THE CHEMISTRY OF SODIUM PHOSPHATES

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I. INTRODUCTION

Terrey's statement (125) regarding the chaotic state of our knowledge of metaphosphate chemistry applied, until quite recently, to a wider range of phosphate compositions,—namely, to the pyro- to meta-phosphate range. The term "condensed phosphates" is convenient for this group, and will include both chemical individuals and glasses in this range of Na_2O–P_2O_5 composition. Even the comparatively well-known orthophosphates have recently yielded some little-appreciated points of departure from the simple picture presented by inorganic textbooks. While greater care in thermal analyses and wider appreciation of the utility of the polarizing microscope[1] would have dispelled some of the confusion, a full grasp of phosphate chemistry was hardly to be expected before the application of x-rays to the characterization of the solid phases.

The water-softening power of glasses approximating $NaPO_3$ in P_2O_5 content (i. e., Graham's salt) and of sodium triphosphate has now become well known. However, such products were known chemically for forty to eighty years before any industrial use was made of them, and then it was not water softening but another property which led to the first real industrial application of these compounds.

In the boiler-water field there was need of a *latent* acid to aid in keeping down alkalinity developed by loss of carbon dioxide from carbonates. A substance was required which would be nearly neutral initially, but which would develop acidity in the boiler and thus counteract the alkalinity similarly developed. As is well known, the condensed phosphates react with water, especially at elevated temperatures, to produce acid orthophosphates as the end products. In 1929 Hall and Jackson (48) sought a patent on metaphosphate for this purpose.

The availability of such a phosphate soon led to the discovery that glasses approximating $NaPO_3$ in P_2O_5 content were quite effective in suppressing calcium ions (45).[2] The superiority of the water-soluble glass over the water-soluble crystalline salt was recognized early (46). This Na_2O–P_2O_5 glass was the first water softener whose addition to calcium hard water did not necessarily yield a precipitate, yet could give water practically as soft as distilled water.

The development of such a product led to a re-investigation of the whole range of condensed sodium phosphates. This search was intensified in Europe by the discovery of the calcium-ion-suppressing power of the Trilons (88), i. e., salts of organic polybasic acids such as $(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$, called Trilon B abroad (or Nullapon B in this country). The Trilons focussed attention on polybasic acids in general, and on polyphosphates in particular, as means of tying up calcium ions in a complex ion. At that time it was still supposed that there might exist a large number of poly-salts in the condensed phosphate region. The patent literature soon contained claims to numerous complex phosphates which were said to be outstanding in water softening, detergent action, wetting, etc. (e. g., 23, 34, 73)[3]. More or less comprehensive studies of the condensed phosphates have since been made in many laboratories.

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[1] For example, by taking the precaution to characterize the triphosphate hydrate microscopically, as yielding twinned rectangular plates showing extinction 8–9° to the twinning plane, Schwarz (117) proved beyond doubt that he had made $Na_5P_3O_{10}$ in 1895, as has been repeatedly demonstrated recently (12, 60, 95, 101).

[2] As pointed out by Partridge (94), the fact that such glasses could suppress magnesium ion and manganous ion had been known prior to this.

[3] The recent review of Easterwood (31) contains many patent references.

This review is an attempt to give a consistent interpretation, primarily from the point of view of the phase rule, of all information now available in the sodium phosphate field. The fundamentals will be stressed more than the practical applications, which have received attention in recent reviews (31, 54, 64, 74, 116).

II. NOMENCLATURE

Metaphosphates differ slightly in classification from other known phosphates, but all condensed phosphates may be regarded as derived from H_3PO_4. They have often been referred to in patent literature as "salts of phosphoric acid poorer in water of constitution than orthophosphoric acid." The basis for this statement is shown in the first two columns of table 1. All except the metaphosphates can also be written in terms of a single general formula, e. g., $Na_{n+2}P_nO_{3n+1}$, as illustrated in the next two columns.

TABLE 1

Nomenclature

DERIVATION OF ACID		NORMAL SALT		FULL NAME OF NORMAL SALT
$nH_3PO_4-(n-1)H_2O$	$1\ H_3PO_4 - 0\ H_2O$	$Na_{n+2}P_nO_{3n+1}$	Na_3PO_4	Trisodium orthophosphate
	$2\ H_3PO_4 - 1\ H_2O$		$Na_4P_2O_7$	Tetrasodium pyrophosphate
	$3\ H_3PO_4 - 2\ H_2O$		$Na_5P_3O_{10}$	Pentasodium triphosphate
	$4\ H_3PO_4 - 3\ H_2O$		"$Na_6P_4O_{13}$"	"Hexasodium tetraphosphate"
$nH_3PO_4-nH_2O$	$3\ H_3PO_4 - 3\ H_2O$	$(NaPO_3)_n$	$Na_3P_3O_9$	Trisodium trimetaphosphate
	$6\ H_3PO_4 - 6\ H_2O$		"$Na_6P_6O_{18}$"*	"Hexasodium hexametaphosphate"

* Some (70, 135) prefer to write the phosphate glasses $Na_2O(NaPO_3)_n = Na_{n+2}P_nO_{3n+1}$. When water of constitution is also present, the formula should be written $(Na,H)_{n+2}P_nO_{3n+1}$. Only when a glass has been made by quenching a melt of $Na_3P_3O_9$ is the formula $(NaPO_3)_n$ acceptable.

Ortho-, pyro-, and tripolyphosphates could quite properly be called mono-, di-, and triphosphates, respectively. Obviously the prefixes "ortho" and "pyro" are too well established to permit changing to the systematic nomenclature. The prefix "tripoly" for the P_3O_{10} ion, though poor chemically, has the advantage of directing one's thoughts more clearly away from Na_3PO_4, which is so often called *tri*sodium phosphate. "Tripoly" is so widely used in industry that it seems likely to prevail, but the shorter prefix will be used here.

It has been common practice to omit the prefix "ortho" when discussing orthophosphates. This is no longer acceptable, for it will inevitably lead to confusion.

The quotation marks in table 1 indicate that "tetraphosphate" and "hexametaphosphate" are not simple chemical individuals. Both will be discussed more fully later.

Another confusing expression needs clarification. One often speaks of glassy metaphosphate or metaphosphate glass. Neither term is free from objections but the former is especially bad, for it implies, particularly when set alongside the expression "crystalline metaphosphate," that a glass of the $NaPO_3$ composition is a particular compound. It is not a compound, but merely a supercooled liquid; not only are its molecular units constrained in some random arrangement, but it probably contains a range of molecular sizes and structures. In the interest of clarity such terms should be avoided.

III. Phase Diagrams

Perhaps the most satisfactory way to get a comprehensive picture of phosphate chemistry and physics is by means of phase diagrams. While the data available are rather limited, nevertheless they suffice to answer many important questions n this complex field.

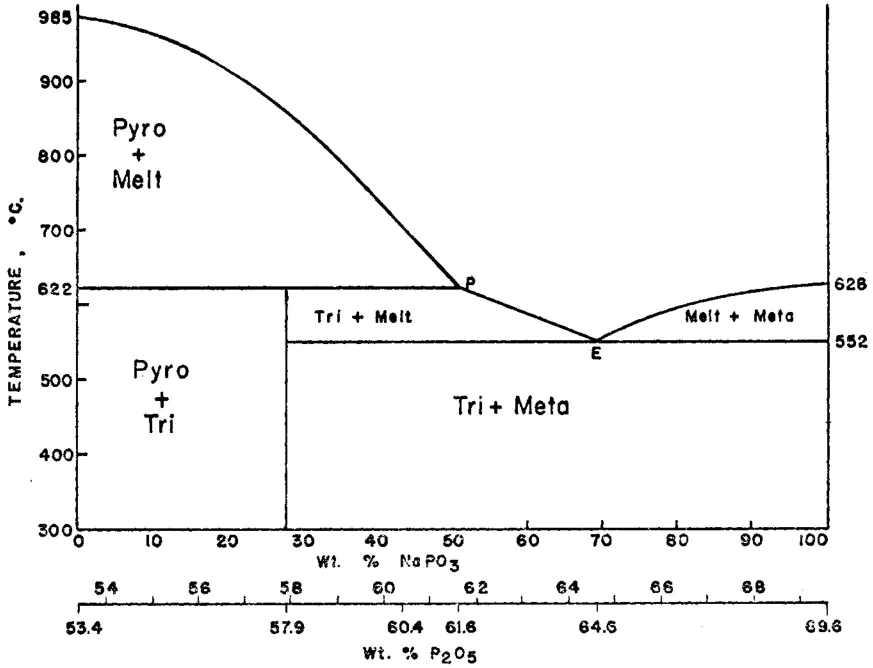

Fig. 1. The $Na_4P_2O_7$–$NaPO_3$ system

A. BINARY SYSTEM Na_2O–P_2O_5

Data are available only for the $Na_4P_2O_7$–$NaPO_3$ portion of the Na_2O–P_2O_5 system, and these are far from complete. Data based on heating curves plus microscopic and x-ray observations are shown in figure 1, which is based on the work of Morey and Ingerson (83) and of Partridge and coworkers (95).[4] The ordinate is temperature in degrees Centigrade and the abscissa is composition expressed in terms of per cent $NaPO_3$, a procedure which is somewhat misleading. A second (per cent P_2O_5) abscissa scale has therefore been added. This diagram does not extend below 300°C., because very little if any change occurs at lower

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[4] It is recognized that the vertical lines at compositions $Na_4P_2O_7$, $Na_5P_3O_{10}$, and $NaPO_3$ cannot represent the true state of affairs, but the necessary solid–solid intersolubilities are lacking for showing them correctly as one-phase areas of finite width.

temperatures. Also not indicated are some solid–solid transformations in the range 400–550°C. for the crystalline salts $Na_4P_2O_7$, $Na_5P_3O_{10}$, and $NaPO_3$.

The meaning of figure 1 may be illustrated in a few cases. Whereas the crystalline salts $Na_4P_2O_7$ and $NaPO_3$ melt to a liquid of the same Na_2O/P_2O_5 ratio, $Na_5P_3O_{10}$ *decomposes as it melts* at 622°C. to give crystals close to $Na_4P_2O_7$ in composition and a liquid indicated by point *P* (61.6 per cent P_2O_5); continued heating simply decreases the amount of $Na_4P_2O_7$-like solid phase until the last crystal disappears at 860°C., giving a melt containing 57.9 per cent P_2O_5. In theory these changes are simply reversed if such a melt is cooled, but in practise the *manner* of cooling has an important bearing on the chemical composition of the product. The reason for this is that reactions involving solid phases are slow and that the liquids involved in phosphate systems are very viscous so that equilibrium is difficult to realize. Sufficiently rapid chilling will give 100 per cent glass. Moderately rapid chilling of a melt made from $Na_5P_3O_{10}$ gives no crystals of $Na_5P_3O_{10}$, but rather fine crystals of $Na_4P_2O_7$ imbedded in a sodium phosphate glass. Slower cooling gives a mixture of $Na_4P_2O_7$, $Na_5P_3O_{10}$, $NaPO_3$, and more or less sodium phosphate glass.

How then is pure sodium triphosphate to be made? Figure 1 indicates that $Na_5P_3O_{10}$ can form in the Na_2O–P_2O_5 system only under conditions that demand reaction between solids. Since such reactions are slow, the reactants must obviously be very finely divided and intimately mixed. This condition can be met either by grinding the reactants together cold, or by quick chilling of the melt. In either case $Na_5P_3O_{10}$ of high purity can be made by heating the intimate mixture for a considerable time at temperatures near 500°C.

Melts containing more than 50 per cent "$NaPO_3$" (61.6 per cent P_2O_5) do not crystallize at all if a fast cooling rate is used, the product being a glass, as recognized by Parravano and Calcagni (92) in 1908. If the cooling rate is about 5°C. per minute, these mixtures supercool about 100°C. (95) before beginning to crystallize; products so cooled to room temperature contain substantial amounts of glass. No one has succeeded in getting equilibrium data by cooling melts in this portion of the Na_2O–P_2O_5 diagram. Because of this fact, investigators have found it easier to determine equilibria by observing the thermal changes upon heating intimate mixtures of various Na_2O–P_2O_5 compositions.

In the "pyro-rich" part of the diagram (61.5–53.4 per cent P_2O_5) there is less tendency toward supercooling the nearer the composition approaches that of $Na_4P_2O_7$. Hence fairly reliable freezing-point data may be obtained (e.g., they are only 10–30°C. low for a cooling rate of 5°C. per minute). Of particular interest is the composition 60.4 per cent P_2O_5, corresponding to the formula "$Na_6P_4O_{13}$" given for the so-called sodium tetraphosphate. While this point has been marked on the P_2O_5 scale for the reader's benefit, the phase diagram gives no evidence for the existence of such a compound. Perhaps it would be well to consider the implications of figure 1 for a melt of the "tetraphosphate" P_2O_5 content, and to simplify the description it may be assumed that equilibrium is attained.

