

# THE COMPOSITION OF THE STRONG PHOSPHORIC ACIDS<sup>1</sup>

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## ABSTRACT

The composition of the strong phosphoric acids was studied in the range 68.8 to 86.3% phosphorus pentoxide by weight. Improved filter-paper chromatography made possible the quantitative determination of the nine lower members of the series, and occasionally up to the twelfth member. It was found that when the strong phosphoric acids are prepared by heating at 350°C., a dynamic equilibrium between the component acids is set up which persists when the mixtures are cooled to room temperature. Only linear condensed polyphosphoric acids were present in the range studied. The composition corresponding to 100% orthophosphoric acid contains about 6 mole per cent each of pyrophosphoric acid and "free water". As the mole ratio of water to phosphorus pentoxide decreases, the number of component acids increases. Orthophosphoric acid is present to an appreciable extent in the stronger phosphoric acids. "Hexametaphosphoric acid" is not a separate chemical entity, but a mixture of higher linear polyphosphoric acids.

## INTRODUCTION

The composition of the strong phosphoric acids,\* i.e. acids containing more than 72.4% by weight of phosphorus pentoxide, the  $P_2O_5$  content of pure orthophosphoric acid, is a subject of considerable interest which has been repeatedly investigated by wet analytical methods. Difficulties in these methods, however, have set a decided limitation on the qualitative and quantitative conclusions possible. A study of this subject by filter-paper chromatography was undertaken, therefore, in order to obtain further and more specific information about compositions having a mole ratio of water to phosphorus pentoxide between 3.6 and 1.2.

It has been shown by means of paper chromatography that by mixing orthophosphoric acid with phosphorus pentoxide at different ratios, and heating the mixture at 350°C., we obtain a mixture containing only linear condensed polyphosphoric acids. No cyclic ones were found. Branched acids, if present, would not be detected, since any ion-molecules with branching are expected to hydrolyze immediately upon dissolution (40). A certain characteristic equilibrium mixture exists for every given ratio of water to phosphorus pentoxide.

The phosphoric acids are very viscous, so that equilibria are attained very slowly; the end result of cooling is an oil in the range 72 to 82%  $P_2O_5$ , a gum in the range 82 to 86%  $P_2O_5$ , and a brittle glass at higher  $P_2O_5$  concentrations. These acids are merely members of a continuous series of amorphous condensed phosphoric acid mixtures which extends from orthophosphoric acid to pure phosphorus pentoxide (38). These mixtures are hygroscopic and hydrolyze upon standing unless stored in tightly closed pyrex containers.

The existence of strong phosphoric acids has been known for many years. Durgin, Lum, and Malowan (14) give a list of several such acids reported

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\*A commercial term, a high degree of ionization not necessarily implied.

previously in the literature. Some of these have since then been positively identified, e.g. the tetrapolyphosphoric acid,  $H_6P_4O_{13}$ , while for others there is enough evidence to date to make their existence highly improbable, e.g. the metaphosphoric acid monomer,  $HPO_3$ . Finally, some of the acids listed by the above-mentioned authors, which at the time represented merely theoretical combinations of phosphorus pentoxide and water, have during the present study been positively identified as far as this is possible by paper chromatography, and their relative concentrations in several mixtures accurately established, e.g. "hexerohexaphosphoric" acid,  $H_8P_6O_{19}$ , better known today as hexapolyphosphoric acid. The same authors checked the analytical methods of Gerber and Miles (19) against those of Britske and Dragunov (6) and found an increasing divergence when acids of high phosphorus pentoxide content were being analyzed. This they considered as evidence that polyphosphoric acids may be present in the strong phosphoric acids.

Bell (3) went a step further by recognizing that tripolyphosphoric acid is present and interferes in some procedures for pyrophosphate determination. By using an analytical method previously developed by the same author (5), he was able to show the presence of ortho-, pyro-, and tripolyphosphoric acids in several of the strong phosphoric acid mixtures, and of "the polymer of metaphosphoric acid commonly known as hexametaphosphoric acid". An "unidentified" acid, indicated by difference, was also present between 78 and 88% phosphorus pentoxide.

Although the exact composition of the strong phosphoric acid mixtures had not been established, several of their physical and chemical properties as a function of their phosphorus pentoxide content were reported in the literature. These include, among others, measurements of densities (14, 23), viscosities (14), vapor pressures (7), boiling points and composition of the vapor over the boiling mixture (38), and heats of vaporization (38). By boiling orthophosphoric acid an azeotropic mixture was obtained (b.p.  $869^{\circ}C$ ., 753 mm. Hg) containing 92.1% phosphorus pentoxide (34). Vapor-density measurements indicated that the vaporized acids dissociate into water and phosphorus pentoxide at temperatures near  $1000^{\circ}C$ . (38).

