American Journal of Science

JANUARY 1944

THE BINARY SYSTEM $NaPO_3$–$Na_4P_2O_7$.

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ABSTRACT. In the binary system $NaPO_3$–$Na_4P_2O_7$ there is a eutectic, at 552° and 0.31 weight fraction $Na_4P_2O_7$, at which the crystalline phases are $NaPO_3$ and $Na_3P_3O_{10}$, the only binary compound between the two end members. $Na_3P_3O_{10}$ melts incongruently at 622°, forming crystals of $Na_4P_2O_7$ and liquid containing 0.495 weight fraction $Na_4P_2O_7$. Optical properties of these three compounds are given.

THE system Na_2O–P_2O_5 resembles the systems Na_2O–SiO_2[1] and Na_2O–B_2O_3[2] in that at the high-alkali end the ortho-compounds crystallize readily; in the intermediate portions glasses are formed which can be crystallized without difficulty to a series of sodium phosphates; and in mixtures low in sodium oxide the tendency toward glass formation greatly increases. Previous studies have made clear the phase equilibrium relationships in the systems with SiO_2 and with B_2O_3, and it was our plan to carry on a similar study in this system. However, other duties have made it necessary to abandon this project, and this paper is a report on the intermediate portion of the system, from the pyrophosphate, $Na_4P_2O_7$ or $2Na_2O.P_2O_5$, to the metaphosphate, $NaPO_3$ or $Na_2O.P_2O_5$. In another paper[3] we have summarized the optical properties of sodium phosphates and sodium phosphate hydrates.

Compounds outside of the range from metaphosphate to pyrophosphate have been described. Excellent crystals of sodium orthophosphate, Na_3PO_4, were obtained by Schroeder, Berk, and Gabriel[4] in studies of solubility in water under pressure. We have prepared it in an impure state by heating $Na_4P_2O_7$ and Na_2CO_3 at 1400°. Rapid loss of P_2O_5 prevented

[1] Morey, G. W., and Bowen, N. L.: 1924, Jour. Phys. Chem., 28, 1167-1179; Kracek, F. C.: 1930, ibid., 34, 1583-1598.

[2] Morey, G. W., and Merwin, H. E.: 1936, Jour. Amer. Chem. Soc., 58, 2248-2254.

[3] Ingerson, Earl, and Morey, G. W.: 1943, Amer. Mineral., 448-455.

[4] Schroeder, W. C., Berk, A. A., and Gabriel, A.: 1937, Jour. Amer. Chem. Soc., 59, 1783.

our determination of its apparently high melting point. When $Na_3PO_4.H_2O$ was heated 16 hours at 600° it appeared to be isotropic; heated 30 minutes at 1400° it remained essentially isotropic with index about 1.487. More study is needed in this region of the diagram.

Another part of the system yet to be studied is that from $NaPO_3$ to P_2O_5. Diphosphates of other bases exist, and a sodium diphosphate, $Na_2O.2P_2O_5$, is to be expected. The compound variously formulated as $NaH_5(PO_4)_2$, or $NaH_2PO_4.H_3PO_4$, or $Na_2O.2P_2O_5.5H_2O$, commonly found in commercial glacial phosphoric acid, may be a diphosphate.

The experimental results were all obtained by the quenching method, which has often been described in papers from this Laboratory. A small amount of the powdered material, about 10 mg., wrapped in platinum foil 0.01 mm. thick, is held at constant temperature long enough for equilibrium to be reached; cooled at such a rate as to freeze that equilibrium; and examined with the petrographic microscope. If all glass, the temperature of treatment was above the liquidus; the presence of crystals indicates that the temperature was below the liquidus; and by successive approximations the liquidus temperature can be located as closely as desired. Moreover, the primary phase, that is, the crystalline phase which separates at the liquidus, can be positively identified by its optical properties, thus leaving no doubt as to the interpretation of the results. This method was particularly suitable for investigating the region from $NaPO_3$ up to 55 per cent $Na_4P_2O_7$. With higher content of $Na_4P_2O_7$, crystallization takes place so readily that the thermal method is more suitable. At the liquidus for the composition of $Na_5P_3O_{10}$ it was necessary to weight the charge and drop into mercury, and it was not possible to prepare glass of the composition of $Na_4P_2O_7$. We have accepted the melting point of 985° determined by Partridge, Hicks, and Smith[5] for $Na_4P_2O_7$.