Cooling such a melt from, say, 800°C. first leads to crystals of $Na_4P_2O_7$, which begin forming at 705°C. As more $Na_4P_2O_7$ crystallizes, the liquid composition moves toward point *P*, which is reached at a temperature of about 622°C. On passing below this peritectic temperature, all $Na_4P_2O_7$, by interaction with the melt, is transformed to $Na_5P_3O_{10}$.[5] On further cooling, more $Na_5P_3O_{10}$ crystallizes and the liquid composition moves toward the eutectic *E*. When the temperature falls below 550°C., the remaining eutectic liquid solidifies. The final mixture is composed of 78.3 per cent triphosphate and 21.7 per cent metaphosphate distributed as follows:

60.6 per cent	$Na_5P_3O_{10}$	crystallized above 550°C.
17.7 per cent	$Na_5P_3O_{10}$	crystallized below 550°C.
21.7 per cent	$NaPO_3$	crystallized below 550°C.

Reversal of thermal changes simply reverses these changes. Thus, products marketed as sodium "tetraphosphate" are mixtures. This has been demonstrated in other ways (10, 22).

Any failure to attain equilibrium conditions in manufacture will complicate the mixture. It may easily cool too fast to convert all $Na_4P_2O_7$ to $Na_5P_3O_{10}$ and this would necessitate more P_2O_5-rich material (either $NaPO_3$ or Na_2O–P_2O_5 glass or both). If the product is made from reactants such as Na_2HPO_4 and NaH_2PO_4, incomplete dehydration may leave acid salts, such as $Na_3HP_2O_7$, $Na_4HP_3O_{10}$, or $(Na,H)_{n+2}P_nO_{3n+1}$.

Before leaving the "tetraphosphate" composition it should be recalled that reaction products in these systems are usually examined cold. Conceivably $Na_6P_4O_{13}$ and/or other higher polyphosphates may be found to have narrow thermal ranges of stability at elevated temperatures, by analogy with sodium pyrosilicate, $Na_6Si_2O_7$ (137), which is stable above 402°C. but decomposes at ordinary temperatures.

B. BINARY SYSTEM H_2O–P_2O_5

This is even less understood than the Na_2O–P_2O_5 system. The phosphoric acids are very viscous, so that equilibria are attained *very* slowly, the usual result of cooling being a glass. Furthermore, they are hygroscopic and attack ordinary glass vessels. All that can be stated relative to the *equilibrium* H_2O–P_2O_5 diagram is that the melting points of three compounds are known, as follows:

COMPOUND	MELTING POINT	REFERENCE
	°C.	
H_3PO_4	42.4	(107, 122, 132)
$H_4P_2O_7$	*ca.* 61	(41)
P_2O_5 (tetragonal?)	580	(57)

By adding P_2O_5 in small increments to water until the mixture contained 84 per cent P_2O_5, Rakuzin and Arsenev (102) obtained a crystalline product

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[5] Practically speaking, this transformation is very difficult to realize quantitatively.

after 5 days. It gave a melting point of 34°C. While this might have been a new compound such as $H_5P_3O_{10}$, no optical or x-ray data were given to show that it differed from H_3PO_4 or $H_4P_2O_7$.

Satisfactory equilibrium data in the H_2O–P_2O_5 system, especially between H_3PO_4 (72.4 per cent P_2O_5) and P_2O_5, will probably not be obtainable by cooling methods. Perhaps one could induce crystallization by the supercooling procedure applied by Schierloh (113) to glycerol. The sample is chilled at some very low temperature for a while and then held at a higher temperature, but below the complete melting point, for crystallization and stabilization. The melting data found upon warming such a stabilized system will probably be close to equilibrium values.

The behavior of P_2O_5 shed some light on the polymer-forming tendency of the complex phosphates. According to Hill, Faust, and Hendricks (57) there are three polymorphic forms. The sublimed P_2O_5 can be resublimed completely at 250°C. and 15 mm. (42) and has a hexagonal crystal structure with four P_2O_5 units in the unit cell. It melts in a closed system at 422°C. but quickly resolidifies in the metastable orthorhombic form; this form melts at about 558°C. and slowly resolidifies to the stable or tetragonal (?) form. The vapor pressure of hexagonal P_2O_5 is highest, that of orthorhombic is much lower, and that of tetragonal is still lower. Hexagonal P_2O_5 reacts violently with water, as everyone knows; orthorhombic P_2O_5 reacts much more slowly (crystals may persist after an hour's contact with water); tetragonal P_2O_5 falls *between* the two. While the x-ray data (57) have not been completely analyzed, the stable (or tetragonal ?) form of P_2O_5 is suspected of being a three-dimensional polymer; it can be superheated to 700°C. for a short time without melting, probably because it cannot depolymerize rapidly enough to melt immediately.

C. TERNARY SYSTEM $NaOH$–H_3PO_4–H_2O

Here again only fragmentary data are available. At room temperature and a pressure of 1 atm., the composition triangle is fairly complete for mixtures of NaOH, H_3PO_4, and H_2O as indicated in figure 2. This graph is based on the data of d'Ans and Schreiner (25) at 25°C. and those of Menzel and von Sahr (82) at 20°C.; the latter have been crudely translated to 25°C. The data are plotted on a right triangle, per cent P_2O_5 along the ordinate and per cent Na_2O along the abscissa; per cent H_2O is found by difference.

A few reference lines are dotted across the triangle to aid in showing chemical relationships. For example, one might ask why not plot the data in terms of NaOH, H_3PO_4, and H_2O, the components mixed. This would reduce the triangle to the position shown by the dotted line running from the NaOH to the H_3PO_4 composition. Now we see that one solid obtained (point *G*, $Na_3PO_4 \cdot \frac{1}{2}H_2O$) lies outside this triangle, so that the results could not be properly expressed in terms of $NaOH$–H_3PO_4–H_2O unless negative values were used. This needless complication is avoided if the data are plotted in terms of Na_2O, P_2O_5, and H_2O. Certain key (molar) ratios of $Na_2O:P_2O_5$ are marked by dotted lines from 100 per cent H_2O (i. e., 0 per cent Na_2O, 0 per cent P_2O_5) to the Na_2O–P_2O_5

side of the triangle. Definitely delineated are one-, two-, and three-phase areas as follows:

1. One-phase areas
    a. Homogeneous solution (liquid)
    b. Seven solid phases (indicated by squares)
2. Six two-phase areas (marked by tie lines)
3. Six three-phase areas (two solids in equilibrium with one liquid solution)

1. Salts not decomposed by water

If we put $NaH_2PO_4 \cdot 2H_2O$ or $Na_2HPO_4 \cdot 12H_2O$ into water, heat the system to produce complete solution, and cool back to 25°C., we shall (at the proper concentrations) recover some of the crystals in a form identical with that put into solution, the remainder being in the saturated solution. This operation can be repeated, using the product of the first crystallization, with the same result. This is possible because the Na_2O/P_2O_5 ratio is the same in the mother liquor as in the solid. While there is nothing unusual about such behavior, many salts, including some sodium phosphates, show a different behavior.

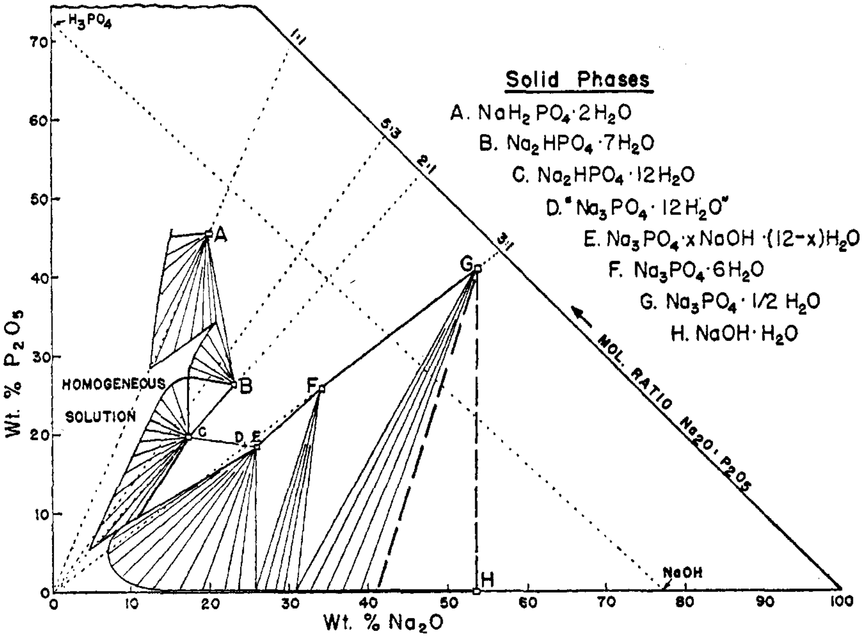

FIG. 2. The system $NaOH-H_3PO_4-H_2O$ at 25°C. and 1 atm.

We could express the above facts in another way. Since the Na_2O/P_2O_5 ratio is the same in crystal as in saturated solution for all NaH_2PO_4 hydrates, NaH_2PO_4 in water (or Na_2HPO_4 in water) can be treated as a two-component system. Examination of Seidell's handbook (118) reveals the following hydrates as the saturating solids:

NaH_2PO_4		Na_2HPO_4	
Hydrate	Temperature range	Hydrate	Temperature range
	°C.		°C.
$2H_2O$	0–41	β $12H_2O$	0–30
$1H_2O$	41–58	α $12H_2O$	30–35
$0H_2O$	Above 58	$7H_2O$	35–48
		$2H_2O$	48–95
		$0H_2O$	Above 95

A single solubility curve can be drawn for either salt as a function of temperature from 0° to 100°C. or above.

Two crystalline phases having the composition $Na_2HPO_4 \cdot 12H_2O$, which are stable in contact with saturated solution, were detected by solubility measurements (49); the α-form is stable at 30–35°C. and the β-form at 0–30°C.

2. Salts decomposed by water

The salt $Na_2HPO_4 \cdot 7H_2O$ can be made not only by crystallization from water at 35–48°C., as indicated above, but can also be crystallized at 25°C. from concentrated solutions containing a suitable excess of H_3PO_4 (see figure 2). Even in such acid solutions the addition of sufficient water will decompose the heptahydrate and crystallize the dodecahydrate. Furthermore, crystals of heptahydrate cannot be purified by recrystallization from water at 25°C., for only the dodecahydrate will be obtained.

A similar but reversed situation exists with respect to the salts $Na_3PO_4 \cdot \frac{1}{2}H_2O$ and $Na_3PO_4 \cdot 6H_2O$. These require an excess of alkali to crystallize at 25°C. A line drawn from a point representing the total composition of a system where $Na_3PO_4 \cdot \frac{1}{2}H_2O$ is in equilibrium with its saturated solution to 100 per cent water (point 0,0 in figure 2) shows how a small amount of water will yield $Na_3PO_4 \cdot 6H_2O$ + saturated solution, while a larger amount will lead to the alkaline complex E. Thus it is impossible to recrystallize the two lower hydrates of Na_3PO_4 from water at 25°C. Either one would yield the alkaline complex.

For most of the crystalline phases in the Na_2O–P_2O_5–H_2O system, the Na_2O/P_2O_5 ratio in the crystal remains constant in spite of (limited) variations of this ratio in the total system and in the saturated solution. This is not true of the crystalline phase represented by square E in figure 2; though plotted as a point this refers to a series of solid solutions which are always richer in Na_2O than $Na_3PO_4 \cdot 12H_2O$, the formula often written for the compound obtained by crystallizing Na_3PO_4 from water at ordinary temperatures. By a study of the isobaric absorption of water vapor at a partial pressure of 10 mm. of mercury, Menzel and von Sahr (82) obtained a crystal analyzing as $Na_3PO_4 \cdot 12H_2O$ and giving an x-ray pattern very similar to that of the more complex hydrate containing the extra sodium hydroxide.[6] The instant one puts this true dodecahy-

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[6] Either Na_3PO_4, $Na_3PO_4 \cdot \frac{1}{2}H_2O$, or $Na_3PO_4 \cdot 6H_2O$ might be used for this vapor hydration, according to Menzel and von Sahr. Addition of water vapor to the hexahydrate leads first to the octahydrate, and then finally at sufficiently low temperature (less than 15°C.) to the

drate into a limited quantity of liquid water, it is converted either to a mixture of $Na_2HPO_4 \cdot 12H_2O$ and $Na_3PO_4 \cdot xNaOH \cdot (12 - x)H_2O$ in contact with solution or to the latter salt alone in contact with solution. The isobaric decomposition curves of these two "dodecahydrates" (82) show that the extra sodium hydroxide stabilizes the product; thus at a partial pressure of 10 mm. of water, dehydration to the octahydrate occurs at 26–26.5°C. for the more alkaline salt and at 15–15.5°C. for the other.

The solid of 3.22 Na_2O/P_2O_5 ratio is the only one that can exist in equilibrium with a saturated solution having the same Na_2O/P_2O_5 ratio. Solids of lower ratio give more acid solutions; those of higher ratio give more alkaline solutions. Thus a tertiary sodium orthophosphate purified by several recrystallizations from water will have an Na_2O/P_2O_5 ratio of 3.22/1. The lowest value of x observed in products crystallized from water was 3.11:1; the original mixture had a 2.80:1 ratio and the mother liquor a 2.69:1 ratio. The highest value observed was 3.25 (large excess of sodium hydroxide in solution). Thus x varies from 0.1 to 0.25.

