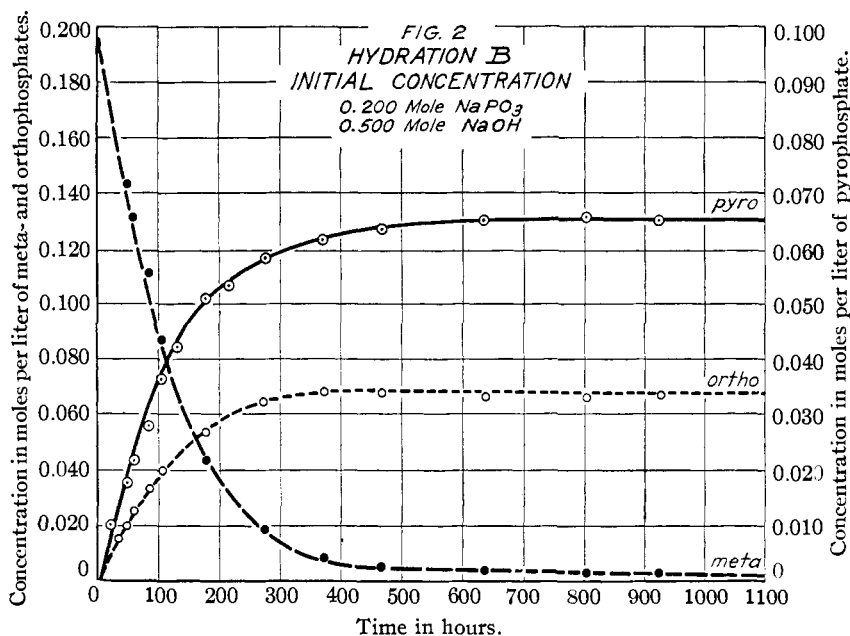
^a Solution A₂ is a duplicate of A given to show the reproducibility of results and the dependability of the method.

TABLE XII

SOLUTION B

$\text{NaPO}_3 = 0.200 \text{ M}$; $\text{NaOH} = 0.500 \text{ M}$; $\mathbf{M} = 0.7620 \text{ g. Zn}_2\text{P}_2\text{O}_7$; $\mathbf{N} = 0.5566 \text{ g. Mg}_2\text{P}_2\text{O}_7$.

Sample	Hours	Zn ₂ P ₂ O ₇ g.	% hydrated to pyro-	Mg ₂ P ₂ O ₇ g.	% hydrated to ortho-	% of meta-by diff.
1	24	0.0782	10.3
2	36	0.0416	7.5	72.5
3	48	.1334	17.5	.0559	10.0	72.5
4	60	.1655	21.7	.0700	12.5	65.8
5	84	.2116	27.8	.0933	16.7	55.5
6	108	.2773	36.4	.1113	20.0	43.6
7	131	.3203	42.1
8	180	.3883	51.0	.1507	27.1	21.9
9	216	.4091	53.7
10	276	.4457	58.5	.1793	32.2	9.3
11	372	.4713	61.9	.1899	34.0	4.1
12	468	.4858	63.7	.1886	33.9	2.4
13	636	.4975	65.2	.1836	33.0	1.8
14	804	.5020	65.8	.1834	33.0	1.2
15	925	.4947	65.0	.1871	33.6	1.4
16	1298	.5014	65.7	.1881	33.8	0.5



hydrated solution was allowed to evaporate at room temperature, at first sodium pyrophosphate only crystallized. When the solution became more concentrated orthophosphate crystallized also. When both types of crystals were carefully freed from the mother liquor and dried, the

sodium orthophosphate crystals became visibly efflorescent within a few hours, while the pyrophosphate crystals remained unchanged. These

TABLE XIII

SOLUTION D

$\text{NaPO}_3 = 0.100 \text{ M}$; $\text{NaOH} = 2.00 \text{ M}$; $\text{M} = 0.3810 \text{ g. Zn}_2\text{P}_2\text{O}_7$; $\text{N} = 0.2783 \text{ g. Mg}_2\text{P}_2\text{O}_7$.