The thermocouples used were calibrated at the melting points of aluminum (B. S. Standard Sample No. 44c, melting point 660.1), potassium chloride, 770.3°, and sodium chloride,[6] 800.4°, and the calibrated points were used in connection with a deviation curve for interpolation in the standard tables of

[5] Partridge, E. P., Hicks, Victor, and Smith, G. W.: 1941, Jour. Amer. Chem. Soc., 63, 454-466.

[6] Roberts, H. S.: 1924, Phys. Rev., 23, 386-395.

TABLE I.

Phase Equilibrium Data for the System $NaPO_3$–$Na_4P_2O_7$.

Weight Fraction $Na_4P_2O_7$	Liquidus ° C.	Primary Phase	Incongruent Melting Temperature ° C.	Eutectic Temperature ° C.
0	627.6	$NaPO_3$	...	...
0.15	607	$NaPO_3$	...	552
0.33	557	$Na_5P_3O_{10}$	...	552
0.40	586.5	$Na_5P_3O_{10}$	...	552
0.45	603	$Na_5P_3O_{10}$	...	...
0.475	615.5	$Na_5P_3O_{10}$	...	...
0.50	631	$Na_4P_2O_7$	622	...
0.5659	704	$Na_4P_2O_7$	622	552
0.57	711	$Na_4P_2O_7$	622	...
0.60	743	$Na_4P_2O_7$	...	...
0.66	801	$Na_4P_2O_7$	...	...
0.72	880	$Na_4P_2O_7$	622	...
(1.00)	(985)			

Adams.[7] The quenching results are given in Table I, and the phase equilibrium diagram in Fig. 1.

The binary system $NaPO_3$–$Na_4P_2O_7$ has been studied by Parravano and Calcagni,[8] Huber,[9] Andress and Wüst,[10] and Partridge, Hicks, and Smith.[11] Parravano and Calcagni found no intermediate compound, but the more recent investigators agree on the formation of sodium tripolyphosphate, $Na_5P_3O_{10}$, or $5Na_2O.3P_2O_5$. Partridge, Hicks, and Smith established the fact that $Na_5P_3O_{10}$ has an incongruent melting point, decomposing to $Na_4P_2O_7$ and liquid. Our results agree closely with theirs, except in the region from the eutectic to the incongruent melting, and in addition we have determined the difference between the forms of $Na_5P_3O_{10}$ and two forms of $NaPO_3$. The $NaPO_3$ III of Partridge, Hicks, and Smith was not obtained by us.

Sodium metaphosphate, $NaPO_3$, affords a convenient secondary standard substance for calibration of thermocouples. It can easily be obtained pure by dehydration of $NaH_2PO_4.H_2O$. The glass resulting from fusion is stable, crystallizes promptly on heating to just below the melting point, and the melt undercools

[7] Adams, L. H.: 1926, International Critical Tables, vol. 1, 57-59. McGraw-Hill, New York.

[8] Parravano, N., and Calcagni, G.: 1910, Z. anorg. Chem., 65, 1-9.

[9] Huber, Hans: 1937, Z. angew. Chem., 50, 323-326.

[10] Andress, K. R., and Wüst, K.: 1938, Z. anorg. Chem., 237, 113-131; 1939, ibid., 241, 196-204.

[11] Partridge, E. P., Hicks, Victor, and Smith, G. W.: op. cit.

