Duhring Lines.—The solubility data for carbon dioxide in the various salt solutions have been represented as Duhring lines[8] by plotting molalities of equal gas solubility using sodium chloride as the reference salt solution. Straight lines can be drawn through the points, the deviation being slight in all cases except with potassium salts where there is some curvature. No improvement in fit of data points is secured by using other salts, or any hypothetical salt, as the reference salt. Similar lines are obtained with other gases and other temperatures. Such a method serves as an excellent approximation method where few data are available, as all lines start from a common origin and but one or two data points are necessary to give a satisfactory approximation.

TABLE V

VALUES OF *a* AND *b* IN EQUATION 1

	Temp., °C.	CO_2 *a*	CO_2 *b*	N_2O *a*	N_2O *b*
NaCl	0.2	−0.0181	0.285	−0.0272	0.346
	25	− .0134	.229	− .0167	.280
	40	− .0113	.217	− .0138	.261
$NaNO_3$	0.2	− .0054	.240		
	25	− .0050	.150		
Na_2SO_4	25	− .0760	.666	− .0746	.834
	40	− .0838	.560	− .0685	.774
KCl	0.2	+ .0207	.216	− .0072	.270
	25	+ .0201	.168	+ .0001	.211
	40	+ .0380	.190	+ .0075	.210
KNO_3	0.2	+ .0350	.170	+ .0733	.350
	25	+ .0248	.088	+ .0243	.170
	40	+ .0343	.086	+ .0203	.130
$Mg(NO_3)_2$	0.2	− .0361	.366	− .0302	.496
	25	− .0268	.257	− .0252	.310
	40	− .0211	.230	− .0159	.280
$MgSO_4$	0.2	− .0852	.701	− .0844	.800
	25	− .0808	.575	− .0781	.665
	40	− .0736	.545	− .0848	.586

Summary

1. An apparatus for the measurement of gas solubility in liquids has been designed in which solubility measurements check within about 0.2 per cent.
2. The solubility of carbon dioxide and nitrous oxide in various aqueous salt solutions has been measured at 0.2, 25 and 40° over a wide range of salt concentrations.
3. It has been shown that the reduction in gas solubility is an additive function of the ion concentrations up to one molal.
4. A new equation is given to express gas solubility in salt solutions as a function of concentration. This equation in most cases fits the data within the experimental error.

SEATTLE, WASHINGTON RECEIVED JUNE 10, 1940

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[8] Perry and Smith, *Ind. Eng. Chem.*, **25**, 195–199 (1933).

[A JOINT CONTRIBUTION FROM HALL LABORATORIES, INC., PITTSBURGH, PA., AND FROM THE COÖPERATIVE X-RAY LABORATORY OF THE UNIVERSITY OF PITTSBURGH]

A Thermal, Microscopic and X-Ray Study of the System $NaPO_3$–$Na_4P_2O_7$[1]

BY EVERETT P. PARTRIDGE,[2] VICTOR HICKS[3] AND G. W. SMITH[2]

The discovery that solutions of sodium metaphosphate glass sequester calcium in a soluble complex corresponding to such a low concentration of calcium ion that addition of carbonate, oxalate, orthophosphate, or soap does not produce a precipitate has led, not only to rapid technical development of the use of this material in all fields of water conditioning, but also to renewed scientific and commercial interest in the meta- and pyrophosphates and in those less well-established compounds of intermediate composition collectively known as the polyphosphates.

The older literature has reference to compounds of empirical formulas $Na_{12}P_{10}O_{31}$, $Na_6P_4O_{13}$, $Na_9P_4O_{17}$ and $Na_5P_3O_{10}$. When Parravano and Calcagni[4] attempted to verify the existence of polyphosphates by studying the cooling curves of melts of sodium pyrophosphate and sodium metaphosphate, they could find no indication of any intermediate anhydrous compounds. More recently, however, the work of Huber[5] and of Andress and Wüst[6,7] has shown that sodium tripolyphosphate, $Na_5P_3O_{10}$, is a real compound. The

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[1] The portion of this investigation dealing with sodium metaphosphate and sodium pyrophosphate was presented at the Pittsburgh Meeting of the American Chemical Society, September 10, 1936, the remainder at the Cincinnati Meeting, April 9, 1940.

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[4] Parravano and Calcagni, *Z. anorg. Chem.*, **65**, 1–9 (1910).

[5] Huber, *Z. angew. Chem.*, **50**, 323–326 (1937).

[6] Andress and Wüst, *Z. anorg. Chem.*, **237**, 113–131 (1938).

[7] Andress and Wüst, *ibid.*, **241**, 196–204 (1939).

new experimental evidence in this paper confirms the contention of the latter investigators that, of the various alleged polyphosphates, only the tripolyphosphate can be isolated in the crystalline state.

Scope.—In this investigation mixtures representing intervals of 10% in composition between the end members of the system $NaPO_3$–$Na_4P_2O_7$ have been studied by four independent methods. Thermal studies, including both heating and cooling curves, have been supplemented by high-temperature microscopy to define the temperature–composition diagram; the crystalline solid phases have then been subjected to examination under the polarizing microscope and their X-ray diffraction patterns have been obtained.

Experimental Methods

Preparation of Materials.—Reagent grade monosodium orthophosphate monohydrate and disodium orthophosphate dodecahydrate served as the starting materials. From the former, anhydrous crystalline sodium metaphosphate was prepared by fusion in platinum at a red heat and slow cooling in an electric muffle furnace. From the latter, anhydrous crystalline tetrasodium pyrophosphate was obtained by initial dehydration in a porcelain dish over a burner, followed by heating in platinum at a red heat in an electric muffle furnace.

From the crystalline anhydrous sodium metaphosphate and sodium pyrophosphate thus obtained, a 20-g. lot of each desired mixture was prepared by fusion in platinum dishes and slow cooling in the electric muffle furnace. During cooling the platinum dishes were expanded noticeably by the crystallization of the melt and, in the range of composition from 60 to 80% of sodium pyrophosphate, as room temperature was approached, the crystalline mass initially formed disintegrated into powder as if under large internal stress.

Each lot of material was reheated to 500° for several hours to ensure complete crystallization and was then ground to a fine powder in an agate mortar immediately preceding its use in the thermal studies described below.

In addition to the series of mixtures just described, a series of samples of sodium metaphosphate was prepared by dehydration of monosodium orthophosphate monohydrate at various constant temperatures in an electric muffle furnace controlled to ±3° by means of a potentiometer-type recording and controlling pyrometer actuated by a chromel-alumel thermocouple. A series of samples of sodium pyrophosphate which had undergone various thermal treatments was likewise prepared.

Thermal Studies.—The heating and cooling curves were determined by measuring the temperature of the material under examination and the temperature difference between this material and a reference point in the wall of the crucible surrounding it. This temperature difference proved to be a sensitive indicator of thermal changes. The apparatus, illustrated in Fig. 1, comprised a small platinum crucible, which just fitted within an alundum standardizing crucible,[8] equipped with a hole in the relatively thick wall in which the reference thermocouple was inserted. The thermocouple which registered the melt temperature was protected by a platinum tube inserted through a hole drilled in the alundum cover of the standardizing crucible. The beads of the chromel-alumel thermocouples were pressed firmly in contact with the alundum and the platinum respectively during use.

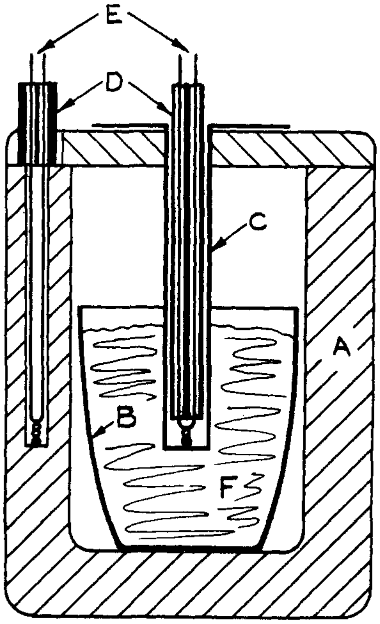

Fig. 1.—Arrangement of crucible for thermal studies by the difference method: A, alundum standardizing crucible; B, platinum crucible; C, platinum shield for thermocouple; D, two-hole porcelain insulators; E, chromel-alumel thermocouple wires; F, finely ground sample.