Analyses of the commercial dodecahydrate have shown repeatedly (e. g., 67, 82, 101) that there is extra alkali in so-called "$Na_3PO_4 \cdot 12H_2O$", the Na_2O/P_2O_5 ratio found varying from 3.14 to 3.20. Menzel and von Sahr (82) found one product to have the ratio 2.98:1, but microscopic examination of the crystals revealed two solid phases: namely, $Na_2HPO_4 \cdot 12H_2O$ and $Na_3PO_4 \cdot xNaOH \cdot (12 - x)H_2O$.

The formula of this tertiary dodecahydrate is written with the x to signify variability. The x-ray data have not been completely interpreted, but they suggest that the extra sodium hydroxide goes into the crystal lattice in the place of some of the water of crystallization, hence the $(12 - x)H_2O$.

It is natural to compare this series of solid solutions for tertiary sodium orthophosphate with those observed among the corresponding calcium phosphates, particularly the apatites. For instance, we may tabulate formulas as follows:

$(Ca_3P_2O_8)_3 \cdot CaF_2$ or $Ca_5P_3O_{12}F$	Apatite
$(Ca_3P_2O_8)_3 \cdot CaCl_2$ or $Ca_5P_3O_{12}Cl$	Chlorapatite
$(Ca_3P_2O_8)_3 \cdot Ca(OH)_2$ or $Ca_5P_3O_{12}(OH)$	Hydroxyapatite
$(Ca_3P_2O_8)_3 \cdot 2H_2O$?	Aquo-apatite?
$Ca_3P_2O_8 \cdot Ca(OH)_2 \cdot 4H_2O$	Isoclasite
$(Na_3PO_4)_2 \cdot NaF \cdot 19H_2O$	Wrongly called "$Na_3PO_4 \cdot 10H_2O$"
$(Na_3PO_4)_4 \cdot NaOH \cdot 47H_2O$ to $(Na_3PO_4)_{10} \cdot NaOH \cdot 119H_2O$	Series of solid solutions

Writing the formulas of the apatites as above is misleading for they suggest definite chemical individuals, whereas actually the compositions indicated are

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dodecahydrate. All of these salts were characterized by analysis for water and by having a distinctive x-ray pattern.

to be taken as illustrations of extremes in systems of solid solutions. For example, the fluoride of apatite can be partially or wholly replaced by one or more radicals such as chloride, carbonate, hydroxy, etc. without destroying or changing greatly the apatite lattice (32). It has even been suggested that there exists an aquo-apatite and a series of solid solutions between it and hydroxyapatite (56), but this is doubted by others (32). Among known sodium compounds is a fluoro derivative (78), but it is hydrated; it was once erroneously reported as $Na_3PO_4 \cdot 10H_2O$ because analyses were not made for fluorine and the water content was close to that for the decahydrate. The extremes of the series of solid solutions denoted by E in figure 2 can be written as $(Na_3PO_4)_4 \cdot NaOH \cdot 47H_2O$ and $(Na_3PO_4)_{10} \cdot NaOH \cdot 119H_2O$. All have the same microscopic appearance and essentially the same x-ray pattern (82), just as do certain series of solid solutions that have been studied among the apatites.

From the foregoing it is evident that we cannot properly speak of the solubility of Na_3PO_4 in water. This is certainly true in the temperature range where the variable alkaline hydrate is the stable saturating phase. In short, Na_3PO_4–H_2O cannot be treated as a two-component system. The fact that the saturated solution and saturating solid may differ from each other and from the initial crystal in Na_2O/P_2O_5 ratio probably accounts for the discordance of Na_3PO_4 "solubility" data. The data quoted by Seidell (118) plus those of Menzel and von Sahr (82) suggest that the saturating phases are as follows:

$Na_3PO_4 \cdot xNaOH \cdot (12 - x)H_2O$	−0.5° to about 43°C.
$Na_3PO_4 \cdot 8H_2O$ (or $7H_2O$?)	43° to 70°C.
$Na_3PO_4 \cdot 6H_2O$	70° to 121°C.
$Na_3PO_4 \cdot \frac{1}{2}H_2O$ (or $1H_2O$?)	121° to 212°C.
Na_3PO_4	Above 212°C.

Four stages of hydration are clearly evident from breaks in the "solubility" curve, and a fifth seems to be present near 43°C. How many hydrates exist in the 6–8 H_2O range is not yet certain and there is still argument over the lower hydrate ($\frac{1}{2}$ or 1 H_2O?). Whether the lower hydrates (8, 6, and $\frac{1}{2}$ H_2O) are variable remains to be demonstrated by careful systematic studies, but Menzel and von Sahr (82) imply that the hexahydrate and the hemihydrate are simple chemical individuals.

3. Discussion

In the $NaOH$–H_3PO_4–H_2O system (figure 2) no evidence was found for pyro-, tri-, or metaphosphates in spite of the fact that the region involving these Na_2O/P_2O_5 ratios was at least partially explored. This is contrary to the behavior of the silicates or vanadates. In the Na_2O–V_2O_5–H_2O system (66, 77, 105), for example, addition of vanadic acid to Na_3VO_4 to reduce the Na_2O/V_2O_5 ratio to about 2 gives crystals of hydrated $Na_4V_2O_7$, not Na_2HVO_4; further addition of V_2O_5 to a Na_2O/V_2O_5 ratio near 1 gives crystals of hydrated $NaVO_3$, not NaH_2VO_4. The different behavior of the phosphates suggests that the orthophosphates are relatively more stable than the corresponding vanadates.

As Hendricks (55) has pointed out, a further indication of orthophosphate stability is to be found in the phosphate minerals. The one hundred and sixty phosphate and arsenate minerals listed in Dana's *Textbook of Mineralogy* (24) are almost exclusively ortho derivatives.

Still further evidence is given by dilute solutions of phosphates in which pyro-, tri-, and metaphosphates tend to hydrate to ortho. In particular, Bamann (5) showed that in the presence of a suitable catalyst at pH 8–9 even pyrophosphate hydrates readily to orthophosphate at 37°C.

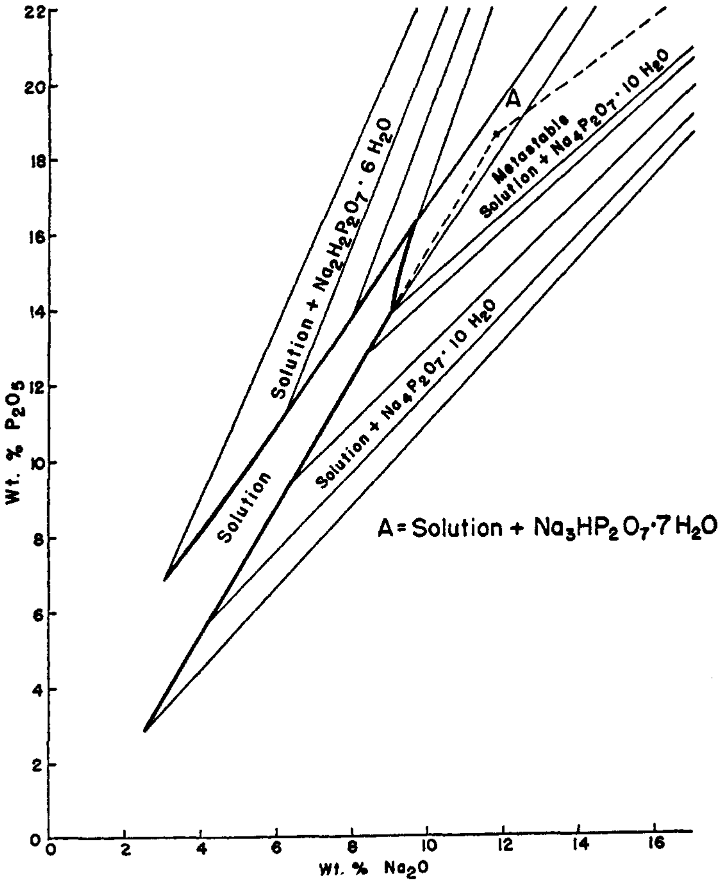

FIG. 3. The system $NaOH\text{-}H_4P_2O_7\text{-}H_2O$ at 20°C. and 1 atm.

It is probably safe to assume that pyrophosphates have either a very limited or even no stable existence in the $Na_2O\text{-}P_2O_5\text{-}H_2O$ system; tri- and metaphosphates are even less stable[7] than pyrophosphates.

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[7] Further discussion of the stability of condensed sodium phosphates will be found in the last section, page 176.

D. TERNARY SYSTEM $NaOH-H_4P_2O_7-H_2O$

While this system is certainly metastable with respect to orthophosphates over part of the range and may be metastable over the whole range, yet pyrophosphates change to ortho slowly enough in the absence of catalysts at ordinary temperatures to permit evaluation of some of the metastable equilibria. Selva's data for 20°C. and 1 atm. (119) are shown in figure 3 for the region 1:1 to 2:1 Na_2O/P_2O_5 ratios; the data are plotted on a right triangle; per cent H_2O is found by difference.

The homogeneous-solution region is much smaller than for orthophosphates. The solid phases which crystallize from solution are $Na_4P_2O_7 \cdot 10H_2O$, $Na_3HP_2O_7 \cdot 7H_2O$, and $Na_2H_2P_2O_7 \cdot 6H_2O$. Again, nothing appears at the 5:3 ratio, which we have in $Na_5P_3O_{10}$, and the salt at the 1:1 ratio is not $NaPO_3$, but $Na_2H_2P_2O_7$. This system could surely be studied in more alkaline systems. The homogeneous-solution branch should bend around and go toward 40.5 per cent Na_2O at 0 per cent P_2O_5, where saturated sodium hydroxide solution would be in equilibrium with solid $NaOH \cdot H_2O$. $Na_4P_2O_7$ or possibly other, lower hydrates of $Na_4P_2O_7$ would probably put in their appearance. Probably more acid systems would be difficult to study, owing to rapid reversion to orthophosphates.

This system has also been studied to the same extent at 30°C. and 1 atm. Here the system differs only in having a slightly larger homogeneous-solution area and in having $Na_2H_2P_2O_7$ and $Na_3HP_2O_7 \cdot H_2O$ as the acid pyrophosphate saturating solids, instead of $Na_2H_2P_2O_7 \cdot 6H_2O$ and $Na_3HP_2O_7 \cdot 7H_2O$, respectively.

Textbooks (e. g., 124) often imply that the salt $Na_3HP_2O_7$ or its hydrates do not exist, and the older literature is (79) certainly confusing on this point. Selva's data suggest reasons for the difficulty. In the first place the range of existence of $Na_3HP_2O_7$ is quite narrow at 20–30°C. Then, a metastable $Na_4P_2O_7 \cdot 10H_2O$–solution equilibrium can be realized without any $Na_3HP_2O_7 \cdot 7H_2O$ being present (figure 3). Also, when drawn on a very large scale, Selva's data suggest that $Na_3HP_2O_7 \cdot 7H_2O$ alone may be unable to exist in equilibrium with a saturated solution of the same Na_2O/P_2O_5 ratio, but require slightly more acid solutions. Contrast with this situation the fact that both $Na_4P_2O_7$ and $Na_2H_2P_2O_7$ can be recrystallized directly from water[8] giving the following salts:

$Na_2H_2P_2O_7 \cdot 6H_2O$ (119)	−0.7°C. to 27°C.
$Na_2H_2P_2O_7$ (119)	Above 27°C.
$Na_4P_2O_7 \cdot 10H_2O$ (80, 81, 119)	−0.4° to 79°C.
$Na_4P_2O_7$ (81)	Above 79°C.

It is not surprising that $Na_4P_2O_7$ and $Na_2H_2P_2O_7$ are better known than $Na_3HP_2O_7$.

Roborgh (106) found $Na_4P_2O_7$ more soluble in glycerol (specific gravity 1.2303, 98 per cent) than in water, as indicated below:

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[8] This ignores the tendency of $Na_2H_2P_2O_7$ to hydrolyze or revert to NaH_2PO_4, which is the true equilibrium salt. Similarly, $Na_4P_2O_7$ probably tends to revert to Na_2HPO_4.

SOLVENT	SOLUBILITY AT 20°C.	SOLID PHASE
	per cent	
H_2O	5.22	$Na_4P_2O_7 \cdot 10H_2O$ (81, 119)
Glycerol	8.8	

E. TERNARY SYSTEMS INVOLVING TRI- OR METAPHOSPHATES

Although the study would probably be more difficult, owing to more rapid reversion toward orthophosphates, a similar study on sodium triphosphates, and perhaps even on sodium metaphosphates, could be made. However, very little such information is available.

A sample of commercial sodium triphosphate, twice recrystallized from water in this laboratory, gave a solubility of 14.5 per cent at about 26°C. (101). Ingerson and Morey (60) found the solubility to be 16.5 per cent at about 25°C., the solid phase being $Na_5P_3O_{10} \cdot 6H_2O$.

The common, water-soluble, crystalline sodium metaphosphate, believed by some to be trimeta $Na_3P_3O_9$, is presumably somewhat more soluble, but quantitative data are lacking. Wiesler (134) gave the solubility as 18 per cent in "cold water", without specifying the temperature. The saturating solid is presumably triclinic $Na_3P_3O_9 \cdot 6H_2O$ (or $NaPO_3 \cdot 2H_2O$).