Sample	Hours	$\text{Zn}_2\text{P}_2\text{O}_7$, g.	% hydrated to pyro-	$\text{Mg}_2\text{P}_2\text{O}_7$, g.	% hydrated to ortho-	% of meta- by diff.
1	23	0.0421	11.1
2	31	.0735	19.3	0.0278	10.0	70.7
3	45	.1030	27.0	.0556	20.0	53.0
4	59	.1372	36.0	.0665	23.9	40.1
5	71	.1715	45.0	.0750	26.9	28.1
6	92	.1932	50.7	.0852	30.6	18.7
7	116	.2129	55.8	.0929	33.3	10.9
8	151	.2249	59.0	.0952	34.1	6.9
9	188	.2400	63.0	.0958	34.4	2.6
10	260	.2478	65.0	.0955	34.4	0.6
11	380	.2494	65.4	.0957	34.4	.2

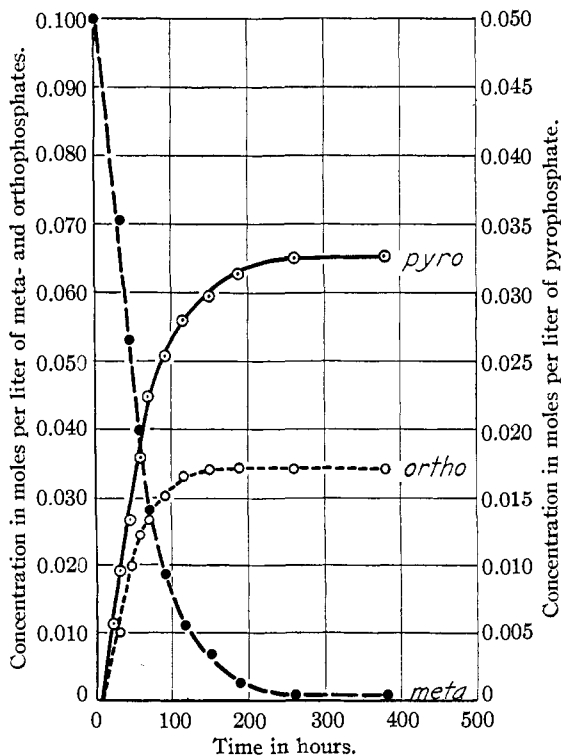


Fig. 3.—Hydration D. Initial concentration. 0.100 M NaPO_3 , 2.00 M NaOH .

TABLE XIV

SOLUTION E

$\text{NaPO}_3 = 0.200 \text{ M}$; $\text{NaOH} = 2.00 \text{ M}$; $\text{M} = 0.7631 \text{ g. Zn}_2\text{P}_2\text{O}_7$; $\text{N} = 0.5584 \text{ g. Mg}_2\text{P}_2\text{O}_7$.

Sample	Hours	$\text{Zn}_2\text{P}_2\text{O}_7$, g.	% hydrated to pyro-	$\text{Mg}_2\text{P}_2\text{O}_7$, g.	% hydrated to ortho-	% of meta-by diff.
1	6.0	0.0373	4.9	0.0126	2.2	92.9
2	15.5	.1013	13.3	.0688	12.3	74.4
3	32.5	.1657	21.7	.0867	15.7	62.6
4	45.5	.2280	29.8	.1218	21.8	48.4
5	57.51451	26.1	..
6	76.5	.3557	46.6	.1639	29.4	24.0
7	94.5	.4015	52.7	.1788	32.0	15.3
8	118.5	.4455	58.5	.1908	34.2	7.3
9	168.5	.4973	65.3	.1881	33.2	1.0
10	292.5	.5011	65.7	.1893	33.8	0.5

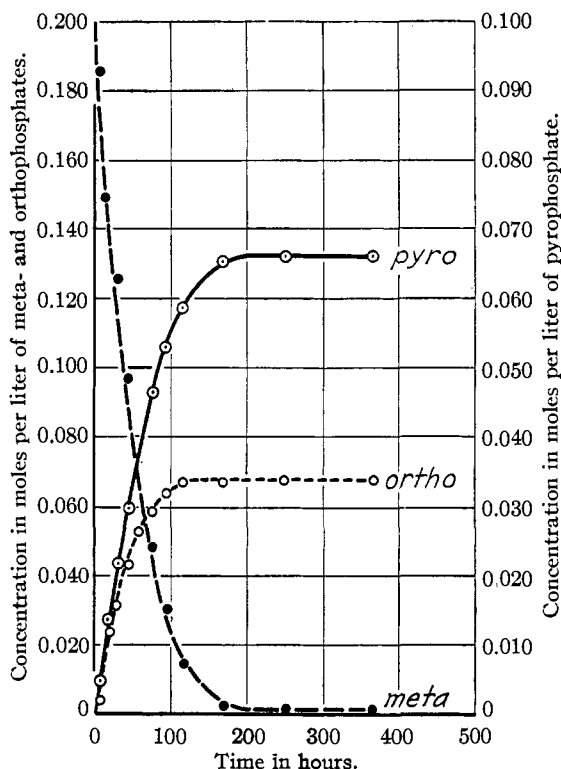


Fig. 4.—Hydration E. Initial concentration. 0.200 M NaPO_3 , 2.00 M NaOH .

efflorescent crystals were separated from the others and tested. They were orthophosphate crystals.