At the beginning of each run the platinum crucible was filled with a weighed amount, from 8 to 15 g., of powdered material and placed in the alundum crucible. After insertion of the thermocouples, the crucible was located in the center of a small electric muffle furnace with the insulated thermocouple leads passing through a small hole in the rear wall to a cold junction at 0° in a thermos bottle. After throwing in the switch to the furnace, readings were taken every minute on a Leeds and Northrup Type K potentiometer, alternately of the potential and potential difference, representing, respectively, the temperature of the sample and the difference between this temperature and that of the wall of the alundum crucible.

The initial swing and the subsequent smooth drift of the temperature difference in the heating and cooling curves, as, for example, those in Fig. 7, represent merely the complex resultant of the rates of heat transfer from the furnace to the two thermocouples. These slow changes are easily distinguishable from the sharp breaks indicating liberation or absorption of heat by the sample. In evaluating the latter, the temperature has been taken at the midpoint of the initial side of the break, corresponding to the greatest rate of change of the temperature difference.

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[8] Catalog No. 8152 A and B, The Norton Co., Worcester, Massachusetts.

The rates of heating of the various samples obtained graphically are shown in Fig. 2, together with the rate of cooling, which was substantially the same in all runs. In the temperature range from 500 to 620° where the thermal effects of significance to the polyphosphate question were found to occur, the rate of change of temperature did not exceed 5° per minute. The writers have therefore felt justified in reporting the temperatures of the various transformations to the nearest 5°.

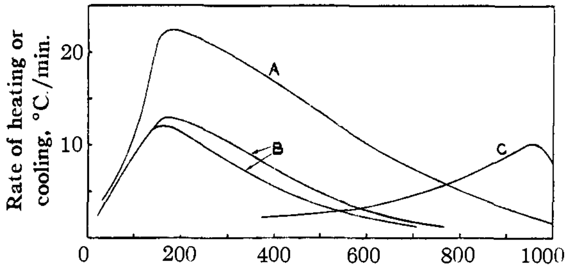

Fig. 2.—Rates of heating and cooling during thermal studies as a function of sample temperature: A, heating rate for $Na_4P_2O_7$ heated to above melting point; B, range of heating rates for all samples other than $Na_4P_2O_7$ heated to above melting point; C, cooling rate for all samples.

The chromel–alumel thermocouples were standardized at two points by measurement of the melting point of sodium chloride and of the transformation of potassium sulfate, which were taken as 800.4 and 583°, respectively,[9] and a calibration curve was constructed using these reference points with the standard potential tables.[10]

High-Temperature Microscopy.—To determine the *liquidus* curves it was necessary to supplement the thermal studies by observations under the microscope over the temperature range up to 1000°. For this work a small furnace, illustrated in Fig. 3, was mounted on the revolving stage of a polarizing microscope.[11]

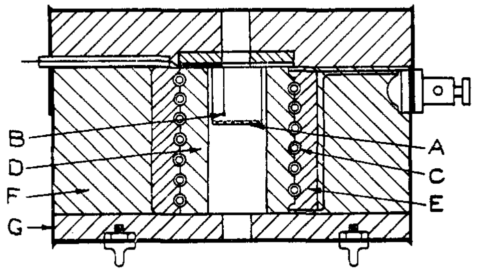

Fig. 3.—Microscope furnace: A, 45-mesh platinum gauze support for sample; B, bead of chromel–alumel thermocouple; C, heating coil; D, alundum furnace core; E, alundum cement; F, insulation; G, cylindrical aluminum shell.

The material under observation was supported on a circle of 45-mesh platinum gauze located at the center of the furnace. By means of a chromel–alumel thermocouple, of no. 28 wire, the bead of which was brought in close proximity to the sample, the temperature could be read continuously on the type K potentiometer.

Each of the mixtures subjected to thermal study was also observed by means of the microscope over the range from room temperature to the disappearance of the last crystal. The liquidus temperature was determined by slowly adjusting the current to the furnace during the final melting until only one tiny crystal remained stable for from ten to fifteen minutes in the melt. Crystallization during cooling was studied both with such melts containing a residual crystal and with those containing no visible solid phase.

By slow cooling over part of the temperature range, comparatively large crystals of the solid phase first separating from each melt could be grown. Then by rapid removal from the furnace it was possible in many cases to quench the residual melt as a glass, so that the initial crystalline phase could subsequently be examined without interference from a second crystalline substance.

Microscopic Identification of Solid Phases.—The crystalline phases obtained by the technique just described as well as the mixtures resulting from the thermal studies, were examined under a polarizing microscope at room temperature by the powder immersion method, using a recently standardized set of refractive index liquids.

X-Ray Identification of Solid Phases.—Independent evidence concerning the crystalline phases in the system $NaPO_3$-$Na_4P_2O_7$ was obtained by a study of X-ray diffraction spectra. Each specimen was powdered, mixed with collodion while minimizing exposure to the air, and then packed into and partially extruded from a capillary tube with an internal diameter of 0.7 mm. When the latter was mounted in the camera, only the extruded portion of the sample intersected the X-ray beam. During exposure, which required, on the average, about an hour, the specimen was continuously rotated by a telechron motor. The diameter of the cylindrical camera was 57.3 mm. Angular divergence of the analyzing beam was limited to approximately 2 degrees.

The analyzing radiation consisted primarily of filtered copper $K\alpha$ lines, obtained from a demountable tube of the Phillips type operated at 50 kilovolts peak and 30 milliamperes. Because some of the samples fluoresced visibly under the X-ray, the film was generally covered with black paper during exposure.

In addition to the X-ray studies at room temperature, a number of photograms were made of sodium metaphosphate and of sodium pyrophosphate at elevated temperatures by mounting powdered samples on a tungsten wire approximately 0.125 mm. in diameter, which could be heated electrically while it was oscillated about its axis in the camera. The approximate temperature of the specimen at different rates of energy input was estimated by observing the current at which reference compounds melted when mounted in powdered form on the wire. A secondary check on the temperature was afforded by the thermal expansion of the tungsten wire, since part or all of its diffraction pattern could be observed on photograms at the higher temperatures.

After preliminary comparison of photograms with those

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(9) "Int. Crit. Tables," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1926, p. 54.

(10) *Ibid.*, Vol. I, p. 59.

(11) Leitz model CM polarizing microscope, equipped with objective H30 and protecting cap, with Polaroid disks substituted for the polarizer and analyzer to avoid possible damage to the Nicol prisms.

of known samples, interplanar spacings for each negative were calculated from direct measurement of the distance between each corresponding pair of diffraction lines, using dividers, a metric steel scale, and a jeweler's magnifying glass. Repeated measurements have shown data thus obtained to be self-consistent within about 2% for the large spacings and within less than 1% for the smaller spacings. Relative intensities of diffraction lines were estimated visually on a scale of 7 for the strongest line in each pattern.

The substances represented by the diffraction data were identified by the method of Hanawalt and Rinn:[12] a preliminary identification was established by comparing three or four stronger lines with those of the reference patterns, and this was confirmed by matching the weaker lines in the order of their intensities; extra lines or lines with excess intensity were then assigned to other reference patterns in a similar manner. Because of the heat treatments employed, certain samples give broad diffraction lines, with occasional lack of resolution; absence of some weaker lines from the patterns, as well as deviations of spacings of up to 2%, or differences of relative intensities of about one unit, arise from this cause and in no way vitiate the identification.