Na_2O–P_2O_5 glasses of P_2O_5 content near that of $NaPO_3$ dissolve to a much greater extent. Strictly speaking, one cannot measure the solubility of a glass, for a solubility determination requires the presence of a definite saturating solid phase in equilibrium with the solution. However, it is useful to know that a clear syrupy solution containing 50–70 per cent of such a glass can be made (20, 64, 121).

F. CRYSTALLINE SODIUM PHOSPHATES

The number of crystalline species in the Na_2O–P_2O_5–H_2O system is evidently quite large. Table 2 lists twenty-nine salts which may be encountered at ordinary temperatures. At temperatures above 300°C. four other forms of $Na_4P_2O_7$ are known (95). It is to be expected that a few more will be found when further systematic studies are made, e. g., $Na_4HP_3O_{10}$ in other levels of hydration than the one listed in table 2. Since any heat treatment may convert the more condensed to less condensed phosphates, this abundance of possible compounds complicates the characterization of such products.

IV. HARDNESS SUPPRESSION

One reason for interest in condensed phosphates is that they possess ability to lock up calcium and magnesium (also ferric) ions and reduce their chance of precipitating soap or other fatty detergents. Even though we limit our attention to one kind of hardness (e. g., calcium) and to one particular soap (e. g., NaMy = sodium myristate), we have increased the complexity of the system to five components Na_2O–CaO–P_2O_5–HMy–H_2O. Very useful information to have on such a system would be the boundary of the homogeneous-solution region, together with the composition of the solid phase in equilibrium with each saturated solution. Needless to say, such data are not available, but their utility and significance can be demonstrated by means of a simpler, analogous system for which data are available. A striking example among three-component systems is $KI{-}HgI_2{-}H_2O$.

TABLE 2

Sodium phosphates

TYPE	NORMAL SALT	ACID SALTS	
Ortho	Na_3PO_4	Na_2HPO_4	NaH_2PO_4
	$Na_3PO_4 \cdot 0.5H_2O$	$Na_2HPO_4 \cdot 2H_2O$	$NaH_2PO_4 \cdot H_2O$
	$Na_3PO_4 \cdot 6H_2O$*	$Na_2HPO_4 \cdot 7H_2O$	$NaH_2PO_4 \cdot 2H_2O$
	$Na_3PO_4 \cdot 8H_2O$*	$Na_2HPO_4 \cdot 12H_2O$ (α)	
	$Na_3PO_4 \cdot xNaOH \cdot (12 - x)H_2O$	$Na_2HPO_4 \cdot 12H_2O$ (β)	
Pyro	$Na_4P_2O_7$	$Na_3HP_2O_7$	$Na_2H_2P_2O_7$
	$Na_4P_2O_7 \cdot 10H_2O$	$Na_3HP_2O_7 \cdot H_2O$	$Na_2H_2P_2O_7 \cdot 6H_2O$
		$Na_3HP_2O_7 \cdot 7H_2O$	
Tri	$Na_5P_3O_{10}$ I	$Na_4HP_3O_{10} \cdot 1.5H_2O$†	
	$Na_5P_3O_{10}$ II		
	$Na_5P_3O_{10} \cdot 6H_2O$		
	$Na_5P_3O_{10} \cdot 8H_2O$‡		
Meta§	$NaPO_3$ I		
	$NaPO_3$ II		
	$NaPO_3$ III		
	$NaPO_3 \cdot 2H_2O$		

* Hall (44) and Ingerson and Morey (60) speak of $Na_3PO_4 \cdot 7H_2O$.

† Obtained by Huber (58) by adding alcohol to an aqueous acetic acid solution of $Na_5P_3O_{10}$.

‡ Both Huber (59) and Bonneman-Bémia (13) claim that this is formed by direct crystallization from water; it readily loses water in air to become the hexahydrate.

§ $NaPO_3$ I is the soluble crystalline variety, Boullé's A (15, 16) and Nylén's $Na_3P_3O_9$. $NaPO_3$ II is an insoluble crystalline variety, Boulé's B. $NaPO_3$ III is also insoluble and crystalline but does not correspond to any form reported by Boullé. $NaPO_3 \cdot 2H_2O$ is the hydrated form of $NaPO_3$ I.

A. SYSTEM $KI{-}HgI_2{-}H_2O$

This system, illustrated for 20°C. in figure 4 (29, 90, 100), has a very large homogeneous-solution area, all of it requiring excess potassium iodide over the 1:1 molar ratio required to form the complex salt $KHgI_3 \cdot H_2O$. Thus mercuric iodide, whose water solubility is comparable to that of calcium carbonate, is very soluble in concentrated potassium iodide solutions, owing to the formation of a soluble complex. Formation of the complex may be expressed by means of equations as follows:

$$\begin{array}{lcl}
HgI_2(\text{solid}) \leftrightarrows HgI_2\ (\text{dissolved}) \leftrightarrows Hg^{++} + 2I^- \\
\qquad\qquad\qquad\quad + \\
KI \leftrightarrows K^+ + \ I^- \\
\qquad\qquad\qquad\quad \upharpoonleft\downharpoonright \\
\qquad\qquad\qquad\quad HgI_3^-
\end{array}$$

This reduces the Hg^{++} concentration below that required to exceed the solubility product and hence no mercuric iodide precipitates.

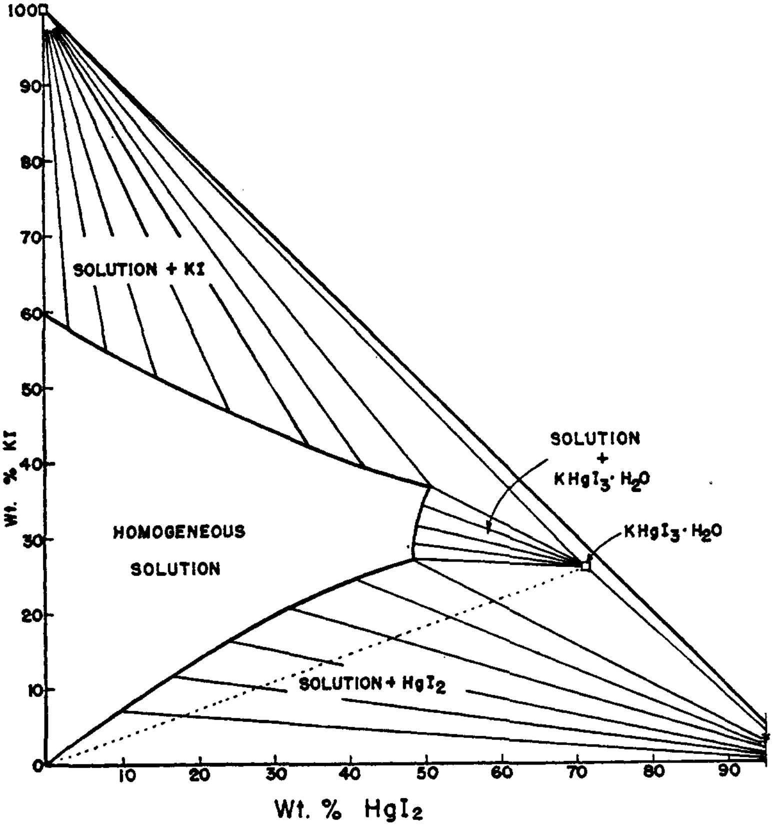

FIG. 4. The system $KI-HgI_2-H_2O$ at 20°C.

B. SUPPRESSION OF Ca^{++}, Mg^{++}, AND Fe^{+++}

While the homogenous-solution region has not been determined in the more complex, practical systems, e. g., $Na_2O-CaO-P_2O_5$-fatty acid-H_2O, nevertheless some parts of this boundary have been located under certain particular conditions. However, the data cannot be presented in the form of a phase diagram.

As a measure of the suppression of calcium, magnesium, or ferric ions it has been customary to determine the minimum amount of the sodium phosphate in question which will (*1*) dissolve a precipitate (101, 126) or more often (*2*) prevent precipitation (4, 22, 36, 40, 52, 59, 101, 108, 110, 126) of some calcium, magnesium, or iron salt. In spite of the abundance of well-known Fe^{+++} complexes (e. g., $Fe(CN)_6^{---}$), the phosphates seem less effective against ferric iron than against calcium or magnesium (121, 126). It has become evident, however, that complexes are more readily formed with magnesium than with calcium. Thus, precipitation of magnesium with calcium as oxalate can be prevented by the addition of a sufficient excess of ammonium oxalate. This trend is confirmed by the data of Hall (47), who found that the addition of 2 moles of $Na_4P_2O_7$ per gram-atom of magnesium in hard water will cause the magnesium to pass through a zeolite softener, but allows calcium removal as usual. The data of Quimby (101) in table 3 also show this same trend, not only for pyrophosphate but for phosphates containing more P_2O_5.

TABLE 3

Comparison of some sodium phosphates in prevention of precipitation of magnesium or calcium soap

0.175 per cent sodium coconut oil soap at 70.5°C.

	CONCENTRATION OF PHOSPHATE REQUIRED, G./100 CC.*			
	Experimental, 5 grain hardness†		Theory (M = Ca or Mg)	
	Mg	Ca	Assumed complex	Minimum concentration
$Na_4P_2O_7$ (purified)		0.81	$Na_2MP_2O_7$	0.023
$Na_4P_2O_7$ (commercial)	0.025	0.82	$Na_2MP_2O_7$	0.023
$Na_5P_3O_{10}$ (laboratory preparation)		0.54	$Na_3MP_3O_{10}$	0.030
			$NaM_2P_3O_{10}$	0.015
"$Na_6P_4O_{13}$" (commercial, crystalline)	0.022	0.35		
Glass (commercial, 65.0 per cent P_2O_5)	0.021	0.085		
$Na_3P_3O_9$ (laboratory preparation)		>1.8		
Glass = "$Na_6P_6O_{18}$" (69.6 per cent P_2O_5)			"$Na_2M_2P_6O_{18}$"	0.026
			"$M_3P_6O_{18}$"	0.017

* *Method:* Two solutions ((A) phosphate + soap and (B) hardness) are heated separately to 70.5°C. and then mixed; the turbidity is read by a photocell 10 min. later. The phosphate concentration is varied until the amount required to transmit 80 per cent of the light transmitted by distilled water is found.

† Equivalent to 85 p.p.m. $CaCO_3$.

In the last column of table 3 are some estimates of the minimum amount of phosphate that would be required to form the indicated complex. While there is no phase diagram available on the nature of the complexes, there is some basis for the complexes $Na_2MP_2O_7$ (40, 136), $Na_3MP_3O_{10}$, $NaM_2P_3O_{10}$ (11, 13, 36, 58, 117), and "$Na_2M_2P_6O_{18}$" (20, 22, 126, 128), the last being accepted merely as a convenient way of expressing the approximate behavior of the glass (69.6 per cent P_2O_5). Whatever the chemical nature of the complexes, it is evident that little or no excess sodium phosphate is required to suppress magnesium, but a large excess is needed to suppress calcium. While the amount of phosphate required for magnesium suppression is practically independent of phosphate composition, the requirement for calcium suppression decreases as the P_2O_5 content of the phosphate increases. This trend was confirmed for a series of sodium phosphates made by neutralizing H_3PO_4–P_2O_5 mixtures homogenized in sealed tubes at 180–400°C.

All sodium phosphates in this composition range show pH sensitivity (101). For example, at 54.5°C. the amount of a glass (65 per cent P_2O_5) required for calcium suppression increased threefold as the sodium phosphate pH (in 2.4 g. per 100 ml. solution) increased from 6.7 to 9.1. Hall (45) has observed a similar result for such a glass, and Rudy *et al.* (110) observed it with $Na_5P_3O_{10}$ as well as with the glass. The effect decreases as the pyrophosphate P_2O_5 content is approached, pyrophosphate itself not being much affected.

Systematic variation of P_2O_5 content in the sodium phosphates made from homogenized H_3PO_4–P_2O_5 mixtures gave the surprising result of defining a curve practically coinciding with the data of table 3 when the amount of phosphate required to suppress calcium was plotted against the P_2O_5 content of the sodium phosphate (101).

The soluble, crystalline salt $NaPO_3$ (or $Na_3P_3O_9$) is quite ineffective as a calcium suppressor, as shown by table 3. This has been observed repeatedly (46, 59, 94).

C. THRESHOLD TREATMENT

Condensed sodium phosphates, especially $Na_5P_3O_{10}$ and the glasses, act as deterrents to the crystallization of calcium carbonate in very low concentrations, e. g., 1–5 parts per million (21, 33, 53, 103, 104). Such concentrations are far below those required for calcium suppression, yet the two phenomena are probably related. The inhibiting action is presumably due to adsorption of the complex phosphate on submicroscopic nuclei (21, 53) so as to prevent growth and hence prevent precipitation. Microscopic studies at concentrations below the threshold show that the sodium phosphates cause distortion of the calcite crystals. This distortion increases and the amount of crystallization decreases as the concentration of complex phosphate increases until, at the threshold concentration, no crystallization occurs.