Since orthophosphate and pyrophosphate were both found when the

metaphosphate was completely hydrated, and since they appeared in each hydration to reach a final value of approximately 34% of the phosphorus in the form of orthophosphate, it would seem that the pyrophosphate and orthophosphate were either end-products or in equilibrium with each other.

That orthophosphate and pyrophosphate were not in equilibrium was shown by the following experiments:

A duplicate of Hydration B was kept in the 75° bath for 419 hours after the metaphosphate had disappeared. No change in the ratio of pyrophosphate to orthophosphate was found. The solution was then placed in the 100° bath and analyzed from time to time for 414 hours more. There was no change in the ratio of pyrophosphate to orthophosphate.

In the D and E hydrations four times as much sodium hydroxide was used as in the A and B hydrations, but the final ratio of pyrophosphate to orthophosphate was the same.

A solution called C, containing 0.5 *M* sodium hydroxide and 0.1 *M* disodium orthophosphate, was kept in the 75° bath for seven days without producing any pyrophosphate.

Another solution, called F, was made of 2.0 *M* sodium hydroxide, and 0.1 *M* phosphorus as ortho- and pyrophosphates. Twenty-five per cent. of the phosphorus was in the form of normal sodium pyrophosphate and 75% disodium orthophosphate. It remained in the 75° bath for 23 days without any orthophosphate reacting to form pyrophosphate, or pyrophosphate to form orthophosphate.

Another solution, called G, was made of 0.2 *M* phosphorus in the form of ortho- and metaphosphates with 2.0 *M* sodium hydroxide. One-third was sodium monometaphosphate and two-thirds disodium orthophosphate. This was kept in the boiling bath for 22 days. The pyrophosphate obtained was that which would result from the hydration of the monometaphosphate added as shown in the preceding tables while the orthophosphate was increased by 34% of the amount of phosphorus added as monometaphosphate. No orthophosphate was transformed to pyrophosphate.

In order to determine if pyrophosphate would hydrate to orthophosphate a solution of 0.2 *M* sodium pyrophosphate and 2.0 *M* sodium hydroxide was kept in the boiling bath for 22 days without a trace of orthophosphate being formed.

A 0.2 *M* sodium pyrophosphate in a 4.0 *M* sodium hydroxide solution was kept in the boiling bath for four days. No orthophosphate was produced.

Since neither increase of temperature nor change of concentration of phosphates and sodium hydroxide altered the ratio of pyrophosphate to

orthophosphate, and since pyrophosphate was not formed from orthophosphate in solution, and since orthophosphate was not formed from pyrophosphate, it seemed reasonably certain that no equilibrium existed under the conditions of our experiments.

All of these experiments were carried out in pure silver flasks.

Graham⁶ states: "But pyrophosphate of soda may be boiled with caustic soda for hours without sensible alteration, provided the solution is not evaporated to dryness; and it crystallizes afterwards in its original form, exhibiting no disposition whatever to form sub-pyrophosphate."

Therefore, since the orthophosphate did not appear from the hydration of pyrophosphate, it must have been produced by the hydration of metaphosphate, and since the pyrophosphate which was present in the hydrations did not result from the dehydration of orthophosphate, it must have occurred from the hydration of the metaphosphate.

It is of interest to note that the orthophosphate and the pyrophosphate were produced in equimolecular quantities. From our work it seems that for every three moles of the sodium monometaphosphate hydrated one mole of orthophosphate and one mole of pyrophosphate were produced simultaneously.



This may mean two independent reactions or one single involved reaction; but since the experimentation has not covered a wide enough range of temperature the decision cannot be made. However, one may conceive of the possibility of two different rates of hydration, if there are two reactions, each affected to a different degree by temperature. Work is planned to elucidate the mechanism and clear this point.

The foregoing experimental data and Figures 1, 2, 3 and 4 demonstrate that an increase in the hydroxyl-ion concentration increases the rate of hydration.

Summary

1. Sodium monometaphosphate dihydrate was prepared.
2. A method of determining pyrophosphate in the presence of meta- and orthophosphate was developed.
3. Sodium monometaphosphate was hydrated to sodium pyrophosphate and sodium orthophosphate in alkaline solution at 75° in silver flasks.
4. Sodium pyrophosphate is an end-product and sodium orthophosphate is an end-product, in the alkaline hydration of sodium monometaphosphate when reactions are carried out in silver flasks.
5. The increase of the sodium hydroxide concentration increased the rate of hydration.

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⁶ Ref. 1, p. 255.