The Forms of Sodium Metaphosphate

Although investigators down to and including Pascal[13] have indicated the possible existence of no less than six different crystalline forms of sodium metaphosphate, only two distinctive X-ray patterns were found by Boulle[14] when he dehydrated monosodium orthophosphate at various temperatures. The latter reported, however, the peculiar observation that while one pattern was shown by material prepared in the temperature interval from 400 to 550°, which he designated "metaphosphate B," the other pattern was produced either by material heated to below 400° (metaphosphate A′) or in the range from 550 to 640° (metaphosphate A). On applying differential thermal analysis, Boulle[15] found the following irreversible transformations

$$\begin{tikzcd}
A' \arrow[r, "430^\circ"] & B \arrow[r, dashed, "525\text{–}590^\circ"] & A \arrow[r, "640^\circ"] & \text{melt} \arrow[d, "\text{rapid cooling}"] \\
 & & & \text{glass} \arrow[ul, "300\text{–}340^\circ"]
\end{tikzcd}$$

Thermal Studies.—Heating curves from the present investigation are represented in Fig. 4. The starting samples of crystalline sodium metaphosphate were made from the same lot of reagent grade $NaH_2PO_4 \cdot H_2O$; A, by heating for eighteen hours at 275°, with a resultant loss in weight which indicated complete dehydration to $NaPO_3$; and B, by heating for nineteen hours at 550°. While the heating curve for the latter sample shows no evidence of any thermal effect up to the melting point, in the curve for the former a definite absorption of energy at 500° is indicated. This apparently corresponds to the inversion from B to A of Boulle.[15] His reported inversion from A′ to B at a lower temperature was not observed in this or other runs.

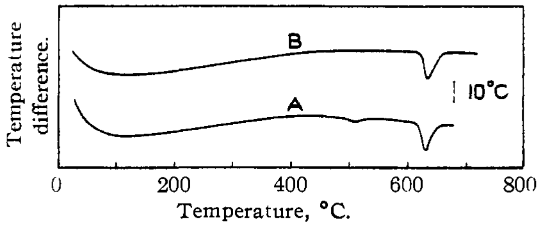

Fig. 4.—Heating curves for sodium metaphosphate prepared at different temperatures: A, $NaH_2PO_4 \cdot H_2O$ heated for eighteen hours at 275°; B, same for nineteen hours at 550°.

The melting point of 625° derived from the present thermal studies is intermediate between the values of 638 and 640° reported, respectively, by Pascal[13] and Boulle,[15] and those of 610° by van Klooster[16] and Tammann and Ruppelt,[17] and of 600° by de Carli[18] and Beans and Kiehl.[19] There was no evidence of any formation of the higher-melting "Kurrol salt" of sodium metaphosphate described by Pascal.[13,20] His observation[20] of the conversion of insoluble into soluble metaphosphate at a temperature close to 500° does, however, agree with the observations of the writers.

X-Ray Patterns.—Although thermal studies yielded evidence of but two crystalline forms of sodium metaphosphate, three X-ray diffraction patterns resulted from the heating of samples of monosodium orthophosphate monohydrate for forty hours at various temperatures. These patterns, which, according to convention, have been numbered downward from the melting point, are compared in Fig. 5. The differences between $NaPO_3$ III, formed at 300 and at 400°, and $NaPO_3$ II, produced at 425, 450 and 475°, are definite, though less obvious than the contrast in pattern between these lower-temperature forms and $NaPO_3$ I made at 500 and at 600°.

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(12) Hanawalt and Rinn, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 244–247 (1936).

(13) Pascal, *Bull. soc. chim.*, **35**, 1131–1141 (1924).

(14) Boulle, *Compt. rend.*, **200**, 635 (1935).

(15) Boulle, *ibid.*, **200**, 832–834 (1935).

(16) Van Klooster, *Z. anorg. Chem.*, **69**, 122–123 (1911).

(17) Tammann and Ruppelt, *ibid.*, **197**, 65–89 (1931).

(18) De Carli, *Atti del II° Congresso Nazionale di Chimica Pura ed Applicata*, **3**, 1146, 55 (1927).

(19) Beans and Kiehl, THIS JOURNAL, **49**, 1878–1891 (1927).

(20) Pascal, *Bull. soc. chim.*, **35**, 1119–1130 (1924).

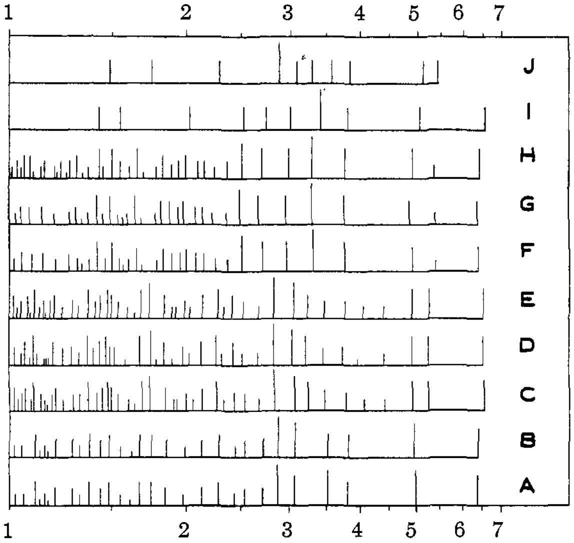

Fig. 5.—Comparison of X-ray diffraction spectra of sodium metaphosphate prepared at various temperatures: $NaH_2PO_4 \cdot H_2O$ was heated for forty hours at various temperatures to produce the samples A to G, inclusive—A, 300°; B, 400°; C, 425°; D, 450°; E, 475°; F, 500°; G, 600°; the $NaPO_3$ glass obtained by quenching from the melt was reheated for forty hours at 300° to produce the sample for H. A and B are $NaPO_3$ III; C, D and E are $NaPO_3$ II; F and G are $NaPO_3$ I. Boulle's forms A and A′, represented by I, apparently are $NaPO_3$ I, his form B, represented by J, apparently is $NaPO_3$ II.

Patterns obtained from specimens at elevated temperatures on the hot tungsten wire verified the formation of $NaPO_3$ I and of $NaPO_3$ II from monosodium orthophosphate monohydrate heated approximately two hours within the temperature ranges indicated by the preceding experiments. In place of $NaPO_3$ III, however, the distinctively different pattern of $Na_2H_2P_2O_7$ resulted from short-time heating on the wire between 300 and 400°, indicating incomplete dehydration.

Optical Properties.—No definite difference in optical properties between $NaPO_3$ III and $NaPO_3$ II could be observed under the polarizing microscope. The polycrystalline character of the samples, and the minute size of individual crystals precluded, however, more than a determination of maximum and minimum refractive indices. As reported in Table IV, while these indices are the same, within the observational uncertainty of ±0.003, for $NaPO_3$ III and $NaPO_3$ II, the values for $NaPO_3$ I are quite different.

Interpretation of Evidence.—While the X-ray evidence of three crystal forms of sodium metaphosphate is superficially at variance with the optical data and with the indication of only one transformation in the thermal studies, an interpretation is possible. Since only a limited rearrangement of structure may be indicated by the shift in pattern from $NaPO_3$ III to $NaPO_3$ II, the refractive indices might be only slightly modified and the energy change might be too small to show up as a break on curve A in Fig. 4, particularly if the transformation occurs slowly rather than instantaneously.

How to correlate the present results with those previously reported by Boulle is difficult. It will be recalled that his low-temperature form, A′, was said to have had the same X-ray pattern as his high-temperature form, A, while an intervening form, B, showed a distinctly different pattern. From Fig. 5, form B would seem to be $NaPO_3$ II, and form A, $NaPO_3$ I. How a pattern identical with that of the latter form could have been obtained by low-temperature dehydration of $NaH_2PO_4 \cdot H_2O$ remains a mystery; perhaps the sample reported as A′ might actually have been $NaPO_3$ I obtained by crystallization from the melt, or by the reheating of $NaPO_3$ glass below 400°. At any rate, the present authors offer, in place of the diagram of Boulle, the following, which they believe more correctly represents the relations between the various forms of sodium metaphosphate

$$\begin{tikzcd}
\text{NaPO}_3\text{ III} \arrow[r, "400\text{–}425^\circ"] & \text{NaPO}_3\text{ II} \arrow[r, "475\text{–}500^\circ"] & \text{NaPO}_3\text{ I} \arrow[r, "625^\circ"] & \text{melt} \arrow[d, "\text{rapid cooling}"] \\
& {} \arrow[u] & \text{reheating to } 300^\circ\text{ C. or above} \arrow[u] \arrow[l, dash] & \text{glass} \arrow[l, dash]
\end{tikzcd}$$

$NaPO_3$ III and $NaPO_3$ II, only very slightly soluble in water, correspond to the Maddrell's salt of the early literature,[21] while the relatively soluble $NaPO_3$ I has usually been referred to as sodium trimetaphosphate, although Beans and Kiehl[19] preferred to call it the monometaphosphate. The glass obtained by quenching the melt is Graham's salt, the so-called sodium hexametaphosphate, which, on reheating, devitrifies chiefly to $NaPO_3$ I, although at lowest temperatures some $NaPO_3$ II also results. Other forms postulated by various investigators down to and including Pascal[13] either are products of the imagination or cannot be obtained by purely thermal processes.