Crystalline $NaPO_3$ has negligible inhibiting action but becomes quite effective in the presence of alkali (21), presumably owing to conversion to $Na_5P_3O_{10}$ (see Bell (10)).

In addition to preventing the deposition of calcium carbonate scale, these low concentrations will dissolve old deposits of calcium carbonate scale if such solutions are kept flowing through the pipes for several months (104).

D. DISCUSSION

Data obtained in this field to date have not been intended to delimit the homogeneous-solution field in a five-component system, such as Na_2O–CaO–P_2O_5–fatty acid–H_2O, but rather as a crude means of detecting differences between complex phosphates made in various ways. Nevertheless, by a suitable modification of the techniques tested one should be able to map out this homogeneous area provided pH were properly controlled. Such a study would add greatly to our understanding of what takes place in the prevention of precipitation of calcium soap, particularly if the work extended far enough over into the heterogeneous area to reveal the composition of the saturating solids.

V. CHARACTERIZATION AND ANALYSIS

Before considering ordinary chemical methods of analysis, attention will be given to some special methods of characterization which tell more about the fundamental nature of the soluble phosphates both as crystals (or glass) and in solutions.

A. ACID DISSOCIATION CONSTANTS

Quite a variety of dissociation constants can be found for H_3PO_4 and $H_4P_2O_7$ (2, 7, 51, 61, 63, 68, 69, 85, 86, 89, 129, 133). For H_3PO_4 the values of Harned and Owen (51) are 7.516×10^{-3} and 6.226×10^{-8} for the first and second hydrogens, respectively, at 25°C. The value for the third hydrogen is probably near 2×10^{-13} (63). For $H_4P_2O_7$ at 18°C. Abbott and Bray (28), whose values for H_3PO_4 are higher than those of Harned and Owen by a factor of 1.5 to 3, reported 1.4×10^{-1}, 1.1×10^{-2}, 2.9×10^{-7}, and 3.6×10^{-9} for the four hydrogens. No data are available for $Na_5P_3O_{10}$ except electrometric titration curves, which show that the first three hydrogens are strong (as are the first two in $H_4P_2O_7$), the fourth is comparable to the third in $H_4P_2O_7$, and the fifth is slightly stronger than the fourth in $H_4P_2O_7$. Treadwell and Leutwyler (129) report that the weakest hydrogen in "hexametaphosphoric acid" has a dissociation constant of 1.6×10^{-2}, i. e., all hydrogens are strong.

B. MOLECULAR WEIGHT

1. Freezing-point lowering in water

If one uses the freezing-point lowering of water for determination of the molecular weights of salts containing polyvalent ions, he must either go to very high dilutions where thermal readings to 0.0001°C. will be needed, or he must make use of the interionic attraction theory at moderately low concentrations. Either method is tedious and exacting, with the result that very few satisfactory determinations of molecular weight have been made using water as the solvent for polyvalent salts. Nylén (91) has applied the latter variation to the common, soluble, crystalline $NaPO_3$, which is thermodynamically stable in the Na_2O–P_2O_5 system at elevated temperatures below the melting point, 620–625°C. He concluded that the salt is the trimer $Na_3P_3O_9$.

2. Eutectic or transition lowering

Muller (87) has developed a much better method, involving either the lowering of some eutectic point or the lowering of some transition point. The plot of molal lowering *vs.* concentration is much less curved, in fact, it is often nearly a straight line even at relatively high concentrations, thus making simpler, cruder technique applicable. Thus for $Na_4P_2O_7$ the KNO_3–ice eutectic gives a line extrapolating back to 5 molal lowerings; $K_4P_2O_7$ would give a line extrapolating to 1 molal lowering, since ions common to both the added salt and the eutectic have no effect in lowering the eutectic point. In the same way one can use the transition point of salt hydrates, e. g.:

$$Na_2SO_4 \cdot 10H_2O \xrightleftharpoons{32.4°C.} Na_2SO_4 + 10H_2O$$

$$CaCl_2 \cdot 6H_2O \xrightleftharpoons{30.2°C.} CaCl_2 \cdot 4H_2O + 2H_2O$$

$Na_4P_2O_7$ would give 1 molal lowering of the $Na_2SO_4 \cdot 10H_2O$ transition, and 5 molal lowerings of the $CaCl_2 \cdot 6H_2O$ transition.

Bonneman-Bémia (13) has made much use of the $Na_2SO_4 \cdot 10H_2O$ transition. For example, purified $Na_5P_3O_{10}$ gave a molecular weight of 372 (theory 368), while metaphosphate made by heating NaH_2PO_4 at temperatures in the interval 300–600°C. gave 307–317 (theory 306 for $Na_3P_3O_9$). But the most interesting use involved dehydration of $Na_5P_3O_{10} \cdot 6H_2O$ in an oven at various temperatures. The molecular weight, calculated to the anhydrous basis, remained constant at nearly the theoretical 368 as the temperature of heating for half-hour periods was raised from 85° to 100°C., but it dropped sharply to a minimum of 245 near 120°C. and then increased gradually back to 368 at temperatures near 300°C. Longer heating, at lower temperatures, e. g., 12 hr. at 150°C., restored the original molecular weight of 368, but heating at 120°C. failed to do so. Bonneman-Bémia postulated that the triphosphate decomposed as follows:

$$2Na_5P_3O_{10} \cdot 6H_2O = 2Na_4P_2O_7 + Na_2P_2O_6$$

This hypothesis ignores the fact that not all of the water was removed in these experiments, and will not explain the pH and acid–base titration data to be presented later.

3. Sedimentation of Na_2O–P_2O_5–H_2O *glasses*

Lamm (69a) has applied the equilibrium ultracentrifuge to glasses made by quenching 0.5-g. charges of melt as follows: *(a)* NaH_2PO_4 heated to 600–650°C. for a short time or *(b)* $Na_3P_3O_9$ heated for 3 hr. at 650°C. For the former Lamm[9] calculated a molecular weight of about 13,000, for the latter a value of 12,600. Such values are equivalent to about 125 monomeric $NaPO_3$ units. While such data should reveal the size of the sedimenting particle under the particular conditions used, they need not necessarily mean that all 125 units are linked by P—O valence bonds. A micelle made up, say, of twenty-one hexameric units associated into some sort of a complex would lead to such a result. There is perhaps less evident reason for such "water-soluble" polyphosphate chains

[9] Tests made in 0.25–0.40 per cent solution of the phosphate glass in 0.1 *N* sodium thiocyanate at 11°C.

to associate than there is for "water-insoluble" hydrocarbon chains in solutions of paraffin chain salts; nevertheless, the evidence available does not exclude the possibility of a micelle. If a micelle forms, its size is probably a function of electrolyte concentration.

Lamm states that these glasses are remarkably monodisperse, differing from synthetic organic polymers, which reveal a rather wide range of molecular sizes in the equilibrium centrifuge. He states also that the particle size decreases with time of heating the melt from NaH_2PO_4.

The significance of these sedimentation data will be more apparent when other methods of determining particle size have been applied. For example, molecular-weight determinations by transition-point lowering with both $Na_2SO_4 \cdot 10H_2O$ and $CaCl_2 \cdot 6H_2O$ would give an idea of what proportion of the sodium ions are free. However, it may be mentioned that evidence is gathering to show that these Na_2O–P_2O_5–H_2O glasses have a high molecular weight. Karbe and Jander (64) interpreted dialysis data as indicating a molecular weight of about 4000 for glass from NaH_2PO_4 heated to 650°C. Samuelson (112a) from titration of acid end groups (see section on acid–base titration) calculated a value of 10,800 for such a product.

C. ELECTRICAL CONDUCTIVITY

The Oswald–Walden–Bredig rule says that, if one determines the equivalent conductance at N/32 and N/1024, the difference divided by 10 gives approximately the product of the ionic valences, e.g., 2 for $MgCl_2$ and 4 for $MgSO_4$ or $Na_4P_2O_7$. Application of this rule to $Na_5P_3O_{10}$ gave 4.9 (13), confirming the pentavalence of the P_3O_{10} ion and the ionization of all five sodium ions. For the common, soluble, crystalline $NaPO_3$ this quantity is 3.0 (97, 134), confirming the trimeric formula $Na_3P_3O_9$.

For glass of approximately the meta P_2O_5 content, e.g., the product of rapidly chilling a melt made from NaH_2PO_4, $Na_2H_2P_2O_7$, or $Na_3P_3O_9$, application of this rule has given values from 2 to 4 (96, 111, 134). On the basis of an assumed hexameric formula, Pascal *et al.* (96, 97) suggested that these glasses are made of complexes such as $Na_2(Na_4P_6O_{18})$, from which only two sodium ions would separate in aqueous solution. As seen under the subject of hardness suppression, such interpretations do not accord with all the facts. How such conductivity data would be interpreted in terms of such high molecular sizes as reported by Lamm (69a) is not clear at present.

Again it is evident that more data are needed. Precise transference plus conductivity data would be very helpful in revealing the manner of ionization of these phosphate glasses.

D. X-RAY PATTERNS

X-rays have been used on sodium phosphates chiefly for identification purposes. However, the structures of the ortho- and pyrophosphate ions have been determined by crystal analysis on less soluble salts.

1. Identification

X-ray patterns are already available in the Dow system (26, 50) for most of the twenty-seven known crystalline sodium phosphates, but some of the patterns refer to substances of doubtful purity. In favorable cases, however, a moderately pure crystalline sodium phosphate can be identified by x-rays alone. Furthermore, the presence of two or more sodium phosphates in a given product has been demonstrated in the phase studies previously described (3, 13, 16, 17, 42, 57, 95, 115).

It should also be possible not only to identify, but also to estimate roughly the concentration of each component present in a complex mixture of crystalline sodium phosphates. However, this requires considerable time and study beforehand with known mixtures to learn how to interpret the complex x-ray pattern which results. Such analysis is often further complicated because the phosphates are mixed with other substances such as silicates, carbonates, soap, or synthetic detergents. Even when x-ray analysis proves inadequate in a particular application, it may prove valuable as a supplement to chemical analyses.

2. Ionic structure

Complete x-ray analysis of phosphate structure has been carried out only for the ortho- (98) and the pyrophosphates (72), with structures established as indicated in table 4. The classical valence formulas do not convey the proper impression. In Na_3PO_4, for example, all four oxygens are known to be equivalent, whereas the classical formula indicates that three are mutually equivalent but different from the fourth. The Werner-type formula is more correct in this respect but does not indicate the structure. The PO_4^{---} ion is tetrahedral, with the P—O distance at 1.54 A. (98).

Studies of crystal structure by x-ray have shown that the pyrophosphate ion does have the oxygen bridge between the two phosphorus atoms (72), as indicated by the classical formula. Here again the classical formula is inadequate, because the six oxygen atoms not in the bridge are equivalent, not divided into two groups (4 and 2). The deficiency of the Werner-type formula is more apparent here than it was for the orthophosphate ion.

By analogy with the pyrophosphate we may represent the triphosphate structure in the same manner by simply adding a second oxygen bridge.

Some investigators have suggested that $Na_3P_3O_9$ is cyclic (101[10], 110, 129), involving three oxygen bridges, but so far there is no proof beyond the molecular-weight and conductivity data already mentioned.

E. OPTICAL DATA

1. Properties of pure compounds

Ingerson and Morey (60) have recently collected all available optical data on sodium phosphates (8, 12, 28, 65, 95, 114) and added a few of their own. Their

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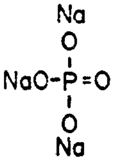
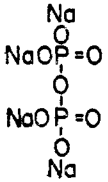
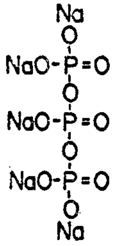
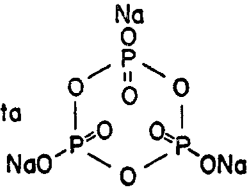
[10] Suggested to the writer by Dr. A. S. Richardson during the course of our studies.

results are collected in table 5, together with a few observations made in this laboratory[11] (101).

The "$Na_3PO_4 \cdot 12H_2O$" is probably the variable hydrate $Na_3PO_4 \cdot xNaOH \cdot (12 - x)H_2O$. The salt $Na_3PO_4 \cdot 7H_2O$ has usually been given as the $8H_2O$ or $6H_2O$ compound, but Hall (44) claimed to have made the heptahydrate by crystallization of the tertiary salt from 50 per cent sodium hydroxide at 77°C If the interpretation given earlier for hydrates of Na_3PO_4 is correct, this salt is probably $Na_3PO_4 \cdot 6H_2O$, since Ingerson and Morey (60) crystallized it by evaporation of its aqueous solution at 83°C. The lower hydrate is given as the monohydrate by several authors (e. g., 60, 114), but as the hemihydrate by others (e. g., 82). More work is obviously needed on hydrates of Na_3PO_4.