## EXPERIMENTAL AND RESULTS

### *Analytical Methods*

Various methods exist for the analysis of phosphate mixtures. Considerable effort has been spent during the last 50 years on developing traditional wet-chemical methods (2, 3, 6, 15, 19, 25, 33) for determining the various species of phosphates in the presence of one another. These methods were not adequate since they could not separate the acids higher than tripolyphosphoric acid. These higher acids are present in many strong phosphoric acid mixtures and interfere with the analysis. None of the methods has proved very satisfactory. This has recently been clearly demonstrated for mixtures of pyro- and tripolyphosphate by Dewald (13). The most commonly used wet-chemical methods are those of Jones (24) and Bell (5). Both these procedures are satisfactory for routine determinations on a given industrial product, although the absolute values may be considerably in error. According to the

Bell procedure, no distinction is possible between polyphosphates with more than four phosphorus atoms in their chain. The zinc precipitation method of Raistrick, Harris, and Lowe (28) does not tolerate large amounts of orthophosphate, while the various X-ray methods, such as the one developed by Raistrick (27), are of course limited to crystalline mixtures. The temperature rise method of McGilvery (26) has so far only found application to sodium tripolyphosphate mixtures containing Phases I and II. The infrared technique of Corbridge and Lowe (10) is sensitive to differences of crystalline form but quantitative methods for amorphous phosphates have not been reported. The sensitivity of the end-group titration methods of Samuelson and Van Wazer (32, 40) decreases with increasing chain length.

As compared with these methods, the paper chromatographic procedure combined with differential spectroscopy (18) permits the direct determination of more species of phosphate anions with as good or better accuracy.

#### *Chromatographic Analysis*

The analyses were made using a procedure developed in this laboratory and described in previous papers (11, 42). This method involves the separation of the phosphate components by filter-paper chromatography and the subsequent colorimetric determination of the phosphorus content of each component. The precision of the method is an absolute figure varying from  $\pm 0.5$  to  $\pm 1.0\%$  of the total phosphorus present, depending on the number and species of phosphates present.

The following modifications of the above-mentioned method have been introduced. In addition to the rectangular chromatographic tanks already in use, cylindrical containers (height 43 cm., diameter 24 cm.) were employed to perform bidimensional base-acid analyses as described by Ebel and his co-workers (16). This method makes possible the clear separation and differentiation of condensed cyclic and linear polyphosphates. The phosphate solution was spotted at the base of a cylindrically shaped 58×22 cm. Schleicher and Schuell No. 589 Green Ribbon filter paper, placed inside the cylindrical tank. This was filled 1 cm. deep with the basic solvent (17) consisting of

40 cc. isopropanol,  
20 cc. isobutanol,  
39 cc. water,  
1 cc. ammonia (25%).

After 24 hr. the paper was dried and placed in a tank containing the acid solvent (31) consisting of

70 cc. isopropanol,  
20 cc. trichloroacetic acid (25%),  
10 cc. water,  
0.3 cc. ammonia (25%).

This solvent is very similar to those described by Volmar, Ebel, and Yacoub (16), and Grunze and Thilo (22). The direction of movement of the solvent in the two cases were perpendicular to each other.

The method of Consden, Gordon, and Martin (9), which uses filter-paper chromatograms with downward solvent flow, has been abandoned in favor of ascending chromatographic techniques. The resulting slowing down of the movement of the solvent produced a better separation of phosphates with chains from 5 to 11 phosphorus atoms. The paper was cut in strips approximately  $30 \times 13$  cm., with the lower end pointed and ending in a narrow projection, 1 cm. wide, dipping into a beaker filled with fresh solvent.

The running time varied from 16 to 24 hr., the temperature being kept constant at  $17^\circ\text{C}$ . No correction was made for any hydrolysis occurring during the running of the chromatogram. Hydrolysis studies since show that the principal effect of hydrolysis would be to reduce the values for hypoly- and raise that for pyro- and to a lesser extent ortho-. Intermediate chain lengths would probably gain as much as they would lose. The hydrolysis error was estimated not to exceed one per cent of the total phosphorus in the values given in Table III except in the cases where hypoly- is a major constituent, in which case the hypoly- may be underestimated by as much as 20% of its true value, the other components being uniformly overestimated accordingly. It has not been possible to compare against standard solutions in the case of acids with more than four phosphorus atoms, since they have so far not been isolated.

#### *Materials*

Orthophosphoric acid, 85%, 0.0001% As, Merck (87.1%  $\text{H}_3\text{PO}_4$  by analysis).

Phosphorus pentoxide, min. 98%, 0.005% As, Merck (98.0%  $\text{P}_2\text{O}_5$  by analysis).

Sodium phosphate monobasic monohydrate, Merck,  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ .

Sodium phosphate dibasic anhydrous, Merck,  $\text{Na}_2\text{HPO}_4$ .

Sodium pyrophosphate decahydrate, Merck,  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

Sodium tripolyphosphate anhydrous, techn. ERCO. Purified by successive recrystallizations from an ethanol-water mixture.

Sodium tetrapolyphosphate. Sodium tetrametaphosphate was hydrolyzed in a 5 *N* sodium hydroxide solution, and precipitated as an oil with ethanol.

Sodium trimetaphosphate.  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  was heated four hours at  $1100^\circ\text{C}$ . and then 24 hr. at  $550^\circ\text{C}$ . It was recrystallized from aqueous solution with ethanol.

Sodium tetrametaphosphate (Cyclophos), Victor Chemical Works. Purified by successive recrystallizations from an ethanol-water mixture.