[21] Maddrell, *Phil. Mag.*, (3) **30**, 322–329 (1847).

The Forms of Tetrasodium Pyrophosphate

Thermal Studies.—The existence of more than one form of tetrasodium pyrophosphate has been indicated previously by the thermal expansion studies of von Sahnen and Tammann,[22] who reported the reversible discontinuities compared in Fig. 6 with the curves from the thermal studies of the present investigation. A single enantiotropic transformation occurs at about 400°, but the behavior between 500 and 550° is more complex. On heating, breaks are evident at 510 and 545°, while on cooling they appear at 545, 515 and 505°. The melting point of 985° is slightly higher than the value of 970° reported by Le Chatelier,[23] but checks very well with that of 988° found by Parravano and Calcagni.[24]

High-Temperature Microscopy.—Study of the behavior of single crystals on heating under the microscope has revealed four inversions, recorded in Table I. Each inversion was evidenced by a change in the interference color of the crystal between crossed polaroids, the change originating at a corner and sweeping like a wave across the crystal. These changes were unmistakable; for example, one crystal which showed a light blue interference color over the temperature range up to the first inversion then became white and, as the temperature was slowly increased, successively changed sharply to purple, to a medium blue, and then to a very dark steel-gray, the latter appearance persisting up to the melting point.

TABLE I

TRANSITION TEMPERATURES OF $Na_4P_2O_7$ DETERMINED BY HIGH-TEMPERATURE STUDIES UNDER THE POLARIZING MICROSCOPE

Inversion	Heating No. obs.	Heating Temp., °C.	Cooling No. obs.	Cooling Temp., °C.	Rounded temperature °C.
V-IV	4	397	3	398	400
IV-III	3	507	4	510	510
III-II	3	516	3	519	520
II-I	3	543	4	546	545

X-Ray Patterns.—As might be expected from the obvious reversibility of the inversions, samples of tetrasodium pyrophosphate with various thermal histories all showed the same X-ray diffraction pattern at room temperature. The patterns obtained from samples mounted on a hot tungsten wire showed, however, definite changes in structure with increase in temperature, at least three different forms being indicated. Uncertainty as to the actual temperature of the surface material by which the X-rays were diffracted prevented definite assignment of the patterns. Attempts to produce a surface temperature known to be above 550° caused rapid failure of the tungsten wire, which was necessarily much hotter than the surface of the sample radiating heat to the cold camera.

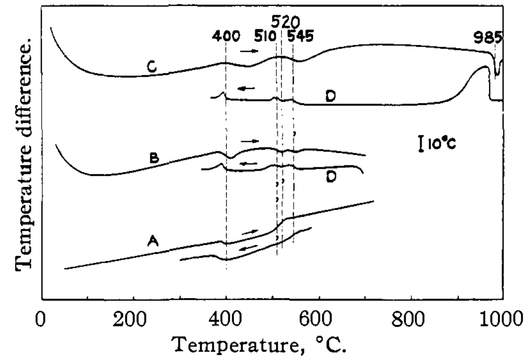

Fig. 6.—The inversions of sodium pyrophosphate: A, thermal expansion curves of von Sahnen and Tammann; B, heating curve (low rate of heating); C, heating curve (high rate of heating); D, cooling curves. Temperatures given for inversions are those derived from high-temperature microscopy.

Interpretation of Evidence.—Even though incompletely verified by the X-ray, the evidence from the thermal studies and the high-temperature microscopy seems adequate to define the reversible transformations of sodium pyrophosphate as follows

$$Na_4P_2O_7\ V \overset{400°}{\rightleftarrows} Na_4P_2O_7\ IV \overset{510°}{\rightleftarrows} Na_4P_2O_7\ III \overset{520°}{\rightleftarrows}$$
$$Na_4P_2O_7\ II \overset{545°}{\rightleftarrows} Na_4P_2O_7\ I \overset{985°}{\rightleftarrows} \text{melt}$$

The System $NaPO_3$–$Na_4P_2O_7$

Thermal Studies.—Starting with end-members of the complexity exhibited by sodium metaphosphate and sodium pyrophosphate, some difficulty might be anticipated in the study of the system containing these components. A logical picture of the phase relations has, however, resulted from the combined evidence from the different methods of attack. Figure 7 presents the results of the individual heating curves for the various mixtures ranging between pure sodium metaphosphate at the bottom and pure sodium pyrophosphate at the top. The significant features of these curves, in order of increasing temperature, are as follows:

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[22] Von Sahnen and Tammann, *Ann. Physik*, (4) **10**, 879–889 (1903).

[23] Le Chatelier, *Compt. rend.*, **118**, 800–804 (1894).

[24] Parravano and Calcagni, *Z. anorg. Chem.*, **65**, 1–9 (1910).

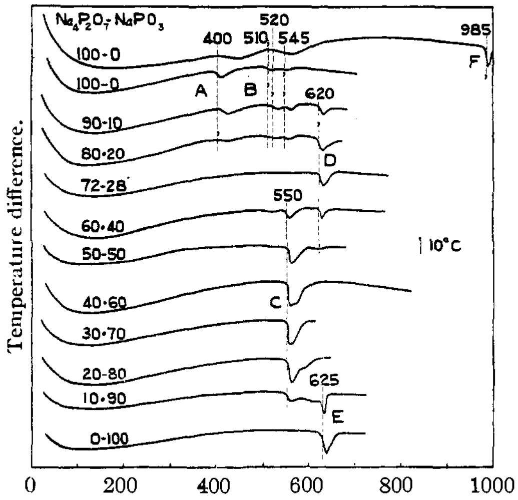

Fig. 7.—Heating curves in the system $NaPO_3$–$Na_4P_2O_7$: A, inversion of $Na_4P_2O_7$ V to $Na_4P_2O_7$ IV; B, inversions of $Na_4P_2O_7$ IV to III to II to I; C, eutectic between $NaPO_3$ and $Na_5P_3O_{10}$; D, peritectic between $Na_5P_3O_{10}$ and $Na_4P_2O_7$; E, melting point of $NaPO_3$; F, melting point of $Na_4P_2O_7$.

A. The inversion of pyrophosphate at 400° is obvious in the case of the 90–10 and 80–20 mixtures, but is barely evident in the 72–28 mixture and does not show at all in the case of mixtures containing still less pyrophosphate.

B. The thermal effects of the other inversions of pyrophosphate between 510 and 545° appear only in the mixtures which show the inversion at 400°, and to the same degree.

C. At 550° the melting of a eutectic is indicated by a break which is evident on the curves of all mixtures containing from 10 to 60% of $Na_4P_2O_7$, but which is strongest in the case of those containing, respectively, 30 and 40%, suggesting that these bracket the eutectic composition. Only the slightest trace of the eutectic break shows on the curve for the 72–28 mixture.

D. At 620° a second pronounced break is apparent on the curves for all mixtures containing more than 50% of pyrophosphate. In the case of the 60 $Na_4P_2O_7$–40 $NaPO_3$ mixture, this thermal effect indicates that the solid phase coexisting with the melt between the eutectic temperature of 550° and the temperature of 620° differs from the solid phase present above the latter temperature.

