PREPARATION AND PROPERTIES OF SOME COMPOUNDS IN THE SYSTEM H_2O–Na_2O–P_2O_5

EARL INGERSON AND GEORGE W. MOREY,
Geophysical Laboratory, Carnegie Institution of Washington.

ABSTRACT

Optical properties of all known compounds of Na_2O and P_2O_5, both hydrous and anhydrous, are given. For eight of these the data are taken entirely from the literature; eight more have been re-studied; five are here described optically for the first time. Crystallographic and density data are given for some of them.

The methods of preparing twelve of these compounds are given, and for the others methods can be obtained from the literature cited. The nomenclature of these phosphates is discussed. Refractive indices are given for eleven glasses in the system $NaPO_3-Na_4P_2O_7$.

The voluminous literature dealing with the system H_2O–Na_2O–P_2O_5 contains descriptions of numerous ternary compounds, together with a large amount of speculation as to the constitution of these compounds and of their aqueous solutions. Much of this speculation about the constitution of solutions is not well founded and postulates hypothetical acids, the existence of which is supported by no real evidence. Nevertheless, some of these solutions do present striking illustrations of the difference in properties of solutions stoichiometrically equivalent, but of different histories. The mass action of water in such solutions ultimately causes them to become identical in properties, but the rate of this change commonly is slow at ordinary temperatures. It is, however, rapidly accelerated by increasing temperature, and the work of Abbot (1) demonstrated that the change to what is described as the orthophosphate condition, which takes months at ordinary temperatures, is complete in a short time at the boiling point.

We thus have in this system the possibility of realization of conditions of metastable equilibrium, and from the exhaustive study of such metastable solutions there appears a possibility of making a real contribution to the general problem of the constitution of liquids in general. An illustration is to be found in the binary system H_2O–$2Na_2O \cdot P_2O_5$, that is, with solutions in which the ratio of Na_2O to P_2O_5 is that of a disodium phosphate. In the series stable at ordinary temperatures there are the following compounds: $Na_2HPO_4 \cdot 12H_2O$ ($2Na_2O \cdot P_2O_5 \cdot 25H_2O$), $Na_2HPO_4 \cdot 7H_2O$ ($2Na_2O \cdot P_2O_5 \cdot 15H_2O$), and $Na_2HPO_4 \cdot 2H_2O$ ($2Na_2O \cdot P_2O_5 \cdot 5H_2O$). Each of these compounds has an incongruent melting point, and in each the solubility increases with temperature. The final compound of this series is Na_2HPO_4 ($2Na_2O \cdot P_2O_5 \cdot H_2O$), the solubility curve of which is strongly retrograde and must terminate at some unknown quadruple point at which the anhydrous compound, $Na_4P_2O_7$ ($2Na_2O \cdot P_2O_5$), is one of the coexisting crystalline phases. When this anhydrous compound is dissolved in water and the solution allowed to evaporate at ordinary temperature, the compound customarily written as $Na_4P_2O_7 \cdot 10H_2O$ ($2Na_2O \cdot P_2O_5 \cdot 10H_2O$) separates. This compound is metastable with respect to the preceding series, and its solution, on long standing or on heating, becomes transformed into one from which one of the compounds of the preceding series will separate. The solubility curve of the 10-hydrate will intersect the metastable prolongation of the solubility curve of $Na_4P_2O_7$ below the quadruple point $Na_4P_2O_7$–Na_2HPO_4–L–V, giving rise to a metastable quadruple point $Na_4P_2O_7$–$Na_4P_2O_7 \cdot 10H_2O$–L–V,