#### *Preparation of the Acids*

A series of mixtures having a mole ratio of  $\text{H}_2\text{O}$  to  $\text{P}_2\text{O}_5$  between 3.6 and 1.2, i.e. a phosphorus pentoxide content between 68.8 and 86.3% by weight, were prepared by placing 15 to 25 gm. phosphoric acid and phosphorus pentoxide in a 50-ml. Erlenmeyer flask, flame sealing, and heating it in a furnace at approximately  $350^\circ\text{C}$ . for about 10 to 20 min. Vigorous shaking in the furnace helped to obtain a uniform mixing of the materials. The heating was interrupted before or immediately after the acids started to attack the Pyrex container. After the mixture had cooled to room temperature, the flask was broken open; a sample was withdrawn and neutralized with 1 *N* sodium

hydroxide to the phenolphthalein end point. All the strong phosphoric acids hydrolyze when dissolved in water and revert finally to orthophosphoric acid. The rate of hydrolysis (12, 21, 39) is very dependent on temperature and the pH of the solution; at room temperature and at a pH 8 to 10 the rate is extremely slow. In order to prevent hydrolysis, care was taken to dilute the acid mixture as quickly as possible, while keeping the pH near the phenolphthalein end point and cooling the sample in crushed ice. A small drop of this solution was analyzed by means of paper chromatography.

For several samples, the phosphorus pentoxide content, calculated from the weight of the starting materials, was found to be in agreement with the total  $P_2O_5$  determined by direct pH titration (1) after complete hydrolysis.

Preliminary experiments were used to assess the importance of the experimental conditions.

(a) It was soon established that the relative proportion of the component phosphoric acids is a function of the over-all concentration of phosphorus pentoxide only and does not depend on the method of preparation. Mixtures were prepared by evaporating orthophosphoric acid in pyrex containers, in a graphite crucible, and in a platinum crucible respectively. In each case the composition of the mixture obtained corresponded to that found when the acids were prepared in sealed Erlenmeyer flasks. Durgin *et al.* (14) and Bell (3) arrived earlier at the same conclusion.

(b) As shown in Table I, the time of heating had no significant effect on the analysis of the solutions obtained, provided a clear melt was obtained before the glass was attacked.

TABLE I  
EFFECT OF TIME OF HEATING ON COMPOSITION OF STRONG PHOSPHORIC ACID MIXTURES  
( $P_2O_5$  content: 77.6%; temperature: 300°C.)

Time (min.)	Distribution of total phosphorus (wt. %)				
	Ortho-	Pyro-	Tri-	Tetra-	Penta-
3	30.9	48.5	14.8	4.3	1.5
5	31.0	48.3	15.7	3.9	1.1
10	32.9	48.1	14.4	3.8	0.8
30	32.6	47.6	14.3	4.5	1.0

TABLE II  
EFFECT OF TEMPERATURE OF PREPARATION ON COMPOSITION OF STRONG PHOSPHORIC ACID MIXTURES  
( $P_2O_5$  content: 77.6%; heating time: 5 min.)

Temp. (°C.)	Distribution of total phosphorus (wt. %)				
	Ortho-	Pyro-	Tri-	Tetra-	Penta-
250	30.6	49.3	14.5	4.8	0.8
300	32.0	47.9	14.3	4.6	1.2
344	30.9	48.2	14.8	4.8	1.3
405	30.8	48.8	14.7	4.8	0.9

(c) The effect of the temperature of preparation on the composition of the mixture is shown in Table II. It will be noted that the temperature range covered was not very large, but was sufficient to show that the temperature of preparation was not a critical factor in these experiments.

The principal experiments were concerned with mixtures having a phosphorus pentoxide content ranging from 68.8 to 86.3%. The results are presented in Table III and plotted in Figs. 2 and 3. In the latter the vertical distance between the curves represents the concentration of the phosphoric acid indicated by number, expressed in per cent  $P_2O_5$  by weight.

TABLE III  
COMPOSITION OF STRONG PHOSPHORIC ACIDS

Composition (wt. % $P_2O_5$ )	Per cent of total phosphorus as:									
	Ortho-	Pyro-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	"Hypoly"
68.80	100.00	Trace								
69.81	97.85	2.15								
70.62	95.22	4.78								
72.04	89.91	10.09								
72.44	87.28	12.72								
73.43	76.69	23.31								
74.26	67.78	29.54	2.67							
75.14	55.81	38.88	5.31							
75.97	48.93	41.76	8.23	1.08						
77.12	39.86	46.70	11.16	2.28						
78.02	26.91	49.30	16.85	5.33	1.60					
78.52	24.43	48.29	18.27	6.75	2.26					
79.45	16.73	43.29	22.09	10.69	4.48	1.92	0.80			
80.51	13.46	35.00	24.98	13.99	6.58	3.14	2.84			
81.60	8.06	27.01	22.28	16.99	11.00	5.78	3.72	2.31	1.55	1.28
82.57	5.10	19.91	16.43	16.01	12.64	8.89	6.41	4.11	3.51	6.99
83.48	4.95	16.94	15.82	15.91	12.46	9.71	6.77	5.04	2.99	9.42
84.20	3.63	10.60	11.63	13.05	12.17	9.75	8.19	5.92	4.91	20.16
84.95	2.32	6.97	7.74	11.00	10.45	9.62	8.62	7.85	6.03	29.41
86.26	1.54	2.97	3.31	5.16	5.32	5.54	3.51	3.30	3.30	66.03

*N.B.* The figures are given to two decimal places for further computation purposes, but the precision may not be better than one per cent total phosphorus in some cases.