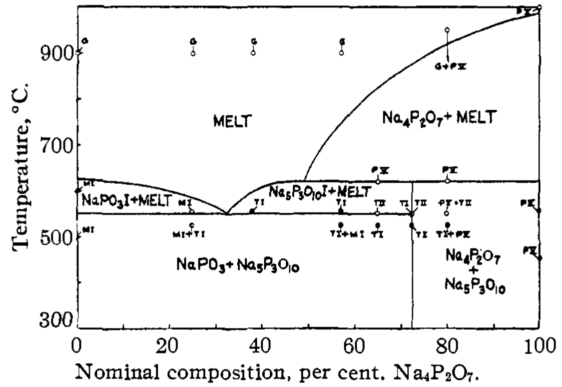

Fig. 8.—The system $NaPO_3$–$Na_4P_2O_7$: open circles represent samples quenched from the indicated temperature; solid circles, samples reheated at the indicated temperature. The identity of the resultant constituents revealed by the X-ray is indicated as follows: G, glass, no crystalline constituent; MI, $NaPO_3$ I; TI, $Na_5P_3O_{10}$ I; TII, $Na_5P_3O_{10}$ II; PV, $Na_4P_2O_7$ V.

The *liquidus* temperatures determined by microscopic study, listed in Table II, have been combined with the temperatures of the thermal effects shown in Fig. 7 to form the diagram of Fig. 8, which represents the system $NaPO_3$–$Na_4P_2O_7$. The presence of a single compound or "polyphosphate" intermediate between sodium metaphosphate and sodium pyrophosphate is indicated. This compound forms a eutectic with sodium metaphosphate at 550° and a nominal composition corresponding to about 33% of pyrophosphate. At 620° the compound melts incongruently, forming sodium pyrophosphate.

TABLE II

LIQUIDUS TEMPERATURES DETERMINED BY HIGH-TEMPERATURE STUDIES UNDER THE POLARIZING MICROSCOPE

Nominal composition, %		*Liquidus* temp., °C.
$Na_4P_2O_7$	$NaPO_3$	
0	100	625
10	90	617
20	80	597
30	70	572
35	65	579
40	60	610
45	55	622
50	50	643
60	40	780
72	28	865
100	0	980[a]

[a] Best value from thermal studies was 985°.

Identity of the Polyphosphate.—The nominal composition of 72.3 $Na_4P_2O_7$–27.7 $NaPO_3$ indicated in Fig. 8 for the compound corresponds to the sodium tripolyphosphate, $Na_5P_3O_{10}$, first reported by Schwarz[25] and recently studied by Huber[5] and by Andress and Wüst.[6,7] That the compound cannot be the $Na_9P_5O_{17}$ tentatively mentioned by Schwarz[25] or the $Na_6P_4O_{13}$ claimed to exist by Fleitmann and Henneberg[26] is evident from the heating curve of Fig. 7. For example,

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(25) Schwarz, *Z. anorg. Chem.*, **9**, 249–266 (1895).

(26) Fleitmann and Henneberg, *Ann.*, **65**, 304–334 (1848).

the nominal composition of 84–16, corresponding to $Na_9P_5O_{17}$, is bracketed by mixtures which show both the inversions of $Na_4P_2O_7$ and the peritectic of the polyphosphate with $Na_4P_2O_7$. Similarly, the nominal composition of 57–43, corresponding to $Na_6P_4O_{13}$, is bracketed by mixtures which exhibit the definite break at 550°, which can only be interpreted as the eutectic of the polyphosphate with $NaPO_3$. This same argument denies the existence as a crystalline phase of $Na_{12}P_{10}O_{31}$, which would have a nominal composition of 25–75, and of any other hypothetical polyphosphate.

In sharp contrast to the preceding is the behavior of the 72–28 mixture corresponding to $Na_5P_3O_{10}$. The heating curve in Fig. 7 shows barely perceptible indications of the presence of a small amount of $Na_4P_2O_7$, but aside from this there is no thermal effect until the sharp break of the peritectic at 620°. This evidence that the single polyphosphate in the system is $Na_5P_3O_{10}$ has been checked by recrystallization of the hydrate, $Na_5P_3O_{10} \cdot 6H_2O$, which characteristically appears as thin rectangular plates. Under the polarizing microscope, these are seen to be twins in which the diagonally opposite quadrants extinguish together, as noted by Bonneman and Bassiere.[27] Chemical analysis of the hydrate yielded the results shown in Table III.

TABLE III

CHEMICAL ANALYSIS OF HYDRATED SODIUM TRIPOLYPHOSPHATE $Na_5P_3O_{10} \cdot 6H_2O$

	Theoretical	Actual	Difference
Na_2O	32.56	32.06	−0.50
P_2O_5	44.73	45.13	+ .60
Loss at 105°	18.92[a]	19.24	+ .32
Ignition loss	22.71	23.01	+ .30
Na_2O/P_2O_5 ratio	1.67	1.63	

[a] Theoretical loss for $5H_2O$.

The Forms of Sodium Tripolyphosphate

That sodium tripolyphosphate, like metaphosphate and pyrophosphate, is polymorphic has been suggested by Huber[5] and demonstrated by Andress and Wüst,[6,7] who observed two different X-ray diffraction spectra in their study of the effect of reheating on the properties of melts of the $Na_5P_3O_{10}$ composition. These differing spectra have been confirmed during the present investigation and the conditions under which the respective forms are obtained have been determined.

When a melt of the $Na_5P_3O_{10}$ or adjacent compositions is quenched very rapidly in very thin layers a glass is obtained which appears clear to the eye. Under the polarizing microscope, however, it will be seen to contain swarms of minute crystallites. Figure 8 indicates that these crystallites are sodium pyrophosphate, since this is the crystalline phase first formed in equilibrium with the melt on cooling any composition containing more than about 50% of nominal $Na_4P_2O_7$. Slightly less drastic cooling, as by pouring the melt on a steel plate, produces a translucent glass in which the crystals of pyrophosphate are larger. Still slower cooling yields a white opaque mass which comprises a large amount of crystalline material in a matrix of residual glass. If this product does not disintegrate to powder as it cools, the X-ray shows predominantly the pattern of $Na_5P_3O_{10}$ I, in Fig. 9, with more or less $Na_4P_2O_7$ V indicated as a secondary constituent.

In contrast, when a melt of the $Na_5P_3O_{10}$ composition is cooled slowly in the furnace to approximately 550° and is then removed, it spontaneously disintegrates, as it approaches room temperature, into a powder which shows the X-ray pattern designated as $Na_5P_3O_{10}$ II in Fig. 9.

If the solid, opaque mass of $Na_5P_3O_{10}$ I in residual glass obtained by moderate cooling is reheated at 500°, and allowed to cool in the air, it disintegrates into $Na_5P_3O_{10}$ II. Reheating of $Na_5P_3O_{10}$ II, obtained in any manner, to a temperature between 500 and 620° transforms it into $Na_5P_3O_{10}$ I which fails to invert on cooling.

Why $Na_5P_3O_{10}$ I developed during the slow cooling of a melt transforms readily into $Na_5P_3O_{10}$ II, while that obtained on reheating the low-temperature form does not is a question for which no good answer can yet be given. The phenomenon has, however, occurred frequently and consistently.

The thermal effect accompanying the inversion on heating $Na_5P_3O_{10}$ II is shown in Fig. 10 to occur at about 515° when the rate of heating near this temperature was not more than 5 degrees per minute. On heating $Na_5P_3O_{10} \cdot 6H_2O$ at various temperatures, $Na_5P_3O_{10}$ I was, however, produced not only at 600 and 550, but also at 500°. The lowest temperature at which the high-temperature form could be formed from the hydrate was not further investigated, but it was noted that at 300°, $Na_5P_3O_{10}$ II was obtained. In none of these experiments was there observed any basis for the statement of Huber[5] that it is impossible to obtain anhydrous sodium tripolyphosphate by direct dehydration of $Na_5P_3O_{10} \cdot 6H_2O$.

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(27) Bonneman and Bassiere, *Compt. rend.*, **206**, 1379–1380 (1938).