TABLE 1. OPTICAL PROPERTIES OF COMPOUNDS

Formula	2V	Sign	α	ω	β	ε	γ
Ratio $Na_2O:P_2O_5=3:1$							
$Na_3PO_4 \cdot 12H_2O$(4)		+		1.4458		1.4524	
$Na_3PO_4 \cdot 7H_2O$*	85°	+	1.462		1.470		1.478
$Na_3PO_4 \cdot H_2O$(10)*		+		1.497		1.522	
Na_3PO_4(10)	76°	+	1.493		1.499		1.508
Ratio $Na_2O:P_2O_5=2:1$							
$Na_2HPO_4 \cdot 12H_2O$(4)	57°	−	1.432		1.436		1.437
$Na_2HPO_4 \cdot 7H_2O$(4)	39°	+	1.4412		1.4424		1.4526
$Na_2HPO_4 \cdot 2H_2O$*	*ca.* 80°	+	1.450		1.461		1.477
Na_2HPO_4*	78°	+	1.483		1.499		1.525
$Na_4P_2O_7$(17)*	40°	+	1.475		1.477		1.496
$Na_2P_4O_7 \cdot 10H_2O$(3),(4)	60½°	+	1.4499		1.4525		1.4604
Ratio $Na_2O:P_2O_5=5:3$							
$Na_5P_3O_{10}$ I(17)*	21°	+	1.477		1.478		1.504
$Na_5P_3O_{10}$ II(17)*	57°	+	1.470		1.477		1.502
$Na_5P_3O_{10} \cdot 6H_2O$(16)*	20°	+	1.449		1.450		1.482
Ratio $Na_2O:P_2O_5=1:1$							
$NaH_2PO_4 \cdot 2H_2O$(2),(4)	82°	−	1.4400		1.4625		1.4818
$NaH_2PO_4 \cdot H_2O$(4)	29°	−	1.4557		1.4852		1.4873
NaH_2PO_4*	64°	−	1.481		1.507		1.517
$NaPO_3$ I(14),(17)*	80°	−	1.474		1.478		1.480
$NaPO_3$ II(17)*	78°	+	1.498		1.510		1.529
$NaPO_3 \cdot 2H_2O$(15)*			1.432				1.441
$Na_2H_2P_2O_7$*			1.510				1.517
$Na_2H_2P_2O_7 \cdot 6H_2O$(3),(4)	32°	−	1.4599		1.4645		1.4649

Numbers in parentheses are those of references at end of paper.

* Studied by Ingerson.

provided that no hydrate of $Na_4P_2O_7$ containing less than 10 molecules of water exists. Similar complex reactions are to be found with other ratios of $Na_2O:P_2O_5$. It appeared to us that the entire relationship of the various compounds in the ternary system $H_2O–Na_2O–P_2O_5$ could best be cleared up by the determination of the phase equilibrium relationships in the system up to the temperatures at which the anhydrous crystalline compounds become the stable solid phases. This research was started, but has been interrupted by the pressure of war work. Accordingly, it seems desirable to place on record a few qualitative observations, as well as the optical descriptions of some of the compounds we have prepared.

Most of the data heretofore available on the phosphates of sodium are contained in articles by Dufet and by Joly and Dufet (2, 3, 4). The accompanying table summarizes the optical properties of all the sodium phosphates of which we have a record, and in the notes which follow are comments on the preparation of these compounds. The new measurements include fair to good data on several sodium phosphates that have not been described optically before, and we have checked and extended measurements on a few others. Where two compounds have quite similar indices, as $Na_5P_3O_{10}$ I and $Na_5P_3O_{10}$ II, the properties were measured very carefully in sodium light, but the properties of a compound quite different from any of the others were determined much more roughly. Our opinion of the relative merits of the various determinations is indicated in the following notes.

NOTES ON THE VARIOUS COMPOUNDS

Ratio $Na_2O:P_2O_5=3:1$

$Na_3PO_4\cdot 12H_2O$. Density 1.645. Melts incongruently at 70.75±.01° (D'Ans and Schreiner, 5), but they did not identify the solid phase formed, which probably was $Na_3PO_4\cdot 7H_2O$. May exist in two forms, one of which is of variable composition (Menzel and Sahr, 6).

"$Na_3PO_4\cdot 10H_2O$." Mentioned as "easily prepared," isotropic by Baker (7), but shown by Mason and Ashcraft (8) to be $NaF\cdot 2Na_3PO_4\cdot 19H_2O$.

$Na_3PO_4\cdot 8H_2O$. Also mentioned by Baker, but not obtained by us or other investigators.

$Na_3PO_4.7H_2O$. Prepared by evaporation of a solution of Na_3PO_4 at 83°; also obtained by Hall (9), who gives a good analysis but no properties. Properties measured in white light without measuring the indices of the oils on a refractometer at the time the determinations were made. Indices probably ±0.002. Beta was determined from alpha, gamma, and 2V, which was measured on the universal stage.

$Na_3PO_4 \cdot H_2O$. Measurements about like those for the 7 hydrate. Obtained by evaporation at 86° of a solution of 100 g. $Na_2HPO_4 \cdot 12H_2O$ and 50 g. NaOH. Analysis of material which probably contained some adhering mother liquor gave 16.6 per cent H_2O; $Na_3PO_4 \cdot 2H_2O$ contains 18 per cent; $Na_3PO_4 \cdot H_2O$, 9.9 per cent. Schroeder, Berk and Gabriel (10) give $\omega = 1.498$, $\epsilon = 1.525$ for crystals of $Na_3PO_4 \cdot H_2O$, without giving evidence of how the composition was determined.

Na_3PO_4. Schroeder, Berk and Gabriel (10) describe anhydrous sodium orthophosphate as monoclinic, 2V calculated from indices; $\rho > v$, distinct; b = acute bisectrix; $Y \wedge c = 10° \pm$. Crystals described show 100, 110, and 001 faces. Twinning on 100 said to be common. They give the solubility curve of Na_3PO_4 from 80° to 350°C.