TABLE 4

Structural formulae of phosphates

	Classical	Werner	Crystal Structure
Ortho		$Na_3^+[PO_4]^{\equiv}$	O O P O O All O alike P-O = 1.54 A.
Pyro		$Na_4^+[P_2O_7]^{\overset{=}{=}}$	O O O P O' P O O O Six O alike one different P-O = 1.56 A. P-O' = 1.52 A.
Tri		$Na_5^+[P_3O_{10}]^{\equiv=}$	
Trimeta		$Na_3^+[P_3O_9]^{\equiv}$	

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[11] The writer is indebted to Dr. F. B. Rosevear of this laboratory for encouragement and assistance in the microscopic study of these compounds.

Our own studies (101) have made it clear that the data of Dufet (28), quoted in table 5, for $Na_2HPO_4 \cdot 12H_2O$ refer to the low-temperature or β-modification.

TABLE 5

Optical properties of sodium phosphates

FORMULA	OPTIC ANGLE	OPTIC SIGN	α	ω	β	ε	γ	REFERENCE
$Na_2O:P_2O_5 = 3:1$								
	degrees							
"$Na_3PO_4 \cdot 12H_2O$"		+		1.4458		1.4524		(28)
"$Na_3PO_4 \cdot 7H_2O$" *	85	+	1.462		1.470		1.478	(60)
"$Na_3PO_4 \cdot H_2O$"		+		1.497		1.522		(60, 114)
Na_3PO_4	76	+	1.493		1.499		1.508	(114)
$Na_2O:P_2O_5 = 2:1$								
$Na_2HPO_4 \cdot 12H_2O$	57	−	1.432		1.436		1.437	(28, 101)
$Na_2HPO_4 \cdot 7H_2O$	39	+	1.4412		1.4424		1.4526	(28)
$Na_2HPO_4 \cdot 2H_2O$	*ca.* 80	+	1.450		1.461		1.477	(60)
Na_2HPO_4	78	+	1.483		1.499		1.525	(60)
$Na_4P_2O_7 \cdot 10H_2O$	60.5	+	1.4499		1.4525		1.4604	(28)
$Na_4P_2O_7$	40	+	1.475		1.477		1.496	(60, 95)
$Na_2O:P_2O_5 = 5:3$								
$Na_5P_3O_{10} \cdot 6H_2O$†	20	+	1.449		1.450		1.482	(12, 60)
$Na_5P_3O_{10}$ I	21	+	1.477		1.478		1.504	(60, 95)
$Na_5P_3O_{10}$ II	57	+	1.470		1.477		1.502	(60, 95)
$Na_2O:P_2O_5 = 1:1$								
$NaH_2PO_4 \cdot 2H_2O$	82	−	1.4400		1.4625		1.4818	(28)
$NaH_2PO_4 \cdot H_2O$	29	−	1.4557		1.4852		1.4873	(28)
NaH_2PO_4	64	−	1.481		1.507		1.517	(60)
$Na_2H_2P_2O_7 \cdot 6H_2O$	32	−	1.4599		1.4645		1.4649	(28)
$Na_2H_2P_2O_7$‡			1.510				1.517	(60)
$Na_3P_3O_9 \cdot 6H_2O$*	77 ± 3	−	1.432				1.441	(60, 65, 101)
$Na_3P_3O_9 = NaPO_3$ I	80	−	1.474		1.478		1.480	(8, 60, 95)
$NaPO_3$ II*	78	+	1.498		1.510		1.529	(60, 95)

* See text.

† Common view of rectangular plate gives $\alpha' = 1.4495$ and $\gamma' = 1.4700 \pm 0.001$ (10 A).

‡ Fine needles, positive elongation; indices really α′ and γ′, since orientation of needles could not be checked.

The α-form was encountered as β-pseudomorphs when β-crystals were warmed up to 31–32°C. on the microscope stage. Crystals of α-$Na_2HPO_4 \cdot 12H_2O$ (e. g., crystals formed directly from aqueous solutions at 30–35°C.) have not been studied microscopically, but Hammick *et al.* (49) stated that these crystals look like the monoclinic β-crystals.

As suggested in Mellor's treatise (79), the soluble sodium metaphosphate usually crystallizes in "triclinic rhombohedra" of $NaPO_3 \cdot 2H_2O$ (or $Na_3P_3O_9 \cdot 6H_2O$). The acute bisectrix interference figure reveals the absence of planes or axes of symmetry and therefore confirms the triclinic nature of this crystal (101). Like Ingerson and Morey we encountered what appeared to be a metastable form,[12] for it was encountered, if at all, only in early stages of fast crystallizations and always disappeared later (if left in contact with the mother liquor), leaving exclusively the triclinic rhombohedra already described.

This "metastable" form is probably the anhydrous salt, as suggested by Ingerson and Morey.

TABLE 6

Microscopic identification of phosphate-type crystals from aqueous solution of pH 9–10

PHOSPHATE		CHARACTERISTIC PROPERTIES
Type	Formula	
Ortho	$Na_2HPO_4 \cdot 12H_2O$ (β)	Diamonds; 60° silhouette angle; symmetrical extinction
Pyro	$Na_4P_2O_7 \cdot 10H_2O$	Columnar to acicular; parallel extinction; negative elongation
Tri	$Na_5P_3O_{10} \cdot 6H_2O$	Rectangular plates; oblique extinction 8–9°; often twinned with extinction 8–9° to twinning plane
Trimeta	$Na_3P_3O_3 \cdot 6H_2O$	Rhombohedra; oblique extinction; 70–75° silhouette angle

2. *Microscopic identification*

Given a sample known to be an Na_2O–P_2O_5–H_2O preparation, the phosphate type among the crystallizable species can be identified microscopically rather simply. The aqueous solution is adjusted to pH 9–10, a drop is allowed to evaporate on a microscope slide below 30°C., and the crystals are examined. Fairly pure compounds reveal the characteristics listed in table 6. Phosphate mixtures give less well defined crystals, but these characteristics are still useful. The presence of Na_2O–P_2O_5–H_2O glass sometimes alters these forms considerably. For example, a rectangular plate of $Na_5P_3O_{10} \cdot 6H_2O$ will be smaller and twins more complex (i.e., appear to be made of four or six instead of two parts), but the 8–9° extinction is still observable. Purification by one or two quick recrystallizations[13] removes enough of the glass to give more simple crystals. Presence of non-phosphatic material may render such simple tests unreliable. In this case

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[12] Near optic axis view was often obtained showing symmetrical extinction, positive, large optic angle, $r > v$, $\gamma' = 1.507$, $\alpha' = 1.495$.

[13] It is very convenient to add alcohol to induce rapid crystallization.

successful microscopic identification is still possible by use of the quantitative data in table 5, which may be applied without pH adjustment provided the unknown does not happen to be a compound for which the optical data are still lacking.

F. CHEMICAL ANALYSIS

From the foregoing discussion, it is evident that there are more than four chemical or ionic types of phosphate to be determined. The glasses act in some respects so differently from the crystallized preparations having the same P_2O_5 content that it often proves useful to estimate this type of phosphate separately. While a mixture of ortho-, pyro-, and metaphosphates can be correctly analyzed by known and reliable chemical methods, the addition of triphosphate and/or phosphate glass greatly complicates the analysis. At present no thoroughly reliable method of analysis is available for complex sodium phosphate mixtures.

Attempts have been made to use prevention of the precipitation of barium ion or calcium ion as the basis of an analytical method (4, 22, 39), but they have not proven successful (38). This is to be expected because of the sensitivity to temperature and pH which leads to a large experimental error. The more reliable chemical methods called upon so far have involved oven-drying, ignition, hydrolysis, precipitation, and acid–base titrations.

1. Oven drying

Many of the salts discussed lose all water of crystallization when dried in an oven at 105°C., e. g., NaH_2PO_4, Na_2HPO_4, $Na_2H_2P_2O_7$,[14] and $Na_4P_2O_7$. Hydrates of Na_3PO_4 dry down to an indefinite water content near that for the formula $Na_3PO_4 \cdot H_2O$; for complete removal of water from "$Na_3PO_4 \cdot 12H_2O$" see the section on ignition below. Both Salzer (112) and Partington and Wallsom (93) say that $Na_3HP_2O_7 \cdot H_2O$ is stable up to 170° to 190°C., but this should be checked by modern methods.

The triphosphate $Na_5P_3O_{10} \cdot 6H_2O$ loses most of its water of crystallization (13) but suffers some hydrolysis to acid pyro- and orthophosphates, as shown in the section on acid–base titrations. The metaphosphate $Na_3P_3O_9 \cdot 6H_2O$ would be expected to behave in a similar manner, but so far proof is lacking.

2. Ignition

Ignition to red heat will dehydrate completely most of the phosphates, removing both water of hydration and water of constitution. Two sources of difficulty are known, however.

The complex salt $Na_3PO_4 \cdot xNaOH \cdot (12 - x)H_2O$ will not lose all its water without heating to a temperature of 1000°C. where it also loses sodium hydroxide (82). But if some $Na_4P_2O_7$ is added to the sample before ignition, the extra sodium oxide is retained while all water is lost, leaving the equivalent of $Na_3PO_4 \cdot xNa_2O$ combined and/or mixed with $Na_4P_2O_7$. Probably moisture in "$Na_3PO_4 \cdot$

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[14] Possibly some hydrolysis to orthophosphate occurs during the drying of $Na_2H_2P_2O_7 \cdot 6H_2O$.

$12H_2O$" or in any hydrate of Na_3PO_4 should be determined by this method regularly; otherwise there is no certainty about the amount of water retained.

The other case requiring caution is any ignition in which the sample melts (especially tri- and metaphosphate samples) at high temperatures (550–900°C.). The last trace of water of constitution is lost extremely slowly from such melts. For example, most preparations of so-called "glassy meta" show an acid reaction, which means incomplete removal of the water of constitution during preparation. Re-ignition of such a glass in the usual way does not remove all water of constitution (101). Better results are obtained by grinding such a glass very fine and heating to constant weight at 500°C. For best results the glass should be mixed intimately with ten times its weight of $Na_4P_2O_7$ and ignited in the usual way.

In short, we can say that best results are obtained by insuring that the final composition of the ignited product will approach that of $Na_4P_2O_7$.

3. Acid–base titrations

(a) Acids

Sample electrometric titration curves for aqueous solutions of phosphoric acids that are commercially available are shown in figure 5. Within the range of the glass electrode it is possible to neutralize only two of the hydrogens in H_3PO_4, one at pH 4.3 and the other at pH 9.3. $H_4P_2O_7$, however, can be completely neutralized,—two hydrogens at pH 4.3, the third at pH 7.2, and the fourth at pH 10.2. The so-called tetraphosphoric acid is a mixture of H_3PO_4, $H_4P_2O_7$, $(HPO_3)_x$, and possibly $H_5P_3O_{10}$ and other polybasic acids. The presence of both ortho- and pyrophosphoric acid can be seen from the fact that the neutralization curve has a very *long* steep portion at the upper end point.

The first (or pH 4.3) end point measures the total P_2O_5 in the acid. When any acid derivable from P_2O_5 and water is titrated to pH 4.3, one titratable H has been neutralized per atom of phosphorus. This relationship seems to be perfectly general, applying to all phosphoric acids including P_2O_5 itself (37, 76, 101). It therefore gives at once the total P_2O_5 content.

Since metaphosphoric acid is already completely neutralized at pH 4.3, the spread between the 4.3 and the upper end point depends in general on ortho-, pyro-, and triphosphates.[15] If we assume with Gerber and Miles (37) that liquid acids in the ortho-to-meta range contain no triphosphoric acid or higher polybasic acids, then this spread gives the sum of the ortho- and pyrophosphoric acids, for each contributes one titratable hydrogen per atom of phosphorus.