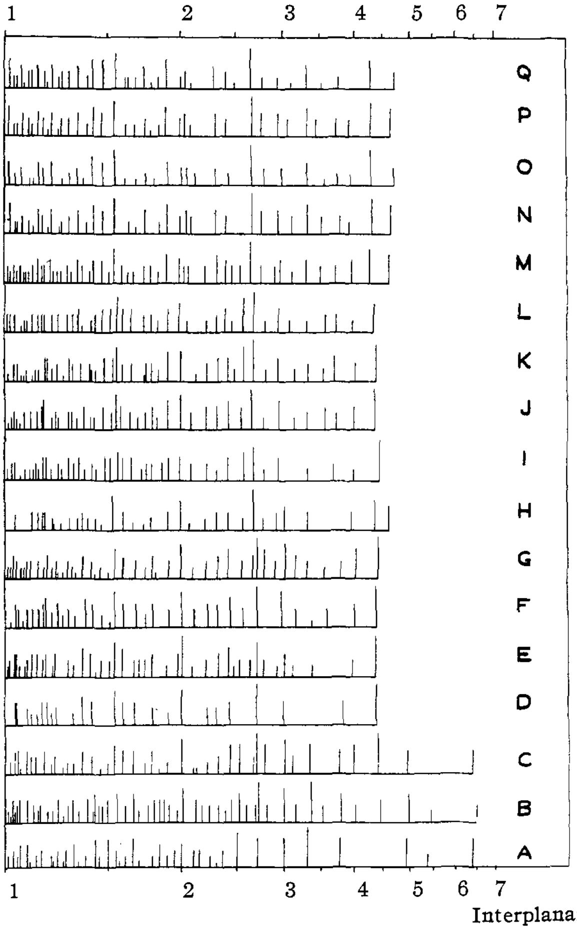

Fig. 9.—Comparison of X-ray diffraction spectra of samples with various compositions and thermal histories

Sample	Nominal composition, % $Na_4P_2O_7$	Nominal composition, % $NaPO_3$	Thermal history Quenched from temp. °C.	Thermal history Reheated at temp. °C.	Reheated for hr.	Predominant constituent	Character of X-ray negative Intensity of pattern	Sharpness of lines	Resolution
A	0	100	...	500	40	$NaPO_3$ I	medium	broad	good
B	25	75	...	525	10	$NaPO_3$ I + $Na_5P_3O_{10}$ I	strong	sharp	good
C	57	43	...	525	8	$Na_5P_3O_{10}$ I + $NaPO_3$ I	medium	broad	medium
D	38	62	555	...	..	$Na_5P_3O_{10}$ I	weak	broad	poor[a]
E	57	43	...	555	7	$Na_5P_3O_{10}$ I	strong	sharp	good
F	65	35	...	525	24	$Na_5P_3O_{10}$ I	medium	broad	medium
G	72	28	...	500	14	$Na_5P_3O_{10}$ I	strong	medium	good
H	57	43	900[b]	...	..	$Na_5P_3O_{10}$ I + $Na_4P_2O_7$ V	strong	medium	poor[a]
I	57	43	slow-cooled in furnace			$Na_5P_3O_{10}$ II	strong	broad	poor[a]
J	65	35	550	...	..	$Na_5P_3O_{10}$ II	weak	broad	poor
K	72	28	550	...	..	$Na_5P_3O_{10}$ II	strong	medium	good
L	72	28	slow-cooled in furnace			$Na_5P_3O_{10}$ II	medium	broad	medium
M	80	20	550	...	..	$Na_4P_2O_7$ V + $Na_5P_3O_{10}$ II	strong	sharp	good
N	65	35	620	...	..	$Na_4P_2O_7$ V	weak	sharp	poor
O	80	20	900	...	..	$Na_4P_2O_7$ V	strong	broad	good
P	80	20	620	...	..	$Na_4P_2O_7$ V	medium	sharp	good
Q	100	0	1000	...	..	$Na_4P_2O_7$ V	strong	sharp	good

[a] Background characteristic of glassy material. [b] Melt poured on steel plate; more drastic quenching yields entirely glassy product.

It will be recalled that, in the preparation of the starting mixtures for the thermal studies, spontaneous disintegration to powder on cooling was exhibited not only by the $72Na_4P_2O_7$–$28NaPO_3$ mixture corresponding to $Na_5P_3O_{10}$, but also by the 80–20 and the 60–40 mixtures. This is scarcely surprising, since the slow cooling in the furnace would have produced in the first case, somewhat more than 70%, and in the second case, somewhat more than 80% of $Na_5P_3O_{10}$ I, the disintegration of which could not be restrained or masked by the residual material.

X-Ray Verification of Temperature–Composition Diagram

On Figure 8 are indicated the composition and thermal history of a series of samples subjected to X-ray examination as an independent check on the identity of the solid phases in the system $NaPO_3$–$Na_4P_2O_7$. Samples quenched from a given temperature are shown as open circles, those reheated at a given temperature as solid circles. The identity of the phase or phases in each sample, determined by comparison of the diffraction spectra, has been indicated for each sample in Fig. 8 by the key letters G for glass, MI for $NaPO_3$ I, TI for $Na_5P_3O_{10}$ I, TII for $Na_5P_3O_{10}$ II, and PV for $Na_4P_2O_7$ V. The spectra of a number of the most significant samples are compared in Fig. 9.

Study of Figs. 8 and 9 reveals complete agreement between the evidence from the X-ray in-

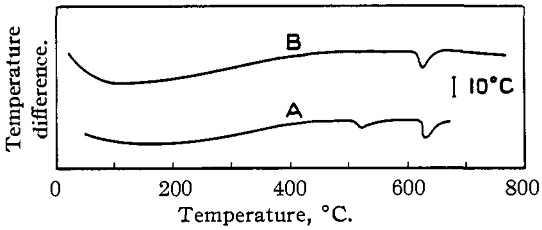

Fig. 10.—Heating curves for two forms of sodium tripolyphosphate: A, sample prepared by cooling from melt to 550° and holding at this temperature (sample disintegrated to powder during subsequent cooling to room temperature); B, sample prepared as above, then reheated to 500°.

vestigation and that from the thermal studies, confirms the work of Andress and Wüst in all essential details, and leaves no place in the system $NaPO_3$–$Na_4P_2O_7$ for any crystalline polyphosphates other than the two forms of sodium tripolyphosphate.

Refractive Indices of Crystalline Phases.—Although by means of the X-ray one can distinguish at room temperature three crystal forms of sodium metaphosphate, two of sodium tripolyphosphate and one of sodium pyrophosphate, differentiation under the polarizing microscope is handicapped by the inherently small particle size of $NaPO_3$ III and II produced thermally, and of $Na_5P_3O_{10}$ II produced by inversion from the higher-temperature form on cooling. Little can be done with these phases beyond measurement of the refractive indices, which are listed in Table IV.

TABLE IV

REFRACTIVE INDICES OF CRYSTALLINE PHASES IN SYSTEM $NaPO_3$–$Na_4P_2O_7$

Substance	Refractive indices[a]	
	N_g	N_p
$NaPO_3$ III	1.525	1.502
$NaPO_3$ II	1.525	1.502
$NaPO_3$ I[b]	1.480	1.474
$Na_5P_3O_{10}$ II	1.500	1.471
$Na_5P_3O_{10}$ I	1.500	1.471
$Na_4P_2O_7$ V[c]	1.496	1.475

[a] White light. [b] This substance was observed to be biaxial (+). Beans and Kiehl[19] report the following data of Colony: N_g 1.486, N_p 1.473, monoclinic (?), biaxial (−). [c] Interference figures show this to be biaxial (+) with small axial angle.

Within the limit of ±0.003 estimated for this type of measurement, the indices of $NaPO_3$ III and II are the same. Similarly, no distinction could be made between those of $Na_5P_3O_{10}$ II and I. The microscope does suffice, however, to distinguish the forms of sodium tripolyphosphate from sodium pyrophosphate with care, and from the forms of sodium metaphosphate with ease.