Ratio $Na_2O : P_2O_5 = 2:1$

$Na_2HPO_4 \cdot 12H_2O$. Monoclinic. $a:b:c = 1.732:1:1.416$. $\beta = 58°36'$. $110 \wedge 1\bar{1}0 = 67°56'$. Dispersion $\rho < v$. Density 1.531.

$Na_2HPO_4 \cdot 7H_2O$. Monoclinic. $a:b:c = 2.871:1:1.859$. $\beta = 83°3'$. $110 \wedge 1\bar{1}0 = 79°48'$. Dispersion $\rho > v$. Density 1.679.

$Na_2HPO_4 \cdot 2H_2O$. Formed by evaporation of solution at 60°. Indices measured in white light, probably ±0.002. Beta calculated from alpha, gamma, and 2V, which was measured on the universal stage. Composition checked by loss in weight.

Na_2HPO_4. Formed by evaporation at 105°. Composition checked by loss in weight. Indices measured in white light, probably ±0.002. Beta calculated from alpha, gamma, and 2V, which was measured on the universal stage.

The solubility curve of Na_2HPO_4 in water has been studied by Menzies and Humphrey (11) and by Hammick, Goadby, and Booth (12). The incongruent melting points as given by them are, respectively: 12Aq, 35.2° and 35°; 7Aq, 48.3° and 48.09°; 2Aq, 95° and 94.97°. Hammick, Goadby, and Booth give evidence indicating that there are two forms of the 12-hydrate, with a transition at 29.6°. No crystallographic or optical details are given in either of the above references.

$Na_4P_2O_7$. Beta calculated from alpha, gamma, and 2V, which was measured on the universal stage.

$Na_4P_2O_7 \cdot 10H_2O$. Obtained by evaporation at room temperature of a solution of $Na_4P_2O_7$ in water. Monoclinic. $a:b:c = 1.287:1:1.895$. $\beta = 81°44'$. $110 \wedge 1\bar{1}0 = 76°16'$. Axial plane $\perp 010$. Dispersion $\rho > v$. Density 1.815.

Ratio $Na_2O : P_2O_5 = 5:3$

$Na_5P_3O_{10}$ I and II. These compounds were made by melting $NaPO_3$

and $Na_4P_2O_7$ in proper proportions and cooling. If the furnace and charge were cooled to room temperature, by cutting off the furnace current, the I-form was usually obtained, and the II-form by removing the crystallized melt at from 500 to 550°. The inversion to the II-form was always accompanied by spontaneous powdering. The relationship between these two forms is not clear. Refractive indices were measured with sodium light, and the oils used were checked on a refractometer at the same temperature and using the same light source. The axial angles were measured on the universal stage, using sodium light. The observed values of 2V agree closely with the values calculated from the indices, which are probably accurate in the third place, 2V to the nearest degree.

$Na_5P_3O_{10} \cdot 6H_2O$. Obtained by dissolving crystalline $Na_5P_3O_{10}$ in water and evaporating at room temperature. The crystals were separated from mother liquor by suction on a sintered glass filter, and crystals and solution analyzed. The crystals gave 44.80 per cent P_2O_5; theory 44.75. The solution represented 45 per cent of the $Na_5P_3O_{10}$ taken, and contained 0.165 g. $Na_5P_3O_{10}$, or 0.213 g. $Na_5P_3O_{10} \cdot 6H_2O$ per gram of solution, the solubility at "room temperature," about 25°. The P_2O_5-content per gram of solution was 0.0945.

When a melt containing more $NaPO_3$ than corresponds to $Na_5P_3O_{10}$, say 43.4 per cent $NaPO_3$ and 56.6 per cent $Na_4P_2O_7$, was quickly cooled to a glass, powdered, dissolved in hot water, and the solution allowed to evaporate at room temperature over sulfuric acid, it dried to a gummy-to-hard glass. When the cooling was so carried out that the product consisted of glass and crystals of $Na_4P_2O_7$, crystals of $Na_4P_2O_7 \cdot 10H_2O$ immersed in a thick, viscous liquid were obtained. When the cooling was so carried out that the product consisted of glass and crystals of $Na_5P_3O_{10}$, the evaporation yielded crystals of $Na_5P_3O_{10} \cdot 6H_2O$ surrounded by liquid too viscous to be separated completely from the crystals, which were identified by their optical properties. Finally, when the cooling was so carried out that the product was completely crystallized to a mixture of $NaPO_3$ and $Na_5P_3O_{10}$, crystals of $NaPO_3 \cdot 2H_2O$ and $Na_5P_3O_{10} \cdot 6H_2O$ were obtained. The above sequence of striking differences in behavior depending on the thermal history of the material which was dissolved to make the aqueous solutions indicates that in the glassy phase there are no "molecular groupings" which on solution give rise to crystals of the several hydrated compounds. It should also be mentioned that each of the above solutions on sufficient boiling will give solutions from which hydrates of NaH_2PO_4 and Na_2HPO_4 will crystallize.