By adding another titration designed to give the amount of orthophosphoric acid, Gerber and Miles were able to express the composition of condensed phosphoric acids in terms of the relative amounts of ortho-, pyro-, and metaphosphoric acids (triphosphoric acid assumed absent). The titration of the orthophosphoric acid involved adding an excess of silver nitrate after having titrated to the end

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[15] This assumes the absence of higher polyphosphoric acids, i.e., $H_{n+2}P_nO_{3n+1}$ with $n > 3$. While there is no evidence at present for the existence of such acids, they may be found in liquid phosphoric acids containing 75 per cent or more of P_2O_5.

point near pH 10; only orthophosphoric acid liberates titratable hydrogen as the phosphates are precipitated by silver, giving one hydrogen for each orthophosphoric acid phosphorus atom.[16]

This type of analysis led Gerber and Miles to the composition diagram of figure 6. Except for the terminal compositions H_3PO_4 and HPO_3, all appear as mixtures of ortho, pyro, and meta acids. The form of the curve defined by the points suggests an equilibrium (homogeneous) of the type indicated by the equation:

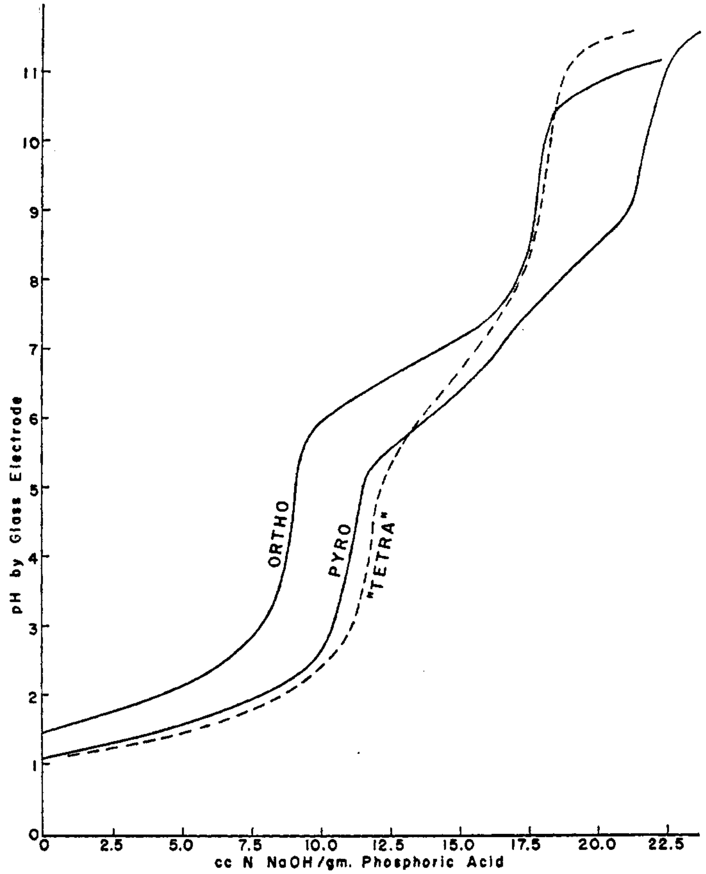

FIG. 5. Electrometric titration of some phosphoric acids

$$\underset{\text{Pyro}}{2P_2O_5\cdot 2H_2O} \rightleftarrows \underset{\text{Ortho}}{P_2O_5\cdot 3H_2O} + \underset{\text{Meta}}{P_2O_5\cdot H_2O}$$

The smooth curve of figure 6 is given by $(P_2O_5\cdot 3H_2O)(P_2O_5\cdot H_2O)/(P_2O_5\cdot 2H_2O)^2 = K = 0.068$ for concentrations in weight per cent. While this equilibrium may

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[16] Treadwell and Leutwyler (129) have used the same procedure for determining ortho P_2O_5, except that Ba^{++} was used to precipitate the phosphates at pH 9.6. Germain (39) used Ca^{++} to precipitate the phosphates, but the results were not quantitative.

not be expressed in the proper terms, it is probable that some such equilibrium will be substantiated by further investigation. $H_5P_3O_{10}$ and higher polybasic acids may be found to exist in such mixtures and other degrees of polymerization, especially for metaphosphoric acid, may be involved.

An appreciation of the significance of the above chemical equilibrium can be obtained by considering an experiment made by Gerber and Miles and checked in our laboratory. Pyrophosphoric acid can be obtained as a crystalline solid and is so sold by chemical distributors. If this acid is dissolved in cold water and analyzed by the titration method of Gerber and Miles, it will be found to contain 95–100 per cent $H_4P_2O_7$. Now if this crystalline acid is heated above its melting point (*ca.* 61°C.) to liquefy it and is restored to room temperature, it remains liquid for a long time (weeks or months) if no $H_4P_2O_7$ seed is added or it is not stirred. A sample of this liquid tested by the Gerber and Miles method yields the composition 65 per cent $H_4P_2O_7$ plus 35 per cent of an equimolar mixture of H_3PO_4 and HPO_3. Evidently when heated above their melting points these acids decompose in accord with some such chemical equilibrium as indicated by the equation above. The true equilibrium is not readily restored by cooling back below the melting point, owing to the very great viscosity of these acids. Thus Gerber and Miles really measured some approach to the chemical equilibrium which obtains at some temperature above the melting point.

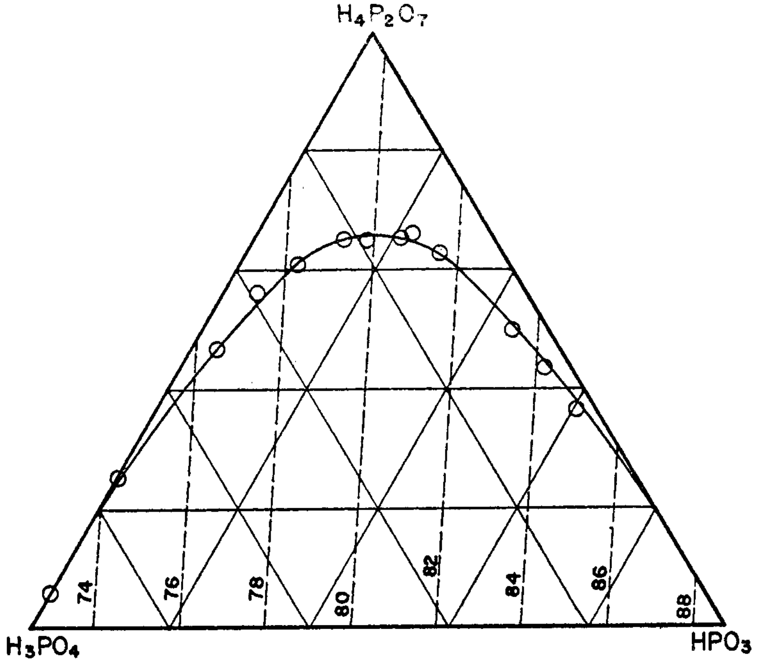

FIG. 6. Compositions of anhydrous phosphoric acids. ———, compositions given by equilibrium constant; O, compositions found by colorimetric pH titration; — — —, lines of equal per cent P_2O_5.

Such data make it very clear why the H_2O–P_2O_5 binary system is so poorly understood. It is probable that true equilibria could be approached by cooling to some low temperature to induce seeding and then restoring to a temperature a few degrees below the stable melting point, as was done by Schierloh (113) for glycerol.

(b) Salts

Acid–base titrations can be used just as effectively on phosphate salts, except that they cannot reveal the P_2O_5 content. Sample curves are given for condensed sodium phosphates by Schwartz and Munter (116). The curve for $Na_4P_2O_7$ shows exactly the same characteristics as the curve for the forward titration of $H_4P_2O_7$ in figure 5—namely, prominent waves at pH 4 and pH 10 and a slight wave at 7. The spread between corresponding end points agrees quantitatively on an equal P_2O_5 basis.

TABLE 7

Chemical equivalents involved in phosphate titrations before and after hydrolysis

PHOSPHATE TYPE*	SPREAD BETWEEN UPPER AND LOWER END POINTS, EQUIVALENTS PER PHOSPHORUS ATOM			SPREAD BETWEEN END POINTS AS MILLILITERS OF *N* REAGENT PER G. P_2O_5		
	Before	After	Difference	Before	After	Difference
Ortho	1	1	0	14.08	14.08	0.00
Pyro	1	1	0	14.08	14.08	0.00
Tri	$\frac{2}{3}$	1	$\frac{1}{3}$	9.39	14.08	4.69
Meta	0	1	1	0.00	14.08	14.08

* Refers to compounds, i.e., crystalline species. Glasses can behave like tri- or metaphosphate, but more generally will act like a mixture of two to four of the above phosphates.

A similar curve for $Na_5P_3O_{10}$ shows that its upper end point is slightly below that of $Na_4P_2O_7$; it shows two other inflections, one at a pH of about 7 and the other at about 4, corresponding to $Na_4HP_3O_{10}$ and $Na_3H_2P_3O_{10}$, respectively (*cf.* Rudy and Schloesser (109)). Taken with the pyrophosphate curve, which also shows a slight inflection near pH 7 corresponding to $Na_3HP_2O_7$, this curve tells us that $Na_4HP_3O_{10}$ exists. Huber (58) has already crystallized one hydrate of it ($Na_4HP_3O_{10} \cdot 1.5H_2O$). The curve tells us further that the third, fourth, and fifth hydrogens of $H_5P_3O_{10}$ are comparable in strength to the second, third, and fourth hydrogens of $H_4P_2O_7$, respectively.

Electrometric titrations of condensed phosphates made so as to define the full course of the curve between pH 2.5 and 11 are very useful in estimating the condition of the product in solution. They are applicable both to crystalline compounds and to glasses (*cf.* Schwartz and Munter). The chemical relationships are summarized in table 7.

The product of heating $Na_5P_3O_{10} \cdot 6H_2O$ for 5.5 hr. at 120°C. (101) is an excellent illustration of the utility of the electrometric titration curve. The pertinent data are given in table 8. These data illustrate the need for titrating the sample both ways from its existing condition. Thus on the anhydrous basis, titration to the lower end point gives nearly the same result for $Na_5P_3O_{10} \cdot 6H_2O$ and its decomposition product. But the *spread* between the two end points is very different. Both the spread and the pH warn of the radical alteration of the $Na_5P_3O_{10}$. As stated in the footnote to table 8, the presence of orthophosphate is indicated. The remainder is largely pyrophosphate.

Utilizing these data and the total P_2O_5 content, one can infer that the decomposition proceeded approximately as follows:

$$32Na_5P_3O_{10} \cdot 6H_2O \xrightarrow{-166H_2O} 13Na_4P_2O_7 + 26Na_3HP_2O_7 + 10NaH_2PO_4 + 8Na_2HPO_4$$

TABLE 8

Decomposition of $Na_5P_3O_{10} \cdot 6H_2O$ *in oven drying at 120°C.*

	$Na_5P_3O_{10} \cdot 6H_2O$		DECOMPOSITION PRODUCTS	
	As is	Anhydrous	As is	Anhydrous
pH of 1 g./100 cc. solution	9.8		8.0	
Milliliters of *N* alkali to pH 10 end point per gram of phosphate	0.03−	0.03	2.45	2.55
Milliliters of *N* acid to pH 4 end point per gram of phosphate	3.91+	5.08	5.12	5.34
Spread between pH 4 and pH 10 phosphate	3.94	5.11	7.57	7.89
Per cent loss on ignition	22.91*		4.01†	
Per cent total P_2O_5	45.42*	58.9	55.59	72.1
Per cent CO_2 by evolution	0.01		None	

* Theory for $Na_5P_3O_{10} \cdot 6H_2O$ is 22.70 per cent H_2O and 44.7 per cent P_2O_5.

† About 0.87 mole $H_2O/Na_5P_3O_{10}$ remains; the titration from pH 8 to pH 10 is equivalent to 2.14 per cent H_2O. If the difference between 4.01 and 2.14 is water of constitution not titrated, i.e., ortho, then there is 10.4 per cent P_2O_5 present in the ortho condition.

The mixture on the right has $\frac{3}{16}$ of its total P_2O_5 in the ortho condition ($55.6 \times 3/16 = 10.4$ per cent P_2O_5). This mixture will give a pH of about 8 in dilute solution and will lose 4.0 per cent H_2O upon ignition; it has a molecular weight of 213, a value appreciably below the 245 minimum obtained by Bonneman-Bémia (13). It is probable that more conversion to orthophosphate occurred in the writer's experiments, for Bonneman-Bémia's sample contained less water of constitution; this would account for the difference in molecular weight. The indicated type of decomposition to pyro- and orthophosphate is more in line with all the facts than Bonneman-Bémia's hypothesis that pyro- and dimetaphosphates are formed.

While their interpretation is attended by more uncertainty, acid-base titration curves are quite as useful for characterizing the Na_2O–P_2O_5–H_2O glasses. The presence of hydrogens titratable between pH 4 and pH 10 (101, 116, 128) reveals at once that a glass is not simply a metaphosphate $(NaPO_3)_n$.[17] In some cases

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[17] This follows from the fact that any phosphoric acid titrated to pH 4 with sodium hydroxide contains one sodium per phosphorus atom; hence $(NaPO_3)_n$ should contain no hydrogen titratable between pH 4 and pH 10.

glasses might conceivably be mixtures of $(NaPO_3)_n$ with acid salts such as NaH_2PO_4, $Na_2H_2P_2O_7$, etc.,[18] but a more likely picture is that of a polyphosphate $(Na,H)_{n+2}P_nO_{3n+1}$ plus small amounts of low-molecular-weight acid salts. When quantitative chemical methods of determining the ortho, pyro, and tri P_2O_5 content of such glasses become available, the part of the titration (pH 4 to 10) due to low-molecular salts can be calculated and deducted from the total. The remainder must be attributed to higher polyphosphates.

On the assumption that glasses made from NaH_2PO_4 can be written $Na_nH_2P_nO_{3n+1}$, Samuelson (112a) has utilized the titration to the phenolphthalein end point to calculate the average molecular weight. The values so calculated varied from 10,800 for a fusion temperature of 650°C. to 17,200 for 950°C. Assuming no ring formation and no loss of P_2O_5 in the fusion process, Samuelson's reasoning should be correct. However, neither ring closure nor loss of P_2O_5 can be regarded as impossible at fusion temperatures. The former would lower the number of titratable hydrogens (by water loss); the latter would increase the number of titratable hydrogens per molecule. Incidentally, flow birefringence studies would be helpful in testing Samuelson's chain model for such glasses.

