Disodium dihydrogen tetrametaphosphate has an X-ray pattern unlike any sodium phosphate previously reported in the literature. It melts near 400°; if the melt is quenched between cold copper plants, a transparent glass is obtained. The glass is much more hygroscopic than the crystalline compound.

$Na_2H(PO_3)_3$-I has properties similar to $Na_2H_2(PO_3)_4$. When methanol is rapidly added to an aqueous solution of the soluble form of $Na_2H(PO_3)_3$, a thick filterable gel-like material is obtained. All of the compositions in the range $0.67 \leq Na_2O/P_2O_5 < 0.75$ exhibit this gel-like formation when methanol is added to an aqueous solution of the salt. The filtered gels are flammable, owing to the very large quantity of methanol contained in them. A fresh precipitate may contain more than 50 weight per cent. methanol even though the sample was precipitated from aqueous solution. If a solution of $Na_2H(PO_3)_3$ is neutralized with NaOH and very slowly precipitated from solution, a white crystalline precipitate is obtained which has an unidentifiable X-ray pattern, but a paper chromatographic analysis of the sample indicates it is sodium trimetaphosphate. This is tentatively accepted as proof that the formula of the salt is $Na_2H(PO_3)_3$. This is in line with the very low intrinsic viscosity of a solution of $Na_2H(PO_3)_3$. The intrinsic viscosity of the solution was too low to be measured accurately.

The crystals formed throughout the entire sodium acid metaphosphate system are of a more or less fibrous nature. This seems to be contradictory to the conclusion that two of the anions of the acid metaphosphate system are of relatively low molecular weight. There is a possibility that the structure reorganizes upon dissolving in water, but this is not believed to be the case. At any rate, the aqueous solutions of the two soluble sodium acid metaphosphates behave as though they were derived from salts of simple anions.

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The Hydration of Sodium Triphosphate

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The anhydrous–hydrate transformation of the two crystalline forms of sodium triphosphate was studied by means of "hydration" vapor pressure and rate of hydration measurements at 25 and 50°. For phase I the "hydration pressures" are 10 and 41 mm. at 25 and 50°, and for phase II, 12 and 64 mm. Phase I hydrates much more rapidly than phase II under similar conditions.

It is well known that anhydrous sodium triphosphate exists in two crystalline forms. Morey and Ingerson[1] in 1944 presented crystallographic data for both phases and designated the high temperature phase as phase I and the low temperature phase as phase II. The transition temperature is said to be approximately 450°. More recently Raistrick[2] discussed an X-ray diffraction method for analyzing the two phases in a mixture. This method has been greatly improved by Mabis and Quimby.[3]

Very little work has been reported concerning differences between these two crystalline forms, except for the crystallographic data mentioned above and the work reported by Dymon and King.[4] However, recently, McGilvery[5] discussed a method for determining the relative amounts of phase I and phase II by means of the difference in their heats of hydration. Hydration of either phase at room temperature produces the hexahydrate, $Na_5P_3O_{10}\cdot 6H_2O$. Although the existence of an octahydrate has been reported,[6,7] it is now generally believed that only the hexahydrate exists.

It must be emphasized that the anhydrous-hydrate transformation is not an equilibrium process. It has not been possible to dehydrate the hexahydrate to the anhydrous salt by any simple method.[8-10] Because of the non-equilibrium conditions, the usual methods of vapor pressure determinations were not feasible. Throughout this paper the data will be designated as "hydration pressures" rather than vapor pressures in order to emphasize this fact.

Materials and Procedure

The anhydrous sodium triphosphate phases I and II were prepared by heating the purified hexahydrate to 600° for phase I and below 450° for phase II. The hexahydrate was purified by repeated crystallization from an aqueous solution of commercial triphosphate (57.5% P_2O_5, 90% tripoly-, 9.5% pyro- and 0.5% ortho-) by the slow addition of ethanol. 90% of the particles of both phases were in the

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range of 10 to 80 μ. The crystallizations removed any pyrophosphate and other phosphates which were present as impurities in the commercial triphosphate. X-Ray powder diffraction patterns of the final product showed no crystalline phosphates present other than the hexahydrate; a similar result was obtained by tris-(ethylenediamine)-cobalt(III) method of Weiser.[11]

The hydration pressures of phase I and phase II at 25 and 50° were determined by measuring the gain in weight of samples of the anhydrous salt which were placed in a series of humidistats. Ten-gram samples of sodium triphosphate phase I and phase II were weighed into tared wide-mouth weighing bottles. The weighing bottles were placed in desiccators at a constant humidity maintained by saturated salt solutions or aqueous solutions of sulfuric acid held at the required temperature in a constant temperature air-bath. Equilibrium was determined by weighing the samples at suitable intervals until a constant weight was obtained.