Behavior of Mixtures on Cooling from the Melt

It should be emphasized that the diagram of Fig. 8 is based upon the effect of increasing temperature upon mixtures made completely crystalline by the preliminary heating at 500°. The curves obtained on cooling these same mixtures from the melt are presented in Fig. 11, with sodium metaphosphate at the bottom and sodium pyrophosphate at the top. In order of descending temperature the significant effects are:

A. The crystallization of pyrophosphate from the melt occurs at progressively lower temperatures as the nominal concentration of metaphosphate in the melt is increased. This thermal effect, which occurs at temperatures consistently below the liquidus as defined by the studies under the high-temperature microscope, does not

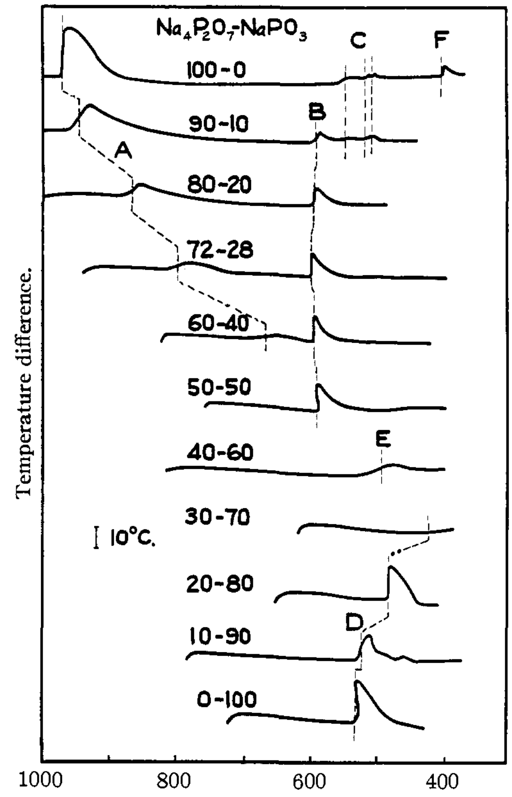

Fig. 11.—Cooling curves for melts prepared from $NaPO_3$ and $Na_4P_2O_7$: A, crystallization of $Na_4P_2O_7$ I from melt; B, replacement of $Na_4P_2O_7$ by $Na_5P_3O_{10}$; C, inversions of $Na_4P_2O_7$ I to II to III to IV; D, crystallization of $NaPO_3$ I from melt; E, crystallization of $Na_5P_3O_{10}$ I from melt; F, inversion of $Na_4P_2O_7$ IV to V.

occur when the melt contains 50% or less of nominal pyrophosphate.

B. The peritectic corresponding to the disappearance of pyrophosphate and the formation of tripolyphosphate is sharply marked in the curves for mixtures containing from 90 to 50% of nominal pyrophosphate, but is not present when the mixture contains 40% or less. The peritectic transformation on cooling occurs at about 590°, 30° below the corresponding change on heating.

C. The inversions of pyrophosphate between 550 and 500° are evident only in the curves for pure pyrophosphate and for the mixture containing 10% of metaphosphate.

D. The crystallization of metaphosphate from mixtures rich in this component occurs only after the melt has been undercooled approximately 100° at the rate of cooling used in this investigation, shown in Fig. 2. Thus the pure metaphosphate, which melts at 625°, did not commence to crystallize until the temperature had dropped to 525°. Mixtures containing from 10 to 30% of nominal pyrophosphate showed progressively lower temperatures of crystallization and smaller thermal effects. With 30% of nominal pyrophosphate in the mixture, little crystallization took place, the final product containing much glass. A considerable amount of glass was also present in the residue from the cooling of the melt containing 40% of nominal pyrophosphate.

With the exception of the initial appearance of pyrophosphate from the melt, the rate of temperature decrease through the range of all changes in phase was less than 5° per minute. Even with this relatively slow rate, the undercooling was pronounced throughout the system except at the extreme pyrophosphate end. Figure 12 compares the results from the cooling curves, in heavy broken lines, with those derived from the heating curves and high-temperature microscopy, in heavy solid lines. In lighter broken lines are shown the course of the liquidus in the system, as indicated by Haddan,[28] and the data of Parravano and Calcagni,[24] whose stirring of the melt apparently allowed less undercooling than occurred in the present study.

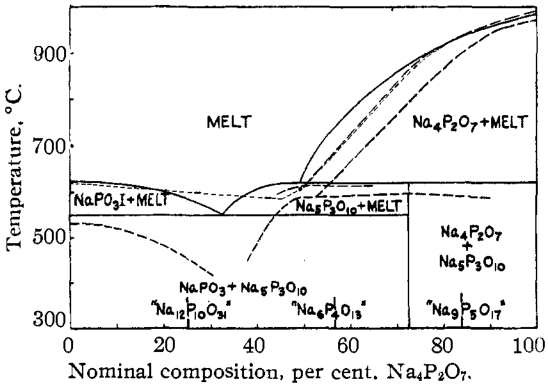

Fig. 12.—Comparison of results from cooling curves with phase diagram based on heating curves: ———, system based on heating curves; — —, thermal behavior on cooling, this paper; — — —, thermal behavior on cooling, Parravano and Calcagni; - - - - -, *liquidus* as given by Haddan.

What Parravano and Calcagni[24] took to be the eutectic between pyrophosphate and metaphosphate is obviously, from Fig. 12, the peritectic between pyrophosphate and tripolyphosphate.

From the behavior on cooling in the furnace, it is evident that only very mild quenching is required to produce a glass from melts near the eutectic composition. Only slightly more rapid cooling will prevent crystallization from melts containing down to 0 or up to 50% of nominal pyrophosphate, as stated by Haddan.[28] Further shift in composition toward the pyrophosphate necessitates progressively stronger quenching to produce a transparent glass. It is, however, feasible commercially to produce a 57–43 glass corresponding to the hypothetical tetraphosphate, and, as previously noted, a glass clear to the eye was obtained with the 72–28 mixture corresponding to the tripolyphosphate, though only by very rapid chilling in very thin layers.

With ordinary quenching, as by pouring the melt on a steel plate, the product changes progressively from transparent to translucent to opaque as the nominal pyrophosphate content is increased above 50%.

Interpretation of Prior Work on Polyphosphates

Together with the recent reports by Huber[5] and by Andress and Wüst,[6,7] the studies presented in this paper clarify much that was obscure in the earlier literature on the polyphosphates. The sodium tripolyphosphate of Schwarz[25] and Stange[29] stands out indubitably as a crystalline chemical individual; the "sodium tetraphosphate" of Fleitmann and Henneberg[26] is seen as sodium tripolyphosphate admixed with residual sodium phosphate glass.

The temperature–composition diagram of Fig. 12 indicates why Huber[5] found that a melt of the

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(28) Haddan, British Patent 378,345, Aug. 11, 1932.

(29) Stange, *Z. anorg. Chem.*, **12**, 444–463 (1896).

$Na_5P_3O_{10}$ composition rapidly quenched produced a glass containing finely dispersed crystals of $Na_4P_2O_7$, and why reheating this glass below the "melting point," *i. e.*, the peritectic at 620°, caused the formation of $Na_5P_3O_{10}$. Huber quite understandably failed to appreciate the significance of the results he obtained when he quenched a melt of the $Na_6P_4O_{13}$ composition, reheated it to below what is now known to be the peritectic, and then rapidly quenched it again. From Fig. 12 it is evident that the product obtained by quenching from between 550 and 620° would comprise crystalline $Na_5P_3O_{10}$ in a matrix of glass and would naturally, when dissolved, exhibit the properties of such a mixture. What Huber referred to as "more highly condensed polyphosphates of the general formula $Na_{n+2}P_nO_{3n+1}$," are simply the infinite number of sodium phosphate glasses, each differing infinitesimally in composition from the next, which may be produced by sufficiently rapid quenching of any melt intermediate between $NaPO_3$ and $Na_5P_3O_{10}$, or, more broadly still, between P_2O_5 and $Na_5P_3O_{10}$.