One use can be made of the titration of any sodium phosphate to the end point near pH 10 which is subject to no uncertainty of interpretation. Knowing the amount of orthophosphate present and the magnitude of this titration, one can calculate the amount of bound water, i.e., water of constitution. If the orthophosphate content is unknown, calculation of the titration to its water equivalent sets a lower limit to the bound-water content. Thus a glass of 66.8 per cent P_2O_5 content was found to contain at least 1.12 per cent combined water. Ignition of this sample above its melting point caused a loss of but 0.71 per cent, illustrating why the final ignition composition should be near that of $Na_4P_2O_7$ for complete water loss. Had the "pyrophosphate" ignition method been applied to the above glass and given a loss greater than 1.12 per cent, the excess could be calculated to orthophosphate at the rate of one PO_4 per hydrogen.

An acid–base titration for determining pyrophosphate was introduced by Britzke and Dragunov (18). Like the Gerber and Miles ortho determination, it is really a combination of precipitation and titration, but it is carried out volumetrically. The pH of the phosphate solution is adjusted to a point near the lower end point, e.g., to pH 3.8, and excess of zinc sulfate is added to precipitate the pyrophosphate as $Zn_2P_2O_7$ and liberate one titratable hydrogen for each pyro phosphorus atom, thus:

$$H_2P_2O_7^{--} + 2ZnSO_4 \rightarrow Zn_2P_2O_7 + 2HSO_4^-$$

The solution becomes more acid and the strong acid is titrated by restoring the pH to 3.8. Britzke and Dragunov were aware that the method was not satis-

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[18] Assuming only four chemical species present—namely, ortho, pyro, tri, and meta—one can calculate the amount of each from four data: initial pH, electrometric titration curve, true ignition loss, and total P_2O_5. Such a result may be far from the truth however, for the calculation makes no allowance for the distribution of titratable hydrogen, P_2O_5, etc., between the simple molecules (ortho, pyro, tri) and the higher polyphosphate molecules probably present in the glass.

factory in the presence of much metaphosphate (see also 76), but orthophosphate does not interfere. It has since been shown that the method is not at all reliable in the presence of triphosphate (9, 62, 76, 101), but Bell has recently developed a promising modification which will be discussed under precipitation methods. It is likely that the polyphosphate molecules in Na_2O–P_2O_5–H_2O glasses also interfere.

4. Hydrolysis

In strongly acid solutions, especially at temperatures near the boiling point of water, all of the condensed phosphates are rapidly hydrated to the ortho condition. This is the basis of the well-known method of determining total P_2O_5 by the precipitation methods to be described below. It is the basis of another hydrolysis method for "apparent meta" P_2O_5.[19] In this case the phosphate mixture is titrated to the upper end point, which is near pH 9 if sufficient sodium nitrate or sodium chloride is added. Here ortho exists as Na_2HPO_4, pyro as $Na_4P_2O_7$, tri as $Na_5P_3O_{10}$, and meta as $(NaPO_3)_x$. A known amount of standard acid is added and the solution boiled to convert all phosphates to the ortho condition. The solution is then back-titrated to the original pH and the known equivalent of hydrolyzing acid deducted. The remainder measures the newly created, titratable hydrogen derived from meta- and triphosphates as indicated in table 7. Meta develops one titratable hydrogen per phosphorus atom, while tri develops $\frac{1}{3}$ of a hydrogen per phosphorus atom. Calculating all the newly created hydrogen to metaphosphate is equivalent to calling $Na_5P_3O_{10}$ a mixture of $Na_4P_2O_7$ and $NaPO_3$; hence the name "apparent meta." This method is sound chemically, but its importance is somewhat diminished by the fact that the same information can be obtained in another way. Note that the spread between the upper and lower end points is 1 H/P for all forms after hydrolysis but was 1, 1, $\frac{2}{3}$, and 0 for ortho, pyro, tri, and meta, respectively, prior to hydrolysis. Thus the difference between these two titrations is precisely equivalent to the "apparent meta" titration. Now consider three phosphate compositions having the same P_2O_5 content, say 60.4, corresponding to the hypothetical $Na_6P_4O_{13}$. We might have, for example

A. 1 mole $Na_5P_3O_{10}$ + $\frac{1}{3}$ mole $Na_3P_3O_9$ (100 per cent crystalline)
B. 0.5 mole $Na_5P_3O_{10}$ + "1 mole" glass $(Na_2O)_{3.5}(P_2O_5)_{2.5}$[20] or
C. 1 mole $Na_4P_2O_7$ + "2 moles" glass $(Na_2O)(P_2O_5)$[20]

Now should the two titrations just mentioned give the same result for all three mixtures, then only one of the two methods need be used. But, should systematic investigation show that these two titrations are frequently independent,[21] then progress in analyzing mixtures containing glass might be possible by proper interpretation of these *two* titrations.

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[19] Jones (62) and Travers and Chu (127) have used modifications of the method described here.

[20] These formulae are not meant in a molecular sense, but are used merely to express the composition of the glass.

[21] This seems rather unlikely to the writer.

5. *Precipitation*

Discussion of precipitation methods will be limited to those which have proved reliable or which give promise. Thus precipitation of orthophosphate as $MgNH_4PO_4$ or as phosphomolybdate can be, and has been, used in a variety of ways. Thus, by acidifying and boiling before precipitation, all phosphorus can be precipitated to give total P_2O_5. The determination is completed according to one of the well-known colorimetric, volumetric, or gravimetric methods given in standard texts on quantitative analysis. Orthophosphate can be determined directly in a complex phosphate mixture by precipitating it as phosphomolybdate in cold acid solution. The determination is frequently completed, after filtering off the phosphomolybdate, by a colorimetric method (14, 30, 35, 123, 130), though volumetric (62) and gravimetric methods (127) have also been used.

Jones (62) experienced difficulty in precipitating pyrophosphate as $Mn_2P_2O_7$ because triphosphate tends to precipitate with the pyrophosphate, giving high pyro P_2O_5 values. The same difficulty is encountered when the precipitation is carried out with zinc (9, 62, 72, 101). In other words, the pyrophosphate and triphosphate ions are so closely related that they undergo very similar reactions. Nevertheless, Bell (9) has succeeded in making the zinc method fairly reliable by a double precipitation; the second precipitation gets rid of the triphosphate which precipitated with pyrophosphate in the first precipitation. The $Zn_2P_2O_7$ from the second precipitation is ignited and weighed.

Bell has further found that a rough measure of the triphosphate content can be obtained by a modification of the old Britzke and Dragunov titration method for pyrophosphate (18). The pH is adjusted to 3.8, a certain excess of zinc sulfate is added, the pH is restored to 3.8 with standard alkali, and the pyrophosphate precipitate is quickly filtered off for the pyrophosphate determination just described. After deducting the pyrophosphate contribution from the sodium hydroxide titration, the remainder is converted to triphosphate by means of an empirical factor established by experiment on synthetic mixtures. While this method gives only approximate results and requires close attention to details, it has the virtue of being a direct determination and should prove useful, at least with essentially crystalline products.

Jones (62) attempted a classification of "metaphosphates" based on precipitation with barium. He found that barium precipitates the "hexametaphosphate" *almost* quantitatively in cold acid solutions, where all crystalline species remain in solution. The precipitate was filtered off, converted to orthophosphate by hydrolysis, and determined in the usual way. Jones further found that the trimetaphosphate remained in solution, while all other crystalline species of phosphate are precipitated by barium in alkaline solution. Acid hydrolysis converts this filtrate to orthophosphate for determination as above.

6. *Discussion*

A test of the Jones method has been made in this laboratory[22] (table 9). For the product of heating $Na_5P_3O_{10} \cdot 6H_2O$ for 5.5 hr. at 120°C., the ortho P_2O_5 figure is

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[22] The analyses were made by Mr. R. H. Lambert under the supervision of Mr. J. T. R. Andrews.

very close to the 10.4 per cent calculated above from the titration plus ignition loss and most of the remainder is in the pyro condition, as previously indicated; the meta P_2O_5 figure (5.25 per cent) is suspected of being high, for the sum of the ortho, pyro, and meta P_2O_5 exceeds the total P_2O_5 by 1.33 per cent. The analyses for both the $Na_5P_3O_{10} \cdot 6H_2O$ and the commercial "tetraphosphate," which appeared wholly crystalline under the polarizing microscope, are about what would be expected for such products.

It is felt that the Jones method represents a distinct advance over earlier methods, but it is not entirely satisfactory, as Jones has realized. Double precipitation of $Mn_2P_2O_7$ would probably improve the accuracy of the Jones pyro P_2O_5 determination; this would help the tri P_2O_5, which is a difference figure, but errors in the two "meta" determinations would still leave this result rather uncertain. The trimeta P_2O_5 figure may often be too high, owing to incomplete precipitation of the other phosphates by barium in alkaline solution (62).

TABLE 9

P_2O_5 *distribution by the Jones method*

	$Na_5P_3O_{10} \cdot 6H_2O$	PRODUCT OF HEATING $Na_5P_3O_{10} \cdot 6H_2O$ FOR 5.5 HR. AT 120°C.	COMMERCIAL "TETRAPHOSPHATE" (CRYSTALLINE)
Total P_2O_5	45.42 per cent	55.59 per cent	56.15 per cent
P_2O_5 distribution by Jones's method:			
"Hexameta" P_2O_5	None	None	None
Trimeta P_2O_5	0.59	5.25	2.84
Ortho P_2O_5	Trace	10.23	3.09
Pyro P_2O_5	0.68	41.44	27.28
Tri P_2O_5 (difference)	44.15	(−1.33?)	22.94

Summarizing the chemical methods of analysis available for complex sodium phosphates, we find that reliable methods have been developed for:

1. Total P_2O_5
2. Ortho P_2O_5 (35, 37, 62)
3. Pyro P_2O_5 (9)

Approximate methods are available for

4. Tri P_2O_5 (9)
5. Meta (trimeta) P_2O_5 (62)
6. P_2O_5 in Na_2O–P_2O_5–H_2O glass ("hexameta," 62)

In addition, there is the spread between the upper and lower end points in acid-base titrations, which measures a sort of sum of ortho P_2O_5 + pyro P_2O_5 + tri P_2O_5 (see table 7) and the reciprocally related result designated as "apparent meta" P_2O_5. It is quite probable that satisfactory analyses for many purposes can be made with the aid of these or variants of these methods. However, products containing Na_2O–P_2O_5–H_2O glass require further analytical study before a generally satisfactory method of analysis can be given.

One must not neglect valuable supplements such as observations with the polarizing microscope, x-ray patterns, or molecular-weight determinations by the methods of Muller (87). Needless to say the more general problem of analyzing complex phosphates in the presence of other substances such as borates, carbonates, silicates, soap, and/or synthetic detergents has not yet been solved.

VI. STABILITY

Discussion of the phase diagrams has already shown that, in contact with water, all phosphates except orthophosphates are thermodynamically unstable. This fact alone does not indicate the "practical" stability of condensed phosphates, for many useful organic compounds are thermodynamically unstable with respect to their elements, yet do not decompose under ordinary conditions (e. g., benzene). The question of importance is: How fast do condensed phosphates revert to orthophosphates in the presence of water under practical working conditions?

Many hydrolysis studies have been made (1, 5, 6, 8, 10, 19, 27, 39, 43, 65, 75, 84, 108, 110, 127, 131), but their utility is often marred by lack of adequate analytical methods (especially in the older work) and in some cases by lack of pH control. Watzel (131) controlled the pH and found the greatest stability for pyro P_2O_5, tri P_2O_5, and the glass of meta P_2O_5 content in the pH range 9–10; in the pH range 3–7 orthophosphate develops fastest for the glass and slowest for pyrophosphate, the triphosphate being intermediate.

Recently Bell (10) has applied more modern methods of analysis to hydration studies in strongly acid or alkaline solutions. He indicates that in hot water the course of the hydrolysis is as follows:

$$
\begin{aligned}
&\text{“}Na_6P_6O_{18}\text{”} + 3H_2O \rightarrow Na_3P_3O_9 + 3NaH_2PO_4\\
&Na_3P_3O_9 + 3H_2O \rightarrow 3NaH_2PO_4\\
&Na_5P_3O_{10} + H_2O \rightarrow Na_3HP_2O_7 + Na_2HPO_4\\
&Na_2H_2P_2O_7 + H_2O \rightarrow 2NaH_2PO_4\\
&Na_3HP_2O_7 + H_2O \rightarrow Na_2HPO_4 + NaH_2PO_4\\
&Na_4P_2O_7 + H_2O \rightarrow 2Na_2HPO_4
\end{aligned}
$$

In hydrolyzing the "hexametaphosphate", the $Na_3P_3O_9$ formed in the first step follows the course taken by pure $Na_3P_3O_9$, as shown in the second equation. Similarly $Na_5P_3O_{10}$, which breaks first into $Na_3HP_2O_7$ and Na_2HPO_4, suffers ultimate hydrolysis to Na_2HPO_4 and NaH_2PO_4, as indicated by the equation for the hydrolysis of $Na_3HP_2O_7$.

In 1 per cent sodium hydroxide solution the hydrolysis of $Na_3P_3O_9$ follows a different course:

$$Na_3P_3O_9 + 2NaOH \rightarrow Na_5P_3O_{10} + H_2O$$

Except during the rapid conversion to triphosphate, no trimetaphosphate is present; hence this hydrolysis follows the course indicated for triphosphate in water above.

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