The final hydration pressures for each phase at each temperature were obtained by gradually narrowing the range covered by each set of humidistats. Aqueous solutions of sulfuric acid were required to produce small differences between desiccators. The compositions of these solutions were checked after each weighing by density measurements, and any deviations from the required compositions were corrected before starting the next equilibrium time interval.

Results and Discussion

The hydration pressures determined in the manner described above are given in Table I.

TABLE I

HYDRATION PRESSURES OF SODIUM TRIPHOSPHATE (MM.), PHASES I AND II

Temp., °C.	Phase I	Phase II
25	10 ± 0.5	12 ± 0.5
50	41 ± 1.0	64 ± 1.0

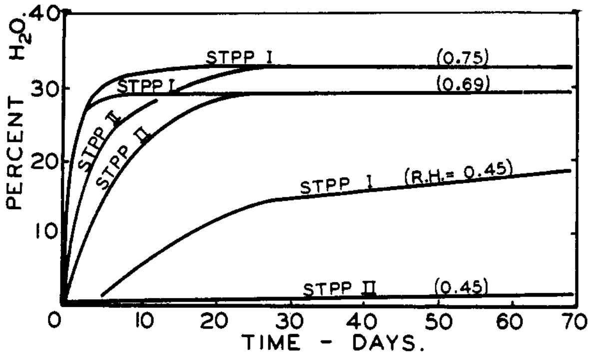

Fig. 1.—Rate of hydration at 50°.

Figure 1 shows the rate of hydration of phase I and phase II at 50° for three of the higher humidities. Phase I hydrates much more rapidly than phase II. At 75% humidity, phase I is completely hydrated in less than five days, while phase II requires twenty-five days. At 25°, on the other hand, the rates of hydration are very slow; complete hydration of phase I requires at least 10 months at 75% humidity and phase II requires a still greater time.

These hydration times are dependent to some extent on the conditions of the experiment. In this work, air was not removed from the desiccators. Therefore, these more practical hydration rates are slower than would be expected if the equilibrium with water vapor were carried out in the absence of air.

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Monohalogen Derivatives of Sulfur Nitride

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The reaction of S_4N_4 with acetyl chloride is shown to produce diacetamide and sulfur dioxide in addition to S_4N_3Cl. The formation of S_4N_3Cl is shown to be caused by the presence of free hydrogen chloride in the acetyl chloride and not to any specific property of the reagent itself. It appears likely that the preparation of S_4N_3Cl from S_4N_4 and sulfur chlorides is due to a similar cause. Hydrogen chloride is shown to react with S_4N_4 under certain conditions to produce S_4N_3Cl, ammonium chloride and chlorine. Analogous reactions appear to take place with hydrogen bromide and hydrogen iodide.

One of the more interesting reactions displayed by sulfur nitride, S_4N_4, is its conversion to thiotrithiazyl "salts".[1-3] These compounds appear to contain an $(S_4N_3)^+$ cation, the nitrate, bisulfate, chloride and perchlorate of which are soluble in water. The bromide, iodide and thiocyanate are insoluble and may be formed by double decomposition reactions from the chloride. The compounds are highly colored and are decomposed by water at a measurable rate.[3]

Thiotrithiazyl chloride, S_4N_3Cl, may be prepared by refluxing sulfur nitride with sulfur chlorides[1,3] or acetyl chloride.[2] No other product of the latter reaction was reported except an unidentified white crystalline substance melting at 125°.

Dry hydrogen chloride gas reacts with sulfur nitride at room temperature to form a brown powder which does not change *in vacuo*. If treated with liquid hydrogen chloride at room temperature in a sealed tube, sulfur nitride completely decomposes to give ammonia, sulfur and chlorine.[4] A benzene solution of sulfur nitride, when treated with dry hydrogen chloride has been reported to form a bright yellow compound of unknown composition.[5]

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