The indices of $Na_5P_3O_{10} \cdot 6H_2O$ were measured in sodium light, probably to ±0.001. When well crystallized it has blocky cleavage in two directions at 90°. When precipitated from solution by alcohol the crystals are intricately twinned in such a manner that γ is difficult to observe. Dispersion, $\rho > v$.

Ratio $Na_2O:P_2O_5 = 1:1$

$NaH_2PO_4 \cdot 2H_2O$ and *$NaH_2PO_4 \cdot H_2O$* are the two commonly obtained hydrates, with incongruent melting points at 40.8° and 57.4°, respectively. NaH_2PO_4 was prepared by evaporation at 95°, and in experiments in closed vessels it was obtained up to 300°. However, at this temperature it looked as if the compound had melted congruently, then solidified. With smaller water contents, $NaPO_3$ II was obtained, sometimes in excellent crystals.

$NaH_2PO_4 \cdot 2H_2O$. Orthorhombic. $a:b:c = 0.915:1:1.569$. $110 \wedge 1\bar{1}0 = 95°6'$. Density $= 1.910$.

$NaH_2PO_4 \cdot H_2O$. Orthorhombic. $a:b:c = 0.934:1:0.962$. $110 \wedge 1\bar{1}0 = 93°56'$. Dispersion, $\rho < v$. Density $= 2.055$.

NaH_2PO_4. Indices measured in white light; probably ± 0.002. 2V was measured on the universal stage in white light.

$NaPO_3$ I. 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 (13), which not only has no justification in modern theory but also is in conflict with modern knowledge of the structure of crystals and glasses. The glassy form, called "sodium hexametaphosphate," 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 glasses. The characterizations of the soluble crystalline form, $NaPO_3$ I, as sodium trimetaphosphate, and of the insoluble $NaPO_3$ II as sodium monometaphosphate are likewise in conflict with our knowledge of crystal structure, in which such molecular aggregations play no part.

$NaPO_3$ I is obtained by crystallizing $NaPO_3$ just below the melting-point. The indices were measured in sodium light, probably ± 0.001; 2V was measured on the universal stage.

$NaPO_3$ II may be obtained by crystallizing the glass at about 450°, but the best crystals were obtained by hydrothermal means, as mentioned above. The indices were measured in sodium light and the oils checked on the refractometer, and are probably accurate in the third decimal place. 2V was measured on the universal stage. It is probably orthorhombic, $110 \wedge 1\bar{1}0$ very nearly 90°, $110 \wedge 101$ *ca.* 55°. Axial plane parallel to 010, acute bisectrix parallel to a-axis.

$NaPO_3 \cdot 2H_2O$. This was prepared by dissolving $NaPO_3$ I in water and evaporating over H_2SO_4. The crystals were not very satisfactory. The

indices are no better than ±0.003, and the high index possibly not that good. Universal stage determinations showed most of the grains to be essentially uniaxial and negative, but a few of them gave values of 2V of approximately 80°, both positive and negative. These were probably grains of the two anhydrous forms, $NaPO_3$ II and I, respectively.

$Na_2H_2P_2O_7$. Material was very fine needles with positive elongation. The indices given are really α' and γ', since it was not possible to check the orientation of the needles.

$Na_2H_2P_2O_7 \cdot 6H_2O$. This was not prepared by us. Monoclinic, $a:b:c = 2.026:1:2.049$. $\beta = 56°41'$. $110 \wedge 1\bar{1}0 = 61°8'$. Dispersion, $\rho < v$, strong.

REFRACTIVE INDICES OF GLASSES

Refractive indices of several sodium phosphate glasses were measured by preparing mixtures of oils to match the glasses in sodium light. The indices of the glasses were then measured on the refractometer. Indices are given to four places, but the fourth place is probably almost entirely without significance because a given glass may vary considerably in index with different heat treatments. The glasses were not annealed, but allowed to cool freely in air, usually in 10-gram lots in the 15-cc. platinum crucible in which they were melted. Following are the compositions, given as weight fractions $Na_4P_2O_7$ in the binary system $NaPO_3$—$Na_4P_2O_7$, followed by their respective indices, n_D: 0 ($NaPO_3$) 1.4847; 0.15, 1.4846; 0.33, 1.4845; 0.40, 1.4843; 0.45, 1.4836; 0.475, 1.4834; 0.50, 1.4831; 0.5659, 1.4825; 0.57, 1.4823; 0.60, 1.4820; 0.72, 1.4814.

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