## DISCUSSION

Both our work and that of earlier authors support the view that, when the strong acids are prepared by heating, a dynamic equilibrium between the component acids is set up which is metastably frozen in when the mixtures are cooled to room temperature. Methods used to date to study these mixtures have been largely based on analytical or crystallization techniques.

### Analysis

Our analyses based on paper chromatography agree roughly with those of Bell (3) based on wet-chemical methods as far as the low molecular weight components are concerned; it appears, however, that what he considered to be tripolyphosphate was actually a mixture of this and various other acids with longer chains. Indeed, as can be seen from Fig. 1, the maximum of the tripolyphosphoric acid curve is at about 25% whereas a maximum of about 60% was reported by Bell for this member of the series. It is conceivable that tetrapolyphosphoric (4) and probably some acids with longer chains would respond to the same analytical test used in the determination of tripolyphosphoric acid by the Bell (3) method.

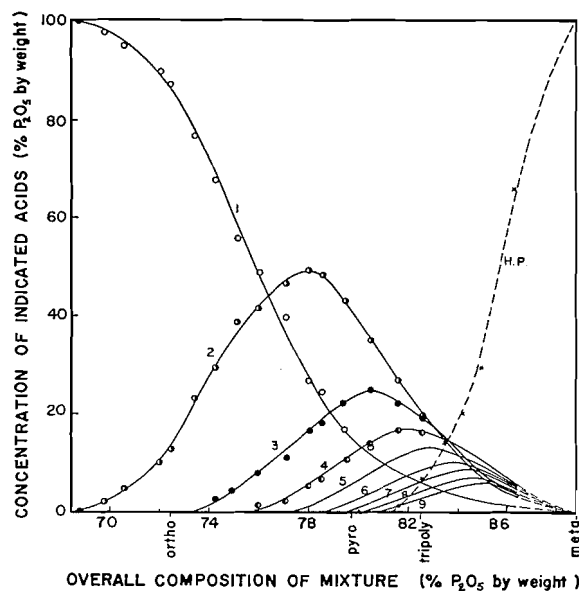


FIG. 1. The composition of the strong phosphoric acids (weight basis); 1 = ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-, 5 = penta-, 6 = hexa-, 7 = hepta-, 8 = octa-, 9 = nona-, and H.P. = "hypoly-".

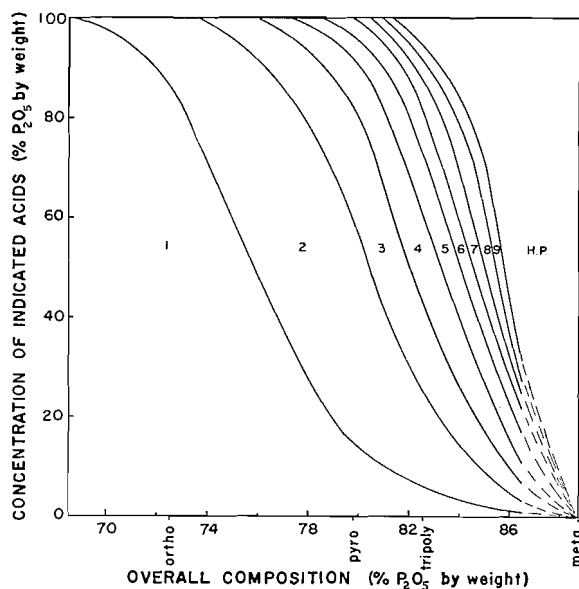


FIG. 2. The composition of the strong phosphoric acids (cumulative) (weight basis); 1 = ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-, 5 = penta-, 6 = hexa-, 7 = hepta-, 8 = octa-, 9 = nona-, and H.P. = "hypoly-".

The "unidentified" acid, believed by him to be a lower polymer of metaphosphoric acid, was found to correspond to the positions of the penta- and hexaphosphoric acids.

A clear separation from the starting line with complete absence of 'ghosting' was noted up to about 83% phosphorus pentoxide content. This behavior is not found when highly polymerized phosphates are chromatographed; from this it was inferred that the acids analyzed as higher polyphosphoric acids (H.P.) were linear acids with not very long chains.

The acid reported by Bell (3) as "hexametaphosphoric acid", a name originally used by Remziye (30) to describe the acid which coagulated albumin, is not a single species. The line indicated in Fig. 1 by H.P., corresponding to Bell's "hexametaphosphoric acid", has no physical meaning and is given for reference reasons only; it includes all acids with a chain containing more than nine phosphorus atoms. Although at times a good separation was possible up to the dodecapolyphosphoric acid, all the results for reasons of uniformity are reported up to the nonapolyphosphoric acid only.