The results reported by Andress and Wüst[6,7] for melts of various compositions reheated to various temperatures may be so readily interpreted against the background of Fig. 8, that further discussion is unnecessary here.

Turning backward from the mutually consistent data of the three independent contemporary investigations, it is not surprising that Fleitmann and Henneberg[26] obtained a glassy product from their melt of the $Na_{12}P_{10}O_{31}$ composition.

Exactly what mixture of crystalline substances and residual glass they removed from their melt of the $Na_6P_4O_{13}$ composition and dissolved in water, no one can prove, but from their description it does seem probable that they worked with a product containing much $Na_5P_3O_{10}$ but not completely devitrified. On recrystallization from solution they obtained a soft, sticky mass of "delicate thin leaflets," found by Bonneman and Bassiere[27] in a repetition of the experiment to be $Na_5P_3O_{10}\cdot 6H_2O$. The crystal crop obtained by Fleitmann and Henneberg held "a large amount of mother liquor," so that, even after being washed with some cold water and pressed between absorbent paper, the analysis of the ignition residue approached the apparent composition of $Na_6P_4O_{13}$ instead of $Na_5P_3O_{10}$.

To Schwarz[25] should be given more credit for having discovered the tripolyphosphate than blame for having failed to realize, with the analytical means at his disposal, that his new compound was the essential crystalline constituent of the "tetraphosphate" he prepared at the same time by the same method. Nor should criticism be leveled at Parravano and Calcagni,[24] the first to use physical rather than analytical methods, for their failure correctly to interpret their essentially correct measurements. As a result of the tendency to yield products completely or partially glassy, the system $NaPO_3$–$Na_4P_2O_7$ has been inherently a difficult one with which to work.

If the unique utility of the sodium phosphate glasses in softening water by forming a soluble complex with calcium had not been realized by Hall,[30] and the so-called sodium hexametaphosphate had not been brought, as a result, from the status of a laboratory curiosity to that of an industrial chemical, it is not likely that anyone would have re-investigated the polyphosphates for years to come. Indeed, there is more than a superficial analogy between the academic search for polyphosphates which followed Graham's classic work on the metaphosphates,[31] and the intense resurgence of interest in the polyphosphates in the wake of Hall's discovery. Paradoxically, this revival has now reversed much of what was previously believed.

Acknowledgments.—Many of the thermal studies were made by Miss Arloa McCanne. Mr. E. R. Burnett carried out the chemical analysis reported in Table III. Dr. T. H. Daugherty and Mr. F. T. Redman assisted in the construction of the microscope furnace. To these and to their other associates of Hall Laboratories, Inc., and to Dr. S. S. Sidhu of the Co-operative X-Ray Laboratory, the writers express their sincere appreciation for assistance.

Summary

From the combined evidence obtained by thermal studies, high-temperature microscopy, and X-ray investigation of the system $NaPO_3$–$Na_4P_2O_7$, it is concluded that:

1. Sodium metaphosphate may be obtained by thermal processes in three crystal forms.

2. Tetrasodium pyrophosphate probably exists in five different crystal forms, but, since all transformations are reversible, only one form can be obtained at ordinary temperatures.

3. Only one of the hypothetical polyphos-

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(30) Hall, U. S. Patent Reissue 19,719, Oct. 8, 1935.

(31) Graham, *Phil. Trans.*, **123**, 253–284 (1833).

phates in the system $NaPO_3$–$Na_4P_2O_7$ actually exists as a crystalline individual. This is sodium tripolyphosphate, $Na_5P_3O_{10}$, which can be obtained at ordinary temperatures in either one of two crystal forms.

Pittsburgh, Penna. Received September 16, 1940

[Contribution from the Gayley Chemical Laboratory, Lafayette College]

Interrelationships between Fluidity, Volume, Pressure and Temperature in Liquids[1]

By Eugene C. Bingham, Harold E. Adams and Gerald R. McCauslin

Introduction.—A relation between the fluidity and volume of liquids has been proposed by Bachinskii[2] but sufficient data were not then available to give this relation a very critical test, particularly where the change in volume was brought about by varying the pressure instead of the temperature. It is desired in this paper to give the results of a more searching test by the use of more recent data by Bridgman[3] on the relative viscosities and compressibilities of eleven liquids at pressures from one to twelve thousand atmospheres, at the two temperatures 30 and 75°.

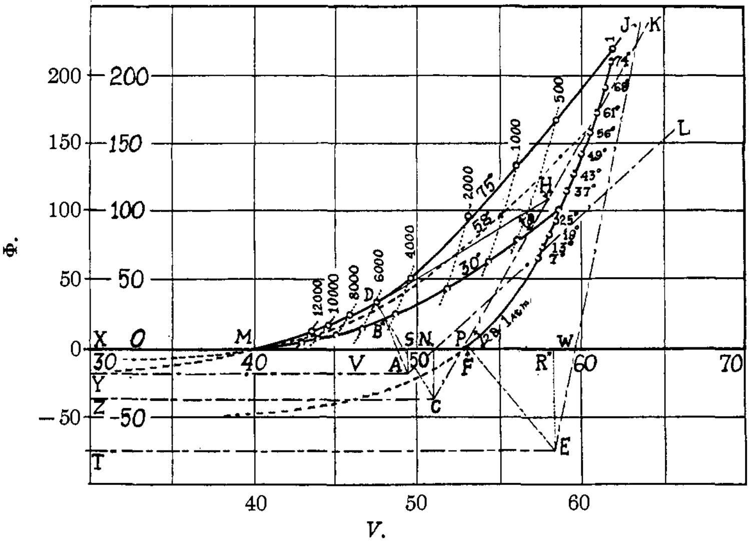

Fig. 1.—Φ *vs.* *V* isotherms of ethyl alcohol at 30 and 75° and isobar at 1 atmosphere.

Neither Bridgman himself nor other worker has found a formula to fit his data. Moreover, Bingham and Coombs,[4] in studying new fluidity temperature data for compounds of high molecular weight, have discovered that in a given homologous series, as the molecular weight increases, the fluidity–volume curves deviate more and more from the linear Bachinskii formula

$$V - \Omega = A\varphi \qquad (1)$$

and pass into a hyperbolic form, which may be written, at least as a first approximation, as

$$V - \Omega = A\varphi - B/\varphi \qquad (2)$$

Bachinskii called Ω the molar limiting volume, $V - \Omega$ the molar free volume which we designate by F_B, and A and B are constants. In comparing the constants of the isobars, where the temperature alone is varied, with those of the isotherms, where the pressure is alone varied, it becomes desirable to distinguish them by subscripts of pressure or temperature as $[A]_P$ and $[A]_T$, etc. Bingham and Coombs found eq. (2) to be sufficiently satisfactory for studying changes in volume and fluidity brought about by varying the temperature and the chemical composition, but it was nevertheless noted that the fit is less perfect when the volume is very small. Time did not permit the elimination of the discrepancy.

As a step in the solution, Bingham, R. G. Volkman[5] and J. L. Petrokubi, working in this Laboratory, found that even a substance which is regarded as obeying the Bachinskii formula particularly well, such as pentane, will, upon severe cooling, reach values of fluidity and volume where the use of the hyperbolic equation is desirable.

Procedure.—The fluidities and molecular volumes were calculated from the original relative values and plotted. A plot of the two isotherms

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(1) Original manuscript received August 15, 1939.

(2) Bachinskii, *Z. physik. Chem.*, **82**, 86 (1931).

(3) Bridgman, *Proc. Am. Acad. Arts Sci.*, **49**, 1 (1931); **61**, 57 (1926); **62**, 187 (1927).

(4) Coombs, Thesis, Lafayette College, 1935, not yet published.

(5) Volkman and Petrokubi, Theses, Lafayette College, 1936, unpublished. The atomic constants most used, for calculating $[\Omega]_P$ as modified from Bachinskii's values by A. E. Holderith and C. E. Grant, using new and more extensive data are CH_2 = 17.76, O = 9.65, H = 4.46, S = 15.63, Cl = 18.79, Br = 21.35, I = 31.74, N = 3.17.