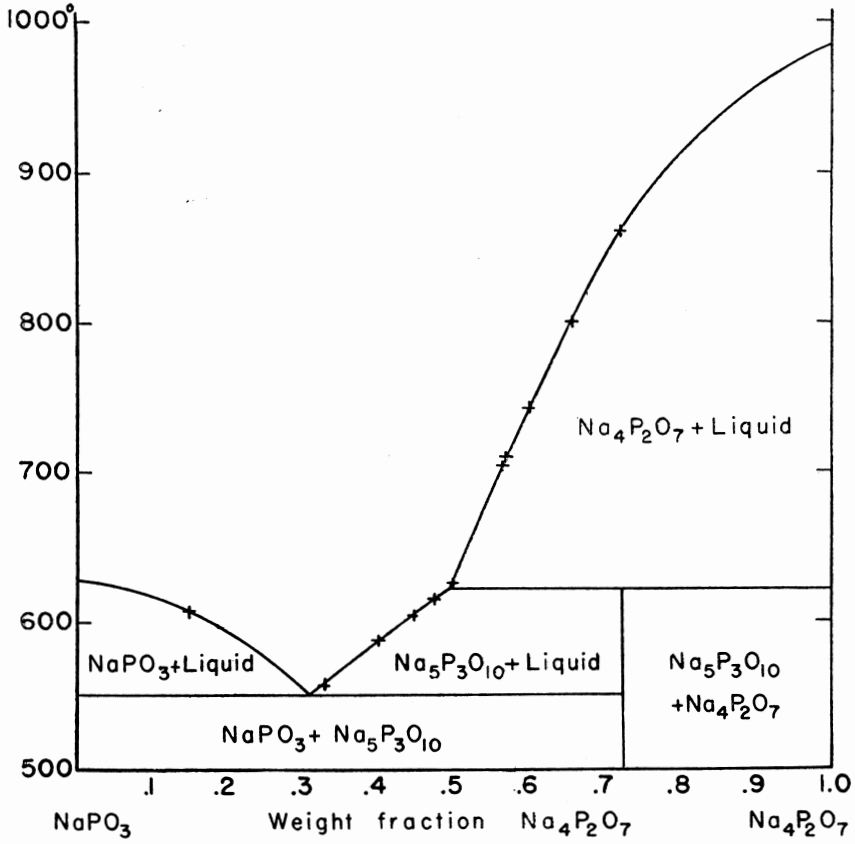

Fig. 1. Phase equilibrium diagram for the system $NaPO_3$–$Na_4P_2O_7$.

so readily that it can be quenched merely by lifting from the furnace. The melting temperature, 627.6,° fills in a gap in the series of secondary standards.

The discussion of the forms of $NaPO_3$ is made more difficult by the persistence of the now absurd system of nomenclature devised almost one hundred years ago by Fleitmann and Henneberg,[12] which not only has no justification in modern theory but also is in conflict with modern knowledge of the structure of glasses. The glassy form, called "sodium hexametaphosphate," and formulated as $(NaPO_3)_6$, is but one of a continuous series of glasses in which the assumption of definite compounds is in conflict with modern theories of the structure of

[12] Fleitmann, Th., and Henneberg, W.: 1848, Ueber phosphorsäure Salze: Liebig's Annalen der Chemie, 65, 304-334.

glass, and the identification of six as the degree of polymerization is without justification.

Sodium metaphosphate exists in at least two crystalline forms. $NaPO_3$ I is obtained by crystallizing just below the melting point. It is biaxial, negative, 2V 80°, α1.474, β1.478, γ1.480. $NaPO_3$ II may be obtained by crystallizing the glass at about 450°. It is probably orthorhombic, and is biaxial, positive, 2V 78°, α1.498, β1.510, γ1.529. The relation between the two forms is not clear. The glass has index 1.4847.

At the binary eutectic, 552° and 0.31 weight fraction $Na_4P_2O_7$, the crystalline phases are $NaPO_3$ and $Na_5P_3O_{10}$, the only compound between the two end-members. It exists in two forms. The high-temperature form, I, is biaxial, positive, 2V 21°, α1.477, β1.478, γ1.504. It was obtained when the melt was quickly cooled to room temperature from about 600°. When the crystallized melt was cooled in the furnace it inverted to the II-form, with spontaneous powdering. $Na_5P_3O_{10}$ II is biaxial, positive, 2V 57°, α1.470, β1.477, γ1.502. Glass of this composition has index 1.4814.

$Na_5P_3O_{10}$ melts incongruently at 622° to form crystalline $Na_4P_2O_7$ and a melt of composition $0.505NaPO_3$, $0.495Na_4P_2O_7$. This melting is very sharp. The pure compound shows no sintering at 620°, much glass and $Na_4P_2O_7$ at 623°. In contrast, a melt containing $0.5659Na_4P_2O_7$ was so sintered at 556° that grinding with mortar and pestle was necessary to obtain a powder, but it was difficult to find the glass under the microscope. This was because each individual crystal of $Na_5P_3O_{10}$ was surrounded by a film of glass so that the true index could not be observed until these individuals were crushed; and the difference in index between glass and the low index of the crystals is so small that the presence of glass could be detected only after careful search. After it was found and its habit had been observed it could be found in every grain, and the properties of the crystals confirmed their identification as $Na_5P_3O_{10}$.

Glass of this composition can be obtained only by rapid and careful quenching. Nevertheless, the liquidus temperature can be determined with greater certainty by the quenching method than by the heating curve method because of the steepness of the melting point curve at this point.

SUMMARY.

A redetermination of the phase equilibrium relationships in the binary system $NaPO_3$–$Na_4P_2O_7$ in general confirms the work of Partridge, Hicks, and Smith. The region between the binary eutectic and $Na_5P_3O_{10}$ has been more precisely located, and the properties of the crystalline compounds were precisely determined.

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