Thilo and Sauer (35), by applying Ebel's bidimensional technique to the investigation of mixtures of phosphoric acids obtained by dehydration of orthophosphoric acid, have confirmed our observation that only linear polyphosphoric acids were present. Traces of cyclic acids were observed in mixtures containing over 84% phosphorus pentoxide. Any branched members are believed (40) to be very unstable in aqueous solution and will degrade to form linear phosphates before any known analytical method can be applied. It is interesting to note that orthophosphate ion is present to an appreciable extent in the strong phosphoric acids. On the contrary, earlier studies (36, 41) showed that glasses in the sodium oxide-phosphorus pentoxide system contain no detectable amounts of orthophosphate. According to Van Wazer (8, 37) "in the derivation of the theoretical distribution function for these glasses, no orthophosphate appeared, because a single  $\text{PO}_4$  group with three negative charges would represent a high charge concentration which would violate the law of detailed distribution of charge". A similar calculation in the case of the acids was inconclusive. However, Van Wazer was able to explain the presence of orthophosphate ions in the acids as follows: "The presence of orthophosphate in the equilibrium mixture of strong phosphoric acids shows that some of the hydrogen atoms are covalently bound to  $\text{PO}_4$  groups, so that the monohydrogen orthophosphate ion can be considered as being unionized in these concentrated acids. Naturally this conclusion is in agreement with the very small ionization constant of the  $\text{HPO}_4^{=}$  ion in dilute aqueous solution".

#### *Crystallization*

The strong phosphoric acid mixtures crystallize upon standing. Rakuzin and Arseniev (29) obtained from a mixture containing 84% phosphorus pentoxide, corresponding to the  $\text{P}_2\text{O}_5$  content of the pure tetrapolyphosphoric acid, a crystalline product after five days of standing. A description by these authors of the solid obtained indicates that the reported crystals were actually pyrophosphoric acid; this lower-strength acid might have been formed by the absorption of moisture from the air (14).

More careful studies by Gerber and Miles (19), Bell (3), and this laboratory showed that mixtures with a phosphorus pentoxide composition corresponding



to the  $P_2O_5$  content of pyrophosphoric acid crystallized on standing. The partially crystallized mixture contained more pyrophosphoric acid than the original mixture but, on remelting, the composition returned to that of the original mixture before crystallization.

All methods of investigation, such as crystallization, which involve a change of phase need careful interpretation. It should not be overlooked that the composition of the primary phase separating from a homogeneous phase containing more than one component may bear no relation to the constitution of that phase.

#### Calculations

By making certain assumptions, it is possible to transform the data of Table III from a weight per cent to a mole per cent basis, and, by using a suitable scale of abscissae, to bring out certain relationships.

The assumptions are:

(a) The component acids (and water) can be represented by the general formula  $H_{n+2}P_nO_{3n+1}$ , where  $n = 0, 1, 2, \dots$ . This enables a free water content to be calculated when the component acids can be determined completely. This water is free only in the stoichiometric sense, i.e. it is not combined with  $P_2O_5$  to form a component acid. Probably it is strongly solvated by  $H_3PO_4$ , here considered the solvent, since it is the predominant component, and this may account for the simultaneous presence of water and condensed acids in an equilibrium mixture.

(b) By extrapolation of calculated "free water" contents, it is assumed that there is no actual "free water" in compositions studied containing more  $P_2O_5$  than the 80.51% mixture. This enables a number average molecular weight to be calculated for the "hypoly" fraction. It neglects the traces of ring compounds present in compositions over 84% phosphorus pentoxide.

The recalculated results are shown in Table IV and are plotted, for the lower acids, in Fig. 3. This figure shows clearly that, as the phosphorus content of the mixture increases, pyrophosphoric acid and "free water" appear before

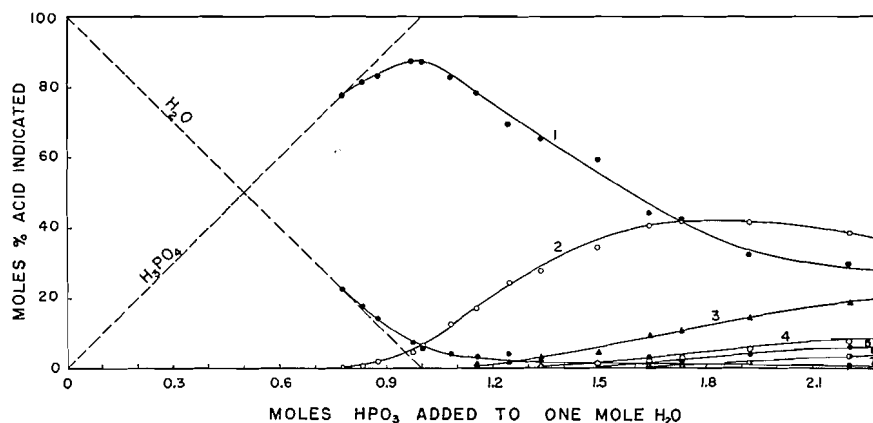


FIG. 3. Computed composition of the strong phosphoric acids (mole basis); 1 = ortho-, 2 = pyro-, 3 = tri-, 4 = tetra-, 5 = penta-, 6 = hexa-, 7 = hepta-.

the over-all composition reaches that of  $\text{H}_3\text{PO}_4$ . At this composition there is only about 88 mole per cent  $\text{H}_3\text{PO}_4$ , with about 6 mole per cent each of "free water" and pyrophosphoric acid. Thus, many of the published properties of "100%  $\text{H}_3\text{PO}_4$ " are subject to a new interpretation.

TABLE IV  
COMPOSITION OF STRONG PHOSPHORIC ACIDS  
(AND NUMBER AVERAGE CHAIN LENGTH OF "HYPOLY" FRACTION)

Over-all composition (moles $\text{HPO}_3/\text{mole H}_2\text{O}$ )	Composition in terms of component acids and water (mole per cent)										Number average chain length
	$n = 1$	2	3	4	5	6	7	8	9 "Hypoly"	Free water	
0.7773	77.74										22.26
0.8308	81.29	0.90									17.81
0.8780	83.60	2.10									14.30
0.9718	87.35	4.90									7.75
1.0012	87.61	6.38									6.01
1.0805	82.88	12.60									4.52
1.1554	78.30	17.07	1.03								3.61
1.2447	69.48	24.20	2.20								4.12
1.3403	65.61	27.99	3.67	0.36							2.37
1.4952	59.60	34.91	5.56	0.85							-0.92
1.6397	44.09	40.38	9.21	2.18	0.52						3.64
1.7310	42.25	41.77	10.54	2.92	0.78						1.74
1.9269	32.22	41.69	14.18	5.15	1.72	0.62	0.22				4.20
2.2041	29.61	38.49	18.31	7.70	2.89	1.14	0.89				0.97
2.5751	21.52	35.97	19.78	11.32	5.86	2.57	1.41	0.77	0.45	0.35	0.9
3.0156	16.48	32.18	17.70	12.93	8.18	4.78	2.96	1.66	1.26	1.87	2.5
3.5765	16.85	28.83	17.96	13.55	8.48	5.51	3.28	2.14	1.12	2.26	—
4.1797	15.17	22.15	16.20	13.65	10.18	6.79	4.89	3.09	2.28	5.60	15.0
5.0519	11.72	17.61	13.03	13.89	10.56	8.11	6.21	4.95	3.38	10.53	14.1
7.8421	12.08	11.65	8.67	10.12	8.35	7.25	3.92	3.25	2.86	31.84	16.3

Figure 3 is also interesting in that it shows that "free water" is present in acid mixtures much higher in phosphorus content than the composition  $\text{H}_3\text{PO}_4$ . When the molecular weight of water, in comparison with the component acids, is considered, a more or less smooth curve for "free water" is obtained, indicating the consistency of the data, until the more complex mixtures are encountered. Here, the analytical difficulties, number of components, and high molecular weights influence the "free water" calculation adversely, although analytical errors in the low molecular weight components may have the greatest effect. Analytical errors which compensated in such a way as not to change the observed number average molecular weight of the component acids would not be detected by this test.

The number average chain lengths calculated for the "hypoly" fraction are shown in Table IV. The inconsistency of the values for the first three mixtures is probably due to the small amounts of the "hypoly" present; however, the number average chain length appears to reach a constant value of about 16 in the rest of the cases, although the amount of "hypoly" increases from 20 to 66% phosphorus pentoxide by weight. Such a maximum might be due to a changing distribution of the molecular weight or the appearance of ring polymers. The latter were not detected chromatographically to any appreciable extent in the compositions analyzed. It is remarkable that the maximum mole per cent is still in the pyrophosphate range, even when about 32 mole per cent of "hypoly" is present. Finally, the general shapes of the curves in Fig. 3 are such that they might be roughly expressed in terms of mass law constants. The average  $K$  value, based on concentrations, for the

second to fifth mixtures in Table IV is  $5 \times 10^{-3}$  (2.43, 4.30, 4.98, 4.99, 8.29 respectively). At most, these indicate some tendency towards a constant value, which might be revealed by more accurate data.

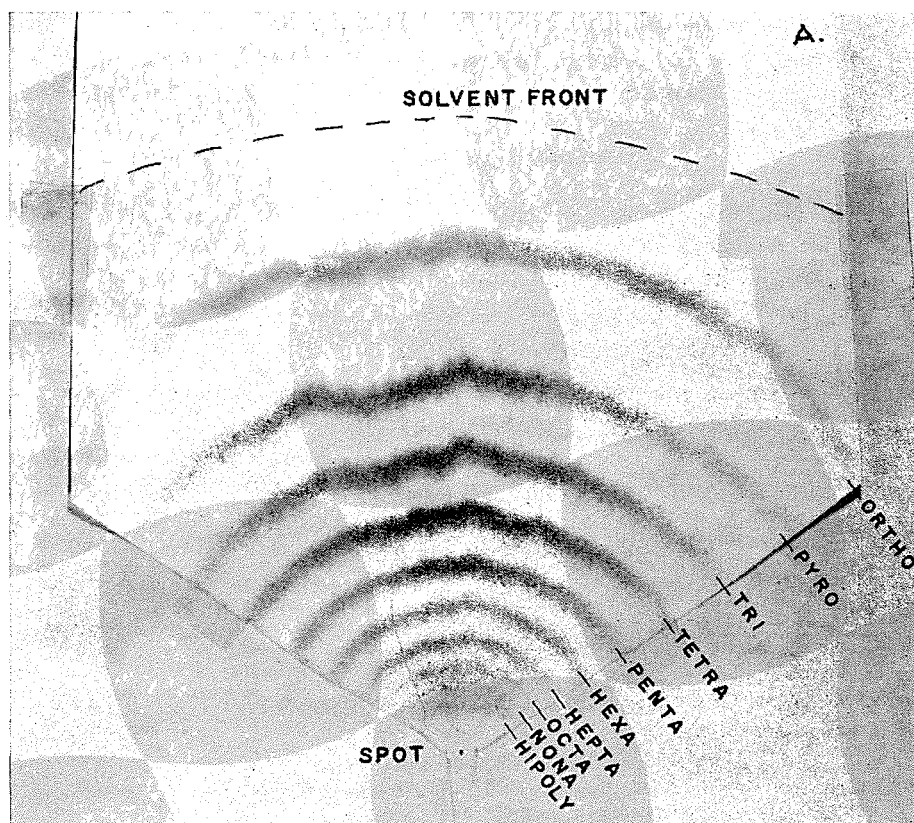


FIG. 4. Chromatographic separation of strong phosphoric acids.

#### *Interpretation*

This paper is concerned largely with presenting experimental results. Their interpretation in terms of chemical theory is a matter of much interest. Two methods are suggested by the current literature. First there is the method of Van Wazer (40) based on statistical models which is an application of modern polymer theory; secondly, there is the ionic and mass law method elaborated by Ingold and his school (20) in interpreting their cryoscopic measurements on sulphuric acid in the immediate neighborhood of the 100% sulphuric acid composition. Since the original derivation of the mass law by Guldberg and Waage was based on essentially a statistical argument, these two methods may not be as far apart as appears at first sight. In both cases, the strong phosphoric acids appear to be suitable materials for study.

#### ACKNOWLEDGMENT

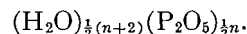
The authors wish to thank Dr. A. E. R. Westman for his interest and help.

APPENDIX. COMPUTATION METHODS

The calculation of Table IV and the data for Fig. 3 from Table III is simple in principle, involving only stoichiometry and simple assumptions. Involved computations can be avoided by the following methods.

*Free Water Content and Mole Percentages* (in absence of "hypoly")

For computing purposes, the component acids, and water, can be represented by the formula



The computation can then be carried through as illustrated in Table V. Essentially, it involves a comparison, in Column (2), of the total water known to be present in the strong-acid mixture with that computed from the chromatographic analysis, Column (5), which does not include "free water".

TABLE V

(1) Over-all composition (wt. %)	(2)* H <sub>2</sub> O	(3) Chromatographic analysis	(4) P <sub>2</sub> O <sub>5</sub>	(5) H <sub>2</sub> O	(6) Components	(7)	(8) Moles HPO <sub>3</sub> per mole of H <sub>2</sub> O
		$n$	$\text{P}_2\text{O}_5$	$(4) \times \frac{n+2}{n}$	$(4) \times \frac{2}{n}$		$\frac{2}{(2)-1}$
		Moles per one mole P <sub>2</sub> O <sub>5</sub> total				Mole %	
		0			(2) 0.1248	6.4	
H <sub>2</sub> O 27.56	2.9976	1	0.8728	2.6184	1.7456	87.4	1.0012
P <sub>2</sub> O <sub>5</sub> 72.44	(5) 2.8728	2	0.1272	0.2544	0.1272	6.4	
	0.1248		1.0000	2.8728	1.9876	100.0	

\*Transferred values have the column of origin indicated in front.

TABLE VI

(1) Over-all composition (wt. %)	(2)* H <sub>2</sub> O	(3) Chromatographic analysis	(4) P <sub>2</sub> O <sub>5</sub>	(5) Component acids	(6)	(7) "Hypoly"	(8) Over-all composition
		$n$	$\text{P}_2\text{O}_5$	$(4) \times \frac{2}{n}$	$\left( \frac{(5)}{(5) \text{ total}} \right) \times 100$	$\frac{\bar{n}}{x-y}$	$\frac{2}{(2)-1}$
		Moles per one mole P <sub>2</sub> O <sub>5</sub> total			(mole %)		(moles)
H <sub>2</sub> O 15.80	1.4785	0					H <sub>2</sub> O 1.000
P <sub>2</sub> O <sub>5</sub> 84.20	(4)+(5) 1.2501	1	0.0363	0.0726	15.17		HPO <sub>3</sub> 4.179
	$x$ 0.2284	2	0.1060	0.1060	22.15		
	(4) $y$ 0.2016	3	0.1163	0.0775	16.20		
	$x-y$ 0.0268	4	0.1305	0.0653	13.65		
		5	0.1217	0.0487	10.18		
		6	0.0975	0.0325	6.79		
		7	0.0819	0.0234	4.89		
		8	0.0592	0.0148	3.09		
		9	0.0491	0.0109	2.28		
		Total	0.7984	0.4517			
	"Hypoly" $y$ 0.2016		(2) 0.0268	5.60	15.0		
				0.4785	100.00		

\*Transferred values have the column of origin indicated in front.

*Number Average Chain Length of "Hypoly" and Mole Percentages* (in absence of "free water")

As illustrated in Table VI, the first part of the computation is the same as in Table V but the water,  $x$ , in the "hypoly" fraction is computed rather than "free water", which is assumed to be absent. The component acid formula can now be written  $H_2O(HPO_3)_n$ . Then, if  $x$  moles of water and  $y$  moles of  $P_2O_5$  are present in the "hypoly" fraction,  $2y$  moles of  $HPO_3$  can be formed, leaving  $x-y$  moles of "hypoly" acids. The number average chain length, i.e. the average number of  $HPO_3$  groups per molecule, will then be  $2y/(x-y)$ .

## REFERENCES

1. American Chemical Society. Reagent chemicals. Am. Chem. Soc. Spec. 1950. p. 240.
2. AOYAMA, S. J. Pharm. Soc. Japan, No. 520: 553. 1925.
3. BELL, R. N. Ind. Eng. Chem. 40: 1464. 1947.
4. BELL, R. N., AUDRIETH, L. F., and HILL, O. F. Ind. Eng. Chem. 44: 568. 1952.
5. BELL, R. N., WREATH, A. R., and CURLESS, W. T. Anal. Chem. 19: 97. 1947; 24: 1997. 1952.
6. BRITSKE, E. V. and DRAGUNOV, S. S. J. Chem. Ind. (U.S.S.R.), 4: 49. 1927.
7. BROWN, E. H. and WHITT, C. D. Ind. Eng. Chem. 44: 615. 1952.
8. CALLIS, C. F., VAN WAZER, J. R., and ARVAN, P. G. Chem. Revs. 54: 777. 1954.
9. CONSDEN, R., GORDON, A. H., and MARTIN, A. J. P. Biochem. J. 38: 224. 1944.
10. CORBRIDGE, D. E. C. and LOWE, E. J. Anal. Chem. 27: 1383. 1955.
11. CROWTHER, J. P. Anal. Chem. 26: 1383. 1954.
12. CROWTHER, J. P. and WESTMAN, A. E. R. Can. J. Chem. 32: 42. 1954.
13. DEWALD, W. Fette u. Seifen, 56: 105. 1954.
14. DURGIN, C. B., LUM, J. H., and MALOWAN, J. E. Trans. Am. Inst. Chem. Engrs. 33: 643. 1937.
15. DWORZAK, R. and REICH-ROHRWIG, W. Z. anal. Chem. 77: 14. 1929.
16. EBEL, J. P. Bull. soc. chim. France, 991, 998, 1085, 1096. 1953.
17. EBEL, J. P. and VOLMAR, Y. Compt. rend. 233: 415. 1951.
18. GEE, A. and DEITZ, V. R. Anal. Chem. 25: 1320. 1953.
19. GERBER, A. B. and MILES, F. T. Ind. Eng. Chem. Anal. Ed. 10: 519. 1938.
20. GILLESPIE, R. J., HUGHES, E. D., and INGOLD, C. K. J. Chem. Soc. 2473. 1950.
21. GREEN, J. Ind. Eng. Chem. 42: 1542. 1950.
22. GRUNZE, H. and THILO, E. Sitzber. deut. Akad. Wiss. Berlin, Math.-Naturw. Kl. No. 5. 1954.
23. International Critical Tables. Vol. 3. McGraw-Hill Book Company, Inc., New York. 1928. p. 61.
24. JONES, L. T. Ind. Eng. Chem. Anal. Ed. 14: 536. 1942.
25. LUM, J. H., MALOWAN, J. E., and DURGIN, C. B. Chem. & Met. Eng. 44: 721. 1937.
26. MCGILVER, J. D. ASTM Bull. No. 191: 22. 1953.
27. RAISTRICK, B. Sci. J. Roy. Coll. Sci. 19: 9. 1948.
28. RAISTRICK, B., HARRIS, F. J., and LOWE, E. J. Analyst, 76: 230. 1951.
29. RAKUZIN, M. A. and ARSENIYEV, A. A. Chem.-Ztg. 47: 195. 1923.
30. REMZIYE, S. Bull. soc. chim. France, 3: 1391. 1936.
31. ROUX, H., THILO, E., GRUNZE, H., and VISCONTINI, M. Helv. Chim. Acta, 38: 15. 1955.
32. SAMUELSON, O. Svensk Kem. Tidskr. 56: 343. 1944.
33. STOLLENWERKE, W. and BAURLE, A. Z. Anal. Chem. 77: 81. 1929.
34. TARBUTTON, G. and DEMING, M. E. J. Am. Chem. Soc. 72: 2086. 1950.
35. THILO, E. and SAUER, R. To be published.
36. VAN WAZER, J. R. J. Am. Chem. Soc. 72: 647. 1950.
37. VAN WAZER, J. R. J. Am. Chem. Soc. 72: 644. 1950.
38. VAN WAZER, J. R. Encyclopedia Chem. Tech. 10: 412. 1953.
39. VAN WAZER, J. R., GRIFFITH, E. J., and MCCULLOUGH, J. F. J. Am. Chem. Soc. 77: 287. 1955.
40. VAN WAZER, J. R. and HOLST, K. A. J. Am. Chem. Soc. 72: 639. 1950.
41. WESTMAN, A. E. R. and CROWTHER, J. J. Am. Ceram. Soc. 37: 420. 1954.
42. WESTMAN, A. E. R. and SCOTT, A. E. Nature, 168: 740. 1951.